# Metallized and Magnetic Polymers

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# Metallized and Magnetic Polymers

## Chemistry and Applications

### Johannes Karl Fink

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# Contents

# Preface

This book focuses on the chemistry of metallized and magnetic polymers, as well as special applications of these materials.

After an introductory section on the general aspects of the field, the types and uses of these polymers are summarized, followed by an overview of some testing methods.

The text focuses on the literature of the past decade. Beyond education, this book may serve the needs of industry engineers and specialists who have only a passing knowledge of these issues, but need to know more.

## *How to Use this Book*

Utmost care has been taken to present reliable data. Because of the vast variety of material presented here, however, the text cannot be complete in all aspects, and it is recommended that the reader study the original literature for more complete information.

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## *Index*

There are three indices: an index of acronyms, an index of chemicals, and a general index. In the index of chemicals, compounds that occur extensively, e.g., *acetone*, are not included at every occurrence, but rather when they appear in an important context. When a compound is found in a figure, the entry is marked in boldface letters in the chemical index.

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Johannes Fink
Leoben, 2nd February 2016

*Metallized and Magnetic Polymers: Chemistry and Applications.* Johannes Karl Fink.

# PART I

# METALLIZED POLYMERS

*Metallized and Magnetic Polymers: Chemistry and Applications.* Johannes Karl Fink.

# 1

# General Aspects

There are monographs on the issues of metallized polymers (1). The topic of metallization of polymers has been reviewed (2).

Metallized plastic components have the same high-quality look and feel as chromium-plated metal parts and are less costly to produce (3). For these reasons, these materials are used in auto manufacturing for radiator grills or mirror caps, as well as for electronic appliances and bathroom fittings.

With a high-quality metallic coating, plastic components take on a luxurious chrome look. thus, they are popularly used in design elements for cars, electrical appliances, kitchens and bathrooms. In vehicles, radiator grills, mirror caps, door handles and trim are some items with such a finish. Push buttons and covers for hi-fi equipment, cell phones and coffee machines, as well as shower heads, are further examples of products coated with this method (3).

Plastic parts can be coated with metal, a process called metallization, for both aesthetic and mechanical purposes (4). Visually, a metal-coated piece of plastic features increased gloss and reflectivity. Other properties, such as abrasion resistance and electric conductivity, which are not innate characteristics of plastic, are often obtained through metallization. Metallized plastic components are used in similar applications as metal-plated parts, but tend to be lower in weight and have higher corrosion resistance, although not in all cases. In addition, electrical conductivity can be controlled in metallized plastic components, and they are inexpensive to manufacture. To metallize a piece of plastic, several common methods are used (4):

1. Vacuum metallization,
2. Arc spraying,
3. Flame spraying, and
4. Plating.

It is also possible to metallize a transfer film, and use alternative methods to apply the film to the surface of the substrate (4).

## 1.1 History

The history of fabrication of metallized polymers has been summarized (5, 6). The first commercial plating of polymers was done in 1905 (7). Also during World War II a fair amount of production took place. The large-scale production started in the mid-1950s (8). An electrical condenser with coated paper was described in 1910 (9).

This was refined some 50 years ago (10). The first metal spraying experiments were done around 1896. However, the zinc arc spray and flame-spray methods were commercialized only after 1910 (5). Sputtering was basically observed in the 1850s by the electric discharges of gases. Metal spraying experiments have already been done in 1896. Practical zinc arc spraying and flame spraying were commercialized after 1910.

### *1.1.1 Capacitors*

Before the introduction of plastic films, capacitors had been fabricated by sandwiching a strip of impregnated paper between strips of metal, and rolling the composite into a cylinder (11).

The manufacture of these types started in 1876. These capacitors were used from the early 20th century onwards (12). With the development of plastic materials, the capacitor industry started to replace paper with thin polymer films. One very early development in film capacitors was described in 1947 (13). The introduction of plastics in plastic film capacitors follows the historic order summarized in Table 1.1.

An early special type of plastic film capacitors were made from cellulose acetate films. The polar insulating dielectric cellulose acetate was a synthetic resin that could be made for metallized capacitors in paint film thickness down to about 3 $\mu m$. A liquid layer

**Table 1.1** Historic order of plastics as capacitors (14).

| Polymer | Abbreviation | Introduced in |
|---|---|---|
| Poly(styrene) | PS | 1949 |
| Poly(ester) | PET | 1951 |
| Cellulose acetate | CA | 1951 |
| Poly(carbonate) | PC | 1953 |
| Poly(tetrafluoroethylene) | PTFE | 1954 |
| Poly(parylene) | | 1954 |
| Poly(propylene) | PP | 1954 |
| Poly(ethylene) | PE | 1958 |
| Poly(phenylene sulfide) | PPS | 1967 |

of cellulose acetate was first applied to a paper carrier, then covered with a wax, dried and then metallized. During the winding of the capacitor body, the paper was removed from the metallized film. The remaining thin cellulose acetate layer showed a dielectric breakdown of 63 $V$. This was sufficient for many general purpose uses. Further, the small thickness of the dielectric material decreased the overall dimensions of these capacitors in comparison to other film capacitors at this time.

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# 2

# Methods of Fabrication

## 2.1 Methods for Metallizing

Common methods for metallizing a polymer film surface are lamination of a metal sheet or foil, wet metal plating, vacuum deposition, sputtering or electrically conductive paint coating (1).

### *2.1.1 Laminating*

In the method for laminating a metal sheet or foil, it is common to use an adhesive, whereby it is difficult to obtain an inexpensive product having a well-balanced property such as adhesive strength between the film and the metal sheet or foil, and it is technically difficult to obtain a smooth well-finished surface (1).

### *2.1.2 Wet Plating*

The wet metal plating is conducted in such a manner that catalysts for metal plating are applied to the portions where a metal layer is to be formed, or the portions where no metal layer is to be formed are covered with metal plating resist, prior to the formation of a metal layer (1). However, it is not easy to roughen the surface of the polymer base sheet to such an extent that adequate adhesion strength can thereby be ensured between the metal layer and the polymer base sheet. Accordingly, the polymer capable of providing adequate practical peeling strength, is rather limited. Further, the selective application of the catalysts for wet metal plating or the precise application of the plating resist, involves technical difficulties. Besides, the process steps are rather complicated, the metal layer-forming speed is rather slow, and there is a problem of how to dispose of the waste plating solution. Thus, the wet metal plating method is costly.

### *2.1.3 Fluid Electrolytic Deposition*

A method for metallizing polymers has been described that is generating anionic sites on the structures, contacting these with a metal cation then reducing the metal cation to metal at the anionic sites or treating the metal cations to form a semiconductor. The metallized polymers are useful as electrical conductors or semiconductors. The process runs as (2,3):

1. The polymer substrate is treated with a solution of a strong base to generate surface anionic sites.
2. These treated structures are then contacted with a solution of the desired metal cation, which is adhered to it via ion exchange.
3. The metal cation is then treated with a compound that forms a semiconductor to yield a semiconductor imbibed polymer or is reduced to the metal state by interaction with the polymer structure to obtain a metal imbibed polymer.
4. If the polymer structure does not have sufficient reduction potential, the cation can be reduced by the interaction with a solution of a strong reducing agent.
5. Optionally, then a second metal can be deposited via electroless plating or electrodeposition to obtain a metal-coated polymer.

Suitable polymers are poly(*p*-phenylene terephthalamide), poly(*m*-phenylene isophthalamide), poly(*p*-benzamide), poly(4,4′-biphenylene isophthalamide), poly(benzimidizole), poly(chloro-*p*-phenylene isophthalamide) and the corresponding copolymers.

Preferred bases are $CH_2SOCH_3^-$, potassium *tert*-butoxide, and the polyanions of the polymers described above either used alone or in the presence of alcohols, amines or nitrates. A preferred mixture of bases is potassium *tert*-butoxide and lithium nitrate.

The preferred solvent to use is dimethyl sulfoxide (DMSO). The combination of base and solvent should cause a swelling of the polymers, as this permits an improved contact with the reagents.

The operating at temperatures depend on the particular solvent that is used, and typically vary between the melting and boiling points of the solvents. For example, when the solvent is DMSO, basically, the temperature range is 17–190°C. However, the preferred temperature range is room temperature to about 60°C. Metals which can be used for the metallization of the polymer substrate are summarized in Table 2.1.

**Table 2.1** Metals for metallization (2).

| Normal use | Semiconductive use |
|---|---|
| Copper | Copper |
| Silver | |
| Gold | |
| Cadmium | Cadmium |
| Zinc | Zinc |
| Platinum | |
| Iron | Iron |
| Cobalt | Cobalt |
| Chromium | |
| Tin | Tin |
| Lead | Lead |
| Rhodium | |
| Ruthenium | |
| Nickel | Nickel |
| | Germanium |
| | Gallium |
| | Aluminum |

Typically, the concentration of the metal cations is about 0.2 $mol\,l^{-1}$. Any metal or metal complex can be used that has appropriate solubility in the solvent of choice (2, 3). Examples for the preparation have been disclosed (2):

**Preparation 2–1:** Silver-imbibed poly(*p*-phenylene terephthalamide) yarn was prepared as follows. Six-inch lengths of poly(*p*-phenylene terephthalamide) yarn were washed with water, followed by acetone and methylene-chloride and then oven dried. Sections of yarn were dipped for 5 *min* into a solution of 0.5 $mol\,l^{-1}$ potassium *tert*-butoxide in DMSO. This generated an orange gel on the surface of the fibers. The yarn was then placed into a solution of 0.5 $mol\,l^{-1}$ silver trifluoroacetate in DMSO for two minutes. This caused the orange gel to become black. The yarn was next placed in a solution of 0.5 $mol\,l^{-1}$ sodium borohydride in DMSO for two minutes. This caused no further color change, but gas evolution took place from the fiber surface. Finally, the yarn was washed with water, followed by acetone, and then hexane. The yarn sample was then air dried. A second section of poly(*p*-phenylene terephthalamide) yarn was similarly treated only with residence times of 2 *min* in the potassium *tert*-butoxide solution, 1 *min* in the silver trifluoroacetate solution, and 2 *min* in the sodium borohydride solution. Conductivity measurements showed that both of these samples were electrical conductors.

Nickel sulfide semiconductor imbibed poly(*p*-phenylene terephthalamide) films were prepared as follows (2):

**Preparation 2–2:** A solution of 0.10 *g* of nickel chloride hydrate in 2 *ml* of DMSO was added to a solution of 74.9 *g* of a 1.33% poly(*p*-phenylene terephthalamide) polyanion solution as the potassium salt. A gel immediately formed, but vigorous stirring restored a viscous solution with some small gel particles. The resulting solution was used to cast a film which was quenched with water to restore the neutral poly(*p*-phenylene terephthalamide) polymer. Treatment of the film with an aqueous solution of sodium sulfide gave a poly(*p*-phenylene terephthalamide) film containing nickel sulfide particles.

### 2.1.4 *Plating-out Method*

The preparation of metallized films using the plating-out method has been demonstrated (4). Various metal powders with lower reduction potential were dispersed in a poly(vinyl alcohol) (PVA) aqueous solution, dried to form a film, then treated with metal salt solutions having metal ions in the metal salt with higher reduction potential.

Metallized PVA films exhibited a low surface resistivity around 100–101 $Ohm\,cm^{-2}$ when using the plating-out method. The surfaces of these films were shown to be metallized by means of X-ray analysis.

### 2.1.5 *Retroplating-out Method*

A method to prepare polymer metallized films was found by using polymer metal chelate films treated with wetted metal plates or metal powders (5). The polymer metal chelate films can be prepared by metal salts mixed with the polymers containing a functional group, such as PVA, poly(amide) (PA), poly(acrylamide), and poly(urethane) (PU). This method is addressed as the retroplating-out method.

Polymer metallized films exhibit a low surface resistivity around 0.1 $Ohm\,cm^{-2}$. The surfaces of these films were shown to be metallized by means of X-ray analysis. The conduction mechanism was verified reasonably well by using a scanning electron microscope and UV-visible absorption data (5).

### 2.1.6 *Electroless Plating*

Since most plastic surfaces are not electrically conductive, the traditional electroplating methods are not quite suitable for providing a metallic coating (6). However, electroless plating is one feasible method for the plating of polymeric materials.

The development of chemical etchants resulted in a controlled microporous surface of the polymeric material and greatly improved electroless plating baths, leading to metal depositions which adhere well to the polymeric surface and which may serve as a conductive preplating for subsequent electroplating.

Electroless plating processes are labor intensive, complicated and hence expensive. For example, a typical electroless plating procedure involves the steps of etching the polymeric material with strongly oxidizing solutions of chromic acid in order to physically roughen the polymeric surface and chemically modifying it to give it a hydrophilic nature; neutralizing it with a mildly acidic or basic reducing agent for removing the detrimental hexavalent chromium; sensitizing it with stannous chloride and palladium chloride for nucleation of palladium, accelerating it with acidic or basic solutions for removing excess tin and exposing palladium nuclei and electroless depositing metals such as nickel and copper on it from a plating bath (6).

### *2.1.7 Vacuum Deposition*

The vacuum deposition method is a good metallizing method (1). However, the adhesive strength of the metal layer with the base film is rather weak, and surface pretreatment of the base film will be required.

In order to form a metal layer only at a predetermined portion, other portions must be covered. A vacuum system or an inert atmosphere is employed and, accordingly, a difficult high technique will be required for a continuous process and the apparatus will be expensive.

Besides, since a vacuum system is employed, an apparatus capable of producing a film having a wide width will be expensive, and a high level of technical skill will be required. Decorative applications account for ca. 80% of metallizing (7).

Metals used in industrial vacuum coating applications are summarized in Table 2.2. Polymers used in industrial metallizing are summarized in Table 2.3.

**Table 2.2** Metals used for vacuum coating (7).

| Metal | Melting point/[°C] | Uses |
|---|---|---|
| Aluminum | 660 | Decorative finish |
| Cadmium | 321 | Aircraft parts |
| Chromium | 1900 | Mirror surface on glass |
| Copper | 1083 | Electronic circuits |
| Gold | 1083 | Electronic circuits |

**Table 2.3** Polymers used for metallizing (7).

| Polymer | Uses |
|---|---|
| Cellulosics | Costume jewelry, toys, appliances |
| Acrylics | Lenses, light diffusers |
| ABS | Auto interiors, housewares |
| Poly(styrene) | Appliances, knobs, cosmetic containers |
| Poly(carbonate) | Automotive applications |
| poly(ethylene) | Housewares, toys, enclosures |

### 2.1.8 *Sputtering*

Sputtering is a material transportation phenomenon caused by energetic ions striking a cathode, causing the material making up the cathode to be transferred to a different surface through a momentum transfer mechanism (8). In the performance of a sputtering technique, the substrate to be coated is placed adjacent to a cathode made of the substance which will form the coating. The cathode is subject to a high negative voltage and is placed in an inert gas atmosphere at low pressure.

Under the influence of the high voltage potential difference, atmospheric ions are accelerated against the surface of the cathode wherein the momentum of the ions is transferred to atoms on the surface of the cathode, ejecting the atoms from the surface of the cathode and causing them to contact and adhere to the adjacent substrate. Such sputtering process parameters which affect the sputtering rate include (8):

1. Mass and energy of the impinging ions,
2. Gas temperature,
3. Electrode spacing,
4. Material and crystallographic orientation of the cathode,
5. Cathode surface, and
6. Cathode shape and shielding.

The inert gases useful for such sputtering techniques include helium, neon, argon, krypton, xenon and nitrogen. Preferably, a chromium metal or chromium alloy is sputtered to a layer having a thickness of 2–100 $Å$ (8).

It has been stated that the sputtering method has disadvantages such as it is difficult to form a thick metal layer and the production rate is slow (1).

### 2.1.9 *Paint Coating*

The electrically conductive paint coating is a simple metallizing method. However, the metal layer thereby formed tends to be peeled off as time passes, and it is therefore difficult to form a thin uniform metal layer on a base film (1). The method of applying a metal sheet or foil on a polymer film surface, followed by removing the metal layer except for the predetermined pattern, is widely used for the production of printed circuit boards.

Electrochemical impedance spectroscopy (EIS) was used to evaluate a high resistance paint coating immersed in a 10% sodium chloride solution. The coating resistance and coating capacitance were extracted from Bode and Nyquist plots during a period of 90 *d* of immersion (9).

A protective paint coating has been described (10). The composition contains a polymeric binder with both hydrophobic and hydrophilic moieties, i.e., an acrylic-graft terpolymer with glycidyl acrylate and an epoxy resin. The preparation of a glycidyl acrylate copolymer runs as (10):

**Preparation 2–3:** Into a 3 *l* round bottom flask fitted with a nitrogen inlet, water cooled condenser, temperature probe, and mechanical stirrer was charged 748.6 *g* of 2-butoxyethanol. The flask was heated to 115°C under nitrogen sparge. A monomer mixture of 1632.0 *g* of 2-ethylhexyl acrylate, 68.0 *g* glycidyl methacrylate, 21.8 *g* dibenzoyl peroxide (78% in water), and 65.0 *g* of 2-butoxyethanol was added to solvent in 2.5 hours. The mixture was held at 115°C for 30 *min*, and then 4.3 *g* of *tert*-butyl perbenzoate were added. The reaction was continued for 1 *h* and then the mixture was allowed to cool. The product obtained was a viscous clear resin solution of 68.2% nonvolatile and 0.38% oxirane.

In addition, several other examples of preparation have been detailed (10).

### 2.1.10 *Pressure-Sensitive Conductive Rubber*

Conventional pressure-sensitive conductive rubber-like polymer films are usually prepared by blending and dispersing into a rubber-like base material, a conductive powder as a conductive material, for instance, a carbon powder such as carbon black or graphite powder, or a metal powder such as gold, silver, nickel, stainless steel or copper stabilized with a noble metal (1).

It is common that the conductive powder is mechanically dispersed into the rubber-like polymer by means of a ball mill, a roll mill, a Bumbury mixer or a screw extruder. However, the degree of dispersion is largely dependent on the dispersing method and the dispersing conditions. Accordingly, it has been difficult to obtain pressure-sensitively conductive rubber-like polymer films which are capable of providing predetermined characteristics consistently. Further, the selection of the conductive powder is also important. Even when the same kind of the conductive powder is used, the pressure-sensitive conductivity or the durability for repeated use, varies to a large extent depending upon the shape, particle size or particle size distribution of the conductive powder.

With the conventional pressure-sensitively conductive rubber-like polymer film, it is intended to utilize the change of electric resistance caused by a strain exerted on the film. However, it used to be difficult to optionally control the electric resistance to change in proportion to the strain. Nevertheless, pressure-sensitively conductive rubber-like polymer film is preferably used for various switches, such as switches for automatic doors, mat switches of electromotive sewing machines, etc., in view of the merits of it containing no mechanical driving parts and thus being free from an electric noise, and it thereby making it possible to substantially reduce the size and the weight. Accordingly, such pressure-sensitively conductive film is expected to find a wider range of applications.

On the other hand, a metal-containing polymer is usually intended for the utilization of the nature of the metal, i.e., the characteristics of the metal against electricity, magnetism, heat, light, sound, chemicals or radiation. Particularly, a polymer in which fine metal particles are uniformly dispersed, is of great interest. As a method for producing a polymer containing a metal, it is known to mix a polymer with metal powder. However, there is a limitation to the size of the metal particles which can be mixed and dispersed with the polymer. For instance, it is practically difficult to uniformly disperse metal particles having a size of not greater than 10 m, in a polymer, and a shaped article thereby obtained tends to be inferior in its mechanical strength.

When metal particles are to be dispersed into the polymer in a high concentration the metal particles are likely to contact one another and, accordingly, the amount of the metal particles to be incorporated is limited to a certain level.

A process for precipitating a metal in a resin by using the pyrolytic characteristics of metal hydrides has been described. However, the metal hydrides have a low pyrolytic temperature and are susceptible to moisture. Thus, such a process is not practical.

### 2.1.11 *Grafting of Polyelectrolytes*

Polyelectrolytes could be grafted onto hydrocarbon surfaces by a dry-process and chemical-free approach using hydrogen projectiles with high kinetic energy but properly controlled to selectively cleave the C–H bonds. Then, electroless plating was carried out after loading Pd moieties by ion exchange (11). This procedure resulted in high quality metallized polymer films with excellent conductivity and mechanical stability.

### 2.1.12 *Selective Deposition of Metal onto Plastic Substrates*

A method of selectively plating a plastic article uses a first polymer resin portion and a second polymer resin portion. The first polymer resin portion is not rendered plateable by sulfonation and the second polymer resin portion is rendered plateable by sulfonation. The method uses the steps of (12):

1. Sulfonating the plastic article, wherein the second polymer resin portion is rendered plateable by sulfonation,
2. Activating the sulfonated plastic article to accept electroless plating thereon, and
3. Plating the sulfonated and activated article in an electroless plating bath.

The plastic article is thereby selectively plated such that the first polymer resin portion does not have plating thereon and the second polymer resin portion is electrolessly plated (12).

## 2.2 Welding

### 2.2.1 *Ultrasonic Welding of Metallized Plastic*

Ultrasonic welding allows accurate and precise application of energy to selectively melt or weld the desired portions of a plastic assembly (13). An ultrasonic assembly is suitable for most thermoplastic materials, and is widely used to weld thermoplastic parts in the automotive, packaging, electronic, and consumer industries. In practice, high-frequency mechanical vibrations are transmitted by the ultrasonic welding machine to mating plastic parts. At the joint or interface of the two parts, a combination of applied force and surface or intermolecular friction increases the temperature until the melting point of the thermoplastic is reached. The ultrasonic energy is then removed and a molecular bond or weld is produced between the two plastic parts.

An ultrasonic welding system typically contains a high-frequency power supply, usually 20–40 *kHz*. The high-frequency energy is directed into a horn, which is a bar or a metal section, typically of titanium, aluminum, or hardened steel, dimensioned to be resident at the applied frequency. The horn contacts the workpiece and transmits the mechanical vibrations into it. A fixture or nest supports and aligns the two parts to be welded. It is generally made of aluminum or steel, and is sometimes lined with cast urethane or another material that is resilient.

Also, a metallized plastic assembly can be effectively created by joining two metal-coated plastic parts using ultrasonic welding. An effective weld, equivalent to that obtained with unplated plastic, can be obtained on plastic parts that are completely plated with metal in the weld joint areas (13).

## 2.3 Molding

### *2.3.1 Molded Products*

Metallized plastic molded products can be made from a plastic and multiple coating layers (14). These layers are a base coat layer, a dry metallic film layer, an inter coat layer and a top coat layer.

As the base coating material, either UV curing coating materials or thermosetting coating materials may be used. They can be selected depending on the particular dry type metal film-forming method used, the type of metal to be coated, and the suitability of the coating. UV curing coating materials are preferred because of various factors such as the inter coating materials and top coating materials used.

The starting materials for the resin used as the inter coat layer are acrylamides. The most preferred special comonomer is *N*-octylacrylamide. This is copolymerized with acrylic acid esters (14).

The top coating material for the top coat layer is an UV curing type coating material. This composition contains 40–90% of a urethane modified polyvinyl compound or epoxy modified polyvinyl compound and 10–60% of a polyvinyl compound which is lower in viscosity than the modified polyvinyl compounds (14). Suitable polyvinyl compounds are summarized in Table 2.4 and in Figure 2.1.

**Table 2.4** Monomers for polyvinyl compounds (14).

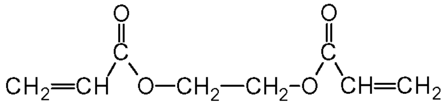
| Monomer |
|---|
| Ethylene glycol di(meth)acrylate |
| Diethylene glycol di(meth)acrylate |
| Triethylene glycol di(meth)acrylate |
| Neopentyl glycol di(meth)acrylate |
| 1,6-Hexanediol di(meth)acrylate |
| Trimethylolpropane tri(meth)acrylate |
| Pentaerythritol tri(meth)acrylate |
| Pentaerythritol tetra(meth)acrylate |
| Bisphenol A dioxypropyl ether di(meth)acrylate |

These compounds preferably can reduce the viscosity of the epoxy or urethane modified polyvinyl compounds when they are mixed together. When curing the inter coating material and top coating material by irradiation with UV rays, it is preferred to add to the coating materials a photopolymerization initiator. Examples of photopolymerization initiators are collected in Table 2.5. Also, some are shown in Figure 2.2.

**Table 2.5** Photopolymerization initiators (14).

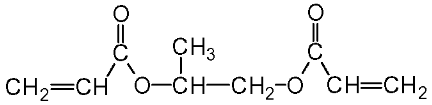
| Initiator | Initiator |
|---|---|
| Benzophenone | 4,4′-Bis(di-methylamino)benzophenone |
| Benzoin | Benzoin methyl ether |
| Benzoin-*n*-butyl ether | Benzoin isobutyl ether |
| Acetophenone | 2,2-Diethoxyacetophenone |
| Propiophenone | Methyl phenylglyoxylate |
| Ethylphenylglyoxylate | 9,10-Phenanthraquinone |

Preferably, the photopolymerization initiator is added in an amount of 0.1–10 *phr* into the coating material. The top coating material may also contain polymeric or silicone coating surface im-



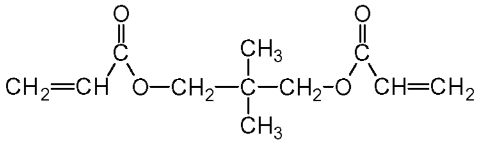
$CH_2{=}CH{-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}C({=}O){-}CH{=}CH_2$

Ethylene glycol diacrylate



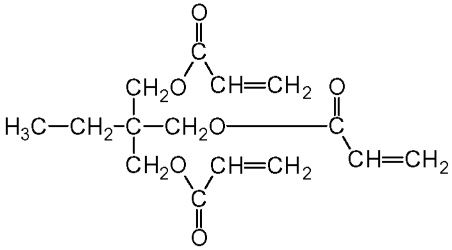
$CH_2{=}CH{-}C({=}O){-}O{-}CH(CH_3){-}CH_2{-}O{-}C({=}O){-}CH{=}CH_2$

Propylene glycol di(meth)acrylate



$CH_2{=}CH{-}C({=}O){-}O{-}CH_2{-}C(CH_3)_2{-}CH_2{-}O{-}C({=}O){-}CH{=}CH_2$

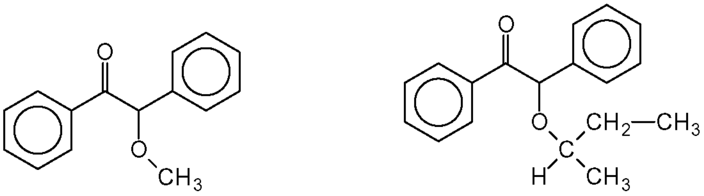
Neopentyl glycol diacrylate



$H_3C{-}CH_2{-}C[CH_2O{-}C({=}O){-}CH{=}CH_2]_3$

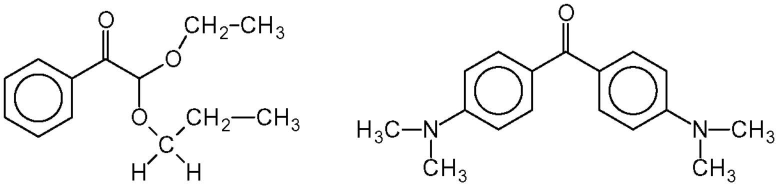
Trimethylolpropane triacrylate

**Figure 2.1** Monomers for polyvinyl compounds.



Benzoinmethyl ether

Benzoin isobutyl ether



2,2-Diethoxyacetophenone

4,4′-Bis(di-methylamino) benzophenone

Methyl phenylglyoxylate

9,10-Phenanthraquinone

**Figure 2.2** Photopolymerization initiators.

provers, flow improvers, various dyes and pigments, which are also commonly added to conventional coating materials (14).

### 2.3.2 *Metallized Plastic Molding*

A metallized plastic molding has been developed that contains a primer on the plastic substrate, on which a metallic film is deposited. Unsaturated compounds which are used for forming a primer layer are summarized in Table 2.6.

**Table 2.6** Unsaturated compounds for primer (15).

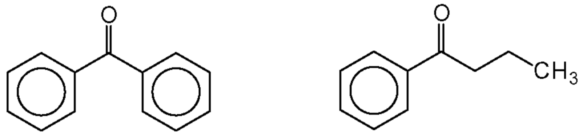
| Compound |
|---|
| Poly(ethylene glycol) diacrylate |
| Poly(ethylene glycol) sebacate diacrylate |
| Bisphenol A dioxyethyl ether diacrylate |
| 1,6-Hexanediol diacrylate |
| Neopentyl glycol diacrylate |
| Trimethylolpropane triacrylate |
| Trimethylolpropane tri(meth)acrylate |
| Pentaerythritol tetracrylate |
| Lauryl acrylate |

The primer is cured by a photopolymerization reaction. For this reason a photoinitiator is added. Suitable examples of the photopolymerization initiators are shown in Table 2.7.

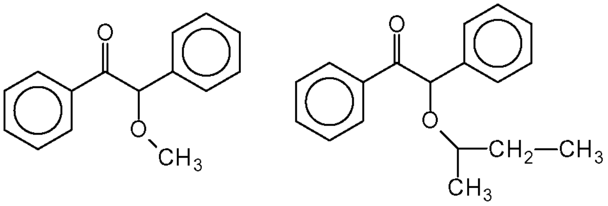
**Table 2.7** Photopolymerization initiators for primer (15).

| Compound | Compound |
|---|---|
| Benzophenone | Propiophenone |
| Benzoin | Benzoin methyl ether |
| Benzoin isobutyl ether | Methylphenyl glyoxime |
| Ethylphenyl glyoxime | Phenanthraquinone |

Photopolymerization initiators are shown in Figure 2.3. The coated substrates were treated using dry type metallic film-forming methods (15).



Benzophenone Propiophenone



Benzoin methyl ether Benzoin isobutyl ether

**Figure 2.3** Photopolymerization initiators.

## 2.4 Special Aspects

### *2.4.1 Metallized Polymer Granules*

Polymer granules which have a metal layer have been developed (16). These can be prepared by currentless chemical metallization or by combined currentless chemical and galvanic metallization.

Organic synthetic and natural polymers are generally electrical insulators. Their specific resistance is between $10^{10}$ and $10^{18}$ *Ohm cm*.

If certain polymers having a main chain with a polyconjugated structure are treated with strong oxidizing or reducing agents, their specific resistance drops from about $10^{9}$ to about $10^{1}$ *Ohm cm* (17).

However, such conjugated polymers cannot be processed by such customary methods in plastics technology, such as injection molding, extruding or laminating, and they are insoluble in conventional organic and inorganic solvents.

Another way of providing polymers with antistatic properties is to add charge transfer complexes, which are based, for example, on tetrathiofulvalene or tetracyanoquinodimethane. The incorporation of these complexes into polymer matrices is very involved, and therefore of no interest to the plastics processing industry save in very special cases.

It is also known to apply antistatic agents to the surface of a prepared plastic component or to incorporate antistatic agents during the preparation directly into the polymer matrices, examples of antistatic agents being fatty alcohols and quaternary ammonium salts.

In the first case only a temporary antistatic effect is obtained, while in the second case the incorporation of antistatic agents has an adverse effect on the original physical and chemical properties of the polymer material.

It is also known that polymer surfaces can be provided by chemical or physical means with an electrically conductive metal surface (18).

However, these metal layers have an undesirably high specific electrical conductivity. Another disadvantage is that this process is only possible in the case of certain polymers.

Another way of imparting antistatic properties to polymers is to incorporate metal filaments, metal fibers, metal powders, metallized glass, or ceramic fibers.

However, this method has the disadvantage that an antistatic effect is only obtained when a substantial amount of metal is incorporated into the polymer. The result is that, again, the physical properties, such as tensile strength, abrasion and tear resistance, the elastic modulus and extensibility, are reduced. It is also unfavorable that the distribution of metal obtained in the shaped polymer article is not homogeneous.

All these disadvantages can be overcome by providing synthetic or natural polymer granules with a metal layer using currentless chemical metallization or combined currentless chemical and galvanic metallization, and then processing the granules thus treated by methods customary in the plastics industry.

Polymer granules having a single particle volume of 0.1 $mm^3$ to 50 $mm^3$ and a metal layer of 3–25% relative to polymer, can be processed by the customary methods of the plastics industry into shaped articles which have permanent antistatic properties and screen off electromagnetic waves. The granules can have any desired shape, i.e., cubes, cylinders, spheres, rods, semispheres or pyramids.

The polymers can be homopolymers, copolymers or graft copolymers. Examples of suitable synthetic polymers are poly(propylene)

(PP), poly(vinyl chloride), poly(vinyl acetate), poly(ethylene) (PE), poly(styrene) (PS), ABS graft or copolymers, poly(butadiene), poly(isoprene), poly(ethylene oxide), polyesters, poly(amide)s, polyhydantoin, poly(urea)s, poly(imide)s (PIs), poly(carbonate)s, epoxy resins and their mixtures and alloys.

The polymers can contain fillers and additives, customary in plastics processing, such as stiffening, reinforcing, shaping or stabilizing agents. Preferable metals are nickel, copper, silver, cobalt, tin, zinc, lead, cadmium, chromium or gold, in particular copper or nickel. The surface of the granules can be activated with palladium, in particular in the form of a metallo-organic compound.

Those groups of the organic part of the above-mentioned metallo-organic compounds which are required to bond the metal are C=C or C=N double bonds and also triple bonds.

Groups which can form a chelate complex are OH, SH, CO, SC or COOH groups.

Groups which are particularly suitable for fixing the activator to the surface of the substrate are summarized in Table 2.8.

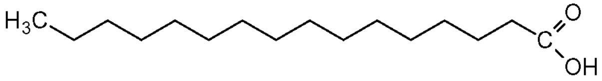
**Table 2.8** Groups for Fixing the Activator (16).

| Group type | Group type | Group type |
|---|---|---|
| Carboxylic acid | Carbonyl halide | Carboxylic anhydride |
| Carboxylate | Carboxamide | Carboximide |
| Aldehyde and ketone | Ether | Sulfonyl halide |
| Sulfonate | Chlorotriazinyl | Chloropyrazinyl |
| Chloropyrimidinyl | Chloroquinoxalinyl | Vinylsulfonic acid |
| Acrylic acid | Amino | Hydroxyl |
| Isocyanate | Olefine | Acetylene Mercapto |
| Epoxide | Oleic acid | Linoleic acid |
| Stearic acid | Palmitic acid | |

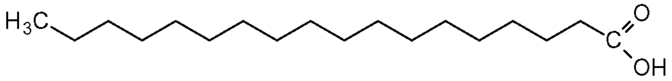
Some long-chain acids are shown in Figure 2.4.

The use of oligomeric, polymeric or prepolymeric metallo-organic compounds has the additional advantage that a smaller amount of noble metal is required per unit area for adequate activation.

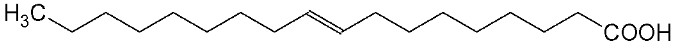
The organometallic activators are used in the form of a solution, dispersion, emulsion or suspension in an organic solvent or in the form of a mixture with an organic solvent. Solvent mixtures can also be used.



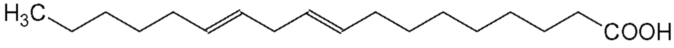
Palmitic acid



Stearic acid



Oleic acid



Linoleic acid

**Figure 2.4** Long-chain acids.

Those organic solvents are preferably used which incipiently swell the surface of the polymer. Swelling agents for specific polymers are described in the Polymer Handbook (19).

Suitable solvents are lower and higher alcohols, aldehydes, ketones, halogenated hydrocarbons, simple or saturated hydrocarbons, organic acids and esters, and liquefied gases, such as butane, propylene and 1,4-*cis*-butadiene.

Solvent mixtures can contain as further solvents naphtha, ligroin, toluene, or *n*-hexane. The activating baths can contain anionic emulsifiers, such as alkali metal salts of palmitic acid, stearic acid, oleic acid, salts of sulfonic acids which are prepared by sulfochlorinating paraffins containing 6–20 carbon atoms, nonionic emulsifiers, which can be prepared, for example, by ethoxylating long-chain alcohols or phenols, cationic emulsifiers, such as salts of long-chain amines having 12–20 carbon atoms or quaternary ammonium compounds having long-chain olefines or paraffin esters, protective colloids based on macromolecular compounds, such as gelatin, pectins, alginates, methylcellulose, ionic and neutral PU dispersions or their oligomeric derivatives, PVAs, poly(vinylpyrrolidone), poly(methyl vinyl acetate), finely divided water soluble minerals, such as alumina, kieselguhr, calcium phosphates, alkali and alkaline earth metal salts, such as NaCl, $CaCl_2$, $MgSO_4$ or $K_3PO_4$. The quantity of the additives listed above can be varied, relative to the given medium, between 0.01 and 20%.

The granules are wetted with the activating baths, the treatment period preferably being between 1 *s* and 90 *min*. After the wetting, the organic solvent is removed and the metallo-organic compound is reduced. It may be necessary to clean the granules by rinsing away reducing agent residues. The granules thus activated are subjected to currentless metallization.

The reduction in the metallization bath is carried out immediately with the reducing agent of the currentless metallization. This procedure is suitable for aminoborane-containing nickel baths or formalin-containing copper baths. Metallization baths suitable for use in the process are preferably baths containing nickel salts, cobalt salts, copper salts, gold or silver salts or their mixtures with one another. Such chemical metallizing baths are known in the technology of currentless metallization.

The granules which have been provided with an electrically conductive metal layer are, if appropriate, galvanically enhanced. Galvanizing baths which are suitable for use in the process are preferably baths containing Ni, Cu, Co, Au, Ag, Sn, Zn, Pb, Cr, or Cd salts or their mixtures. Such galvanizing baths are known in the electroplating technology.

The granules which have been provided with a metal layer are processed by means of processes customary in the plastics industry, such as extruding, calendering, blow molding, compression molding or injection molding, the last two methods being preferable. The distribution of the metal in the shaped articles obtained is largely homogeneous.

The shaped polymer articles have excellent, permanent antistatic properties. They also screen off electromagnetic waves, so that it is possible to make out of them, for example, casings for electronic calculators, which are protected against the damaging effect of such waves.

Another important use of metallized polymer granules is in the decorative field, where granules metallized with a metal layer of 0.5–5%.

Polymeric materials based on the above-mentioned granules have a high metallic effect and a completely smooth and shiny surface. Unlike present polymeric materials bearing metallic paints they are scratchproof and impact-resistant, since not only the surface but also the matrix contains metal agglomerates, i.e., pigments.

It is of course possible to obtain the same metallic effect by incorporating such granules in thermosetting plastics, such as epoxy resins and phenolic resins, or by admixing to or mixing with non-metallized polymer granules (16).

### *2.4.2 Functional Poly(propylene)*

Antioxidants that contain a PP backbone and pendant hindered phenol groups (PP-HP), with both random and tapered copolymer microstructures, have been discussed (20).

These compounds can be effectively prepared by a Steglich esterification (21, 22) of the corresponding hydroxylated PP (PP-OH) copolymers with the hindered phenol molecule containing a carboxylic acid moiety.

In the Steglich esterification, the addition of 4-dimethylaminopyridine accelerates the dicyclohexylcarbodiimide-activated esterification of carboxylic acids to such an extent that side reactions are eliminated and even sensitive acids such 2,5-cyclohexadiene-1-carboxylic acid readily form the *tert*-butyl ester (21).

Some resulting PP-HP copolymers show a significantly higher thermal-oxidative stability than a pristine PP polymer and the commercial PP products that contain a small amount of organic hindered phenol stabilizers.

A better oxidative stability was also observed in PP/PP-HP blends under elevated temperatures. Overall, the PP chain degradation temperature increases with the increase of HP concentration in the matrix. The effectiveness of the PP-HP stabilizer is attributed to its comparability and co-crystallization with the PP homopolymer, which result in a uniform distribution of hindered phenol moieties (20).

Thermograms of these compositions are shown in Figure 2.5.

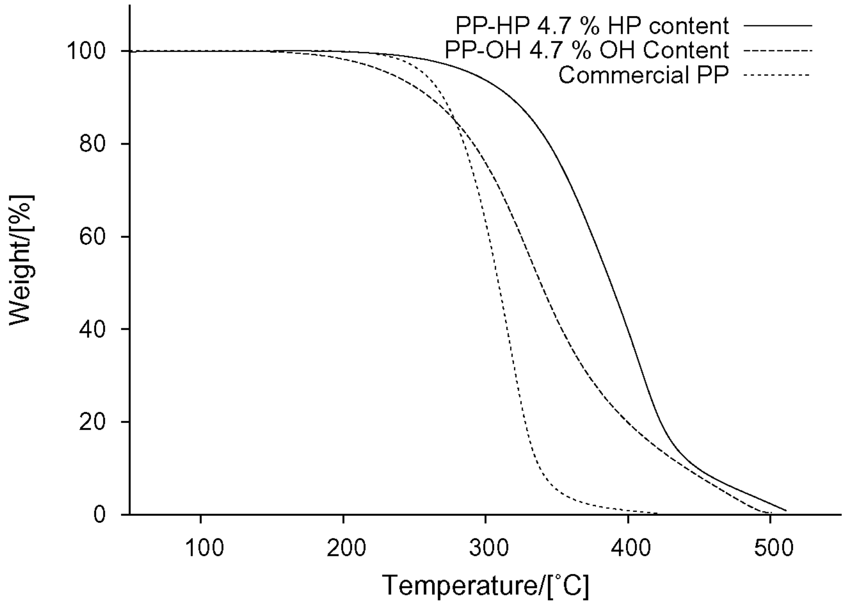


**Figure 2.5** Thermograms of compositions with hindered phenol moieties (HP) and hydroxylated PP (PP-OH) (20).

It also allows the relatively higher concentration of hindered phenol (polar) moieties in the nonpolar PP matrix without phase separation. In addition to the known advantages of polymer-bonded stabilizers, with low mobility and volatility to prevent loss through diffusion or extraction, PP-HP thin dielectric films with uniform morphology show a higher dielectric constant and maintain low dielectric loss, particularly for the tapered PP-HP copolymers with high crystallinity.

Therefore, these types of polymers may find applications in metallized polymer film capacitors (20).

### 2.4.3 *Poly(amide)*

Metallized PA films can be obtained by the reduction of PA metal chelate films using reducing agents (23,24).

In the preparation of PA metal chelate solution, a small amount of precipitate forms when a certain stoichiometric ratio of formic acid, PA, and metal salts is mixed. The precipitate formation rate is affected by the nature and the concentrations of the metal salts, the molecular weight of the PA used, and the solution temperature.

In addition, the precipitate formation rate affects the conducting surface metallic substance of reduced nylon/$CuCl_2$/$NiCl_2$ complex metal chelate film. The conducting surface is metallic Ni for low-molecular-weight nylon 4/$CuCl_2$/$NiCl_2$ film and metallic Cu for high-molecular-weight nylon 4/$CuCl_2$/$NiCl_2$ film reduced by $NaBH_4$ aqueous solution.

The precipitate consists of PA, metal salt, and formic acid. The interaction among the PA, metal salt, and formic acid appears to be by means of hydrogen bonds and ionic bonds (24).

PA metal chelate films exhibit an excellent surface resistivity around 10–10 $Ohm\,cm^{-2}$ when treated with sodium borohydride aqueous solutions.

Aqueous solutions of PA-formic acid with metal salts, and films prepared from those solutions, were analyzed by UV-visible and IR spectroscopy, respectively, in order to investigate and identify the structure of the poly(amide) metal chelates.

The factors that include the nature and concentrations of the metal salts, and the concentrations of the reducing agents, and the reduction time, which may affect the conductivity of metallized films, were investigated.

A treatment of the surfaces of these films with an aqueous solution of sodium borohydride forms a definite metallic luster appearance. The surfaces of these conductive films could be proved to be metallized by means of ESCA analysis. ESCA stands for electron spectroscopy for chemical analysis (25).

The strongly adhered metal on the films is believed to be responsible for the improvement in the electrical conductivity (23).

### *2.4.4 Poly(imide)s*

Metallized films of PIs are particularly desirable in the fabrication of large-scale integrated circuits (26). The PI is primarily used as an insulating dielectric layer. Other uses are flexible printed circuitry and photovoltaic devices. Photovoltaics are devices primarily fabricated as a flexible substrate which can withstand the temperatures associated with the deposition of amorphous silicon.

A major concern in the metallizing PI films, particularly for electronic applications, is the adhesion of the metal film to the polymeric substrate. It is necessary that the metal film will stay well-adhered to the polymer during and after processing, which often involves electroplating and selective etching of metal film off the substrate by strong acids.

This processing can lead to an undercutting of metal film and loss of adhesion. The most popular method of achieving well-adhered copper films on PI is done by sputtering. In this process, chromium is sputtered in the presence of oxygen onto the PI substrate and then copper is sputtered onto this primed substrate. It has been claimed that this pre-sputtering with chrome in the presence of oxygen results in the covalent bonding of the chrome oxide layer to the substrate. This covalent bonding mechanism may be subject to hydrolysis reaction and may generally be expected to show reduced persistence after exposure to ambient conditions (26).

An electroless plating process on a surface of an aromatic PI substrate has been described (27,28). This consists of the steps of forming a nonaqueous solution containing a Zn complex, a salt or alloy of an alkali metal in a positive valence state and at least one polyatomic association of a main group metal in a negative valence state. The polyatomic main group metal is selected from Ge, Sn, Pb, As, Sb, Bi, Si, and Te.

An aromatic polymeric substrate is chosen which is reducible by the solubilized salt and is resistant to degradation during the reaction. A redox reaction is effected between the salt in solution and the substrate by contacting the solution with the substrate for a sufficient time to simultaneously oxidize and deposit the main group metal in elemental form to produce a plated substrate. The alkali metal is then retained in the plated substrate, and the substrate becomes negatively charged by electrons transferred from the main group metal during the redox reaction (28).

A metallization process has been developed for diffusing metals into the surface of a polymeric substrate having electroactive centers and subsequently plating a metal to a desired thickness (26). A charge is first injected and reversibly stored in the PI, whose charge is subsequently used for the reduction and deposition of transition metal in elemental form.

A significant advancement of this process is the use of aqueous or methanolic solutions to carry the chemical reducing agent for the PI and the use of monoatomic ions or complexed transition metal ions capable of reducing an electroactive center in the polymer (26).

The reduction of the PI with $Te^{2-}$ is best accomplished in methanol, although the half-wave potentials for the oxidation of $Te^{2-}$ in water or methanol are essentially the same. The differences in reducing PI in water, as opposed to methanol, appear to arise from the inability of water solutions to adequately wet the polymer and facilitate rapid electron transfer. Reduction of PI using aqueous $Te^{2-}$ is generally a much slower reduction step and can produce inhomogeneous results. Surfactants added to these aqueous $Te^{2-}$ solutions have reduced the inhomogeneity.

The reductants are easily regenerated electrochemically by applying a suitable potential to the solution (26). This makes possible the use of a closed-loop system for the reduction of PI. Only electrolyte need be added to the system to make the film reduction continuous. Additionally, no special environmental problems are encountered in the use of this system. Films of copper, cobalt, cobalt/phosphorous alloy, gold and nickel can be deposited on a PI film. In detail, the metallization of PI runs as follows (26):

**Preparation 2–4:** All reductions and some oxidations are performed in an oxygen-free inert atmosphere such as nitrogen or argon. Most of the operations can be conducted in a glove box under an argon atmosphere. In this example 1 *g* of $K_2Te$, obtained from Cerac/Pure, Inc., was dissolved in 100 *ml* of methanol. Approximately 30 *min* are allowed for the dissolution of the salt. A 75 $\mu m$ thick strip of an aromatic PI, (Kapton®) was immersed into the solution for about 30 *s*, removed, rinsed in methanol and wiped clean. The resultant deeply green colored PI film strip was then ready for metallization.

An oxidizing solution of $Cu(OCOCH_3)_2 \times H_2O$ in methanol 1 $g\,l^{-1}$was prepared. The above prepared reduced green colored PI film strip was then immersed for 60 seconds in this oxidizing solution. A brilliant mirror-like reflective copper film was obtained. The copper film was thin (partially transparent when held up to the light) and electrically conductive.

**Preparation 2–5:** An aqueous solution was prepared using 0.4 *g* $VOSO_4 \times 2H_2O$ plus 3.7 *g* ethylenediaminetetraacetic acid dihydrate in 100 *ml* deionized water. Tetramethylammonium hydroxide was added in sufficient quantity to dissolve the Na2 EDTA salt and to raise the initial pH to between 8 and 9. This solution was electrolyzed at −1.4 *V* versus a Ag/AgCl reference electrode. The final pH was about 9.

A 75 $\mu m$ thick strip of an aromatic PI (Kapton®) was immersed into the solution prepared above for about 30 seconds, removed and wiped dry. The resultant deeply green colored PI strip was metallized in the absence of oxygen. An electroless copper solution held at a temperature of 43°C. was utilized. The reduced PI strip was immersed for 5 *min*. A well-adhered bright copper layer with bulk electrical conductivity was obtained.

Several other examples have been disclosed (26).

The adhesion of the metal films is quite good. Tape peel tests with an aggressive tape did not result in failure of the metal/polymer adhesion. The adhesion appears to be good even immediately after the film formation in the electroless oxidants. This promotes processing in a continuous manner when copper thickness is to be increased to 1 mil or greater by electroplating.

It is commonly observed that the adhesion of metal to polymer increases with time as metal establishes a mechanical anchorage. Copper films deposited upon PI by the above described technique were investigated by transmission electron microscopy in order to characterize the polymer/metal interface. These investigations show that the adhesion of the film to the polymer is due to a mechanical anchorage of the metal caused by the immediate diffusion of the metal complex just within the polymer surface where the reduction occurs. Metal builds on top of this diffused region forming the thick, conductive, copper film (26).

### 2.4.5 *Poly(amide-imide)s*

Poly(amide imide)s (PAIs) were synthesized by a direct polycondensation method (29). A series of PAI metal chelate films was prepared using $AgNO_3$, $CuCl_2$, and $CoCl_2$ mixed with the PAIs in *N*-methyl-2-pyrrolidone solution. These PAI metal chelate films were reduced by various reducing agents, and the reduced films exhibited low surface resistivity around 100 $Ohm\,cm^{-2}$. Using X-ray analysis, the surfaces of these conductive films could be shown to be metallized (29).

### 2.4.6 *Poly(acetylene)s*

Polymers of acetylene derivatives have a one-dimensional main chain having a $\pi$-electron conjugated bond system, and therefore exhibit electrical conductivity and also nonlinear optical effects (30). For this reason, they are under study in many areas as optical function materials and electronic function materials. Unfortunately, common poly(acetylene) derivatives are unstable to heat, pressure, and to UV light in an oxygen-containing environment.

When a compound having a diacetylenic group in part of its linear hydrocarbon chain is used to carry out chemisorption, it is possible to deposit a chemisorbed layer of a diacetylene derivative having a monolayer film thickness of the order of several tens *Å*, and it is further possible to easily obtain a chemisorbed built-up film.

Further, when chemisorption is carried out using a compound having an acetylenic group in part of its linear hydrocarbon chain, it is possible to deposit a chemisorbed layer of an acetylene derivative having a monolayer film thickness of the order of several tens *Å*, and it is also possible to easily obtain a chemisorbed built-up film.

On the other hand, in a monomolecular layer formation, when an amphiphilic acetylene derivative having hydrophobic and hydrophilic groups is used, a monomolecular film can be formed on a water surface, and further, a built-up film can be formed according to a *Langmuir-Blodgett* technique.

It has been found that a metallized poly(acetylene) having an ultrahigh molecular weight and a very long conjugated bond system which is stable in an oxygen-containing atmosphere can be formed by preparing a monomolecular layer by chemisorption (30).

$\omega$-Nonadecylynoictrichlorosilane, tricosadiynoictrichlorosilane and 1-(trimethylsilyl)-$\omega$-nonadecylynoictrichlorosilane are silane-type surfactants that can be used for chemisorption.

Then the deposited monomolecular layer is immersed in an aqueous solution containing a metal ion of Ag or Cu, to replace a hydrogen atom connected to the acetylenic group or diacetylenic group by the above metal atom under an acetylide reaction, and then immersing the deposited monomolecular layer in an organic solution containing a metal salt catalyst to polymerize the molecules at the acetylenic group in the above monomolecular layer. In this way a metallized poly(acetylene)-type ultralong conjugated polymer can be produced (30).

### *2.4.7 Silaferrocenophanes*

The synthesis of highly metallized polymers has been described (31). Acetylide-substituted silaferrocenophanes with pendent cobalt or molybdenum clusters or mononuclear organonickel substituents have been synthesized by the complexation of the triple bond (32).

Attempts to synthesize analogous platinum species yielded a platinasila[2]ferrocenophane, a result of the oxidative insertion of platinum into an ipso-cyclopentadienyl carbon-silicon bond. The synthesis is shown in Figure 2.6.

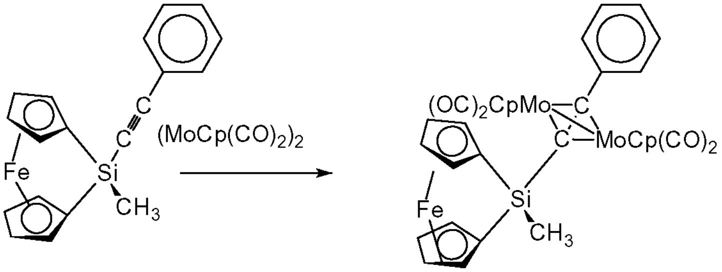


**Figure 2.6** Synthesis of acetylide-substituted silaferrocenophane (32).

Further, the compounds have been prepared via macromolecular clusterization of acetylide-substituted poly(ferrocenylsilanes). The extent of clusterization achieved was in the range of 70–75% (31).

All the highly metallized polymers were demonstrated to function as negative-tone resists in electron-beam lithography, while Co-PFS and Mo-PFS were successfully patterned by UV-photolithography, allowing the fabrication of micron-sized bars, dots, and lines. These studies suggest that the highly metallized polymers may be useful in the fabrication of patterned arrays of alloy nanoparticles for both materials science and catalytic applications (31).

### *2.4.8 Metallized Hybrid Polymers*

A hybrid polymer film consists of a base polymer film having a plasma-treated surface and a second polymer film having different surfaces (33). The first surface of the second polymer film is disposed along the first plasma-treated surface of the first polymer film.

The base polymer is chosen from thermoplastic films, including PP, poly(ethylene terephthalate), or poly(vinylidene fluoride), and others. On the other hand, thermoset films are cellulose derivatives, PI, and poly(benzoaxozole).

The second polymer films are radiation-polymerized monomer films from multifunctional acrylate or acrylated monomers that contain double bonds capable of radical polymerization.

Plasma treatment is done with gases from the group of $N_2$, Ar, Ne, $O_2$, $CO_2$, and $CF_4$. This effects a functionalization of the base film, to further improve the crosslinking of the acrylate film surface, and to remove surface charge, which improves winding and unwinding of the hybrid film.

Also, inorganic layers may be used in combination with the polymer layers to produce hybrid films for special end use. Inorganic layers include metals, metal alloys, and ceramics.

The hybrid polymer film shows both an improved corrosion resistance and an improved current carrying ability in metallized capacitors. When used in food packaging, the presence of the acrylate polymer on the top of a thermoplastic polymer, such as PP, improves the oxygen and moisture barrier of the metallized and ceramic-coated films. It also improves the mechanical properties of the barrier layer to such an extent that there is less damage of the barrier layer as a function of film elongation (33).

By adjusting the chemistry of the acrylate coatings, the surface of the hybrid films can be made hydrophobic or hydrophilic. This is useful for the application of printing inks for packaging films.

The metallized printable film can be produced in a one-step process, which eliminates the lamination of an additional polymer film that is used to protect the metal layer and provide a printable surface.

When used in electrical flexible cables, fluorinated acrylate polymers deposited on such thermoset polymer films as PI, poly(imide benzoxazole), and poly(benzoaxozole) prevent electrical tracking, and they only carbonize in the presence of electrical arcing (33).

### *2.4.9 Radiation Curable Compositions*

A thin film of metal to a nonmetallic substrate can be applied to make a metallized substrate and to provide the metallized substrate with a protective coating (34). Such coated, metallized substrates are useful for containers and container caps for cosmetics.

The substrates for such articles often are composed of heat-sensitive materials, such as heat-sensitive plastics, which can distort when exposed to elevated temperatures. So, it would be desirable to provide coatings for such metallized substrates that can be cured efficiently at temperatures below the temperatures at which such heat-sensitive substrates distort.

Moreover, the coatings for such substrates should not only be decorative, but also should be highly adherent to the metallized substrate. Further, they should be mar resistant and resistant to degradation by various solvents (34).

A radiation curable composition has been developed based on curable esters of polyfunctional hydroxyl groups containing carboxylic acids. When the resin is utilized in a composition for application to a metallized substrate, the composition also contains a polymer having a glass transition temperature equal to or higher than −17°C. This polymer is selected from an acrylic polymer or a polyester polymer.

In a preferred procedure for preparing such a resin, dimethylol propionic acid is reacted at 150–210°C. An esterification catalyst is utilized, such as butyl stannoic acid, dibutyl tin oxide, antimony oxide, dibutyl tin dilaurate, *p*-toluene sulfonic acid, and methane sulfonic acid (34).

Then, this reaction product is reacted with an $\alpha,\beta$-ethylenically unsaturated carboxylic acid, e.g., acrylic acid or methacrylic acid.

These radiation curable resins are particularly useful for coatings over nonmetallic substrates such as acrylonitrile-butadiene-styrene plastics, having an adherent, thin film of metal deposited by vacuum metallizing, sputtering, electroless deposition, or electroplating. The products can be cured by UV radiation. Preferred are UV light emitting lamps of the medium pressure mercury vapor type (34).

### 2.4.10 Heat Treatment

Metallized polymer films were prepared from poly(acrylonitrile) (PAN) or PVA silver chelate solution by heat treatment (35). These metallized films exhibited low surface resistivity around 100

*Ohm* $cm^{-2}$. The surface of these conductive films was proved to be metallized using X-ray analysis. The metal adhered on the film was believed to be responsible for the improvement of electrical conductivity. The effects of types and concentrations of silver salt, types and volume of solvent, and drying time on the conductivity of metallized films were investigated.

Also, polymer metal chelate solutions could be prepared by metal salts mixed with the polymers containing functional groups such as PAN or PVA, and PU (36). These polymer metal chelate solutions were cast onto metal plates, whose oxidation potentials were greater than those of the metal of polymer metal chelate solutions. After a heat treatment, the metal ions in the polymer films were reduced to metal on the surface, thus, metallized conductive polymer films could be obtained.

## 2.5 Special Uses

### 2.5.1 *Films for Packaging Oxygen-Sensitive Materials*

In the manufacture of films for packaging oxygen-sensitive materials, including meats and dairy products, the resinous material should be impermeable to atmospheric gases and other vapors.

Unfortunately, most common organic polymers, such as PE, PS and many other polymers, are not sufficiently resistant as such to the transmission of atmospheric gases to be useful for applications that require impermeable resinous materials.

Therefore, it has become a common practice to coat such polymers with suitable materials in order to make the polymers more resistant to the transmission of gases (37).

A barrier polymer, such as a polymer of vinylidene chloride or vinyl chloride, has been suggested to improve the impermeability of the resinous substrate (38).

Alternatively, the permeability of the resinous material can be decreased using a metal coating. A surface of a plastic article can be metallized without substantial pinholes, holidays and other defects by initially coating the surface with an aqueous colloidal dispersion of an organic polymer, particularly a barrier polymer such as poly(vinylidene chloride) (PVDC).

Then, the organic polymer coating is treated in order to make it metallizable. Subsequently, an overcoating of the treated organic polymer coating is done with a metal to form a thin metal layer adherent to the organic polymer layer.

The resulting metallized plastic article can be optionally treated with an additional amount of an aqueous colloidal dispersion of an organic polymer or metal that is essentially impermeable to atmospheric gases and other vapors. Subsequently, an example of preparation is given (37):

**Preparation 2–6:** PS is extruded into a film having a thickness of 95 *μm*. One surface of the film is surface sulfonated to a degree of about 0.2 $\mu g cm^{-2}$ of sulfur trioxide equivalents by contacting the surface with dry air containing 2 % sulfur trioxide at 25°C for approximately 1 *s*.

Then, the surface sulfonated film is coated with a vinylidene chloride polymer by applying a 35% solid aqueous colloidal dispersion having an average particle size of 0.22 *μm* using a Meyer rod. Excess amounts of the dispersion are allowed to drain off and the remaining dispersion dried to a continuous coating.

The coated surface of the film is then surface sulfonated to a degree of about 0.2 $\mu g cm^{-2}$ of sulfur trioxide equivalents per square centimeter by contacting the surface with dry air containing 2% sulfur trioxide at 25°C for approximately 1 *s*.

A metallizing bath is prepared by mixing one part each of the following solutions:

0.6% $Ag(NH_3)_2NO_3$ in $H_2O$,
0.30% NaOH in $H_2O$, and
0.15% glucose and 0.15% fructose in $H_2O$.

The surface sulfonated coated film is dipped into the bath and metallization is completed within 1 *min*. The metallized film is removed from the bath and washed with water. The resultant film shows essentially no pinholes, holidays or similar defects on visual inspection.

The metallized film is overcoated using the polymer and techniques employed in coating the plastic substrate. The latex is dried to a continuous overcoat. A cross-section of the resultant metallized film is prepared and examined under a magnification of 1900. A four-layer film is seen having a total thickness of about 108.5 *μm* of which 95 *μm* is attributable to the substrate. The PVDC coating on the substrate is measured to be 8.8 *μm* thick, the silver layer is 0.31 *μm* thick and the PVDC coating over the silver layer has a thickness of 4.4 *μm*. When tested for permeability, the oxygen transmission rate of the resultant film is found to be about 0.131 $cm^3 d^{-1} at^{-1}$, wherein the oxygen transmission rate is determined using a mass spectrometer to measure permeated oxygen at 20°C for 24 *h*.

Glucose and fructose are shown as Fischer projection in Figure 2.7.

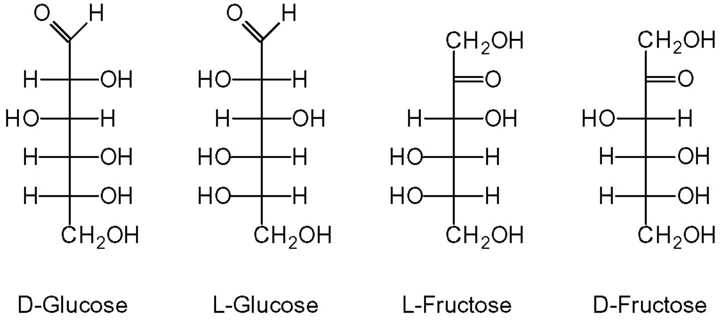


**Figure 2.7** Glucose and fructose.

### 2.5.2 *Margin Pattern Forming*

A process for producing a metallized plastic film consists of the steps of (39):

1. Applying to the outer surface of a rotating rubber roll a masking oil selected from the group consisting of oils which have such evaporation characteristics so as to be suitable for use in evacuation systems wherein a pressure of $10^{-2}$ to $10^{-3}$ *torr* is maintained, the outer surface of the rubber roll being provided with a pattern of projections and indentations,
2. Transferring the masking oil present on the surface of the projections on the rubber roll to a continuously moving plastic film to form an oil pattern on the plastic film, wherein sufficient oil is applied in step 1 to the rubber roll in order for the thickness of the oil pattern on the plastic film to be in the range of 2 $\mathring{A}$ to $5 \times 10^3 \mathring{A}$,
3. Immediately subjecting the plastic film coated with the oil pattern to a process of vacuum evaporation and deposition of a metal, wherein the presence on the plastic film of the oil having the explained evaporation characteristics and thickness prevents the metal from depositing on the portions of the surface of the plastic film which are coated with oil,

whereby a film of the metal is deposited only on the portions of the surface of the plastic film which are not coated with the oil, and

4. After the deposit of the metal film, allowing the oil present in the form of a pattern on the surface of the plastic film to evaporate completely, whereby a patterned metal coating remains on the surface of the plastic film.

The margin pattern forming method is useful for the fabrication of metallized film capacitors, but is also useful for forming intricate patterns of ornamental vacuum-evaporated films (39).

### *2.5.3 Surface Reflectors*

By manufacturing articles from thermoplastic materials and metallizing the articles at their surface reflectors can be formed (40).

Most thermoplastic materials require extra processing steps prior to the metallization, e.g., application of primers or chemical etching. However, certain types of materials can be metallized without any extra processing steps. These materials are poly(ester carbonate)s or blends of poly(ester carbonate)s and poly(carbonate) (PC). This is surprising since PC cannot be metallized in good quality without extra processing steps prior to the metallization step (41).

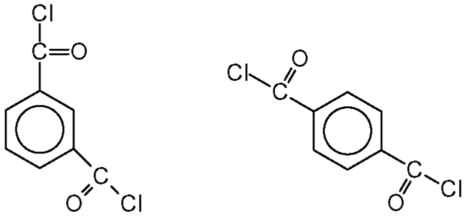
Suitable poly(ester carbonate)s can be obtained by an esterification reaction of a carbonate precursor such as phosgene or diphenylcarbonate, a diphenol such as bisphenol A and an ester precursor such as a difunctional carboxylic acid such as terephthalic acid or an ester-forming derivative thereof. Poly(ester carbonate)s have ester bonds and carbonate bonds in their polymer chain. Suitable poly(ester carbonate)s have been described (42). A process for the preparation of poly(ester carbonate)s has been described (43,44).

The ester bonds can also be obtained from aliphatic dicarboxylic acids or mixtures of aliphatic and aromatic dicarboxylic acids (45, 46).

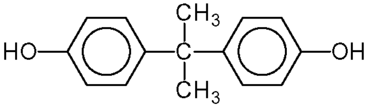
Aromatic PCs are generally prepared by reacting a dihydric phenol compound with a carbonate precursor, for example, phosgene, a halogen formate or a carbonate ester.

Dihydric phenols which may be used in the preparation of the aromatic PCs are mononuclear or polynuclear aromatic compounds which comprise two hydroxy radicals each directly bonded to a carbon atom of an aromatic nucleus. The dihydride phenols may be substituted with one or more halogen atoms or one or more alkyl groups. Branched PCs are also known to be suitable (47).

In detail, the following materials have been tested: A polyestercarbonate in the form of pellets derived from bisphenol A, terephthaloylchloride and isophthaloylchloride. As aromatic PC a homopolymer in the form of pellets derived from phosgene and bisphenol A was used (40,41). These monomers are shown in Figure 2.8.



Isophthaloylchloride Terephthaloylchloride



Bisphenol A

**Figure 2.8** Polyestercarbonate monomers.

## 2.5.4 *Electrical Applications*

### 2.5.4.1 *Stripping Apparatus for Condenser*

A stripping apparatus for stripping a metal film from a metallized plastic film has been developed (48). A metallized plastic film for a condenser is prepared by vacuum vapor deposition of a metal film, such as aluminum, onto one side of an extremely thin plastic film. In a condenser using such a metallized plastic film, when wound the cut ends of metal film wound one upon another, often contacting to cause a short circuit.

In order to prevent such a short circuit it is necessary to partially strip the deposited metal film from the plastic film. In such a metallized plastic film, the beginning part of the winding is stripped and also a fixed length of metal film at regular intervals is stripped according to volume and pressure conditions.

The stripping apparatus is simple and compact, in comparison with a conventional apparatus. Here, the aluminum foil is not wastefully used, thereby resulting in remarkable cost savings (48).

### 2.5.4.2 *Electrical Capacitor*

A method for the manufacture of a capacitor composed of a consolidated winding of metallized plastic has been disclosed (49).

Here, two regenerably thin, metallized bands on plastic plies are layered on a drum to form an initial capacitor. The initial capacitor is subdivided into the desired individual capacitors perpendicular to the layer planes. For a plurality of plastic plies and coatings forming a potential mother capacitor, non-active cover plies are provided, parting plies are arranged thereon and cover plies are in turn arranged thereon and the plastic plies that have the coatings are in turn arranged thereon for the next mother capacitor.

The initial capacitor which has been formed in this fashion is established with end contact layers and is subsequently subdivided in the region of the intermediate parting plies and in a perpendicular direction. In particular, the steps of fabrication are as follows (49):

1. The two metallized bands are provided with intermittent, metal-free insulating strips before or during winding. Laser beams generate the metal-free strips in the regions of the edges of the metallized bands and spaced at intervals in a winding direction such that the insulating strips lie in a plane perpendicular to the winding axis when wound onto the drum. Both the ends as well as the beginnings of the insulating strips extend into the region of the subsequent incision or go slightly beyond this region.
2. When being wound onto the drum, the bands are guided such that the centers of the insulating strips of the upper

band are arranged symmetrically above the centers of the interstices between the insulating strips of the lower band in the finished mother capacitors.

3. After the winding and consolidation of the initial capacitor or, respectively, the mother capacitors, and while still on the drum, at least those end faces formed by the edges are provided with a metal layer by metal spraying.
4. Before or after dividing the initial capacitor into individual mother capacitors, incisions are made perpendicular to the winding direction in the middle between two respective cut lines from both sides of the mother capacitor. The two projections of each capacitor arise due to the width and depth of these incisions.
5. The mother capacitors are separated into the individual capacitors, potentially after fastening power leads thereto, by making insulating saw cuts both along cut lines which proceed through the centers of the insulating strips, as well as along a cut line which lies parallel to the edges in the middle of the mother capacitor.
6. Finally, the individual capacitors are finished by applying cap-shaped or other power leads, insofar as these were not already attached in the step before.

The extremely thin plastic layer is produced by means of a lacquering process and is composed of a material selected from acetylcellulose, PC or an epoxy resin lacquer. It is especially advantageous when the plastic layers are manufactured by glow polymerization from the vapor phase. The metal layers are manufactured by the Schoopage process, i.e., metal spraying (50).

This metallizing process is named Schoopage process after the Swiss engineer *Max Ulrich Schoop*, who invented a combustion spray application for tin and lead (51–53).

### *2.5.4.3 Printed Circuit Boards*

The fabrication of molded, one-piece blanks for printed circuit boards and molded one-piece articles, such as printed circuit boards, has been described. The processes for forming the blanks and metallized articles include two separate molding steps to form portions of the articles (54).

It has been discovered that a polymer article with an adherent metallic surface pattern may be formed by a two-shot molding technique in which one molding shot utilizes a crystalline polymer resin and the other molding shot utilizes an amorphous polymer resin. The surface areas of the article which are to have a metallic area thereon are formed of the amorphous polymer resin and the surface areas of the amorphous polymer resin, and the surface areas of the article which will not have metal are formed of the crystalline polymer resin.

The article formed by two-shot molding is adhesion promoted by conventional treatment techniques such as exposing the surface areas of the article to strong oxidizers or to a solvent followed by strong oxidizers. The portion of the surface formed of amorphous polymer resin is made hydrophilic and receptive to adherent metallization by the adhesion promotion treatment. The portion of the surface formed of crystalline polymer resins is substantially unaffected by the adhesion promotion treatment and remains hydrophobic and resistant to adherent metallization. Metallization is accomplished by conventional techniques such as activation and electroless plating.

The crystalline thermoplastic resin can be selected from the group of polyesters, poly(phenylene sulfide) and poly(ether ether ketone). The amorphous, high temperature thermoplastic resin compound includes a catalyst treated filler for electroless metal deposition and can be selected from the group consisting of poly(sulfone), poly(ether sulfone), and poly(ether imide). In detail, the process consists of the steps of (54):

1. Molding a first electrically insulating material into at least one first predetermined shape, the first material being either resistant to adhesion by an adhesion promotion process, or non-catalytic and incapable of being rendered catalytic for adherent metallization by an activating process, and
2. Forming a second electrically insulating material into at least one second predetermined shape, the second material being capable of adhesion promotion by an adhesion promotion process and either catalytic for adherent metallization, or capable of being rendered catalytic for adherent metallization by an activating process, and interconnecting the first and second shapes to produce the one-piece, non-conductive ar-

ticle wherein selected surface areas of the article are suitable for adherent metallization and remaining areas defined by the first shape are resistant to adherent metallization.

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# 3

# Properties and Methods of Measurement

## 3.1 Standard Test Methods

Test methods for metallized plastics are summarized in Table 3.1.

**Table 3.1** Test methods for metallized plastics.

| Standard | Description | Reference |
|---|---|---|
| ASTM B117 | Salt Spray Test | (1) |
| ASTM B380-97 | Corrodkote Test | (2) |
| ASTM B368 | CASS Test | (3) |
| ASTM B532 | Recommended Practice for Evaluation of Appearance of Plated Plastics | (4) |
| ASTM B533 | Peel Strength Measurement of Plated Plastics | (5) |
| ASTM B659 | Standard Guide for Measuring Thickness of Metallic and Inorganic Coatings | (6) |
| ASTM B571 | Adhesion of Metallic Coatings | (7) |
| ASTM B604 | Decorative Electroplated Coatings for Plastics | (8) |
| ASTM D2247 | Humidity Test | (9) |

### *3.1.1 Requirements for Decorative Coatings*

The ISO standard 4525:2003 specifies the requirements for decorative, electroplated coatings of nickel plus chromium with and without copper undercoats on plastics materials (10). It permits the use of either a copper or ductile nickel undercoat to satisfy thermal cycle requirements.

### *3.1.2 Corrodkote Method*

The standard ASTM B380-97 deals with the the Corrodkote method of evaluating the corrosion performance of copper/nickel/chromium and nickel/chromium coatings electrodeposited on steel, zinc alloys, aluminum alloys, plastics and other substrates (2). The Corrodkote test is an accelerated test used for determining plating corrosion resistance of electrodeposits. It is performed by putting Corrodkote mud as well as a dried specimen under testing within a moist chamber (11). In this test, a Corrodkote mud is made by combining:

1. 7 $ml$ of copper nitrate at 5 $g\,l^{-1}$,
2. 33 $ml$ of ferric chloride at 5 $g\,l^{-1}$,
3. 10 $ml$ of ammonium chloride at 100 $g\,l^{-1}$, and
4. 30 $g$ of kaolin clay.

### *3.1.3 Copper-Accelerated Salt Spray Test*

The CASS test is a copper-accelerated acetic acid salt spray test (12). It was discovered in 1945. The method involves adding acetic acid to a solution containing salt used in salt spray tests. This method is much more corrosive than the ordinary salt spray method of testing. The CASS test is widely employed and is useful for specification acceptance, simulated service evaluation, manufacturing control, and research and development (3). It was developed specifically for use with decorative, electrodeposited nickel/chromium and copper/nickel/chromium coatings. Use of the test has improved the quality of electroplated parts and led to the development of new and superior electroplating processes.

### *3.1.4 Visual Defects*

The ASTM standard B532-85 limits the amounts and types of visual defects that can be tolerated on decoratively electroplated surfaces of plastic products. The appearance of surfaces will be separately evaluated depending on the prominence of the surface under conditions of ordinary use (4).

### *3.1.5 Peel Strength*

The peel strength of metal electroplated plastics can be evaluated by ASTM B533-85 (5). The force required to separate a metallic coating from its plastic substrate is determined by the interaction of several factors:

- The generic type and quality of the plastic molding compound,
- The molding process,
- The process used to prepare the substrate for electroplating, and
- The thickness and mechanical properties of the metallic coating.

By holding all others constant, the effect on the peel strength by a change in any one of the above-listed factors may be noted. Routine use of the test in a production operation can detect changes in any of the above-listed factors. The peel test values do not directly correlate to the adhesion of metallic coatings on the actual product.

When the peel test is used to monitor the coating process, a large number of plaques should be molded at one time from the same batch of molding compound used in the production moldings to minimize the effects on the measurements of variations in the plastic and the molding process.

The ASTM B533-85 test method gives two procedures for measuring the force required to peel a metallic coating from a plastic substrate (5).

1. One procedure utilizes a universal testing machine and yields reproducible measurements that can be used in research and development, in quality control and product ac-

ceptance, in the description of material and process characteristics, and in communications.

2. The other procedure utilizes an indicating force instrument that is less accurate and that is sensitive to operator technique. It is suitable for process control use.

### 3.1.6 *Thickness*

The standard ASTM B659-90 summarizes the methods for measuring the thickness of metallic and inorganic coatings, including electrodeposited, mechanically deposited, vacuum deposited, anodic oxide, and chemical conversion coatings (6).

### 3.1.7 *Adhesion*

ASTM B571-97 describes tests that are useful for production control and for acceptance testing of the adhesion of coatings (7). A perfect adhesion exists if the bonding between the coating and the substrate is greater than the cohesive strength of either. Such adhesion is usually obtained if good electroplating practices are followed.

### 3.1.8 *Thermal Cycling*

ASTM B604-91 establishes the requirements for several grades and types of electrodeposited copper plus nickel plus chromium coatings on plateable plastic substrates where appearance, durability and resistance to thermal cycling are important to service performance (8).

### 3.1.9 *Water Resistance*

ASTM D2247-11 covers the basic principles and operating procedures for testing water resistance of coatings by exposing coated specimens in an atmosphere maintained at 100% relative humidity so that condensation forms on the test specimens (9).

Water can cause the degradation of coatings, so knowledge of how a coating resists water is helpful for assessing how it will perform in actual service. Failure in tests at 100% relative humidity may be caused by a number of factors, including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. This practice is therefore useful for evaluating coatings alone or complete coating systems. Tests at 100% relative humidity are used for quality control for coatings and substrate treatments.

The test chamber can be a small laboratory cabinet or a room large enough to hold an automobile or a truck. Some automobile manufacturers test completed vehicles in rooms maintained at 100% relative humidity. Corrosion tests can be conducted, as the condensate dripping off the test articles is not recirculated (9).

## 3.2 Interface Properties

To understand the macroscopic adhesion of metallized plastics, the metal-organic bonding chemistry at metal-polymer interfaces must be investigated. Studies of the electronic and vibrational structure and the morphology of metal-polymer interfaces have been reviewed (13).

### 3.2.1 *Morphology*

The morphology of a metal-polymer interface is important for many properties, e.g., the adhesional strength (14). By varying of the conditions of preparation it is possible to obtain different morphologies.

Examples have been summarized, on how metal-polymer interfaces with different morphologies can be prepared by evaporating noble metals onto chemically different polymers, i.e,. bisphenol-trimethyl cyclohexane poly(carbonate), pyromellitic dianhydride-oxydianiline poly(imide), and on Teflon® AF 1601.

The interfaces were characterized using transmission electron microscopy, X-ray photoelectron spectroscopy, and atomic force microscopy. The combination of these techniques allows one to determine morphological parameters such as the concentration and distribution of metal clusters at the surface and in the near-surface region.

Using low deposition rates and elevated temperatures, spread-out metal/polymer interfaces can be formed, whereas the use of high deposition rates and moderate temperatures results in relatively sharp interfaces (14).

Another approach to obtain a defined morphology is to form large metal clusters of 10–30 *nm* diameter on the polymer surface and embed them into the polymer in a controlled manner by a subsequent annealing process (14).

#### 3.2.1.1 XPS Investigation

The chemical interactions of thermally evaporated gold and aluminium with polymer substrates have been elucidated by X-ray photoelectron spectroscopy (15). As polymers, poly(ethylene), poly(propylene), poly(styrene), poly(ethylene terephthalate), poly(ether ether ketone), poly(vinyl alcohol) and silicone polymers were tested.

From the core level shifts in X-ray photoelectron spectroscopy and intensity measurements, the mechanism of adsorption of metal atoms on specific acidic sites on polymer surfaces has been investigated.

The detailed mechanism and also the interface morphology and the growth mechanism are governed by metal-metal and metal-polymer interactions (15).

### 3.2.2 *Sliding Wear*

The particles that are generated in sliding wear can be analyzed by coupling a modified Taber abraser test with a liquid particle count analysis of the generated particles (16).

By combining these two methods, a differential analysis of the size of particles as a function of sliding distance can be obtained, thus making it possible to qualify metal coatings on plastics for use in particle-sensitive environments.

The particle generation function for plastics metallized by a magnetron sputter deposition method was determined. The counterbody was an aluminium slider (16).

### 3.2.3 *Promoting Adhesion*

In the manufacture of printed circuit cards and boards, a dielectric sheet material is employed as the substrate (17). A conductive circuit pattern is provided on one or both of the major surfaces of the substrate. A conductive pattern can be formed on the surface of the substrate using a variety of known techniques, including the subtractive technique and the additive technique.

In the subtractive technique, a blanket layer of copper on the substrate is selectively etched to form the desired circuit pattern. A pattern in the metallic surface such as copper can be etched by applying to the surface a photoresist, exposing the photoresist through a pattern of actinic radiation, removing the exposed or unexposed portion of the resist depending upon the type of resist to expose the underlying metal, and then etching the exposed metal with a suitable etchant.

In the additive process, the photoresist is applied to the surface of the substrate, followed by being exposed through a pattern to actinic radiation and removing the exposed or unexposed portions of the resist depending upon the type of resist employed to expose the underlying substrate and the desired circuitry to be subsequently provided. Next, the exposed substrate is typically coated with a metallic layer, such as copper, from an electroless plating bath followed by electroplating to achieve the desired line thickness.

However, the bond of the photoresist or photoactive layer to the metal surface has not always been adequate, especially for exposure to various plating baths or etching compositions. The adhesion of photoresists to the underlying metallic surface is critical not only in fine-line subtractive circuitization, but also in other photoresist-based manufacturing processes such as pattern electroplating and solder mask applications. In solder mask applications, a photoactive polymeric solder mask is applied and defined by photolithographic techniques to uncover those underlying portions whereby solder is to be deposited while protecting other areas from having the solder deposit.

In view of the adhesion problems between these polymers and underlying metallic surfaces, a number of surface texturing/screening processes have been suggested for enhancing such adhesion.

For example, a pumice on foil copper to roughen its surface is done. In the case of subtractive circuitization, a sulfuric acid pretreatment is done. A vapor blast treatment of gold can be done in the case of certain solder mask applications.

A method for improved bonding of polymers to metallic surfaces has been described (17). It has been found that polymers can be firmly and adherently bound to the desired metallic surface by employing a water-soluble polymeric material, which prevents curling or lifting of the other polymer from the metallic surface and, consequently, prevents undercutting during etching in the case of photoactive polymers. Examples of some water-soluble polymeric materials include polymers from acrylamides, amidoamines and acrylic acids (17).

A suitable cationic poly(acrylamide) (PAAm) is commercially available under the tradename POLYTEC® 7M from Polyset, Inc. Another commercially available cationic polymer is a cationic poly(amidoamine) under the tradename Cartaretin® available from Sandoz Chemicals. A commercial nonionic PAAm is POLYTEC® 31PX from Polytec, Inc. (17).

## 3.3 Combustion of Metallized Polymers

The combustion of metallized polymers has been reviewed (18).

Ceramics with magnetic cobalt iron alloy nanoparticles can be obtained by the pyrolysis of a highly metallized organometallic polymer precursor (19). This precursor is a poly(ferrocenylsilane) with pendant cobalt clusters. Depending on the pyrolysis temperature, either superparamagnetic or ferromagnetic particles may be formed.

### *3.3.1 Cobalt Nanoparticles*

Polyhedral oligomeric silsesquioxane (POSS) moieties have been introduced into an organometallic polymer to aid the formation of stable Co nanoparticles through the solid state pyrolysis process (20). The polymers were synthesized as shown in Figure 3.1.

Also, the analogue material without POSS groups was prepared. The characterization of both materials revealed that the introduction of POSS groups into the polymer could effectively hinder cobalt nanoparticles from sintering into larger particles, even at high pyrolysis temperatures.

In particular, the silicon-oxygen cage of the POSS groups could be converted into silicone oxide materials, which cover the surface of cobalt particles after pyrolysis. Thus, the obtained nanospheres had a unique architecture with a much smaller and uniform size. The Co nanoparticles formed were in the range of 30–80 *nm* (20).

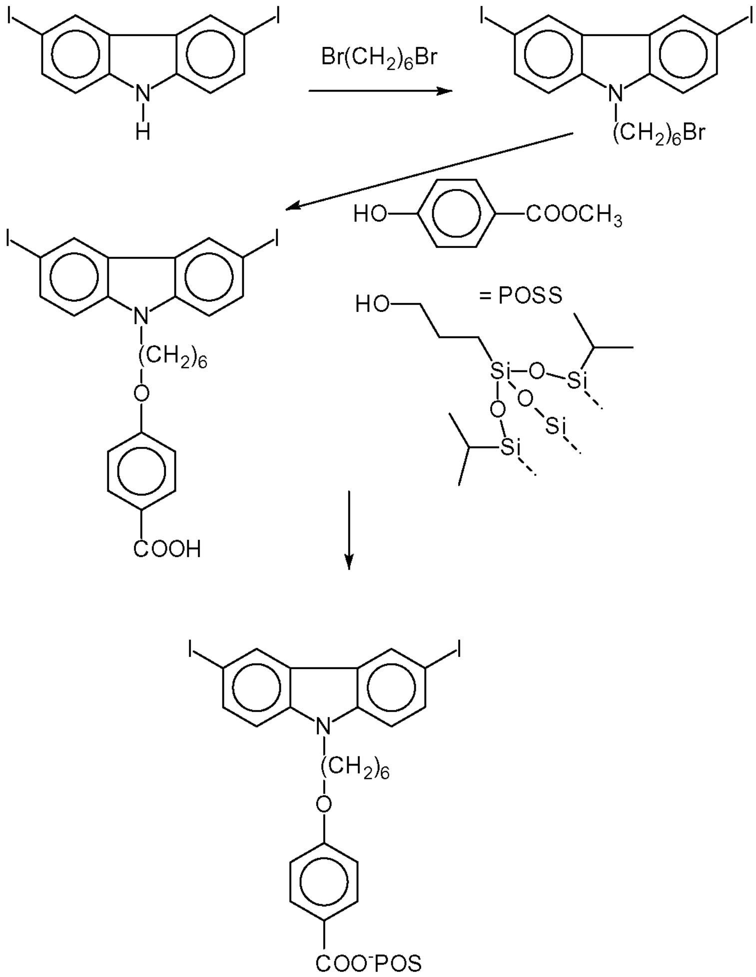

**Figure 3.1** Introduction of POSS moieties into an organometallic polymer (20).

## 3.4 Fluorine Diffusion in Metallized Polymers

A $^{19}F^{16}O$ nuclear reaction analysis technique has been used to quantitatively determine fluorine concentration and distribution in fluorinated polymeric films (21). By varying the proton beam energy over a suitable range and measuring the $\gamma$-ray yield at each step, combined with the knowledge of energy loss per unit length of the film, the fluorine depth profile can be obtained.

The diffusion of fluorine at the aluminum/fluorinated parylene interface could be clearly identified after the sample was annealed at 450°C for 2 *h*. The ion beam technique provides an attractive method to characterize the stability of the metal-fluorinated film interface (21).

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*Metallized and Magnetic Polymers: Chemistry and Applications.* Johannes Karl Fink.

# 4

# Fields of Application

The replacement of metal articles by plastic items offers the advantages of lower cost, higher production speed, wider design latitude, weight savings and fewer corrosion problems in view of the applicable extrusion and injection molding techniques (1).

However, for many applications, a metallic coating of the polymeric article is desirable, since in that way the hardness, wear resistance, shiny appearance and metallic feel characteristic of metals is imparted to the polymeric substitutes (1).

Metallized polymeric films are commonly employed for heat panels, printed circuit boards, electromagnetic shielding plates, capacitors, acoustic diaphragms, heat-reflecting boards, antistatic boards, or electrophotography (2).

The plating of plastic articles has found application in shielding electromagnetic interference from electronic equipment. This effect causes problems to advanced electronic devices of great sensitivity (1).

## 4.1 Shielding Electromagnetic Interference

There are many methods available for shielding electromagnetic interference (EMI). However, shields made from metal are heavy and complex in form. On the other hand, a metal coating on the surface of a plastic article for making EMI shield may be easily scratched to partially lose its shielding efficiency. Once the scratched scraps, which are electrically conductive, drop onto a printed circuit board of an electronic product, a short circuit may be caused to deteriorate the electronic product. Also, a metal coating may increase the problems of environmental protection.

Several plastic molding processes have been published. These processes incorporate metal materials into the resin compositions for making EMI shields.

For example, a molding composition has been developed that contains a thermosetting resin binder and an electrically conductive filler, such as particles of carbon black, graphite, and a conductive metal for achieving a shielding effect to the emissions of electromagnetic interference (3). However, in the process of blending the resin with the fillers, the fillers can be easily clustered, resulting in an inhomogeneous dispersion. This diminishes the shielding effectiveness.

Also, fiber fillers and flake fillers may also be considered to substitute the particulate fillers. However, the process of using fiber fillers is costly and uneconomical for commercial production (4). Another disadvantage is that flake fillers, when used in the processing steps of resin blending, pelleting and injection molding, may be easily broken to reduce the electrical conductivity, thereby also decreasing the EMI shielding effect of the molded product.

An improved process for making homogeneously metallized plastic pellets for molding effective EMI shields has been developed. This process uses the steps of (4):

1. Metallizing a laminated plastic sheet by sandwiching an electrically conductive metal foil in between two plastic films,
2. Slicing the metallized laminated plastic sheet into a plurality of metallized plastic strips,
3. Wetting and binding the metallized plastic strips, which have been radially arranged, with a thermoplastic resin matrix to form a metallized plastic bar by pultrusion processing,
4. Cutting the pultruded metallized bar to obtain homogeneously metallized plastic pellets for making effective EMI shields.

The thermoplastic film can be selected from an acrylonitrile-butadiene-styrene copolymer or poly(ethylene) (PE). The electrically conductive metal foil may be selected from aluminum, copper, silver, or nickel. The metal foil in between the two plastic films is bonded by a coupling agent to form the metallized laminated plastic sheet. As coupling agent, zircoaluminate or tri(dioctylpyrophosphato)titanate can be used (4).

## 4.2 Microwave Components

A method of fabricating a microwave waveguide component that is capable of transmitting microwave energy can be performed by the steps of (5):

1. Preparing the surface of the component by immersing the component into a preselected swellent to chemically sensitize the surface, etching the component to chemically roughen the surface, rinsing the component in cold water to remove etchant residue, immersing the component in a preselected neutralizer to stop the etching process, rinsing the component in cold water to remove neutralizer residue, and etching the component in ammonium bifluoride/sulfuric acid to remove residual glass fibers exposed during the initial etching step,
2. Catalyzing the surface of the component by immersing the component into a preselected catalyst preparation solution to remove excess water from the surface, catalyzing the component using a palladium-tin colloidal solution to promote copper deposition, rinsing the component in cold water to remove residual solution, activating the catalyst by stripping excess tin from the catalyzed surface, and rinsing the component in cold water to remove solution residue,
3. Depositing a thin copper layer by immersing the parts into a copper strike solution, and rinsing the component in cold water to remove residual solution,
4. Drying the component to increase copper adhesion, and
5. Depositing a thick copper layer by electroless copper plating the surface of the component to achieve a plating thickness of approximately 7.6 $\mu m$ (300 $\mu in$), rinsing the component in cold water to remove residual solution, and drying the component.

As plastic materials, a modified poly(phenylene oxide), a 30% glass filled poly(ether imide), and fiber reinforced thermosetting plastics have been used (5).

When a thermoset would be used in place of a thermoplastic in the fabrication of microwave components, it is expected that increased dimensional tolerances would be obtainable, since the crosslinked plastic will not creep This dimensional stability is achieved at the expense of molding rate, since thermoset molding time is longer than that for a thermoplastic to allow for material curing (5).

## 4.3 Conductive Fibers

Conductive fibers play a significant role in the areas of aerospace, microelectronics, medicine, precision vehicles, and the automotive industry due to their electric properties (6).

Ultra-high molecular weight poly(ethylene) (UHMWPE) fibers are one of the materials for conductive fibers. This is because the fibers have high tensile strength and module, lower density than any other organic fibers, perfect wear resistance, low friction, and excellent toughness.

Also, the comprehensive properties of UHMWPE fibers are better than other high-performance materials such as amide fibers, carbon fibers, and glass fibers.

There are several conventional procedures to fabricate conductive fibers, such as doping or coating with conductive materials, spinning conductive polymer into yarn, and surface metallization (6). Surface metallization is a facile way to get surface-metallized fibers.

In general a multistep pretreatment of cleaning is required, surface sensitization, or activation before plating. This arises because of the infeasibility of directly depositing metals on the inactive polymeric surface. Thus, the pretreatment step is crucial to prepare conductive fibers.

A problem in the case of UHMWPE is that the surface is extremely chemically inert and smooth. Therefore, an important issue for the preparation of conductive UHMWPE fibers is an effective way to activate their surface.

Mussels show adhesion on many natural or artificial organic and inorganic substrates. Thus the mechanisms of how mussels adhere can be transformed into synthetic materials. 3,4-Dihydroxyphenethylamine, i.e., dopamine, can polymerize into a monolayer strongly attached to the surface of substrate with the assistance of oxygen in alkaline aqueous solution. The structure of dopamine is shown in Figure 4.1.

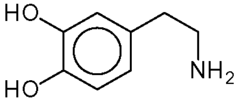


**Figure 4.1** Dopamine.

A poly(dopamine) monolayer contains much hydroxyl groups and amide groups. These groups can effectively chelate metallic cations. In this way, dopamine can activate the surface of UHMWPE fibers.

Conductive UHMWPE fibers have been prepared via electroless silver plating by utilizing dopamine as an activating agent. In the plating bath, $Ag(NH_3)^{2+}$ ions that are absorbed by the poly-(dopamine) monolayer are reduced to metallic silver particles by reducing agents (6).

The conditions of silver electroless plating influence the weight increment and the resistance of silver-coated fibers. The plating time controls the quantity of metal particles deposited on the surface. The plating temperature controls the redox reaction rate and the deposition rate of the metal. The silver-coated fibers show a strong electrical conductivity (6).

## 4.4 Intermetallic Layers

Polymers can be metallized with intermetallic compounds (1). Specific intermetallic compounds are $Cu_2Sb$, $FeSb_2$, SbZn, $Sb_3Zn_4$ and InSb. Such intermetallic surface layers appear to adhere well to the various polymer compositions.

They are electrically conductive to an extent, depending upon the nature of the intermetallic compound and the thickness of the layer. For many of the applications the electric conductively is sufficiently high and the metallized polymer materials are useful as such. If desired, the intermetallic surface layers may be plated with any further metal or metal combination, which is effected most conveniently by electrodeposition in that the surface has become electrically conductive (1).

## 4.5 Metallized Polymer Mirror

Conventional polymer mirror designs use a vacuum metallized polymer that is attached by an adhesive layer to a substrate (7). But in harsh, outdoor environments, these polymer mirror designs tend to degrade by delamination and by silver corrosion. In particular, it has been noted in these designs with conventional constructions that the adhesion between the polymer (i.e., poly(methyl methacrylate) (PMMA)) and silver is weak and deteriorates in the presence of moisture. Further, the polymer can delaminate from the silver and degrade specular reflectance.

The identification of metallized polymer constructions capable of resolving the problems would reside in selecting the proper choice and placement of materials, so that the factors that contribute to the degradation of the reflective surface are controlled and isolated from that surface.

Metallized polymer mirror constructions with improved durability have been developed (7). These have an oxide layer interposed between an outer layer of the polymeric material and the reflective layer of silver. The oxide acts as an adhesive layer and impedes the initiation of delamination as well as the propagation of delamination, i.e., tunneling, if initiation of delamination occurs.

The interposed oxide layer further provides a protection to the silver layer and slows down the corrosion of the silver layer. In a preferred construction, a copper layer is disposed between the layer of silver and the adhesive layer, and in this preferred construction, the copper also helps slow corrosion of the silver (7).

### *4.5.1 Poly(urethane) Insulating Fluid*

The insulating fluid must be compatible with the polymer film forming the metallized film capacitor element in the event that such fluid contacts the film. Compatibility with the polymer film means that the fluid must not act as a solvent towards the polymer film. It is believed that fluids that act as a solvent towards the polymer film, which is typically formed from a polyolefin such as poly(propylene) (PP), can cause swelling and wrinkling of the film, which is undesirable because it can lead to premature capacitor failure.

The insulating fluid should have good heat transfer capability, sufficient viscosity to impede leaking and suitable compatibility with outgassing byproducts caused by corona discharge and clearing phenomena. Also, the fluid should not attack the metal on the metallized polymer film.

A metallized film capacitor has been developed with a poly(urethane) (PU) oil insulating fluid that is compatible with the polymer substrate and metal material forming the metallized film (8).

The overall NCO to OH ratio to produce the high viscosity PU oil will typically range from about 0.6 to 1. The NCO to OH ratio and the particular materials chosen for the reaction will dictate the final viscosity of the resulting PU oil insulating fluid. Typically, any reaction done with an NCO to OH ratio higher than 0.6 to 1 will produce a solid elastomeric material which is unsuitable for use as an insulating oil in metallized film capacitors (8).

## 4.6 In-Mold Metallized Polymer Articles

The common method of metallizing a polymer component after it has been net shape molded has several drawbacks (9). Basically, metallizing dramatically increases the cost and time required to manufacture the part. Metallizing requires that the part, once removed from the mold, is treated using a chemical bath, subsequently plated using vapor deposition and then finally clear-coated to protect the thin layer of metal that was deposited onto the part. These additional steps introduce a great deal of additional handling of the part before it attains its finished state and result in nearly doubling the cost associated with manufacturing the part.

Molded polymer components with a metallic layer on their exterior surface can be fabricated where the metallic layer is entirely formed within the mold cavity before the part is removed from the mold (9).

There, a metal alloy and a polymer resin are selected so that they are carefully matched with respect to their relative melting points and in order to ensure that the polymer and metal are not miscible. It is particularly important that the melting point of the metallic alloy is tailored to fall towards the upper end of the desired molding range of the base polymer resin and above the temperature at which the resin is typically compounded.

Further, it is also important that the melting point of the alloy fall at a temperature that will not be reached within the extrusion barrel of the molding machine until the polymer composite passes the check ring on the extrusion barrel. Since the metallic alloy has a very low viscosity in its molten state, maintaining the metallic alloy in a solid state until it passes the check ring prevents the possibility that molten metal flow rearwardly through the barrel past the extrusion screw.

After the flow of material passes the check ring on the extruder barrel, the flow of material reaches a temperature wherein both the polymer and metallic alloy are in a molten state and are subsequently injected into the mold cavity. As the pressure within the molding cavity increases, the lower viscosity material tends to migrate to the exterior surfaces of the mold cavity where the differential pressure is greatest and the higher viscosity material remains in the central region of the mold cavity. Accordingly, since the molten metal has the lower viscosity, the molten metal is driven out of the mixture and to the outer surfaces of the mold cavity while the polymer, having a higher viscosity, remains at the core of the mold cavity. Once the part is allowed to cool, the resultant part is a net shape molded part having a polymer core with a metallic coating or layer disposed on or at the exterior surfaces thereof (9).

## 4.7 Camera Housing

Camera housings have been made from diverse forms of material over the history of photography (10). The initial materials selected were primarily designed to provide a relatively lightweight camera structure while insuring that the interior of the camera was kept free of any undesired light. While these requirements are still germane to the present modern day camera, additional and more complex requirements have been added. The high labor cost associated with the assembling of the more expensive 35 *mm* cameras has required the camera manufacturers to seek alternative methods of providing housing assemblies. Heretofore, the quality required in the higher priced cameras has been met by the use of metal camera bodies. The economies presented with the use of plastic injection molding is now attracting the manufacturers of expensive cameras to switch to plastic camera housing assemblies (10).

Originally, cameras were made of wood and fiberboard, frequently covered with cloth. Subsequently, sheet metal, aluminum and zinc die cast parts were utilized. In 1934, Eastman Kodak Company introduced their first Brownie camera molded from phenol-based resins. Nowadays, most fixed-focus cameras are all plastic.

Various types of plastics, such as cellulosics, PE, UHMWPE, Nylon, phenolics, styrene polymers, epoxies and methacrylate polymers, have been utilized (10).

While plastic has been utilized in the relatively inexpensive fixed-focus camera bodies, there has been a recognition that problems can exist with the use of plastics in the proper alignment and positioning of lenses.

Plastic has a relatively low melting point and will deform if it is heated above 150°C. Preferably, the plastic camera part should not be heated above 75°C. Without heating, however, it is difficult to achieve a strong adhesive coating of a metal. A further problem occurs when utilizing a vacuum, since the heating of the plastic will produce various gases that will themselves react and leave undesirable byproducts on the surface of the camera part.

While it has been recognized that it would be highly desirable to provide an abrasion resistant metal coating, the adhesion of a metal coating to a plastic substrate has been difficult to achieve. Again, the thermal problems dealing with the plastic has created certain barriers. The discrepancy in the coefficients of thermal expansion between metal and plastic has created cracks when the camera housing is utilized in wide extremes of ambient temperature.

An improved plastic camera housing having an exterior metallized decorative coating and method of achieving the same has been developed (10).

The camera housing assembly part can be formed from a glass fiber filled plastic such as poly(carbonate). The plastic housing part can be pretreated with a lacquer or plastic subcoating such as a PU-based resin with carbon powder, graphite powder, copper powder, or chromium powder added thereto in the size range of 1–5 *μm*. A magnetron process is utilized for both pretreating the plastic housing and for the sputtering depositing of a soft intermediate layer of metal to assist in the adhesion of a hard exterior metal coating. The camera housing surface is preliminarily plasma etched in an environment of argon gas at a pressure of $10^{-2}$ *torr* for a period of about 2 *min*.

Subsequently, while still maintaining the argon gas environment, copper is sputtered onto the prepared surface to a thickness of approximately 1–3 *μm*. Finally, chromium is subsequently sputtered in the same environment to provide the abrasion resistant exterior coating of approximately 0.3 *μm*. The housing part can be rotated during sputtering to further insure that it is kept at a relatively cool condition below 75°C. The rotation also reduces the sputtering rate required compared to that of a stationary sputtering condition (10).

## 4.8 Metallized Polymer Film Capacitors

Metallized film capacitors are typically used for starting and running motors and also in lighting applications (8). The capacitive element of a metallized film capacitor is typically formed by very tightly co-rolling two polymer films having metal layers deposited thereon around a core to form two spaced apart electrodes. Generally, the tightly co-rolled metallized polymer films are placed in a container, which is typically metal.

Electrical leads are connected between the metal sprayed ends of the metallized polymer films and terminals mounted on a top. The container is filled with an insulating fluid and the top is sealed to the container.

In some capacitors, insulative sheetlike material may be placed in the container between the co-rolled metallized polymer films and the metal container. Also, in some capacitors, a pressure activated circuit interrupter is employed.

## 4.9 Micro-fuel Cell

The fabrication and characterization of a micro-fuel cell prototype based on PMMA has been described (11). The material has low aspect ratio micro-channels, which were superficially metallized by a sputter deposition technique.

For current collector and anticorrosion coatings different high electrical conductivity materials such as copper, molybdenum and gold were employed. Metallic coatings were physically and chemically characterized by using scanning electron microscopy for the topographical analysis, X-ray diffraction for the structural analysis and energy dispersive spectroscopy for composition analysis.

The electrical and electrochemical parameters obtained for the prototype cell were: a mean open circuit potential of 855 $mV$, a maximum electrical power density of 73 $\mu Wcm^{-2}$ at 182 $\mu Acm^{-2}$ and 380 $mV$ (11).

## 4.10 Printed Circuit Boards

A heat treatment of a composition of a polymer and an organic complex of a transition metal element is known to metallize polymer compositions. A metallized surface film is obtained when the heat treatment is conducted with the polymer composition being in intimate contact with a metallizing board, which had to be made of a material having adequate heat resistance and to be readily releasable from the metallized film (12).

A polymer composition containing an organic metal complex has been described for the purpose of producing a metallized polymer from the polymer composition (2).

The process for the production of a printed circuit board comprises applying a copper foil onto a laminated board made of, e.g., an epoxy resin or a phenol resin, or a film made of a poly(imide) (PI) or a polyester, then covering the necessary circuit portions with an etching resist, such as a photo-sensitive polymer, chemically removing the exposed copper portions with an etchant solution, such as an iron chloride solution, and then removing the etching resist from the circuit portions to obtain a printed circuit board (2).

However, the above process has disadvantages such as the process steps being rather complicated, and since a corrosive compound is used for etching, it tends to have adverse effects on the properties of the product unless it is adequately washed away with water; and the treatment of the waste etching solution is also a problem.

Further, it is necessary to use an adhesive for the bonding of the copper foil to the polymer base sheet, whereby there are various problems, such as deterioration of the original thermal resistance or electrical characteristics of the polymer base sheet, in addition to the question of adequate adhesive strength.

### *4.10.1 Solderable Metallized Plastic Contact*

Attempts have been made to solder a metallized plastic part to a printed circuit board to make an electrical contact between the printed circuit board and the electrically conductive coating of the metallized plastic part (13). However, the electrically conductive material covering the plastic part may be delaminated or blistered away from the surface of the plastic part. Such a delamination is not acceptable in the electronics industry since the bond between the two components is not adequate. The bond between the two components is subject to tearing and thus subject to loss of electrical continuity between the two components.

A conductive element has been developed that includes a substrate made of a polymer where a solderable electrically conductive material covers a surface of the substrate to form an electrically conductive region on the substrate. By using high temperature polymers, such as liquid crystal polymers, a delamination or deformation of the metallized plastic will not occur (13).

### *4.10.2 Polymer Compositions for Metallized Polymers*

A polymer composition containing an organic metal complex has been described for the purpose of producing a metallized polymer from the polymer composition (2).

The organic metal complex should be soluble in an organic solvent and capable of freeing the metal when heated. As the central metal of the organic metal complex to be used, titanium, zirconium, vanadium, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, ruthenium, iridium, rhodium, palladium, osmium, platinum, copper, silver and gold, are preferred.

The organic metal complex containing such metals, is preferably stable against oxygen or moisture. The organic ligand may be a tertiary phosphine, a tertiary phosphite, carbon monoxide, an aliphatic or alicyclic olefin, a conjugated olefin, an aryl compound, a heterocyclic compound, an organic cyano compound, an organic isonitrile compound, an organic mercapto compound, a compound having an alkyl group, a vinyl group, an allyl group, an ethynyl group or an acyl group, halogen, oxygen, hydrogen and nitrogen. Specific examples are collected in Table 4.1.

**Table 4.1** Organic ligands (2).

| Ligand | Ligand | Ligand |
|---|---|---|
| Triphenylphosphine | Tributylphosphine | Triethylphosphine |
| Triphenylphosphite | Tributylphosphite | Triethylphosphite |
| Carbon monoxide | Cyclooctadiene | Cyclopentadiene |
| Cyclooctatetraene | Ethylene | Butadiene |
| Pentadiene | Acetonitrile | Benzonitrile |
| Isobutylene | *tert*-Butyl-isonitrile | Vinylisonitrile |
| Benzoisonitrile | Acetylacetone | Ethyl acetyl acetonate |
| Pyridine | Thiophene | Quinoline |
| Furan | 2,2′-Dipyridyl | |
| Ethylenedithiol | Toluene-3,4-dithiol | |

Some of these compounds are shown in Figure 4.2.

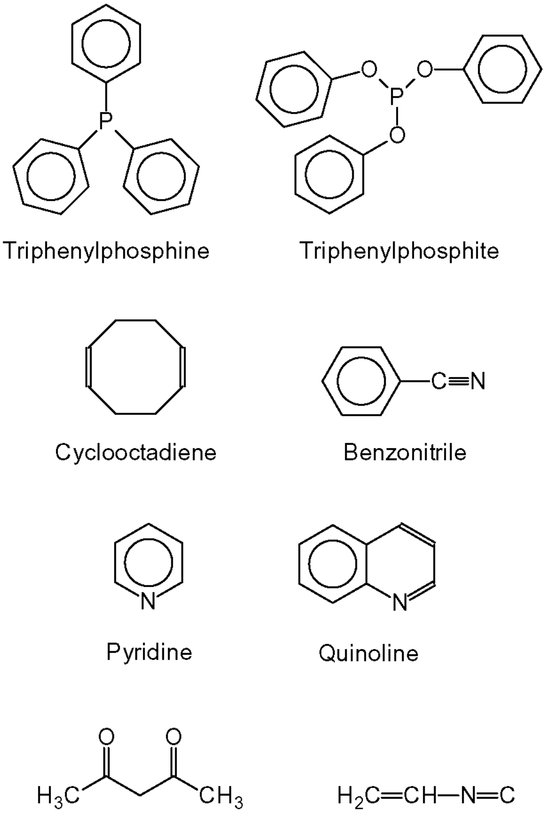
From the viewpoint of the heat treatment of the organic metal complex, the boiling point of the ligand is preferably not higher than 400°C.

The heat treatment may be conducted in atmospheric air or in an inert gas atmosphere. It is usual to conduct the heat treatment in atmospheric air. The polymer types that can be used are listed in Table 4.2.

These polymers may be used alone or in combination as a mixture. Further, these polymers may be used in the form of a powder, granules or a mass, or may be used in the form of a dispersion or a solution of a polymer in a proper solvent.

The polymers to be used for the preparation of a film having a metallized surface or a film having a metal layer pattern on its surface, are required to be soluble in an organic solvent.

On the other hand, the polymers to be used for the preparation of a polymer with fine metal particles dispersed therein, such as a dielectric polymer composition, are not restricted as much. The



Triphenylphosphine
Triphenylphosphite
Cyclooctadiene
Benzonitrile
Pyridine
Quinoline
Acetylacetone
Vinylisonitrile

**Figure 4.2** Organic ligands.

**Table 4.2** Rubber-like polymers for printed circuit boards (2).

| Polymer | Polymer |
|---|---|
| Ionomer resin | Acrylonitrile-acrylic-styrene |
| Acrylonitrile-styrene resin | Acrylonitrile-butadiene-styrene |
| Phenoxy resin | MMA-butadiene-styrene resin |
| Ethylene-vinylchloride copolymer | Ethylene-vinylacetate copolymer |
| Poly(styrene) | Poly(vinylidene chloride) |
| Vinyl acetate | Poly(ethylene) |
| Poly(propylene) | Poly(butadiene) |
| Poly(vinylidene fluoride) | Poly(tetrafluoroethylene) |
| Polyacetal | Poly(amide) |
| Poly(amide-imide) | Polyarylate |
| Polyether-imide | Polyether-ether ketone |
| Poly(ethylene terephthalate) | Poly(butylene terephthalate) |
| Poly(carbonate) | Poly(sulfone) |
| Poly(ethersulfone) | Poly(phenylene oxide) |
| Poly(phenylene sulfide) | Poly(methyl methacrylate) |
| Guanamine resin | Diallylphthalate resin |
| Vinyl ester resin | Phenol resin |
| Unsaturated polyester resin | Furan resin |
| Polyimide resin | Poly-*p*-hydroxybenzoate |
| Urethane resin | Melamine-formaldehyde resin |
| Urea-formaldehyde resin | Epoxy resin |

polymers to be used for a high dielectric polymer composition are preferably selected from polymers exhibiting a high anti-breakdown voltage and a low dielectric loss tangent.

To permit the uniform dispersion of the organic metal complex, the rubber-like polymer is preferably the one which is soluble in a solvent in an unvulcanized state. Particularly preferred is a rubber-like polymer which is durable for repeated deformations and which has excellent heat resistance.

There is no particular restriction on the solvent for the polymer or the solvent for the metal complex. The solvents may be used alone or in combination as a mixture of solvents. Examples of solvents are summarized in Table 4.3 and some of these compounds are shown in Figure 4.3.

**Table 4.3** Solvents for preparation (2).

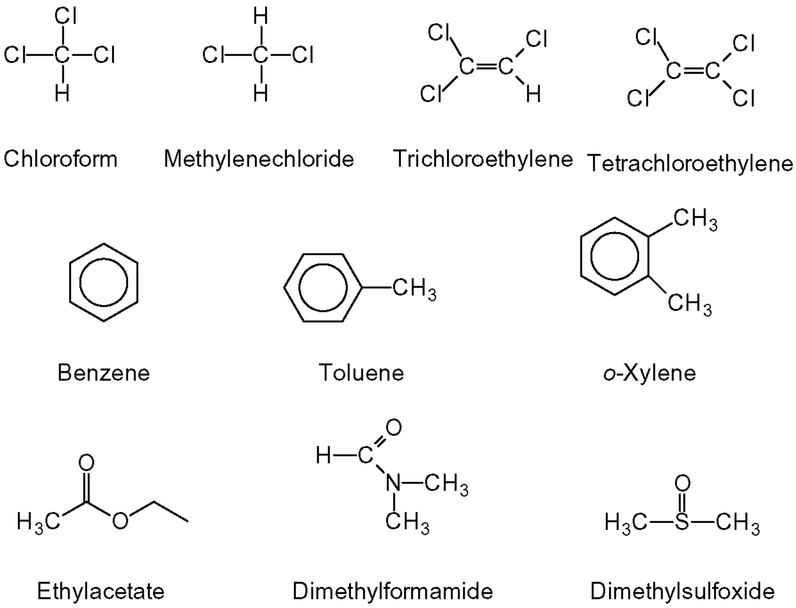
| Solvent | Solvent | Solvent |
|---|---|---|
| Chloroform | Methylenechloride | Trichloroethylene |
| Tetrachloroethylene | Benzene | Toluene |
| Xylene | Acetone | Ethylacetate |
| Dimethylformamide | Dimethylsulfoxide | |

These solvents are used for the preparation of a polymer composition, wherein an organic metal complex is uniformly dispersed, or for the control of the viscosity of such a composition to provide it with proper processability.

The method for the production of a metallized polymer involves a heat treatment of the polymer composition. The heat treatment is conducted at a temperature sufficient to let the organic metal complex free the metal. Therefore, the temperature may not necessarily be as high as the decomposition temperature of the organic metal complex. Namely, the temperature for the heat treatment is usually selected within a range of from 100–350°C so that the polymer does not undergo a thermal deterioration.

### *4.10.3 Metallized Films*

In the case of metallized films, films with metal layer patterns and pressure-sensitive conductive films, a mixture of a polymer and an organic metal complex in a weight ratio of the polymer to the metal



Chloroform Methylenechloride Trichloroethylene Tetrachloroethylene

Benzene Toluene *o*-Xylene

Ethylacetate Dimethylformamide Dimethylsulfoxide

**Figure 4.3** Solvents for preparation.

of the organic metal complex of 99.9:0.1 to 80:20, is dissolved or dispersed in the organic solvent to obtain a solution of the polymer composition comprising the organic metal complex (2). In the case of metallized films and films with metal layer patterns, the polymer concentration in the solution is usually 5–30%.

In the case of the highly dielectric polymer with fine metal particles uniformly dispersed therein, the metal content is 5–30% by volume. If the metal content is less than 2%, the permittivity will be too small. If it exceeds 70%, the moldability will be poor.

A uniform composition of the polymer and the organic metal complex can be prepared by mixing by means of a mixer, followed by removing the solvent. Another method is to mix a polymer solution and an organic metal complex solution uniformly, followed by the removal of the solvent.

Then, the solution of the polymer composition with the organic metal complex may be cast on a casting board to form a film, or may be coated on a substrate to form a coating film.

A solution of the polymer composition containing the organic metal complex can be cast on a casting board or coated on a substrate, and the film thereby formed is then subjected to heat treatment with a metallizing board. The solution of the polymer composition may be applied directly onto the metallizing board to form a film thereon, which is afterwards subjected to a heat treatment.

The metallizing board must be formed from a material which has adequate heat resistance at the temperature of the heat treatment and which can be readily released from the metallized film. For example, copper, a copper alloy, aluminum, glass and a resin such as poly(ethylene terephthalate) (PET) are suitable.

When the solution of the polymer composition containing the organic metal complex is cast on the metallizing board, followed by the heat treatment, it is possible to obtain a film metallized only on its lower surface. Further, when the above-mentioned steel or chrome-plated steel is used as the casting board and the metallizing board is brought in contact with the upper surface of the film during the heat treatment, it is possible to obtain a film metallized only on its upper surface. It is possible to metallize both surfaces of the film by subjecting it to heat treatment by placing the metallizing board on each surface. In this case, the metallizing board may be used as the casting board, so that the film formed on the board can be subjected to the heat treatment as it is. Otherwise, the formed film may be peeled off from the casting board, and then subjected to the heat treatment by bringing it in contact with a metallizing board.

In the case of the coating method, it is possible to metallize the surface of the coating film in the same manner as the metallization of the upper surface of the film formed by the casting method, after coating the solution of the polymer composition containing the organic metal complex on the coating substrate.

Thus, it is possible to optionally select the kind of the organic metal complex, the metal content in the complex and the concentration of the polymer composition containing the organic metal complex depending upon the particular applications, e.g., as a heat-reflecting board, a heat panel, a printed circuit board or a capacitor having a semi-specular metal surface.

Further, it is also possible to metallize and make electroconductive both surfaces of the polymer film containing the organic metal complex by sandwiching the polymer film with a pair of metallizing boards made of glass, copper, aluminum or resin during the heat treatment.

With respect to the metallized film thus obtained, the formed metal can be identified and the formed state of the metal can be investigated by an X-ray diffractometer, an X-ray spectroscopy or a scanning electron microscope. The metal formed by the heat treatment of the organic metal complex is localized in its substantial entirety on the surface of the film which is in contact with the metallizing board, and the metal is integral with the polymer and thus has strong adhesion strength (2).

### *4.10.4 Pattern Forming*

A polymer film having a metal layer of a predetermined pattern on its surface, can be formed by heat-treating the polymer composition in the same manner as described above, except that a pattern-forming board is used in place of the metallizing board (2). Namely, the polymer film is subjected to heat treatment under such condition that it is brought in contact with the pattern-forming board. As such a pattern-forming board, mentioned may be made of a board made of a material capable of inducing the metallization, as mentioned above, and partially coated with a resin which does not induce the metallization, for instance, a board made of copper, a copper alloy, aluminum or glass, on which a film of a polyester, poly(tetrafluoroethylene) (PTFE) or PP cut into a predetermined pattern is intimately bonded or a board capable of inducing the metallization, which is coated with an organic paint or a polymer solution, such as an epoxy resin or a silicone resin by means of screen printing, except for the portions corresponding to the predetermined pattern.

However, the pattern-forming board is not restricted to such boards. For instance, there may be employed a resin board made of PET, on which an organic metal complex solution has been applied in the predetermined pattern, by means of screen printing; or a resin board made of a resin which does not induce the metallization, such as PET, an epoxy resin or a phenol resin, on which a material capable of inducing the metallization, such as copper, a copper alloy, aluminum or glass, is formed in the predetermined pattern, for instance, a copper printed epoxy resin or phenol resin board, or a flexible printed PI or PET board (2).

A solution of the polymer composition containing the organic metal complex is cast on a casting board made of PET, PE, PP or PTFE which does not induce the metallization and which is durable against the solvent used for the preparation of the polymer composition, and adjusted to a predetermined film thickness by means of a doctor knife. After removing the solvent by heating at a temperature which does not bring about the thermal decomposition of the organic metal complex, the formed film is peeled off from the casting board, whereby a polymer film containing the organic metal complex is obtained.

The polymer film is brought in contact with the above-mentioned specific pattern-forming board and subjected to heat treatment, whereby a film having a metal layer of a predetermined pattern formed only on the surface which is in contact with the pattern-forming board, is obtained.

It is also possible to form the metal layer patterns on both sides of the polymer film by subjecting the polymer film to the heat treatment under such condition that both surfaces of the polymer film are in contact with the pattern-forming boards. Further, it is also possible to cast the solution of the polymer composition containing the organic metal complex directly on the pattern-forming boards and subject it to the heat treatment after removal of the solvent, whereby a film having a metal layer pattern formed only on the surface which is in contact with the pattern forming board, is obtained.

Further, it is possible to form a metal layer pattern on a coating film surface by coating the polymer composition on a shaped resin article made of a resin which does not induce the metallization and which is durable against the solvent used for the preparation of the polymer composition containing the organic metal complex and has good adhesion to the polymer composition, such as PET, an epoxy resin or a phenol resin, then drying the coated polymer composition, and heat-treating it with the pattern-forming board placed thereon (2).

### *4.10.5 Pressure-Sensitive Conductive Film*

A pressure-sensitive conductive rubber-like polymer film can be obtained by heat-treating a polymer composition of a rubber-like polymer containing an organic metal complex (2).

There, an unvulcanized rubber-like polymer solution containing an organic metal complex is cast on a prescribed metallizing board. After the removal of the solvent, the matter is subjected to a heat treatment, whereby only the surface which is in contact with the metallizing board, will be metallized.

Alternatively, the polymer solution is cast on a prescribed casting board, and after the removal of the solvent subjected to a heat treatment with a metallizing board placed intimately on the formed film. Here, only the surface which is in contact with the metallizing board will be metallized.

In order to selectively metallize the film surface, it is necessary that the polymer film is intimately in contact with the metallizing board during the heat treatment.

From the observation of the metallized layer on the surface by means of a scanning-type electron microscope, it has been found that the metallized layer is composed of a highly dense aggregation of very fine metal particles and usually constitutes a layer having a thickness of from 1 to 20 $\mu m$, depending upon the production conditions. The metallized layer is integral with the rubber-like polymer and firmly bonded to the rubber-like polymer. In this state, the metal layer on the surface conducts electricity and exhibits a certain conductivity.

When a strain is exerted on the metallized rubber-like polymer film, the metal layer on the surface deforms along with the deformation of the rubber-like polymer film and, accordingly, the state of contact of the fine metal particles changes, whereby the conductivity decreases depending upon the degree of the deformation of the metal layer on the surface.

The change of the state of contact of the fine metal particles resulting from the deformation of the rubber-like polymer film, is very well reproducible and highly dependent on the deformation, and thus is excellently interrelated with the change of the conductivity or the electric resistance.

When the strain is released to permit the rubber-like polymer film to return to the initial state, the state of contact of the fine metal particles likewise returns to the initial state and thus presents the same level of electric conductivity as prior to the deformation.

As opposed to the conventional pressure-sensitive conductive rubber-like polymer film, wherein conductive particles are dispersed in a rubber-like polymer, here the pressure-sensitively conductive rubber-like polymer film is a conductor at the normal state, and its electric resistance increases as it deforms and finally reaches an insulated state, and upon release from the deformation, it returns to the initial conductor.

Further, the metal layer on the surface of the pressure-sensitive conductive rubber-like polymer film may be coated with a rubber-like polymer for the purpose of improving the durability under various environments. In such a case, there will be no change in the intrinsic properties of the pressure-sensitive conductive rubber-like polymer film. The preparation of pressure-sensitive conductive films is done as (2):

**Preparation 4–1:** A poly(vinyl chloride) (PVC) paste sol was prepared by mixing 100 *ppw* of a PVC paste with 65 *ppw* of a dioctylphthalate plasticizer. To 100 *ppw* of the PVC paste sol, 0.926 *part* of a di-$\mu$-chloro-bis($\varepsilon$-2-methylallyl) dipalladium (II) complex dissolved in a small amount of chloroform was added and thoroughly stirred and mixed. Then, the mixture was subjected to degassing under reduced pressure at 40°C and chloroform was removed. The PVC paste sol containing the di-$\mu$-chloro-bis($\varepsilon$-2-methylallyl) dipalladium (II) complex thus obtained was cast on a copper plate having a thickness of 100 $\mu m$ as a metallizing board, in a thickness of 400 $\mu m$, by means of a doctor knife.

The film thus formed on the copper plate was heated at 180°C for 5 minutes in atmospheric air, and then peeled from the copper plate, whereby a pressure-sensitive conductive PVC film having a thickness of 290 *μm* and metallized on one surface, was obtained.

A sample having a length of 50 *mm* and a width of 8 *mm* was taken from the film, and a pair of copper wires having a diameter of 0.2 *mm* were attached to the center portion of the sample by means of an electroconductive silver-type adhesive (Eccobond Solder 56C, manufactured by Emerson & Cuming Japan K.K.) with a distance of 20 *mm* in the longitudinal direction of the sample to form fixed electrodes extending in parallel with each other and perpendicular to the film surface. The sample provided with the electrodes was mounted on a tensile test machine (Tensilon UTM-5, manufactured by Toyo Baldwin Co., Ltd.), and the electrodes were connected to an electric resistance meter (LCR meter AG-4311, manufactured by Ando Electric Co., Ltd.) by means of lead wires.

The sample was stretched to a predetermined extent, and the length between the electrodes at that time was measured and divided by the initial length, whereby the value obtained by the division was taken as a stretching rate. Further, the electric resistance at that time was measured.

The film stretching was stopped at a stretching rate of 8%, and while permitting the stretched film to return to the initial state, the stretching rates and the corresponding electric resistance values were measured, whereby the results as shown in Figure 4.4 were obtained.

The measurements were repeated 1000 times by repeating the stretching and releasing of the film, whereby the same electric resistance values were obtained at the same stretching rates.

### *4.10.6 Polymer with Finely Dispersed Metal Particles*

According to a fourth embodiment, a polymer containing finely dispersed metal particles may be obtained by heating the above-mentioned polymer composition containing the organic metal complex (2). The pyrolytic reaction of the organic metal complex is utilized to form fine metal particles in the polymer.

Organic metal complexes have been studied mainly in the field of chemistry of catalysts, and in recent years, they have been studied for their applications in such fields as synthetic organic chemistry and biological chemistry. However, no substantial study has been made on the use of the organic metal complexes for the purpose of uniformly dispersing metal particles in polymers. The present inventors have studied various organic metal complexes for their pyrolytic properties and their thermal decomposition products. As

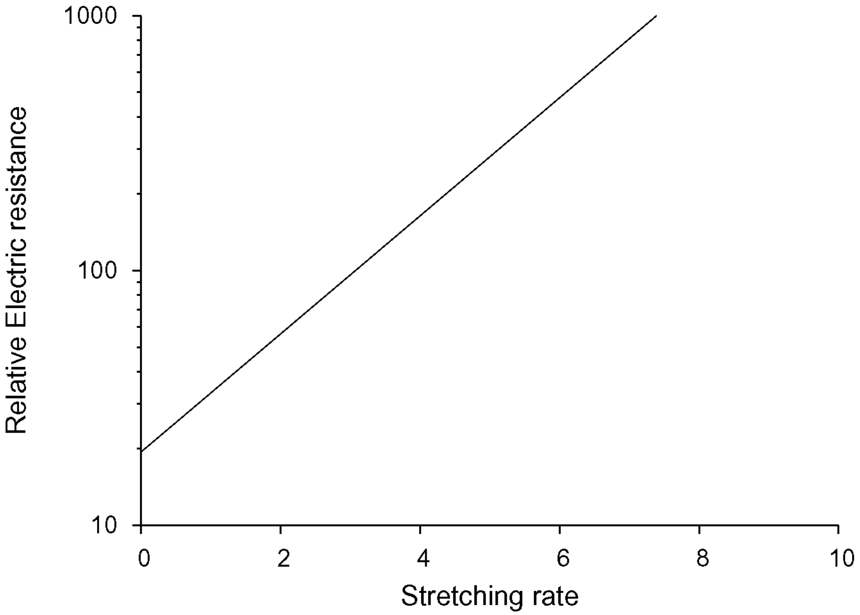


**Figure 4.4** Electric resistance values (2).

a result, it has been found that the complexes which are capable of releasing metals when heated, are extremely effective for the purpose of obtaining polymer compositions containing finely dispersed metals.

It is known that when a polymer composition containing metal particles dispersed therein is placed under an electric field, interfacial polarization appears at the interface between the metal particles and the polymer, and thus such a composition gives high permittivity.

The intensity of the interfacial polarization varies depending on the eccentricity of metal particles when the metal particles are assumed to be an ellipsoid of revolution, the conductivity or surface area of the metal particles, or the volume ratio of the metal particles in the polymer.

Accordingly, it should be possible to obtain a metal particle-dispersed polymer composition having a high permittivity, by dispersing fine metal particles having great eccentricity, i.e., being elongated in the direction of the electric field and highly conductive in a high concentration (2).

However, when dispersion of metal particles in a high concentration by conventional processes is attempted, the metal particles tend to contact one another and they are hardly uniformly dispersed. Thus, the amount of metal particles to be incorporated is limited.

If the dispersion of the metal particles is poor, it is likely that the particles contact one another locally, and the dielectric breakdown voltage of the polymer composition containing the metal particles will be so low that it is no longer practically useful.

Thus, it is theoretically known that if fine metal particles can be incorporated in a high concentration into a polymer, it is possible to obtain a useful dielectric. However, there has been no practical means to accomplish it because of the difficulties in obtaining a uniform dispersion of fine metal particles in a polymer.

Under these circumstances, it is extremely significant that this process provides an efficient method for the production of a polymer composition wherein fine metal particles are uniformly dispersed. The metal particles dispersed in the polymer are very fine and have an average particle size of from 20 to 200 $\mu m$ although the particle size varies depending upon the type of metal, the type of polymer or the conditions for the heat treatment. Further, the metal particles formed are present independently from one another in the polymer. Thus, the polymer composition containing uniformly dispersed fine metal particles exhibits superior dielectric characteristics and high permittivity when placed in an electric field (2).

A polymer in an optional form is mixed with a solution of an organic metal complex in a solvent to form a polymer composition containing the organic metal complex, whereby the two components are much more uniformly mixed as compared with the case where no solution of the organic metal complex is used (2). Accordingly, it is thereby possible to obtain a polymer containing fine metal particles uniformly dispersed. The mixing is preferably conducted at a temperature at which no substantial pyrolysis of the organic metal complex proceeds. Further, other additives, such as another stabilizer, a plasticizer or a colorant, may optionally be incorporated as the case requires.

The polymer containing the finely dispersed metal particles may be molded into an optional shape depending upon the particular use. The molding may be conducted simultaneously at the time of the above heating, or may be conducted prior to or after the heating, as the case requires. For instance, in order to obtain a molded product of the polymer containing finely dispersed metal particles, a usual molding method, such as compression molding, injection molding or extrusion molding, may be conducted at the same time as or subsequent to the heating, or a coating method or casting method may be employed, whereby a molded product such as a film, a sheet or a coating film is obtainable (2).

### *4.10.7 Flexible Metallized Polymer Film*

Circuit cards and devices have been protected from environmental effects by polymeric encapsulation, metal covers, hermetically sealed metal or ceramic covers (14).

The encapsulation or potting methods provide conformal coating but the coating does not provide a hermetic barrier to moisture permeation or chemical diffusion.

Hermetically sealed covers of ceramic or metal do provide environmental protection but tend to be bulky, heavy and expensive (14).

However, new and existing film metallization processes, such as magnetron sputtering and roll plating, along with the development of high performance polymer films, are allowing for the feasible design of lightweight, formable and hermetic metallized polymer film covers to replace or enhance the above techniques for protection of electronic devices and assemblies.

The use of a metallized film with one metal surface and the other an insulative polymer, creates a fully integrated cover that can be hermetically sealed over an assembly, individual components or over integrated circuit chips. This cover is thinner than conventional covers and flexible, so it can be formed to the contours of the assembly, thus cutting down on excess dead space above the assembly.

The fabrication of the film is done by either lamination or physical vapor deposition, i.e., sputtering (14). Lamination requires that a sheet of polymer, not fully cured or hardened, is placed on a metal foil in a platen press. The press is activated by applying a large force to the laminate and heat is typically added to promote the polymeric/metal adhesion. After the cycle, the sheets are now joined as one and are referred to as a laminate.

The sputtering process is quite different from the lamination process. This requires a film of polymer to be sputtered coated with metal from a given target. This occurs in equipment referred to as a sputter chamber. This process is generally referred to as a glow discharge process, employing a voltage-induced plasma to generate metal atoms from a given target, which are then transported through the plasma and deposited on the substrate, in this case the polymer. The metallizing sequence and process parameters are critical in controlling this process. Once the initial metal layer is applied to the polymer, the roll can be further plated to any given thickness by traditional electroplating techniques. Finally, the edge border of the film is created in the same manner as for the lamination process, typically by etching.

The thickness of the metal film is less than in the traditional methods but is designed to provide the environmental protection required for the life of the assembly (14).

## 4.11 Electrostatic Miniature Valve

A low cost concept for the fabrication of micromechanical electrostatic actuators has been reported. The fabrication is done by microinjection molding of 3D polymer devices followed by electroless plating and laser patterning of the metal layer (15).

The polymer-based valve consists of a bottom cap, an actuator and a top cap fabricated by microinjection molding from the liquid crystal polymer Vectra® E820i Pd from Ticona. This is covered by an electroless deposited metal layer, which is patterned by laser ablation to form the electrical conductors, the electrodes and isolation. In addition, the valve contains two gasket seals and a metal spring.

## 4.12 Antennas

### *4.12.1 Antenna Reflector*

A method of manufacturing a metallized plastic reflector for the reflection of electromagnetic radiation has been described. A curved top layer of a fiber reinforced synthetic resin is coated on its convex side with a metal layer which in turn is connected with a supporting layer of a synthetic resin reinforced with fibrous material.

For example, an unsaturated polyester resin is first provided over the surface of the mold (16). A completely resin-impregnated glass fiber is then laid on the resin layer and the assembly is hardened at a temperature of approximately 120°C for a few hours. After hardening, the surface is roughened by sandblasting. A fabric of metal strips is manufactured separately and, after having been etched, is provided with a layer of a phenolic adhesive.

The fabric of metal strips is deformed in accordance with the shape of the fiberglass mat disposed on the mold and is then adhered to the roughened surface of the mat. Thereafter a second layer of resin-impregnated glass fiber cloth is provided on the metal fabric, the assembly is evacuated, then hardened, and the resulting laminate is finally removed mechanically from the mold (16).

This method has the drawback of being time-consuming, expensive and, in particular, less suitable for mass production of reflectors (17). In addition, the fabric structure of the metal strips must be very fine to obtain optimum electrical properties, which impedes the deformation of the fabric and the correct permanent positioning thereof. Another drawback of this method is that the mold which determines the shape of the surface of the metal layer, has to be removed in between. This may give rise to deformation, however small. This may be on the concave surface of the supporting layer on which the metal layer is provided.

It has also been suggested to provide the convex surface of a mold with a film of poly(vinyl alcohol), spraying thereon a metal layer and finally providing a supporting layer of, for example, glass fiber reinforced polyester (18). This method has the advantage that the surface of the metal layer is less rough and more accurately conforms to the desired surface as determined by the mold. The drawback of the method is that the metal layer of the resulting reflector is not protected from attack by the surroundings, for example, weather influences.

An improved method has been described (17). The curved top layer is manufactured from a fiber reinforced unsaturated polyester resin by using a mold provided on its convex side with a metal layer which in turn is provided with a supporting layer of the reinforced resin. As compared with a polyester resin, an epoxy resin is slightly more viscous, and generally requires a longer hardening time and is slightly more difficult to process, so polyester resin is preferred.

A film or fabric of fibrous material is provided over a convex surface of a mold and is saturated with the resin. After partial hardening of the resin, a layer of metal is then applied on the resin by a spraying process. Thereafter, a supporting layer of the resin reinforced with fibrous material is placed on the metal layer and finally, after hardening of the assembly, the mold is removed. The fibrous material preferably consists of glass fibers.

The hardener for the unsaturated polyester resin is dibenzoyl peroxide. An accelerator is also added, for example, dimethylaniline, c.f. Figure 4.5. The resin is not hardened entirely. This can be achieved by omitting paraffin from the resin so that the outermost layer of the resin exposed to air is not fully hardened and has a slightly sticky consistency.

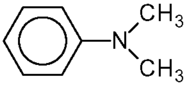


**Figure 4.5** Dimethylaniline.

After hardening the resin at room temperature, a layer of metal is sprayed on the surface with a usual spraying method. A layer of Sn/Sb metal alloy having a melting range of 240–350°C. is applied by flame spraying. The metal adheres very readily to the substratum and furthermore does not crack after a longer period of time. This very favorable characteristic is obtained as the surface the top layer onto which the liquid metal particles are sprayed is not fully hardened and the fibrous layer is just saturated with resin. The top layer need not be roughened. Further, no adhesives are used.

The electromagnetic radiation reflecting metal layer fabricated is very accurate, that is, conforms very accurately to the convex surface of the mold which corresponds to the desired theoretical surface, for example, a parabolic surface.

The reflector is suitable for application in the high frequency and super high frequency range of approximately 1–20 *GHz*. In particular, the reflector may be used in antennas, especially satellite antennas, operating at a power of 200 *W* (17).

In Figure 4.6 a reflector, 9, having a parabolic surface, 10, with a diameter of 1.6 *m* is shown (17). On its circumference the reflector has an upright edge, 11, 10 *cm* wide, and centrally it is provided with a supporting member, 12, for a reflector horn, 13. Supporting member, 12, has a stabilizer, 14. The reflector furthermore comprises, on the side remote from the supporting member, 12, a reinforcement ridge, 15, to which is connected an apparatus, in this case a motor, 16, with stand, 17.

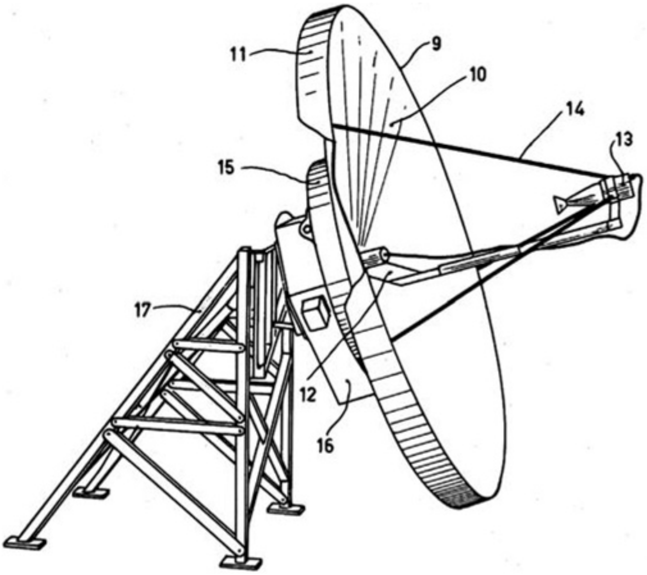


**Figure 4.6** Reflector with parabolic surface (17).

### *4.12.2 Rear Projection Television Receiver Mirrors*

Rear projection type television receivers have become very popular due to the large display screens that are available without necessitating special installations or large viewing areas (19). In such receivers, three color cathode ray tubes, i.e., red, green, and blue, project an image onto a mirror, with the image being reflected (and magnified) onto a display screen that may comprise a fresnel lens arrangement. However, the large mirrors, on the order of 100 × 76 *cm* (40 × 30 *in*), are not only expensive, but heavy.

Some rear projection television receiver mirrors have been fabricated of a metallized plastic film that is tightly stretched and secured to a relatively lightweight aluminum frame. The technique utilizes a trapezoidal shape, an U-shaped frame that is secured to the cabinet by brackets at its corners, or by welding.

A rigid backing, in the form of about a one-half inch thick sheet of styrofoam is secured in the frame very close to the metallized plastic film. The metallized plastic film is stretched, wrapped around the frame and secured to both the backing and to the back of the frame by an adhesive. The excess metallized plastic film is trimmed and the assembly is subjected to heat for a short time to cause the stretched metallized plastic film to shrink somewhat. Suitable mounting brackets are affixed to the frame. The result is a very flat, lightweight mirror.

A drawback of such a mirror is that it is very labor intensive, since the adhesive is manually applied and the metallized plastic film must be hand-wrapped about the frame.

A method has been developed for the fabrication of metallized plastic film mirrors which eliminates a majority of the hand operations. This includes machine forming the frame from aluminum roll stock and reducing the likelihood of wrinkling of the metallized plastic film by supporting it on a smooth peripheral edge that is raised from the frame surface (19).

### *4.12.3 Metallized Foams*

The technology of metallized foam offers a sophisticated approach to the design of wire-like, flat, and 3D antennas (20). Foam-like materials are very lightweight due to their intrinsic structure. In addition, these materials typically exhibit a low dielectric constant and loss tangent. Such properties make the foams attractive for use as substrates for the fabrication of antennas in applications that require lightweight and low loss. Only the necessary metal skin depth is deposited over arbitrary shaped structures. This new antenna design technology offers low weight, possible shaping, and innovative architectures.

Some developments of antennas for several applications needing either size reduction, limited weight, good efficiency, or using new materials, have been presented (21) .

To meet the constraints of size, weight and efficiency, it is important to make proper choices in design and technology. Various shapes, using standard laminates, have been developed to simplify the feeding, for size reduction and multiple frequency resonances.

A metallization process of foam has been developed in order to realize low weight structures, but also to improve the efficiency, obtain three-dimensional antennas or build new artificial materials (21).

## 4.13 Gas Transmission

### *4.13.1 Oxygen Barrier*

#### *4.13.1.1 Aluminium Layers*

The structure of thin (10–50 *nm*) aluminium layers vacuum deposited onto polyester film has been examined using both transmission electron microscopy and light microscopy (22).

The density of the pinhole defects in the aluminium coating, quantified by an image analyzing microscope, governs the permeability of the film to oxygen.

Finite element calculations of the effect of various pinhole diameters and densities on the permeability agree with the experimental data. It has also been shown that the barrier properties of the polymer layers immediately adjacent to the metal coating are critical in determining the deleterious effect of the pinhole defects (22).

#### *4.13.1.2 Aluminium Oxynitride*

Metal oxide layers deposited on polymer substrates have been utilized as gas barrier films in food packaging as an alternative to the traditional aluminium foil (23). The resistance of these composite films to gas transmission is controlled predominantly by nanoscale defects created during the fabrication of the oxide layer.

The size and density of these defects are believed to be strongly dependent on the intrinsic properties of the metal oxide layer. Changing the chemical composition of these coatings is a possible method to enhance the gas barrier properties of the films.

Aluminium oxynitride $AlO_xN_y$ gas barrier films were produced by medium frequency of 40 *kHz* AC magnetron sputtering, using a co-axial dual magnetron source with commercial Al targets. Argon was used as the background gas and nitrogen as the reactive gas during the sputtering process. The target-substrate distance was kept constant at 11 *cm* throughout all depositions. The layers were deposited on untreated, optical grade PET of 50 $\mu m$ thickness, n-type Si(100) wafers and mica substrates. The depositions were carried out in plasmas created in both pure nitrogen gas and argon/nitrogen gas mixtures.

These aluminium oxynitride films, fabricated on poly(ethylene terephthalate) substrates, have been investigated using various techniques, among others, scanning proton microprobe, atomic force microscopy, scanning electron microscope; transmission electron microscopy, and gas permeation measurements.

The structural observations have been correlated with the measurements of the oxygen and water vapor permeation of the composite. Oxygen transmission rates are as low as 1 $cm^3m^{-2}d^{-1}atm^{-1}$ and the water vapor transmission rates are below 0.2 $g\,m^{-2}d^{-1}$ (23).

## 4.14 Micromechanical Sensor and Actuator Devices

An innovative concept for the fabrication of micromechanical sensors and actuators has been described where the polymer devices fabricated by injection molding are covered by metal layers of copper, nickel-phosphorus and gold using electroless plating (24). At a sufficient metal layer thickness the mechanical properties of the beams are dominated by the metal cover surrounding the beam.

A differential accelerometer has been fabricated from the metallized liquid crystal polymer. The sensitivity and frequency response is well suited to cover a broad band of applications. So it has been concluded that this technology can be used to fabricate diverse micromechanical sensor or actuator devices (24).

## 4.15 Medical Uses

The characteristics and suitability of various types of electrodes for biomedical applications have been reviewed (25). Electrode geometry, design, surface modification, and stimulation wave forms have been discussed.

### *4.15.1 Leadwires and Intrafascicular Microelectrodes*

A process has been developed for producing fine, very flexible microwires suitable for use as small signal leadwires or nerve electrodes (26).

This process uses the metallization of high-performance monofilament polymer fibers to yield electrically conductive fibers with greatly improved flexibility over solid metal wires of similar strength. The metallization layers are produced by serial vacuum deposition of a 0.3 $\mu m$ thick coating of three metals, titanium-tungsten, gold, and platinum, onto monofilament poly(*p*-phenyl-terephthalate aramid) fibers, i.e., Kevlar®.

The metallization was performed without pre-etching by vacuum deposition using sputter targets. The conditions are shown in Table 4.4.

**Table 4.4** Processing conditions (26).

| Sputter target | Time/*min* | Power/*W* | Thickness/*nm* |
|---|---|---|---|
| Titanium/tungsten | 2 | 320 | 30 |
| Gold | 5 | 400 | 200 |
| Platinum | 4 | 380 | 70 |

The three different metallization layers were deposited sequentially in the order given in Table 4.4, without breaking the vacuum between the changes of the target. This metallization structure achieves a high electrical conductivity without adding significant stiffness to the fiber and has good malleability so as to be resistant to metal fatigue and microcracking (26).

The metallized fibers are then insulated with a 1 $\mu m$ thick layer of silicone elastomer. This elastomer was Silastic® MDX4-4210 from Dow Corning. In the final step, the insulated electrode fibers were attached to tungsten needles, 50 $\mu m$ in diameter and 2 *cm* long.

The result is a microlead with high electrical conductivity, i.e., a linear resistance of 30 *Ohm cm*$^{-1}$, desirable interfacial properties, excellent mechanical stability and extremely high flexibility. These physical characteristics are appropriate for application as signal leadwires or recording electrodes or stimulating electrodes, where a small size and a high flexibility are important.

The use of these materials as intrafascicular electrodes for recording multi-unit neural activity in feline peripheral nerves has been demonstrated (26).

Also, electrochemical gold plating processes were examined for the metallization of Kevlar yarn (27). A conventional $Sn^{2+}/Pt^{2+}$ surface activation coupled with electroless Ni deposition made the fibers conductive enough to serve as cathodes for electrochemical plating.

X-ray diffraction data showed that metallic Pd were formed during the surface activation. In contrast, amorphous phases and trace amounts of pure Ni metal were plated by the electroless process.

The electrodeposition in a thiosulfate bath was the most efficient Au coating process in comparison to the analogous electroless procedure, and electroplating using a commercial cyanide method (27).

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# 5

# Environmental Issues

## 5.1 Recycling

Reclamation of materials from spent or otherwise normally discarded articles has obvious potential for financial as well as environmental benefits (1). Reclamation of plastic or metal from articles consisting of metal or plastic alone may not require a specialized approach. On the other hand, the reclamation of metal, plastic or both from articles comprising intimately combined metal and plastic presents liberation and separation considerations. Several approaches have been proposed.

The reclamation of plastics from metallized plastics presents especially difficult liberation as well as separation problems. For example, a metallized plastic is designed to resist breaking away of metal from plastic. Thus, prior to metallization, such as plating, the plastic may be etched, abraded or otherwise treated to tenaciously adhere metal to plastic.

Even after liberation of metal from plastic, however, separation can be further complicated by additional aspects of certain metallized plastics. For example, the metal may contain nonferrous or essentially nonferrous metal layers. Still further, even low levels of minute particles can render reclaimed plastic unacceptable for return to higher uses, e.g., plating grade thermoplastic.

Metallized plastic, such as chrome-plated plastic, can be processed to separate metal from plastic and especially to recover reusable, essentially metal-free plastic (1). The metallized plastic is comminuted, as necessary, to suitably sized pieces which then are exposed to a cryogenic temperature and impacted in a rotary mill to form a mixture of plastic and metal particles.

Subsequently, most of the metal particles are removed from the mixture by effecting particle size and magnetic separation steps. Oversized particles can be recycled for further processing. The recovered plastic is then extruded, under conditions which render it molten, through one or more screens (1).

## 5.2 Metallized Plastic Packages

Metallized plastic samples were collected from packages of foodstuffs and cosmetics. Analytical results of metallized plastic materials obtained by neutron activation analysis have been presented (2,3).

The polymers could be identified by infrared spectroscopy and differential scanning calorimetry. The results indicated that poly(ethylene), poly(propylene), poly(ethylene terephthalate) and poly(styrene) are polymers used in metallized plastics.

The neutron activation analysis was done by irradiating the samples with a thermal neutron flux of a nuclear reactor, followed by induced $\gamma$-ray activities measurements using a hyperpure germanium detector coupled to a $\gamma$-ray spectrometer. In this way, toxic elements such as arsenic, cadmium, chromium, nickel, and antimony, as well as nontoxic elements, such as barium, calcium, cobalt, iron, scandium, selenium and zinc, could be measured. Their concentrations presented a large variability among the samples.

Analyzing the polymer and toxic elements is of great interest to develop adequate and safe processes for the recycling or the incineration of metallized plastic packages without causing damage to the environment (2).

The range of elemental concentrations in metallized plastics of compact discs, telephones, cards and automobile accessories, food and cosmetic packagings, and toys and housewares has been detailed (3), c.f. Tables 5.1 and 5.2.

**Table 5.1** Range of elemental concentrations (3).

| Element/<br>Amount | Food packagings<br>Range | Cosmetic packagings<br>Range |
|---|---|---|
| As $/\mu g\, kg^{-1}$ | 122 – 191 | 1.4 – 386 |
| Ba $/\mu g\, g^{-1}$ | 35 – 280 | 14 – 908 |
| Br $/\mu g\, kg^{-1}$ | 552 – 1752 | 95 – 3039 |
| Ca $/\mu g\, g^{-1}$ | 306 ± 77 | 134 – 675 |
| Cd $/\mu g\, g^{-1}$ | 0.98 ± 0.14 | 0.029 – 518.2 |
| Co $/\mu g\, kg^{-1}$ | 14 – 3922 | 8 – 8458 |
| Cr $/\mu g\, g^{-1}$ | 0.17 – 163 | 0.08 – 54.9 |
| Fe $/\mu g\, g^{-1}$ | 10 – 918 | 7 – 58 |
| Sb $/\mu g\, kg^{-1}$ | 7.2 – 44346 | 3.8 – 5888 |
| Sc $/\mu g\, kg^{-1}$ | 2.1 – 135.5 | 0.45 – 114 |
| Se $/\mu g\, kg^{-1}$ | 38 – 3591 | 36 – 33006 |
| Zn $/\mu g\, g^{-1}$ | 10.1 – 1088 | 4 – 593 |

**Table 5.2** Range of elemental concentrations (3).

| Element/<br>Amount | Toys<br>Range | Housewares<br>Range |
|---|---|---|
| As $/\mu g\, kg^{-1}$ | 96 ± 3 | 17 – 811 |
| Ba $/\mu g\, g^{-1}$ | — | 13 ± 2 |
| Br $/\mu g\, kg^{-1}$ | 298 – 436 | 163 – 2685 |
| Ca $/\mu g\, g^{-1}$ | 67 ± 27 | 246 – 1872 |
| Cd $/\mu g\, g^{-1}$ | — | 21.3 – 28.0 |
| Co $/\mu g\, kg^{-1}$ | 1715 – 12390 | 45 – 4541 |
| Cr $/\mu g\, g^{-1}$ | 0.024 – 0.67 | 1.8 – 9.3 |
| Fe $/\mu g\, g^{-1}$ | 5 – 135 | 44 – 852 |
| Sb $/\mu g\, kg^{-1}$ | 4.4 – 35 | 19.0 – 3898 |
| Sc $/\mu g\, kg^{-1}$ | 10.2 ± 0.3 | 2.3 – 107.5 |
| Se $/\mu g\, kg^{-1}$ | — | 64 – 5673 |
| Zn $/\mu g\, g^{-1}$ | 113.3 – 154.1 | 37.1 – 124.3 |

## 5.3 Biodegradable Metallized Polymers

Recently, metallized polymers with unconventional properties have become objects of significant research interest for environmental protection, bionanotechnology, or radiophysics (4).

A biocompatible, biodegradable and bacteriostatic siloxane/carbonate copolymer has been used as a support for magnetronic and ion-plasma deposition. These methods were developed for the preparation of Cu-containing hybrid or Ni and Au coating.

The surface structure, optical and mechanical properties were found to be dependent on deposition time, temperature, and coating thickness. For gold coatings with a thickness of about 80 *nm* the most favorable results on durability, were obtained, its defectless area was 43 *nm* (4).

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*Metallized and Magnetic Polymers: Chemistry and Applications.* Johannes Karl Fink.

# PART II

# MAGNETIC POLYMERS

*Metallized and Magnetic Polymers: Chemistry and Applications.* Johannes Karl Fink.

# 6

# General Aspects

Magnetic polymers can be fabricated by incorporating small magnetic metal particles into the conventional polymer. On the other hand, pure organic materials with magnetic properties have been discovered. These structures can be incorporated by a chemical reaction into a polymer, either by attaching polymerizing groups to these materials and starting a polymerization reaction or by grafting these materials onto already existing polymers. The issue of magnetic polymers has been reviewed (1).

Also, magnetic polymer nanocomposites have been reviewed in a monograph (2). In 1992, there were warnings about the nature of magnetic polymers (3):

> Numerous reports claiming ferromagnetic behavior in organic polymers exist. However, the reported materials have been plagued by ill-defined compositions, low yields on a magnetic basis, and poor reproducibility (3).
>
> Such low values of saturation magnetization cause serious concern as to whether the magnetic behavior arises from extrinsic sources and thus obligate the researcher to provide a persuasive case that when a material has a low saturation magnetization, suggesting that the magnetic fraction is only a small portion of the bulk, that the magnetic behavior is in fact intrinsic and not of extrinsic origin.
>
> In several cases, when reinvestigated, the magnetic behavior of reported polymeric magnetic materials has been attributed to extrinsic sources. In the cases where extrinsic sources have not been identified, verification of

> the magnetic behavior has not been reported by independent laboratories. Thus, until 1992 there have not been any reports of a bulk polymer that have stood the test of confirmation for ferromagnetic or even ferrimagnetic behavior (3).

On the other hand, some time later, the same author reviewed magnets composed of molecular components (4).

## 6.1 History

Synthetic organic polymers have been compounded with magnetic materials to result in a magnetic gum and in magnetic tapes. These materials have been made by dispersing an inorganic magnetic substance in a synthetic rubber, or by kinking ferrite onto a polymer film. The polymers themselves are not magnetic substances. Most organic compounds have no unpaired electrons. The exceptions are free radicals and carbenes, which are unstable at room temperature.

For this reason, organic compounds have not been of great interest as magnetic materials, although a few papers have pointed out the theoretical possibility of ferromagnetic organic compounds. Organic polymers containing paramagnetic substances have been of interest for their usage as conducting materials, redox resins, and antioxidants (5–9).

In 1967, it was discovered that the electronic ground state of bis-(phenylmethylenyl)-*m*-phenylene, a dicarbene, is the quintet state. The magnitudes of the observed zero-field splittings agreed with the theoretical prediction made by Higuchi (10–12). This compound is shown in Figure 6.1.

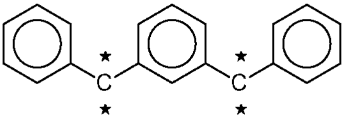

**Figure 6.1** Bis(phenylmethylenyl)-*m*-phenylene.

Afterwards, it has been proposed that hypothetical polymers with a conjugated *p*-electron system, c.f. Figure 6.2, could show a ferromagnetic spin-alignment due to the topological assignment of their molecular orbits (13).

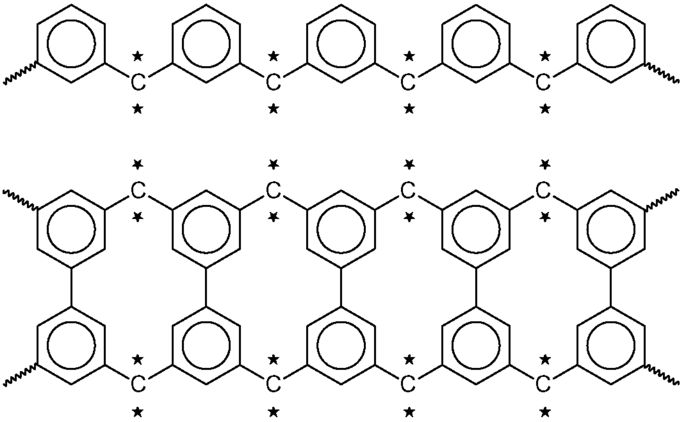

Figure 6.2 Polymers with a conjugated *p*-electron system.

1.5-Diphenyl-3-(*p*-methacryloyloxymethylphenyl) verdazyl and related compounds have been synthesized and anionically polymerized using *n*-butylmagnesium bromide or sodium naphthalene as initiator. Dark green polymers with a molecular weight of about 2300 *Dalton* could be obtained (14).

Already in 1984, some poly(carbene)s were prepared by an *in-situ* photolysis of polydiazo derivatives. Measurements of their magnetic susceptibility showed that the poly(carbene)s have the highest possible spin multiplicities in the ground state.

In 1986, the first organic ferromagnet was reported (15). The magnetic properties of these compounds were attributed to interactions of the *p*-electrons of C, O, and N. This behavior is different from the magnetism in conventional atom-based and d-f electron inorganic materials.

The magnetic properties of organic compounds can be tailored by flexible organic synthetic methods. This possibility may expand the potential applications (1). In 1990, a polymer with an indigo unit in the main chain was prepared. The structure is shown in Figure 6.3.

This polymer contains some material that can be attracted to a permanent magnet (16). Evidence for hysteresis loop at room temperature was reported.

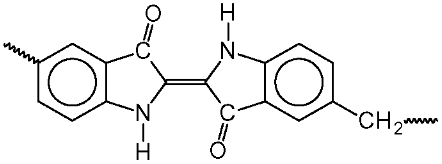

Figure 6.3 Polymer with an indigo unit.

Polymers synthesized from the 1,3-dipolar cycloaddition of 1,3-bis-(3-sydnone) and *N′*,*N′*-(1,4- phenylene)bismaleimide exhibit a magnetic behavior similar to ferromagnets, even at room temperature (17). The structure is shown in Figure 6.4.

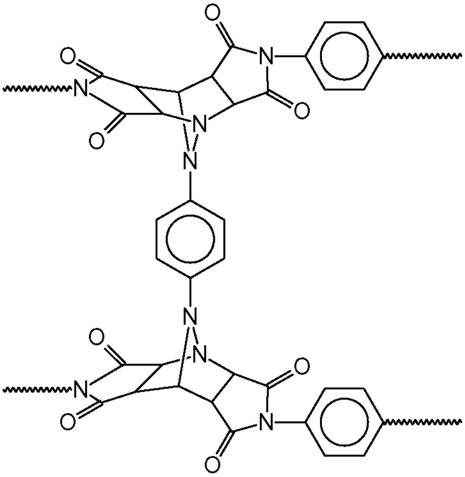

Figure 6.4 1,3-Bis-(3-sydnone)-based polymer (17).

## 6.2 Basic Issues of Magnetism

When a substance is exposed to a magnetic field *H*, the magnetic induction *B* of the substance can be expressed as

$$B = H + 4\pi M \quad . \tag{6.1}$$

In Equation 6.1, *M* is the magnetization. The magnetic susceptibility $\chi$ of a material in a magnetic field is the ratio of the magnetization to the magnitude of the magnetic field:

$$\chi = \frac{M}{H} \quad . \tag{6.2}$$

The sign of the magnetic susceptibility usually depends on whether the electrons in a particular molecule are paired or unpaired. All of the matter can be divided into two categories relative to their magnetic properties:

1. Diamagnetic, and
2. Paramagnetic.

Paramagnetic materials have unpaired electron spins in a molecule or ion. On the other hand, diamagnetism is generated by paired electrons moving in a closed orbital. In a diamagnetic molecule, where the magnetic induction $B$ is smaller than the magnetic field $H$, the a negative value of $\chi$ is experienced. In a paramagnetic molecule, in which the value of $B$ is larger than that of $H$, the value of $\chi$ is positive (1).

In paramagnetic species, four types of magnetization are possible. This is a result of the magnetic interaction among randomly oriented spins. These types are paramagnetism as such, ferromagnetism, antiferromagnetism, and ferrimagnetism (1).

In paramagnetism the spins are oriented randomly as there is no magnetic interaction among the spins. In ferromagnetism the randomly oriented spins of a paramagnetic substance orient themselves parallel to one another. In antiferromagnetism, the situation is reverse, the spins orient themselves antiparallel. In ferrimagnetism the spins orientate antiparallel alternately to one another. A two-dimensional model of the spin orientation is shown in Figure 6.5.

## 6.3 Types of Magnetic Organic Polymers

Organic polymers for magnetism have been classified into three categories (1):

1. Polymers with organic radicals in the side chains,

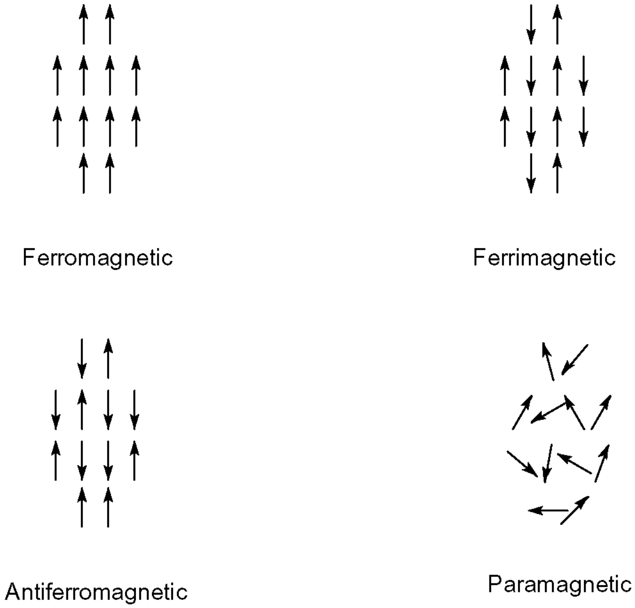

**Figure 6.5** Basic spin orientation in magnetic types (1).

2. Main-chain conjugated polymers with organic radicals, and
3. Two-dimensional polyradicals.

### *6.3.1 Organic Radicals in the Side Chains*

Since magnetism develops by a spin-alignment owing to an intermolecular exchange interaction of electrons in the d- or f-orbitals of metal ions, the magnetic behavior of organic polymers containing paramagnetic metal ions is of interest for developing ferromagnetism in polymers.

Polymers with tetraphenylporphyrin side chains and metals attached to these side chains interact antiferromagnetically (18, 19). The interaction is much larger than that of the corresponding monomer units. The basic structure of these polymers is shown in Figure 6.6.

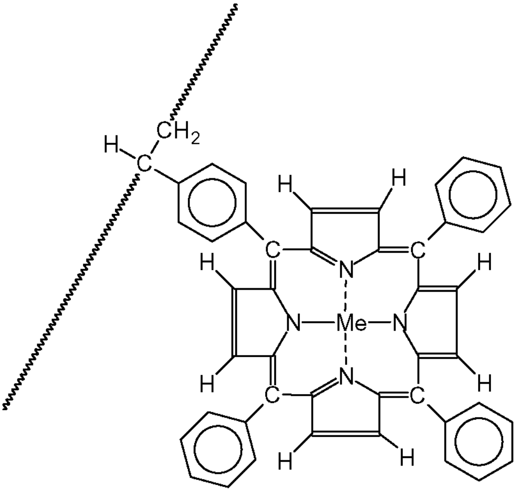

**Figure 6.6** Polymers with tetraphenylporphyrin side chains (1).

In 1989, it was found that ferromagnetic polymers can be formed by the dehydrogenation of triarylmethane resins by irradiation of UV light or laser light in the presence of photo-oxidizing agents (20). The basic structure of these polymers is shown in Figure 6.7. This finding confirmed that conjugated polymer chains are necessary for the occurrence of ferromagnetism.

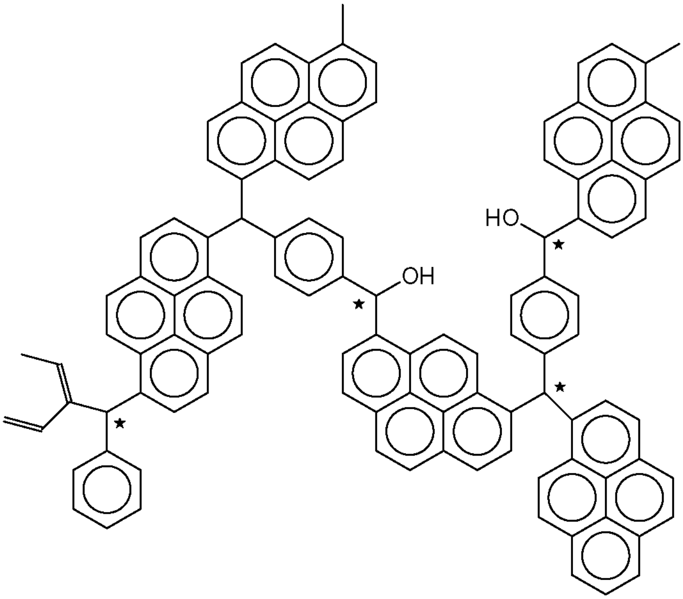

**Figure 6.7** Triarylmethane resins (20).

### 6.3.1.1 *Ferromagnetic Porphin Compounds*

There is an increasing need for insulating magnetic materials which are chemically stable up to critical or Curie temperatures in excess of 125°C. Such magnetic materials may be substituted for ferrites and other insulating magnetic compounds in applications such as radio frequency transformers, bulk magnets, magnetic and magneto-optic recording materials. The magnetic materials may also be included in photomagnetic switches, integrated optical devices, colloidal dispersions, i.e., ferrofluids and magnetic inks, thin film and multilayer magnets, magnetostrictive sensors, microwave materials, magnetic bubbles and soft magnetic materials with low coercive fields for AC motors, generators and transformers, as well as for magnetic imaging and transducers for medical implants, if the magnetic material is biocompatible.

Ferromagnetic porphin compounds can be produced by heating a non-ferromagnetic porphin compound having a central transition metal atom in the non-ferromagnetic porphin molecule and at least some of the pyrrole rings of the non-ferromagnetic porphin molecule having benzene or phenyl groups substituted on or integral with said rings (21). The non-ferromagnetic porphin compound is heated in the substantial absence of oxygen to a temperature sufficient to pyrolyze at least a portion of the benzene or phenyl groups of the non-ferromagnetic porphin compound. A ferromagnetic porphin compound is formed, which is inherently magnetic and is capable of retaining magnetism when exposed to a magnetic field. The resulting ferromagnetic porphin compounds retain their ferromagnetic properties even up to about 473 $K$ in air and at much higher temperatures in vacuum or an inert atmosphere (21).

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# 7

# Methods of Fabrication

## 7.1 Preparation of Magnetic Polymer Particles

### 7.1.1 *Coprecipitation*

Magnetic polymer particles can be produced by the coprecipitation of transition metals in the presence of a polymer having available coordination sites (1). These particles are capable of forming stable aqueous suspensions and may be easily resuspended after agglomeration.

For the preparation, a solution containing $FeCl_2$ and $FeCl_2$ and a polymer, such as a protein, having available coordination sites is treated with a strong base, such as ammonium hydroxide $NH_4OH$ in order to precipitate magnetic iron oxides such as magnetite ($Fe_3O_4$) in a form which is intimately combined with the polymer. The precipitation is typically carried out with rapid stirring and optional agitation by sonication, in order to produce resuspendable magnetic-polymer particles. After precipitation, the particles are washed and subsequently resuspended in a buffer solution at approximately neutral pH (1).

Subsequent to precipitation and resuspension, the particles may be treated with a bifunctional reagent in order to effect crosslinking of reactive sites present on the polymer.

This crosslinking may be effective as either an intra-particulate crosslinking in which reactive sites are bound on the same particle, or may be a reaction of an extra-particulate ligand which is then crosslinked to the polymer on a given particle. In the second case, a bifunctional reagent having a relatively short distance between its two functional groupings is desirable to promote the linkage between the particle polymer and the extra-particulate species. Conversely, intra-particulate crosslinking is promoted by the use of a bifunctional reagent which is longer and is not sterically hindered from bending, so that two reactive sites on a single particle may be linked by a single bifunctional molecule.

The magnetic polymer particles prepared in this way exhibit many useful properties. The particles are magnetic due to the inclusion of a form of magnetic metal compound. The particles may be formulated to be resuspendable after aggregation and to produce relatively stable suspensions which do not settle even after several days of quiescent storage. Furthermore, the particles may be relatively small (approximately 0.01–0.2 $\mu m$) and therefore filter sterilizable. Also, the particles can be tailored to include specific biofunctional ligands useful in various analytical, diagnostic, and other biological or medical applications (1).

Special examples have been detailed, such as coupling to antibodies, particles containing a radioiostope of iodine, and a magnetic immunoassay (1).

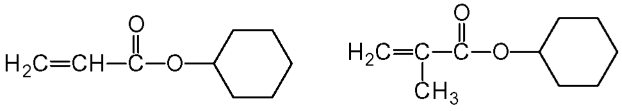
### *7.1.2 Superparamagnetic Substances*

Aromatic monomers have the problem of the absorption of UV lights and emission of fluorescent lights (2). Therefore, magnetic polymer particles that contain a large amount of styrene monomers may have a problem when physiologically active compounds are to be detected or identified. The strong nonspecific absorbency of the styrene polymer particles with proteins may cause a problem when the magnetic polymer particles containing styrene monomers are used for diagnostics.

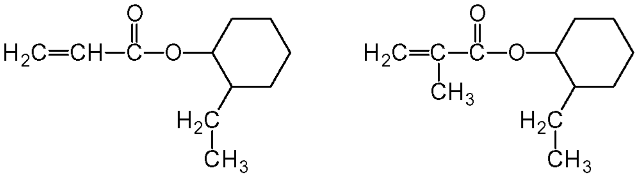
Also, when magnetic polymer particles have the problem of elution of iron ions, they are applicable only in fields where the elution of iron ions has no influence. The problem of elution of iron ions can be circumvented by a process described below (2).

A superparamagnetic substance can be used in the process for manufacturing magnetic polymer particles (2). The superparamagnetic substance should be lipophilic. Examples of a superparamagnetic substance contained in the magnetic polymer particles are metals such as triiron tetroxide ($Fe_3O_4$) and ferrites.

As monomers for inclusion, 2-ethylcyclohexyl acrylate, 2-ethylcyclohexyl methacrylate, cyclohexyl acrylate, and cyclohexyl methacrylate have been proposed. These compounds are shown in Figure 7.1.



Cyclohexyl acrylate Cyclohexyl methacrylate



2-Ethylcyclohexyl acrylate 2-Ethylcyclohexyl methacrylate

**Figure 7.1** Monomers for inclusion.

The monomers are added to a superparamagnetic substance and the organic phase is premixed with a water phase using a homogenizer and then dispersed using an ultrasonic dispersing machine to prepare an oil-in-water type emulsion with the average diameter of the oil droplets being 2 $\mu m$. Then the polymerization is started.

The following processes may be used to prevent a superparamagnetic substance from flowing out of the magnetic polymer particles (2):

1. Additional polymerizing a vinyl monomer in the presence of already fabricated magnetic polymer particles.
2. Bringing an iron solubilizer into contact with the magnetic polymer particles, dissolving and removing the superparamagnetic substance remaining around the surface of the magnetic polymer particles after the polymerization reaction.
3. Bringing an organic base or a water-soluble solvent into con-

tact with the resulting magnetic polymer particles after the polymerization reaction.

### 7.1.3 *Conventional Processes*

Conventional processes for preparing polymer particles containing magnetite ($Fe_3O_4$) coat the magnetite particles with a polymeric material (3).

$Fe_3O_4$-based magnetic nanoparticles can be used in wastewater treatment and biological fields for such applications as magnetic resonance imaging contrast agents, hyperthermia therapy and protein separation. The $Fe_3O_4$-based magnetic nanoparticles are attractive because they combine the advantages of magnetism and polymers together. In order to obtain practical application in the above-mentioned areas, the bare $Fe_3O_4$ needs to be functionalized with different kinds of molecules like organic small molecules and polymers and some inorganic molecules like silica, metals and carbon. The chemical preparation methods, different modification methods and various applications of the $Fe_3O_4$-based magnetic nanoparticles have been reviewed (4).

A commonly used method uses magnetite powder which is mixed mechanically with a molten polymer. After this treatment, the magnetite-containing polymeric material is finely divided. However, this procedure results in particles having an uneven shape with different sizes. Particles prepared in this manner are often used as toner, but the uneven shape is undesired since it will result in uneven and unsharp edges on the characters.

Another method uses finely divided magnetite, to which a vinyl monomer and an initiator are added in water to form a polymer around the magnetite grains. Here also magnetic particles having an undefined and highly variable size and shape are formed. Further, only some of the particles will be magnetic, and the content of magnetite in the particles is usually very unequal. Other methods employ the admixture of albumin and other proteins with magnetite and vigorous stirring in water with emulsifier to form drops which contain magnetite and protein. Still another method consists of the treatment of swelling polymer particles with finely divided magnetite to obtain magnetite on, and possibly some inside, the particles.

### 7.1.4 *Iron Salt Modification*

Magnetic iron oxide can be homogeneously placed in a polymer latex by chemical reaction. Iron is introduced into the particles in the form of salts and is then converted to magnetic iron oxide, which to a great extent will be magnetite ($Fe_3O_4$) or oxides having corresponding magnetism.

A great advantage of the process is that it allows all of the particles to have the same concentration of magnetic iron oxide. When monodisperse polymer particles are formed as starting material, the process will in particular provide monodisperse magnetic polymer particles which all contain the same amount of magnetic iron oxide. The procedure may run as follows (3):

**Preparation 7–1:** 100 *ml* of methyl methacrylate, 90 *ml* of glycidyl methacrylate, 10 *ml* of ethyleneglycol dimethacrylate and 1750 *ml* of $H_2O$ were mixed in a reactor. The mixture was then subjected to rapid stirring for 30 *min*. Then, 2.0 *g* of $(NH_4)_2S_2O_8$ dissolved in 50 *ml* of water were added. The temperature was raised to 65°C, and polymerization was carried out for 6 *h*. After polymerization a latex containing 10% of polymer, particle size 0.2–0.3 *μm*, was obtained.

100 *ml* of the latex were treated with 100 *ml* of ethylene diamine at 80°C for 3 *h*. After the reaction, excess ethylene diamine was removed by dialysis for 10 *d*, with change of water every day.

Elementary analysis showed that the particles contained 4.6% of N. 50 *ml* of dialyzed latex containing 5 *g* of particles treated with ethylene diamine were cooled down to 10°C.

811 *mg* $FeCl_3 \times 6H_2O$ were dissolved in 20 *ml* of water and cooled down to 10°C. Similarly, 338 *mg* $FeCl_2 \times 4H_2O$ were dissolved in 20 *ml* of water and cooled down to 10°C. The two iron chloride solutions were combined and then mixed with the latex in a rotating container, which was rapidly evacuated down to 10 *mmHg*. After 20 *min*, 10 *ml* cold (10°C) ammonia solution (25%) were added by suction.

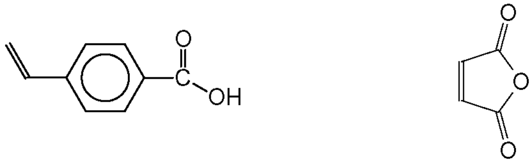
The vacuum was then eliminated, and the temperature was raised to 80°C. After 30 *min* at 80°C, the mixture was cooled and the particles separated from the solution by centrifugation. The particles were washed several times with water to remove excess ammonia and ammonium chloride formed. After this treatment the particles contain magnetic iron oxide. The iron content in the particles was found to be 4.9%.

It is also possible to bind the iron by means of ionic bonds (3). Having acid groups on and inside the particles, the iron may be transported from the outer phase of the dissolved iron salt to be bound to these groups.

Examples of monomers which will provide such acid groups are methacrylic acid, *p*-vinyl benzoic acid and maleic anhydride. These monomers are shown in Figure 7.2.

Acrylic acid

Methacrylic acid



*p*-Vinyl benzoic acid

Maleic anhydride

**Figure 7.2** Monomers that provide acid groups.

The iron salt-binding groups may also be attached to the previously formed polymers. Thus, it is possible to prepare a copolymer from a monomer mixture, which essentially consists of vinyl monomer with epoxy groups such as glycidyl methacrylate.

By treating the final polymer with substances which react with epoxy groups and which contain N-groups, the groups will become covalently bonded on and inside the particles. It is possible to treat polymer particles containing epoxy groups with ethylenediamine to form $-CH_2-NH-CH_2-CH_2-NH_2$ groups.

Another method for the introduction of iron-binding groups comprises the introduction of $-NH_2$ groups or $-CH_2-NH_2$ groups on the benzene nucleus in the polymer particles prepared by polymerization of an aromatic monomer (3).

Similarly, acid groups may be introduced into the final polymer particles. This may be obtained by hydrolyzing a polymer which contains ester groups. It is also possible to introduce sulfonic acid groups and carboxylic acid groups.

The suggestions above and still more, e.g., iron binding by the introduction of hydrazine groups or nitrogen dioxide groups, have been exemplified in detail (3,5).

### *7.1.5 Fluorescent Magnetic Polymer Particles*

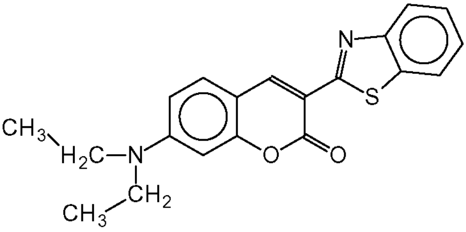
Magnetically responsive fluorescent polymer particles can be used as highly sensitive quantitative reagents for biochemical and immunological studies (6). The fluorescent magnetic particles can serve as a marker for a correct number of particles being delivered to an assay well and for detecting particle loss during the assay.

These fluorescent magnetic particles, with or without coupling to biological material, can be incorporated at various ratios into nonmagnetic particles for various assays to serve as markers for making sure that the correct number of particles are being delivered into the well and for checking the particle loss during the assay.

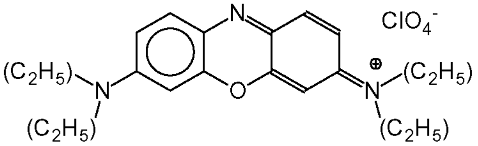
The fluorescent magnetic particles may be prepared by first producing a magnetically responsive metal oxide with an average size of about 1 $\mu m$ or less and then coating a fluorescent polymeric core particle with a layer of polymer containing metal oxide. The surface of these fluorescent magnetic particles can be coated further with another layer of polymer or functionalized polymer to provide the desired surface characteristics (6).

The spectral characteristics of the fluorescent magnetic particles can be varied by using core particles incorporated with various fluorescent dyes, either a single fluorescent dye or a combination of several fluorescent dyes. Alternatively, the fluorescent magnetic particles can be prepared by incorporating various fluorescent dyes, either a single fluorescent dye or a combination of several fluorescent dyes, which are soluble in the monomer and can withstand the polymerization conditions in the presence of nonfluorescent polymeric core particles, metal oxide, and monomer. Suitable fluorescent materials are collected in Table 7.1. Some fluorescent dyes are shown in Figure 7.3.

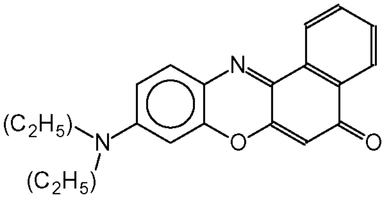
The particles have been found to he useful in immunoassays and a wide variety of biomedical applications. The fluorescent magnetic particles can be used for passive or covalent coupling of biological



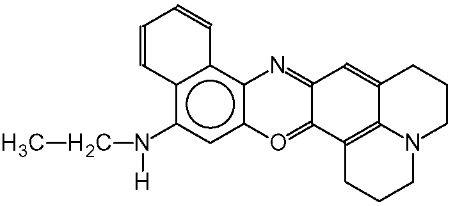
Coumarin 6



Oxazine 725
(3,7-Bis(diethylamino)phenoxazin-5-ium perchlorate)



Nile red



Oxazine 750

**Figure 7.3** Coumarin 6, Oxazine 725 (3,7-bis(diethylamino)phenoxazin-5-ium perchlorate), Oxazine 750 .

**Table 7.1** Fluorescent dyes (6).

| Compound | Compound |
|---|---|
| Nile red | Nile blue |
| Coumarin 4 | Coumarin 6 |
| Oxazine 725 | Oxazine 750 |
| Rhodamine B | |

material such as antigens, antibodies, enzymes or deoxyribonucleic acid (DNA)/RNA and used as solid phase for various types of immunoassays, DNA/RNA hybridization assays, affinity purification, cell separation, phagocytosis, and other biomedical applications (6). An electron micrograph of the magnetic particles described above is shown in Figure 7.4.

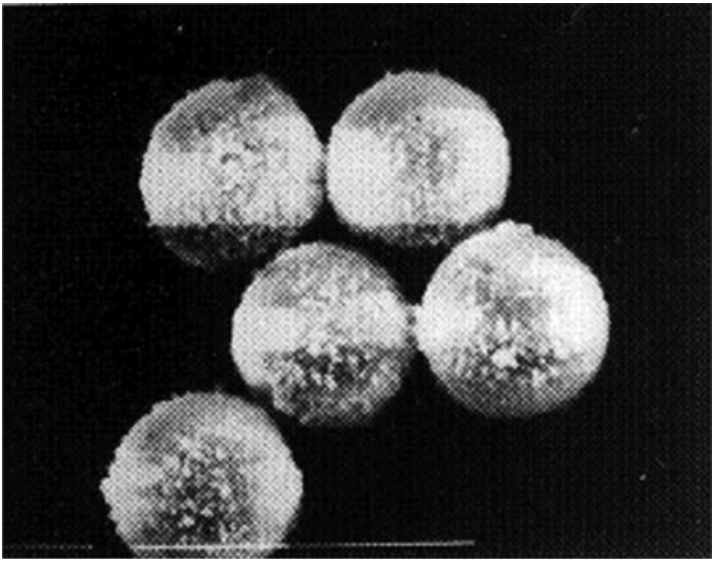


**Figure 7.4** Electron micrograph of magnetic fluorescent particles (6).

## 7.2 Special Types

### 7.2.1 *Spherical Iron Nanoparticles*

Spherical iron nanoparticles with a diameter of 10 *nm* have been synthesized using water in oil reverse micelle systems (7). The particles were encapsulated in styrene polymer by an emulsion polymerization method. The resulting beads were 150 ± 50 *nm* in diameter, having a saturation magnetization of 23.5 $emug^{-1}$ . The styrene-coated iron particles exhibited a superparamagnetism, as confirmed by Mössbauer spectroscopy, and dispersed well in water. The saturation magnetization was higher than reported for commercially available polymer-coated micron sized beads. The styrene-coated iron nanobeads are intended for medical use.

In particular, certain magnetic ionic liquid monomers, such as 1-vinyl-3-dodecyl-imidazolium monomers with metal halides counter-anions, have been synthesized. These ionic liquid monomers were homopolymerized to get magnetic poly(ionic liquids). Then, magnetic latexes were synthesized by using the magnetic ionic liquids as surfmers using an emulsion polymerization of methyl methacrylate/*n*-butyl acrylate. It was found that the powders obtained by freeze-drying showed a paramagnetic behavior with weak antiferromagnetic interactions between the adjacent metal ions.

Even when the ratio of magnetic ionic liquid to monomer was only 2%, these poly(methyl methacrylate-*co*-butyl acrylate) powders and latexes responded to a magnetic field due to the surfmer paramagnetic nature (7).

### 7.2.2 *Magnetic Polymer Latex*

Magnetic polymers in the form of gels or particles are generally obtained by mixing a magnetically charged material into a polymer prepared by conventional bulk, solution, emulsion or suspension polymerization methods (8). In the preparation of magnetic polymers, an additional stage, such as atomization, coagulation, extrusion and distillation of the solvent is often required, thus necessitating both suitable equipment and the expenditure of more than trivial energy.

Often, difficulties in the dispersion are encountered. This results in polymer particles having both defective magnetic charge distributions and modified properties.

Special latex polymers are required to disperse the magnetic charge. A method for dispersion has been suggested. This is the addition of a magnetically charged material during the emulsion polymerization of a mixture of monomers. At least one of the monomers should be water soluble. However, with this method, hydrophilic polymers of restricted applicability are formed. These disadvantages can be overcome by the following method (8):

1. Dispersing a magnetically charged material into an organic phase comprising an organically-soluble initiator and an organic monomeric component selected from the group consisting of a single vinyl aromatic monomer and a combination of a single vinyl aromatic monomer and a copolymerizing monomer,
2. Preparing an aqueous solution comprising water and at least one emulsifier,
3. Mixing the organic phase containing the dispersed magnetically charged material with the prepared aqueous solution,
4. Homogenizing the mixture of the organic phase containing the dispersed magnetically charged material and the prepared aqueous solution, and
5. Polymerizing the homogenized mixture to obtain a magnetic-polymer latex containing hydrophobic vinyl aromatic polymer particles.

The magnetic polymer lattices are stable, comprise polymer particles containing therein well-dispersed magnetically charged materials, and are easily obtained by polymerizing water-insoluble monomers in the presence of a magnetically charged material.

The magnetically charged material is selected from iron oxide, chromium dioxide and iron oxide combined or mixed with a metal oxide. The metal oxide is selected from cobalt oxide, manganese oxide, zinc oxide, barium oxide and rare earth oxides. Suitable magnetically-charge materials are (8):

- Metals such as iron, iron-silicon, nickel, and cobalt,

- Metal alloys of any one of iron, iron-silicon, nickel or cobalt with at least one of molybdenum, chromium, copper, vanadium, manganese, aluminum, and titanium,
- Pure iron oxides such as $Fe_3O_4$ or $\gamma-Fe_2O_3$,
- Iron oxides such as $Fe_3O_4$ or $\gamma-Fe_2O_3$, combined with other metal oxides such as cobalt oxide, manganese oxide, zinc oxide, barium oxide, and rare earth oxides, and
- Chromium dioxide.

Suitable monomers for hydrophobic vinyl aromatic polymers and copolymers, respectively are collected in Table 7.2. Suitable polymerization initiators are collected in Table 7.3 and some are shown in Figure 7.5.

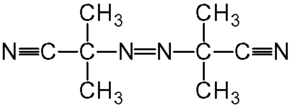
**Table 7.2** Monomers for hydrophobic vinyl aromatic polymers (8).

| Aromatic monomer | Aromatic monomer |
|---|---|
| Styrene<br>Ethylstyrene<br>Vinyltoluene | $\alpha$-Methylstyrene<br>*tert*-Butylstyrene |
| Ester monomer | Ester monomer |
| Heptyl fumarate<br>Methyl itaconate | Octyl fumarate<br>Ethyl itaconate |
| Diene monomer | Diene monomer |
| Butadiene | Isoprene |

To produce the magnetic polymer lattices, the magnetically charged materials are dispersed into an organic phase together with the monomers and the initiator.

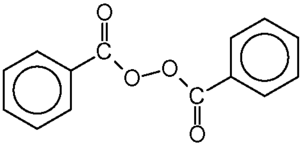
Before the polymerization starts, in order to get a latex, the organic phase is dispersed in water together with an emulgator, such as sodium laurylsulfate and oxyethylenated nonyl phenol. The magnetic-polymer lattices obtained are useful in paints, magnetic tapes, recordings, and biological applications (8).

The final polymer particles are readily attracted by a magnet even when the concentration thereof in the latex is very low. In certain applications, therefore, the magnetic polymer particles may be easily

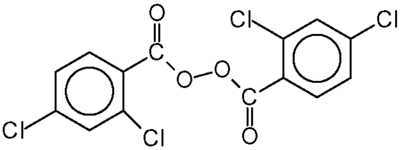


Azobisisobutyronitrile

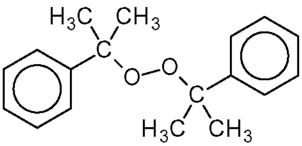
1,1′-Azobis(cyclohexanecarbonitrile)



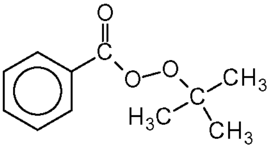
Benzoyl peroxide



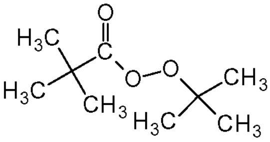
2.4-Dichlororo benzoyl peroxide



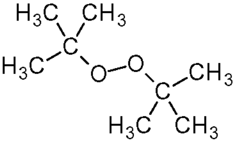
Dicumyl peroxide



*tert*-Butyl peroxybenzoate



*tert*-Butyl perpivalate



Di-*tert*-butyl peroxide

**Figure 7.5** Polymerization initiators.

**Table 7.3** Polymerization initiators (8).

| Initiator | Initiator |
|---|---|
| Azobisisobutyronitrile | 1,1′-Azobis(cyclohexanecarbonitrile) |
| Dibenzoyl peroxide | Dicumyl peroxide |
| Di-*tert*-butyl peroxide | Diacetyl peroxide |
| Dioctanyl peroxide | Lauroyl peroxide |
| Methyl ethyl ketone peroxide | Caprylyl peroxide |
| Dichloro-2,4-benzoyl peroxide | *p*-Chlorobenzoyl peroxide |
| *tert*-Butyl perpivalate | *tert*-Butyl diethylperacetate |
| *tert*-Butyl peroxybenzoate | Di-*tert*-butyl diperphthalate |
| 1,1-Di-*tert*-butyl-peroxide-3,3,5-trimethylcyclohexane | |

separated from the ambient liquid medium without resorting to the conventional methods of coagulation and atomization.

### 7.2.3 *Imprinted Polymer Particles*

Magnetic hydrophilic molecularly imprinted polymer particles were successfully synthesized via an inverse suspension polymerization in silicone oil, using methacryloxypropyltrimethoxysilane modified $Fe_3O_4$ nanoparticles as magnetic particles, 2,4-dichlorophenoxyacetic acid as template, hydroxyethyl methacrylate as hydrophilic monomer, and acetonitrile as a high polar porogen (9).

The synthesized magnetic hydrophilic molecularly imprinted polymer particles could be separated rapidly under an external magnetic field. About 94% transmittance of the particle/water suspension could be reached within 20 *min* by magnetic separation, whereas about 84% transmittance was achieved after at least 180 *min* by sedimentation.

The hydrophilic molecularly imprinted polymer particles showed a higher selectivity for templates. Hydrophilic molecularly imprinted polymer particles took on a higher imprinting factor than hydrophobic molecularly imprinted polymer particles and were able to rebind hydrophilic molecularly imprinted polymer particles more easily than 4-chorophenoxyacetic acid (9).

### *7.2.4 Magnetic Polymers from Maghemite and Poly(vinyl alcohol)*

Oxide particles synthesized and dispersed in aqueous medium, containing different polymeric forms, can be trapped in solid matrices, keeping a high dispersion degree (10). The oxide/polymer mass ratio determines the average distance between the particles existing in the sol. In this work, ultrafine maghemite particles were prepared in aqueous solution containing different concentrations of poly(vinyl alcohol) (PVA). The average diameter of the obtained particles was below 20 *nm*.

The adsorption of PVA on the surface of maghemite was examined by infrared spectra and thermogravimetry (TG). The dispersion and agglomeration of the particles were different in an aqueous solution at 4% because the magnetite particles were of a small diameter. The magnetic properties of these composites are preserved (10).

### *7.2.5 Ethylenediamine-Functionalized Magnetic Polymers*

A series of ethylenediamine (EDA)-functionalized magnetic polymers have been prepared using the suspension polymerization technique with a varied amount of glycidyl methacrylate during the suspension polymerization procedure (11). The EDA-functionalized magnetic polymers were characterized by transmission electron microscopy, vibrating sample magnetometer, X-ray diffractometer, TG.

The adsorption properties of the EDA-functionalized magnetic polymers for the removal of chromium (VI) in wastewater were studied. The results showed that the adsorption efficiency was highly pH dependent and decreased with the increasing of initial concentration of chromium (VI). The adsorption data obtained at optimized conditions, i.e., 35°C and a pH of 2.5, could be well fitted with a Langmuir isotherm.

The maximum adsorption capacities of the EDA-functionalized magnetic polymers to Cr(VI) were highly related to the contents of EDA-functionalized magnetic polymers. The adsorption kinetic data were modeled by a pseudo-second-order rate equation, and the adsorption of Cr(VI) by all the present EDA-functionalized magnetic polymers reached equilibrium in 60 *min* (11).

### 7.2.6 *Magnetic Fluids*

Two room-temperature ionic liquids containing tetrachloroferrate-(III) ions, 1-butyl-3-methylimidazolium tetrachloroferrate and 1-butyronitrile-3-methylimidazolium tetrachloroferrate have been compared (12). Their magnetic susceptibilities are similar, but the observed responses are distinct from each other, suggesting that the response is determined not only by the magnetic susceptibility but also by the other factors, including density, viscosity, and surface tension.

These magnetic ionic liquids constitute a new class of magnetic fluids that hold many attractive physical properties for practical applications (12).

A magnetic ionic liquid, which shows a strong response to magnetic field, has been synthesized in an ionic liquid by mixing 1-butyl-3-methylimidazolium chloride and $FeCl_3$. Visible absorption spectroscopy showed that this liquid contains the high spin $FeCl^{4-}$ as the anion. This ionic liquid responded strongly to a magnetic field (12).

### 7.2.7 *Magnetic Ceramic Thin Films*

Magnetic ceramic thin films containing Co–Fe alloy nanoparticles have been prepared by the pyrolysis of a highly metallized polymer precursor composed of a poly(ferrocenylsilane) with pendant cobalt clusters under a reductive atmosphere (13).

The variation of the pyrolysis conditions results in changes in the nanoparticle size, size distribution, and composition, as well as the ceramic film structure, all of which influence the magnetic properties of the material.

When pyrolyzed at 500°C, the nucleation and growth afford uniform size, larger Co–Fe nanoparticles on the film surface, and smaller nanoparticles in the underlying layer of the ceramic films.

The nanoparticle-containing films are superparamagnetic when pyrolyzed at 600°C and are ferromagnetic at higher pyrolysis temperatures (13).

### 7.2.8 *Iron-Schiff-Base Magnetic Polymers*

A magnetically active organometallic iron-Schiff-base polymer, with a molecular weight between 4–50 *k Dalton*, was synthesized (14). This polymer comprised a multiplicity of Schiff-base tridentate chelating groups having the capacity to combine with the iron (II) or iron (III) ion of an organic salt.

The magnetic susceptibility of this organic polymer was between about $1 \times 10^{-6}$ and $1 \times 10^{-2}$ $cc\,g^{-1}$ at ambient temperature. When this polymer, which was a useful tough film, was heated up to about 200°C and held for approximately 1 *min*, the magnetic susceptibility increased from $1 \times 10^{-4}$ $cc\,g^{-1}$ to $6 \times 10^{-4}$ $cc\,g^{-1}$.

This surprising permanent residual enhancement of the magnetic susceptibility of this polymer should be useful in the storage of information in optical magnetic devices (14).

### 7.2.9 *Bisverdazyl Diradicals*

Stable free radicals stem from their potential as building blocks for the formation of molecular magnetic materials. In addition, there is great potential for the formation of magnetic polymers from them. The synthesis of polymers has been detailed (15).

#### 7.2.9.1 *Singlet-Triplet Splitting*

Density functional calculations were performed on the 1,1′,5,5′-tetramethyl-6,6′-dioxo-3,3′-biverdazyl diradical, c.f. Figure 7.6, and some of these complexes in order to investigate how Cu chelation affects the singlet-triplet splitting of the verdazyl system (16).

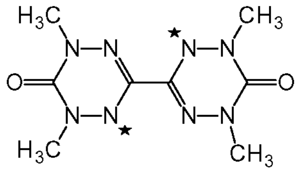


**Figure 7.6** 1,1′,5,5′-Tetramethyl-6,6′-dioxo-3,3′-biverdazyl diradical.

It was found that Cu coordination delocalizes the singlet state, resulting in increased electron-electron interactions, which favor the triplet state. In addition, it was found that the size of the singlet-triplet splitting can be tuned by varying the donating ability, as well as the size, of the ligand on Cu (16).

### *7.2.10 Non-Kekulé Biradicals*

The functionalization of [60]fullerene is a promising method for the synthesis of ferromagnetic materials (17).

This arises because of its unique spherical structure, photochemistry, and radical quenching properties. The Diels-Alder reaction of [60]fullerene with *o*-quinodimethanes has been developed and is one of the most powerful methods for synthesizing a large variety of functionalized fullerenes. Fullerenes have been summarized (18).

*o*-Quinodimethanes can be obtained from the thermal or the photochemical elimination of a small molecule from various precursors, as shown in Figure 7.7.

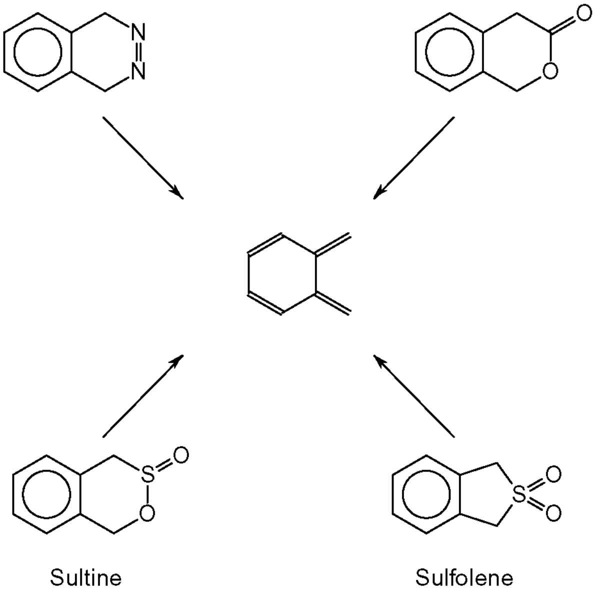


**Figure 7.7** Synthesis of *o*-quinodimethanes (17).

Among the precursors for *o*-quinodimethanes, sulfolene and sultine are good choices because they undergo their pyrolysis at reasonably low temperatures (17). So, they are usually stable at room temperature, in contrast to the other precursors shown in Figure 7.7.

Methods have been described for the synthesis of bis-diazene precursors of catenated tetraradicals (19). The photodeazetation in a low-temperature matrix of the *N*-tosylpyrrole compound results mainly in the monodeazetated biradical.

### *7.2.11 m-Chloroaniline for Magnetic Polymers*

Modeling with a one-dimensional tight-binding crystal orbital method shows that the cationic and the dehydrogenated forms of poly(*m*-aniline) can form an organic ferromagnet with high spin multiplicity (20).

Based on these calculations, the synthesis and the electron spin resonance measurements of the derivatives of this polymer have been performed. It has been concluded that free radicals are created on the nitrogen sites of the cationic and the dehydrogenated forms of this polymer. Although the spin concentration is small, this polymer may be an interesting approach to magnetic polymers (20).

### *7.2.12 Porous Magnetic Polymer Microspheres*

An inverse replication method based on porous $CaCO_3$ templates was developed to fabricate porous magnetic polymer microspheres composed of biocompatible poly(dopamine) and magnetic $Fe_3O_4$ nanoparticles (21). The procedure of preparation involved the synthesis of $Fe_3O_4/CaCO_3$ templates, the infiltration and the spontaneous polymerization of dopamine in the template pores. Finally a mild removal of templates occurred.

The particle size, the surface morphology and the pore structure of the porous microspheres could be easily tailored by altering the templates. The poly(dopamine) microspheres could be used to covalently immobilize yeast alcohol dehydrogenase for catalyzing the conversion of formaldehyde to methanol (21).

### *7.2.13 Magnetic Nanoporous Coordination Polymers*

The use of organic molecules as an alternative strategy for achieving new nanoporous metal-organic materials has become an attractive prospect (22).

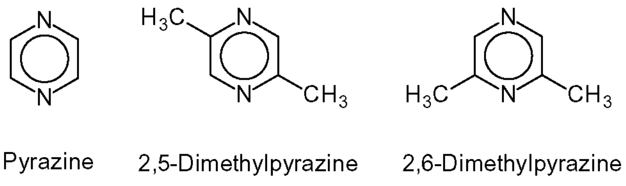
Using chemical coordination or crystal engineering techniques allows the systematic design of open-framework structures with a considerable range of modulated pore sizes and functionalities using different organic ligands such as phosphane, cyano groups, *N,N′*-type ligands and polycarboxylic acids.

In addition, the use of transition metal ions opens the possibility to get nanoporous materials with additional electrical, optical or magnetic properties. Potential applications are low density magnetic materials, magnetic sensors and intelligent or multifunctional materials (22).

#### *7.2.13.1 Mercury-Based Coordination Polymers*

Mercury coordination polymers using pyrazine ligands, i.e., 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, and pyrazine as such have been prepared by the reaction with $HgCl_2$, $HgBr_2$, $HgI_2$, and $Hg(S{-}C{\equiv}N)_2$ under thermal gradient conditions using the branched tube method and by simple solvent evaporation from the reactant mixtures (23).

The pyrazine derivates are shown in Figure 7.8.



Pyrazine 2,5-Dimethylpyrazine 2,6-Dimethylpyrazine

**Figure 7.8** Pyrazine derivates.

Structural characterization by single-crystal X-ray diffraction indicated that the substitution pattern of the pyrazine derivatives and the counter ions play important roles in the framework formation of the mercury(II) polymers. Two general types of mercury(II) pyrazine derivatives could be thus identified (23):

1. Coordination complexes with $HgX_2L$ stoichiometry with usually no holes, and
2. $(HgX_2)_2L$ complexes with one or two holes or vacant sites at the mercury atoms.

### 7.2.14 *Magnetic Polymer Composites*

Permanent magnets, comprising an object made from magnetized typically inorganic materials, used as a polymer composite that creates a magnetic field have been described (24). Materials that can be magnetized include ferromagnetic or ferrimagnetic materials including cobalt, nickel, iron, rare earth metals and naturally occurring materials and various alloys and mixtures.

A melt molded magnetic polymer composite in a form suitable for loading into, and being applied by, hot-melt hand-held or hand-actuated applicators that can melt and apply the melt materials, such as hot-melt adhesive applicators, is used.

The useful form is a rod-shaped material that can be magnetized before dispensing. The polymer composite includes magnetic particulates of increased or high density material, such as metals, mixed metals, alloys and inorganic compounds, dispersed or embedded in a thermoplastic or thermoset polymer binder or matrix, as well as low density particles, e.g., hollow glass spheres.

The composite may further include filler materials, an interfacial modifier to improve the association between the particulate and the polymer and to enhance rheological properties of the composite materials (24).

For example, a hot-melt poly(amide) (nylon) adhesive (HB Fuller HL6608) was used as the polymer matrix. This particular product has a viscosity of 4,175 *cP* at 190°C and 1,800–3,800 *cP* at 204 °C. The product is advantageous due to its crystallization point and hardening at a distinct temperature.

Compounded glue sticks with packing fractions of 0.4–0.7 using stainless steel particles were interfacially modified at a 0.40%. The sticks were compounded using a 19 *mm* laboratory twin screw compounder at a target melt temperature of 165°C directly out of a cylindrical die. Die diameters of 5/8 *inch* and 1 *inch* were used to create cylindrical densified melt molding material compatible with industrial 3M glue guns. The sticks were then melted within the glue guns at temperatures of 190–220°C and successfully shot into a fishing jig head and sinker molds produced by Do-It Molds. The material showed a softening point of 174–184°C and a density of 0.98 $gcm^{-3}$ (24).

Other polymers have also been successfully processed into cylindrical glue sticks and injected into molds via hot-melt glue guns.

### 7.2.15 Polymer-Coated Magnetic Particles

A method for preparing microparticles with an optional polymeric coating has been described. The method comprises (25):

1. Providing nanoparticles of a superparamagnetic material, preferably having a size of between 1 *nm* and 100 *nm*,
2. Optionally adding a hydrophobic surface layer to the particles, preferably by combining them with a material having a first end that adsorbs into the surface of the nanoparticle and a second end that extends away from the nanoparticle and imparts hydrophobicity to the particles;
3. Making a suspension of the hydrophobic nanoparticles and a polymerization initiator in the hydrophobic solvent,
4. Optionally adding a polymerizable monomer to the hydrophobic solvent;
5. Making an emulsion of the hydrophobic phase in a continuous aqueous phase with an emulsifier, wherein the hydrophobic phase comprises droplets in which polymerization initiator, hydrophobic nanoparticles; and optionally polymer monomer, are dissolved therein, and the aqueous phase optionally comprises a viscoelastic additive;
6. Optionally sizing the first emulsion to provide a second emulsion of the same basic components but in which the droplets are substantially uniformly between 2 and 20 $\mu m$ in size;
7. Evaporating at least a substantial portion of the hydrophobic solvent to assemble nanoparticles suspended in the hydrophobic solvent to form micron size aggregates;
8. Optionally replacing the first surfactant with a second surfactant, which is preferably a polymerizable surfactant;
9. Optionally adding at least one polymerizable monomer to the aqueous medium;

10. Polymerizing the monomers to provide a polymer layer on the microparticles; and
11. Optionally functionalizing the polymer layer of the microparticles with one or more polymer, nanoparticle, or biological macromolecular layers.

An emulsion is used to facilitate assembly of the microparticles. Emulsions are formed from two immiscible phases and are stabilized through the use of emulsifiers. When the nanoparticles are suspended in a hydrophobic phase, an oil-in-water emulsion may be prepared by adding a sufficient quantity of an aqueous solution containing surfactant to the hydrophobic phase and vigorously stirring the mixture to produce a polydispersed hydrophobic phase in the continuous aqueous phase. When the nanoparticles are suspended in a hydrophilic phase, a water-in-oil emulsion may be prepared by adding a sufficient quantity of a hydrophobic solution containing surfactant to the hydrophilic phase and vigorously stirring the mixture to produce a polydispersed hydrophilic phase in the continuous hydrophobic phase.

A variety of hydrophobic fluids may be used for the hydrophobic phase, including, alkane, alkene, cycloalkane, aromatic and nonpolar organic solvents, for example, hexane, octane, cyclohexane, toluene, benzene, xylene, styrene, acrylate compounds, etc. Hexane is the preferred hydrophobic phase as it has a low enough vapor pressure at room temperature that the emulsion can be processed, but the hexane can easily be removed by evaporation.

The hydrophobic phase also may provide a vehicle for adding polymerization initiator and monomer to the assembled microparticles. The preferred initiators are ones that can be activated by UV light, such as benzophenone derivatives, thioxanthone derivatives, phenyl propane-one derivatives, acetophenone derivatives, phenyl ketone derivatives, phosphine oxide derivatives. UV initiator synergists, such as aminobenzoate derivatives and benzoyl benzoate, may be used with UV photoinitiators for more effective UV reaction. Benzophenone has been the preferred initiator. The polymerization initiator should be soluble in the hydrophobic phase, and is added by dissolving the initiator in the hydrophobic phase. The amount of polymerization initiator is selected according to the monomers used, the amount of monomer to be polymerized (25).

### 7.2.16 *Magnetic Polymers with High Curie Temperature*

Monomers having multiple unpaired electrons, i.e., spins, have been prepared, which then play the role of electron-donators, resulting in the formation of donor-acceptor polymers with an electron acceptor with at least one transition metal, e.g., iron, cobalt, or nickel, that is located within a ferrocene-, cobaltocene-, or nickelocene-containing monomer (26).

The magnetic properties of molecule-based polymers are dependent upon the chemical nature of electron donating and electron accepting units as well as the bridge linking these units. The following magnetic polymers based on 11,11,12,12-tetracyano-9,10-anthraquinodimethane, 7,7,8,8-tetracyano-*p*-quinodiamine, and tetracyanoethylene have been synthesized.

The monomers can be polymerized to obtain covalently linked molecule-based magnetic polymers. The synthesized polymers are soluble in organic solvents, since they may have long flexible, bulky side chains.

The Curie temperature of a magnetic polymer depends on the chemical structure of the particular molecule-based magnetic polymer, and can vary accordingly. The Curie temperature denotes the highest temperature at which magnetic behavior can be observed, i.e., at temperatures above the Curie temperature of a magnetic polymer, the polymer ceases to exhibit magnetic characteristics. The Curie temperature should be above the temperatures to be expected in the application and environment in which the magnetic polymer is to be used to prevent the degradation of the magnetic characteristics (26).

### 7.2.17 *Shaped Ceramics*

Shaped ceramics with tunable magnetic properties from metal-containing polymers have been reviewed (27).

Ceramic materials are generally prepared from powders in the sequence of synthesis, processing, shaping, and sintering steps. Organosilicon polymers and inorganic glasses may be particularly suitable precursors to advanced ceramics, since they have the advantage of a three-dimensional network of covalent bonds (28,29).

The design, synthesis, characterization and applications of poly(borazylene) and poly(borosilazane) polymers have been reviewed (30). The use of these polymers as processable precursors to BN and SiNCB composites has been described. A design strategy is based on the controlled functionalization of preformed polymers with pendant groups of suitable compositions and crosslinking properties to yield second-generation dipentylamine-poly(borazylene) and pinacolborane–hydridopolysilazane polymers which are stable as melts and can be easily melt-spun into polymer fibers. Subsequent pyrolysis processes of these polymer fibers then provide excellent routes to BN and SiNCB ceramic fibers.

The ring-opening polymerization of strained silaferrocenophanes is a well-established route to high molecular weight poly(ferrocenylsilane)s (31).

Poly(ferrocenylsilane)s are transition metal-containing macromolecules with a backbone that consists of alternating ferrocene and organosilane units. High molecular weight products of these materials have been prepared by thermal ring-opening polymerization of silicon-bridged silaferrocenophanes (32).

Block copolymers from ferrocenylsilanes can self-assemble in the solid state to form ordered arrays of nanoscale redox-active organometallic domains, and in solution they can form well-defined supramolecular organometallic polymer aggregates such as spheres, cylinders and also still more complex architectures (32). At pyrolysis at 1000°C in nitrogen atmosphere, a poly(ferrocenylsilane) yields a magnetic ceramic powder.

It has been shown that the pyrolysis of nanoscale cylinders of poly(ferrocenylsilane) in hexagonal mesoporous silica at 900°C yields iron nanocrystals with a diameter constrained by the width of the channels (27,33).

Crosslinking the preceramic polymers is the recommended method for increasing the ceramic yield because crosslinking reduces the amount of volatile decomposition products (27).

A crosslinked structure is obtained from a spirocyclic silaferrocenophane (27).

### *7.2.18 Magnetic Polymer Microbeads*

Magnetic polymer microbeads can be widely used in magnetic bioseparation for clinical testing, and they function as carriers for enzyme immobilization, bacterial separation, cell separation, and the separation of nucleic acid and protein. Magnetic polymer microbeads can also be used as carriers of medicines and for gene delivery. A method for preparing magnetic polymer microbeads has been presented (34). The method uses the following steps:

1. Preparation of the polymer particles,
2. Immersing the polymer particles into a solution in order to swell the particles,
3. Adding magnetic nanoparticles to the solution and allowing the magnetic nanoparticle to enter the interior of the polymer particles, and
4. Separating the polymer particles from the solution.

The polymer particles are made of poly(styrene), or a related copolymer such as poly(styrene-glycidyl methacrylate). A variety of magnetic nanoparticles can be chosen, because the magnetic nanoparticles are pre-prepared. A wide variety of functional groups can be introduced onto the surfaces of magnetic nanoparticles. Therefore, magnetic polymer microbeads can be applied in many areas (34).

A micrograph of polymer particles formed in this way is shown in Figure 7.9.

Similarly, a magnetic ion exchange resin can be formed in this way (35). A scanning electron microscope photograph of a magnetic ion exchange resin manufactured by using 5 $mg\ ml^{-1}$ nanoscale magnetic iron oxide ($Fe_3O_4$) solution is shown in Figure 7.10.

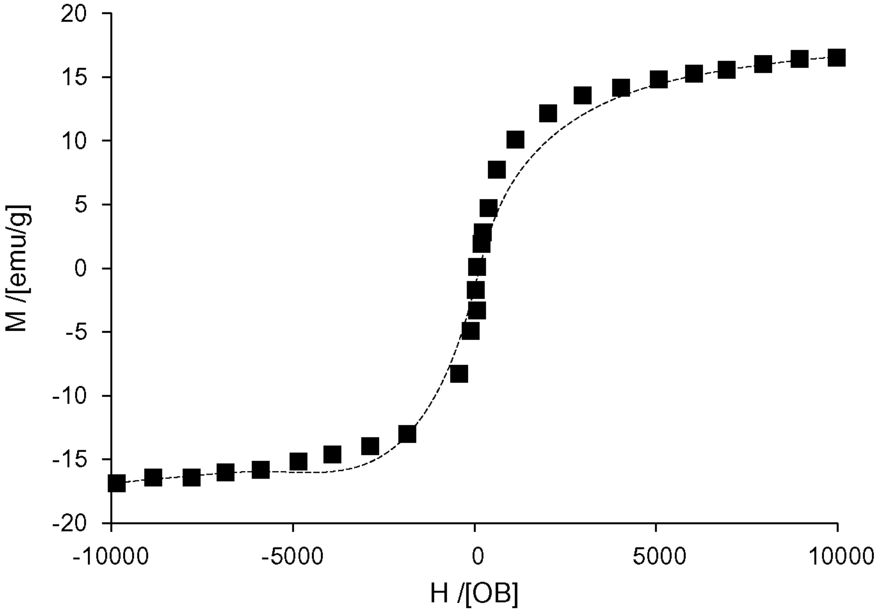


**Figure 7.9** Micrograph of polymer particles (34).

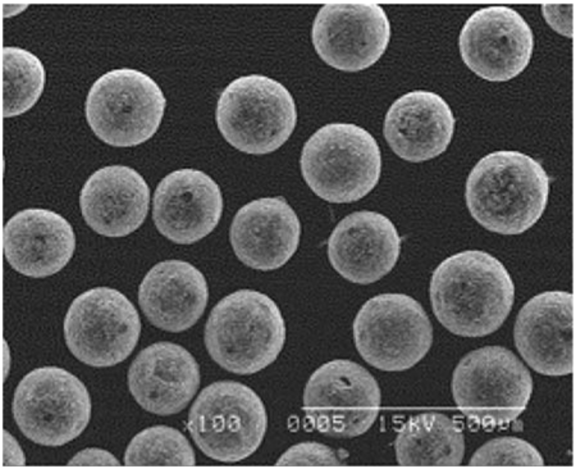


**Figure 7.10** Scanning electron microscope photograph of a magnetic ion exchange resin (35).

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# 8

# Properties and Methods of Measurement

## 8.1 Standard Test Methods

The ASTM standard E709-15 (1) describes techniques for both dry and wet magnetic particle testing, a nondestructive method for detecting cracks and other discontinuities at or near the surface in ferromagnetic materials. Magnetic particle testing may be applied to raw material, semifinished material, i.e., billets, blooms, castings, and forgings, finished material and welds, regardless of heat treatment or lack thereof. The methods are also useful for preventive maintenance testing.

The ASTM standard E1444 (2) establishes the basic parameters for controlling the application of the magnetic particle testing method. The minimum requirements for magnetic particle testing used for the detection of surface or slightly subsurface discontinuities in ferromagnetic material have been documented.

The ASTM standard A275/A275M (3) covers the procedures for magnetic particle examination on steel forgings. The inspection medium shall consist of finely divided ferromagnetic particles, whose size, shape and magnetic properties, both individually and collectively, shall be taken into account. Forgings may be magnetized in the longitudinal or circular direction by employing the surge or continuous current flow methods. Magnetization may be applied by passing current through the piece or by inducing a magnetic field by means of a central conductor, such as a prod or yoke, or by coils. While the material is properly magnetized, the magnetic particles may be applied by either the dry method, wet method, or fluorescent method.

## 8.2 Phase Diagram of Magnetic Polymers

Polymers made of magnetic monomers, such as Ising or Heisenberg-like, in a good solvent have been investigated (4).

These polymers can be modeled as self-avoiding walks on a cubic lattice, and the ferromagnetic interaction between the spins is established by the monomers short-ranged in space. The physics of the model can be described as following (4):

1. At a high temperature, entropy is dominating, and the chain is swollen. As a result, the number of nearest neighbor contacts is small, and from a magnetic point of view, the system is equivalent to a one-dimensional Ising model.
2. At a low temperature, the magnetic energy is larger than the entropy loss due to confinement. Therefore, the chain collapses. The polymers are undergoing a magnetic induced first order collapse transition.

There is a strong jump in the polymer density, as well as in its magnetization. In the presence of a magnetic field, the collapse temperature increases, while the discontinuities decrease. Beyond a multicritical point, the transition becomes second order. Monte Carlo simulations for the Ising case are in qualitative agreement with these results (4).

The studies revealed that ferromagnetic interactions may drive the collapse of a polymer, even in a good solvent. This collapse is very sensitive to the presence of an external magnetic field. Thus, it might be possible to design new polymeric magnetic materials, for which the collapse transition is triggered by a magnetic field, at room temperature (4).

## 8.3 Adsorption Mechanism of Amino-Functionalized Magnetic Polymers

A series of $NH_2$-functionalized nanomagnetic polymer adsorbents coupled with different multi-amino groups, i.e., ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine have been prepared (5). These compounds have been used for the investigation of the adsorption mechanism of a Cu(II) and Cr(VI) coexisting water system.

The amino compounds are shown in Figure 8.1. Three methods of adsorption were tested to elucidate the adsorption mechanism (5):

$$H_2N{-}CH_2{-}CH_2{-}NH_2$$

Ethylenediamine

$$H_2N{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH_2$$

Diethylenetriamine

$$H_2N{-}CH_2{-}CH_2{-}NH_2{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH_2$$

Triethylenetetramine

**Figure 8.1** Amino compounds.

1. Adsorbing Cu(II), Cr(VI) from water simultaneously,
2. Adsorbing Cr(VI) followed by adsorbing Cu(II), and
3. Adsorbing Cu(II) followed by adsorbing Cr(VI).

The results indicated that the adsorption of Cu(II) and/or Cr(VI) on functionalized nanomagnetic polymers was competitive, as well as cooperative.

The adsorption mechanisms of the Cu(II), Cr(VI) coexisting system could be related with coordination interactions, electrostatic attraction, and ion exchange (5).

## 8.4 Cyano-Bridged Coordination Polymers

Rings of 24 atoms form part of the two-dimensional structure of the novel compounds $[NdM(bpym)(H_2O)4(CN)_6] \times 3H_2O$, (M = Fe (1), Co (2) and bpym = 2,2′-bipyrimidine) (6). These compounds are the first two-dimensional cyano-bridged species containing lanthanide and transition metal centers. The structures and magnetic properties have been investigated.

## 8.5 Spin-Glass Behavior in Some Schiff-Base Co-containing Magnetic Polymers

The magnetic properties in the temperature range of 4.2–300 $K$ as a function of the frequency of the excitation current of a series of Cobalt-containing polymers have been reported (7). At high temperature, the substances follow a Curie-Weiss law. However, in the low-temperature region the ac susceptibility presents a peak which is accompanied by an out-of-phase component. The frequency dependence of the magnetic susceptibility at zero dc magnetic field is characteristic of spin-glass behavior (7).

## 8.6 Neutron Scattering from Magnetic Polymers

Some of the static and dynamic properties of a simple magnetic polymer have been calculated (8). The localized magnetic moments on each monomer interact via a nearest neighbor Heisenberg exchange. While $\vec{k}$ -independent quantities, like the free energy and the spin-wave density of states, are independent of polymer conformation, $\vec{k}$ -dependent quantities like the wave-vector-dependent susceptibility $\chi(\vec{k}$ and the neutron scattering law $S(\vec{k}, \omega)$ can yield useful information about the polymer conformation statistics.

It has been shown that the inverse correlation length in a ferromagnetic polymer, which can be determined from $\chi(\vec{k}$, runs with the square root of the absolute temperature. The neutron scattering law $S(\vec{k}, \omega)$ measures essentially the spin-wave density of states at low temperatures, although there is a weak $\vec{k}$ dependence (8).

## 8.7 Shape-Memory Effect

In shape-memory polymers, the changes in shape are usually induced by heating. When the polymers cannot be warmed up by heat transfer using a hot liquid or gaseous medium, a noncontact triggering will be required. The magnetically induced shape-memory effect of composites from magnetic nanoparticles and thermoplastic shape-memory polymers has been discussed (9).

A poly(ether urethane) as well as a biodegradable multiblock copolymer with poly($p$-dioxanone) as hard segment and poly(caprolactone) as soft segment have been used as matrix components. Nanoparticles consisting of an iron(III)oxide core in a silica matrix could be incorporated into both polymers. A shape-memory effect in both composite systems could be induced by inductive heating in an alternating magnetic field (9).

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# 9

# Fields of Application

The fields of application of magnetic polymers include a wide variety of issues:

- Electronic uses,
- Supports for biological molecules,
- Biotechnology, and
- Medical uses.

These fields of application are dealt with subsequently in detail.

## 9.1 Improvement of Drilling Performance

When improving the hydrocarbon recovery or drilling performance, there are several aspects to consider, such as (1):

- Reducing the nonproductive time,
- Increasing the life of the well, and
- Preventing formation damage.

Reducing the nonproductive time may be accomplished by increasing the rate of penetration (ROP), or reducing frictional pressure. Preventing or inhibiting corrosion of the well may reduce failure of downhole tools or extend the life of the well. Preventing or inhibiting lost circulation may prevent formation damage, as well as improve the hydrocarbon recovery.

One of the primary concerns in upstream deepwater operations is the operational narrow window between pore pressure and fracture gradient that often results in major fluid losses during drilling, running, casing, and cementing processes. Thus, the lost circulation prevention and control are crucial for successful drilling and completion activities. Loss of circulation is one of the biggest contributors to drilling nonproductive time, and is the most difficult segment of drilling in which to make economic decisions.

The loss of circulation is the phenomenon in which drilling fluid leaks away via fractures or openings in the wellbore or in the formation. This loss of fluid can be quantified according to its severity, including: seepage losses, partial losses, severe, and total or catastrophic losses.

Each situation must be specifically handled depending on the operational, personnel and economic risks involved. One of the main causes of loss of circulation includes exceeding the fracture gradient with excessive fluid weights or high surge pressures and equivalent circulating densities, which induces fractures in the formations and produces fluid losses while tripping pipe, breaking circulation, or raising fluid weights.

The ROP is the speed at which a drill bit breaks the formation under it to deepen the borehole. Increasing the ROP may reduce the nonproductive time. Mechanical aspects of the drill bit may be altered to enhance the ROP, or chemicals may be added. ROP enhancers may include surfactants and polymers, in a synthetic base oil carrier, such as a synthetic-based olefin or ester.

Highly-permeable formations may be massive sands, pea gravel, shell beds, reef deposits, and combinations of these. Cavernous and vugular formations may include limestone, dolomite, chalk, and other formations with secondary porosity, which may be indicated by sudden and severe to complete loss of returns of downhole fluids that may be accompanied by sudden erratic rates of penetration.

Depending on the reason for the loss of circulation, remedial procedures involve reducing the pressure exceeded by the circulating fluid, or filling the openings through which a downhole fluid is escaping. A slurry may be added that can become stiff on standing for filling the fractures or opening of the wellbore to prevent or inhibit lost circulation, or introducing a bridging or plugging solid so that normal filtration can occur.

A type of lost circulation material may include a poly(acrylamide) (PAAm) dispersion in water that is emulsified in paraffinic oil, where bentonite is added into the external oil phase. Near the drill bit, where high shear rates are prevailing, the emulsion may be broken, and the bentonite is wetted by water and crosslinked with PAAm, resulting in a viscoelastic material in the formation. Crosslinked polymers have been used for severe lost circulation control, since they are not easily reversible.

A crosslinked polymer has a high apparent viscosity and strong cohesive force and may not be easily diluted by downhole fluids. The crosslinked polymer may be pumped normally, becoming viscoelastic in the weak zone. The crosslinked polymer has good chemical compatibility with various other components of lost circulation material. Inorganic bridge materials may be combined with crosslinked materials to enhance thermal stability and optimize particle size distribution. Free chain movement may be prevented by crosslinking between chains of the polymer matrix. This, in turn, results in an increased strength, decreased flexibility, and increased brittleness of the polymer matrix. Physical crosslinking occurs when long chains entangle, effectively forming chemical knots between them. Crosslinking may be carried out by applying: heat, mechanical force, exposure to ionizing and nonionizing radiation (such as microwave), exposure to active chemical agents, or any combination of these. As the extent of crosslinking increases, there is a rapid increase in viscosity and the material becomes viscoelastic; at this point the system becomes gelled.

Industrially important crosslinked polymers include: phenol and amino resins, alkyl resins, unsaturated polyesters, epoxy resins, concrete, silicon dioxide, carbon, siloxanes, isocyanates, acrylic copolymers, unsaturated and saturated hydrocarbons, halogen-containing hydrocarbons, ionomers, and combinations thereof.

Horizontal sections may be drilled with a drilling fluid containing a polymer, e.g., a viscosifier agent, sized calcium carbonate, calcium chloride, or sodium chloride. Field experience has demonstrated that mixtures, heterogeneous in shape, size, and strength, are usually more likely to form a seal than is a single material. The lost circulation material specifications frequently involve laboratory performance tests in addition to certain physical properties, such as screen size distribution and bulk density.

### 9.1.1 *Wall Coating*

It has been discovered that at least partially coating a wall of a wellbore with magnetic polymers may improve hydrocarbon recovery or drilling performance (1).

Magnetic polymers may respond to externally applied stimuli, such as, but not limited to, electrical stimuli, stress and strain stimuli, magnetic stimuli, thermal stimuli, light, solvent composition, and others. Magnetic polymers may react to external stimuli to result in a defined engineering or scientific goal. Much of the strength of the magnetic polymer comes from the contact of the magnetic particle with the polymeric matrix. The polymeric matrix also allows the magnetic polymer to swell and gives the magnetic polymer elasticity.

Each magnetic polymer may have a magnetic particle embedded within a polymer matrix. The magnetic particle may be or include, but not be limited to iron, cobalt, nickel, magnesium, molybdenum, tantalum, alloys thereof, spinels thereof, oxides thereof, and combinations thereof, as well as alloys and spinels. Among these magnetic particles, metal oxides may be more resistant to oxidation. The polymer matrix may be or include poly(styrene) (PS), PAAm, dextran, poly(vinyl alcohol) (PVA), poly(methyl methacrylate) and related copolymers.

Nanoparticles present single domain structures, which include groups of spins all pointing in the same direction and acting cooperatively. By contrast, microparticles exhibit multidomain structures consisting of many single domains, separated by walls that generate magnetic flux closures rendered to the materials nonmagnetic behavior. Generally, nanoparticles have an average particle size of 999 $nm$ or less whereas macroparticles are larger than 1 $\mu m$ or larger.

The size of the magnetic particle distinguishes the magnetic polymers as one of two different types: superparamagnetics and ferromagnetics, and the dispersions formed from them are called ferrofluids and magnetorheological fluids, respectively. Ferrofluids may be used to switch off the magnetic state after usage of the magnetic polymer, e.g., when it may be desirable for the magnetic particle to have a minimum disturbance on the process or when the surface-to-volume ratio needs to be large. On the other hand, magnetorheological fluids present applicability when yield stress has to be accurately controlled by changing the magnetization, or when it is desirable to have a strong response to the magnetization (1).

### 9.1.2 *Magnetically Controlled Delivery*

If a subterranean fluid additive is a cement activator, upon release, the activator can interact with a cement slurry in the downhole environment to provide setting of the cement slurry on demand in a desired location within a wellbore or a subterranean formation (2). This may be useful to activate hydration of a cement composition downhole.

The release of the magnetically sensitive component can result in a *flash set* of at least a portion of the cement composition. The term flash set will be understood to be an irreversible setting of at least a portion of the cement composition within a time in the range of from about 1 *min* to about 5 *min* after contacting the cement composition with an activator that is released from the magnetically sensitive component.

Suitable mechanically activated devices can be activated by a magnetic force to cause a mechanical release of a subterranean fluid additive. An example of a mechanically activated device is a remotely controlled device that is activated by a magnetic force generated from a magnetic source so as to release a contained or enclosed subterranean fluid additive downhole. By repeating the on-off operation of the magnetic force, a controllable release of the subterranean fluid additive from the mechanically activated device can be programmably designed (2).

## 9.2 Electronic Uses

### 9.2.1 *High Frequency Transformers*

Magnetic electrical components, such as inductors that operate at a radio-frequency of up to several hundred *MHz* or more with a high quality factor, are of general interest (3).

Conventionally, such electrical components are fabricated using air or powdered iron cores, with the powdered iron cores being used when a high quality factor is required. For certain uses, the powdered iron cores must be machined to shape for a particular inductor application. This demand substantially increases the costs of the inductor. Also, the machining of very small cores is difficult.

Electrical components, including high quality factor inductors and high-frequency transformers, have been developed that can be formed from one or more electrically conductive coils located proximate to a magnetic polymer material which is an epoxy material that contains copolymerized ferromagnetic molecules (3).

Advantageously, the electrical components can be formed in many different sizes and shapes, including planar chip inductors down to one millimeter in size. Further, these components can be formed at low cost, and without the need of being machined to shape.

A method has been described that relates to an electrical component comprising an electrically conductive coil and a magnetic polymer material located proximate to the coil.

The magnetic polymer material is made from a cured epoxy that contains a mercaptan derivative which has a ferromagnetic atom chemically bonded onto its sulfur atoms.

The epoxy resin is made from a diglycidol ether of bisphenol A. The mercaptan may be a polymer from dimercaptopropanol or dimercaptoethanol. The ferromagnetic atom may be Fe, V, Mn, Ni, Co, Cr, or combinations of these metals (3). The epoxy monomer is shown in Figure 9.1.

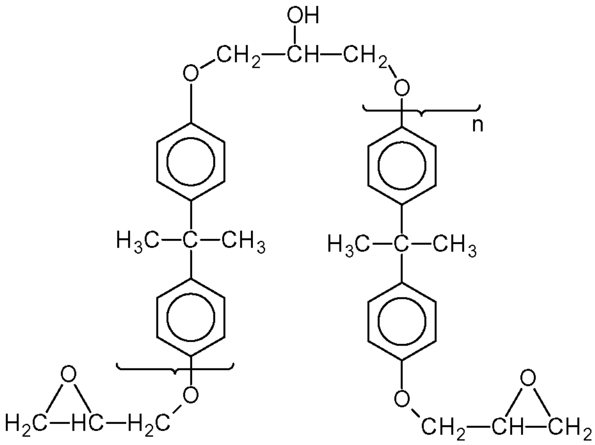


**Figure 9.1** Diglycidol ether of bisphenol A (3).

Further, an inductor using a magnetic polymer material as an example of an application is shown in Figure 9.2.

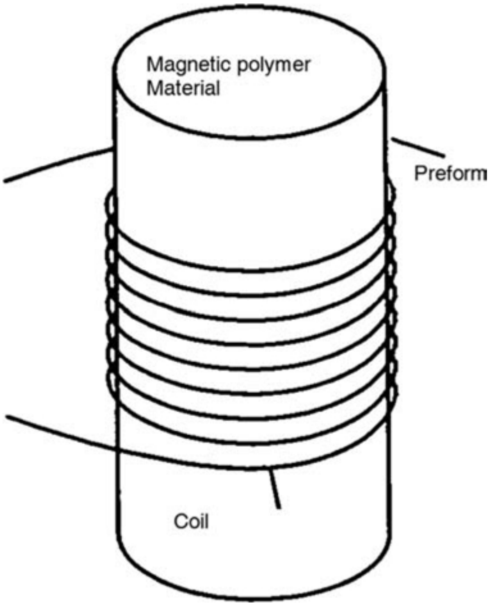


**Figure 9.2** Inductor as an example of application (3).

## 9.2.2 *Electrophotography*

### 9.2.2.1 *Basic Methods*

Several methods for the formation and development of images on the surface of photoconductive materials are known (4). The basic electrostatographic process places a uniform electrostatic charge on a photoconductive insulating layer (5). Then, the layer is exposed to a light and shadow image to dissipate the charge on the areas of the layer exposed to the light. Afterwards, the resultant electrostatic latent image is developed by depositing on the image a finely divided electroscopic material, i.e., the toner. The toner is attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the electrostatic latent image. Then, this powder image can be transferred to a support surface, i.e., paper. Finally, the powder image may be permanently affixed, e.g., by the application of heat.

In the magnetic brush process the developer material containing the toner and magnetic carrier particles is carried by a magnet (6). The magnetic field of the magnet causes the alignment of the magnetic carriers in a brushlike configuration. The toner particles are drawn from the brush to the electrostatic image by electrostatic attraction. Here the developer is usually a triboelectric mixture of the finely divided toner powder. The powder contains a dyed or pigmented thermoplastic resin mixed with coarser carrier particles of a soft magnetic material.

Disadvantages of conventional developing materials may be their tendency to cake, bridge and agglomerate during handling and storage. Another factor affecting the stability of the triboelectric properties of the carrier particles is the susceptibility of the carrier particles to impaction.

When carrier particles are used in automatic machines and recycled through many cycles, the collisions between the carrier particles and other surfaces in the machine may cause the toner particles to be welded or otherwise forced into the carrier surfaces. This may cause a change of the triboelectric value of the carrier and thus effects a loss of the copy quality.

### 9.2.2.2 *Carrier Materials*

Carrier materials have been developed that overcome the above-mentioned disadvantages (4). Electrostatographic carrier materials with low bulk densities and high magnetic permeabilities can be obtained by impregnating low density imbibitive polymer particles with magnetic metals or metal oxides (4).

Low density magnetic composite carrier particles are prepared by metallizing the polymer beads electrolessly by the thermal decomposition of a transition metal carbonyl to the elemental metal or metal oxide in the presence of the beads with a suitable suspending medium. The polymer beads are impregnated with magnetic iron or its magnetic oxidized salts by placing them in a suitable vessel with iron pentacarbonyl and a suspending medium such as *n*-octane.

Air and moisture are excluded by displacement with a dry inert gas, such as nitrogen, and the contents are heated and stirred so that the iron pentacarbonyl boils, and the mixture is refluxed until the temperature rises to that of the suspending medium, whereupon impregnation of the beads with iron or its oxides is complete. The mixture is then cooled, the beads are washed with fresh suspending medium and with diethyl ether to remove any fines, air dried with heat and vibration, and the beads recovered. The magnetic low density particles obtained typically are dull black to gray in color depending upon metallic loading.

Mixing with toner particles, the carrier materials provide a significantly reduced toner impaction and a longer life (4).

### *9.2.2.3 Magnetic Polymer Particles*

Magnetic polymer particles have been developed that exhibit excellent water dispersibility and are fixable on paper. When a hydrophobic monomer and a monomer with a pendent hydroxyl group are mixed and are suspension polymerized in water, the particles are apt to agglomerate during the polymerization, and it is difficult to obtain a polymer having a desired copolymerization ratio.

The reason for this is that the monomer having a hydroxyl group is diffused from oil drops, which are dispersed in the water as a monomer mixture, to the water as well, so as to polymerize in the water in addition to in the oil drops (7).

When the polymer includes a hydrophobic component, it is difficult to include the magnetic powder in the polymer particle since the surface of the magnetic powder is relatively hydrophilic and, further, when a hydrophobic monomer polymerization component and a hydrophilic monomer polymerization component are phase separated in the polymer particle, the dispersibility of the magnetic powder tends not to be uniform. When the amount of hydroxyl groups in a particle is too small, the redispersibility of the fabricated polymer particles in water tends to be deteriorated.

The types of monomers used must be added in certain ratios to overcome the difficulties described above (7). The usable monomers for use are collected in Table 9.1.

The formation of tris-(2-hydroxyethyl)isocyanurate is shown in Figure 9.3. In the next step an esterification with acrylic acid or a related compound, e.g, an acid chloride, follows.

Monomers for use as crosslinking agents are shown in Figure 9.4.

The monomers must be radically polymerized by oil-soluble initiators. Oil-soluble initiators are given in Table 9.2.

**Table 9.1** Monomers (7).

| Hydroxy Monomers |
|---|
| 2-Hydroxylethyl(meth)acrylate |
| 2-Hydroxypropyl(meth)acrylate |
| 3-Hydroxypropyl(meth)acrylate |
| Glycerin di(meth)acrylate |
| 1,6-Bis(3-acryloxy-2-hydroxypropyl)-hexyl ether |
| Pentaerythritol tri(meth)acrylate |
| Tris-(2-hydroxyethyl)isocyanurate (meth)acrylate |
| Polyethylene glycol (meth)acrylate |
| Carboxy Monomers |
| Acrylic acid |
| Methacrylic acid |
| Methacryloyloxyethyl monophthalate |
| Methacryloyloxyethyl monohexahydrophthalate |
| Methacryloyloxyethyl monomaleate |
| Methacryloyloxyethyl monosuccinate |
| Hydrophobic monomers |
| Styrene |
| Methyl(meth)acrylate |
| Butyl(meth)acrylate |
| 2-Ethylhexyl(meth)acrylate |
| Lauryl(meth)acrylate |
| Ethoxybutyl(meth)acrylate |
| Benzyl(meth)acrylate |
| Diethylaminoethyl(meth)acrylate |
| Crosslinking monomers |
| Divinylbenzene |
| Ethylene glycol di(meth)acrylate |
| Diethylene glycol di(meth)acrylate |

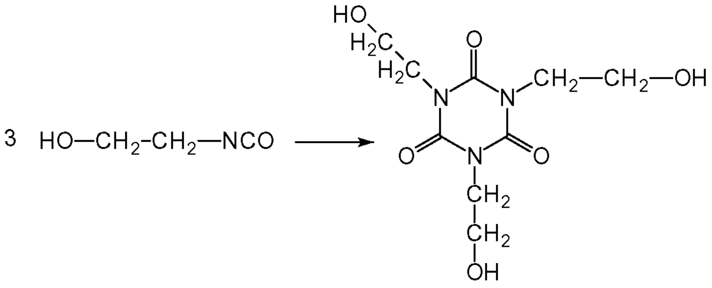
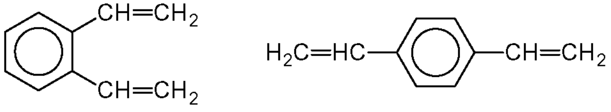
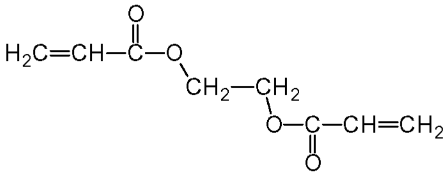


**Figure 9.3** Formation of tris-(2-hydroxyethyl)isocyanurate.



1,2-Divinyl benzene

1,4-Divinyl benzene



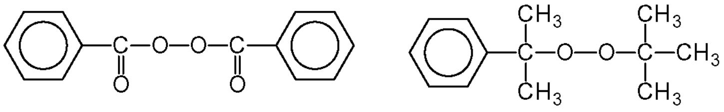
Ethylene glycol diacrylate

**Figure 9.4** Monomers for use as crosslinking agents.

**Table 9.2** Oil-soluble initiators (7).

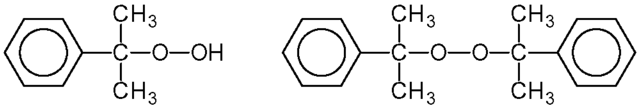
| Azo initiators |
|---|
| Azobisisobutyronitrile |
| 2,2′-Azobis(2-methylbutyronitrile) |
| 2,2′-Azobis(2,4-dimethylvaleronitrile) |
| Dimethyl-2,2′-azobis(2-methylpropionate) |
| 1,1′-Azobiseyelohexane-1-carbonitrile |
| Peroxide initiators |
| Dibenzoyl peroxide |
| Diacetyl peroxide |
| Decanoyl peroxide |
| Lauroyl peroxide |
| *o*-Methoxybenzoyl peroxide |
| *p*-Chlorobenzoyl peroxide |
| 2,4-Dichlorobenzoyl peroxide |
| Diisopropyl percarbonate |
| Di-2-ethylhexyl peroxidicarbonate |
| Acetylcyclohexylsulfonyl peroxide |
| *tert*-Butyl perisobutyrate |
| *tert*-Butyl perpivalate |
| *tert*-Butyl 2-perethylhexanoate |
| *tert*-Butyl peroxide |
| *tert*-Butylcumyl peroxide |
| Dicumyl peroxide |
| Methyl ethyl ketone peroxide |
| Cumene hydroperoxide |
| *tert*-Butyl hydroperoxide |

Some peroxides are shown in Figure 9.5. Further, non-crosslinked resins for use are collected in Table 9.3.



Dibenzoyl peroxide

*tert*-Butylcumyl peroxide



Cumene hydroperoxide

Dicumyl peroxide

**Figure 9.5** Peroxides.

**Table 9.3** Non-crosslinked resins (7).

| Resin |
|---|
| Poly(styrene) |
| Styrene-acrylic acid alkyl copolymers |
| Styrene-methacrylic acid alkyl copolymers |
| Styrene-acrylonitrile copolymers |
| Styrene-butadiene copolymers |
| Styrene-maleic anhydride copolymers |
| Bisphenol A poly(ester)s |
| Poly(ethylene) |
| Poly(propylene) |
| Poly(urethane) |
| Epoxy resins |
| Silicone resins |

It was found that when the monomers are mixed with the non-crosslinked resins in an amount so that the sum of the monomers is less than that of the amount of crosslinked resin, suspension particles that are stable in an aqueous medium may be formed (7).

A styrene-acrylic acid alkyl copolymer and a styrene-methacrylic acid alkyl copolymer may be used because the physical properties may be readily controlled and the mixing and dispersion process of the magnetic powder may be conveniently carried out.

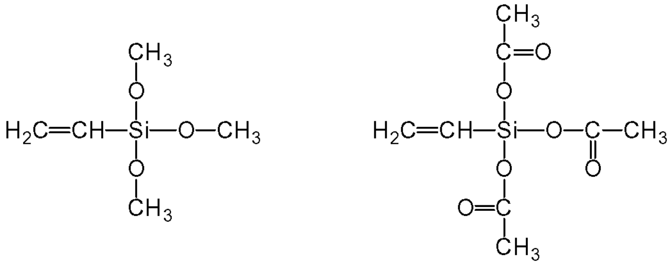
As the magnetic powder, magnetite or ferrite may be used. An average primary particle diameter of the magnetic powder before being subjected to a hydrophobizing treatment is preferably in the range of 0.02–2.0 $\mu m$. When the average primary particle diameter of the magnetic powder is set in the range, the magnetic powder merely agglomerates and can be readily uniformly dispersed in the monomer mixture.

The magnetic powders must be hydrophobized on their surfaces. The method of the hydrophobizing treatment is done by covering the surface of a magnetic powder with a hydrophobizing agent such as various types of coupling agents, silicone oils, and resins. Examples of hydrophobizing agents are listed in Table 9.4. Some are shown in Figure 9.6.

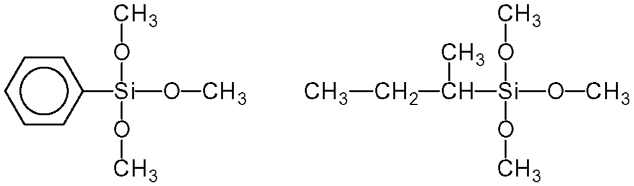
**Table 9.4** Hydrophobizing agents (7).

| Compound |
|---|
| Vinyltrimetoxysilane |
| Vinyltriethoxysilane |
| $\gamma$-Methacryloxypropyltrimethoxysilane |
| Vinyltriacetoxysilane |
| Methyltrimethoxysilane |
| Methyltriethoxysilane |
| Isobutyltrimethoxysilane |
| Dimethyldimethoxysilane |
| Dimethyldiethoxysilane |
| Trimethylmethoxysilane |
| Hydroxypropyltrimethoxysilane |
| Phenyltrimethoxysilane |
| Phenethyltrimethoxysilane |
| *n*-Hexadecyltrimethoxysilane |
| *n*-Octadecyltrimethoxysilane |

A mixture including the hydrophilic monomer, the hydrophobic monomer, a non-crosslinked resin, a magnetic powder, the polymerization initiator, and a crosslinking agent, is mixed and suspended in an aqueous medium (7). Optionally, for use in electrophotography, colorants in the form of pigments are added (8). Pigments are listed in Table 9.5.



Vinyltrimetoxysilane Vinyltriacetoxysilane



Phenyltrimethoxysilane Isobutyltrimethoxysilane

**Figure 9.6** Hydrophobizing agents.

**Table 9.5** Pigments (8).

| Compound | Compound |
|---|---|
| Chrome yellow | Hansa yellow |
| Benzidine yellow | Threne yellow |
| Quinoline yellow | Permanent orange GTR |
| Pyralozone orange | Vulcan orange |
| Watch young red | Permanent red |
| Dupont oil red | Lithol red |
| Rhodamine B lake | Lake red C |
| Rose bengal | Aniline blue |
| Ultramarine blue | Calco oil blue |
| Methylene blue chloride | Phthalocyanine blue |
| Phthalocyanine green | Malachite green oxalate |

As the suspension method, mechanical suspension or ultrasonic suspension may be used. The particles including the suspended monomer and the magnetic powder are suspended, then polymerized, to obtain the magnetic polymer particles. The polymerization may be carried out not only under atmospheric pressure but also under pressure (7).

The magnetic polymer particles formed in this way can be used in magnetic ink or an image-forming material used for a wet image-forming method (7).

In Figure 9.7 a schematic configurational view showing an example of a portion of an image-forming apparatus in which images are formed by magnetography is shown.

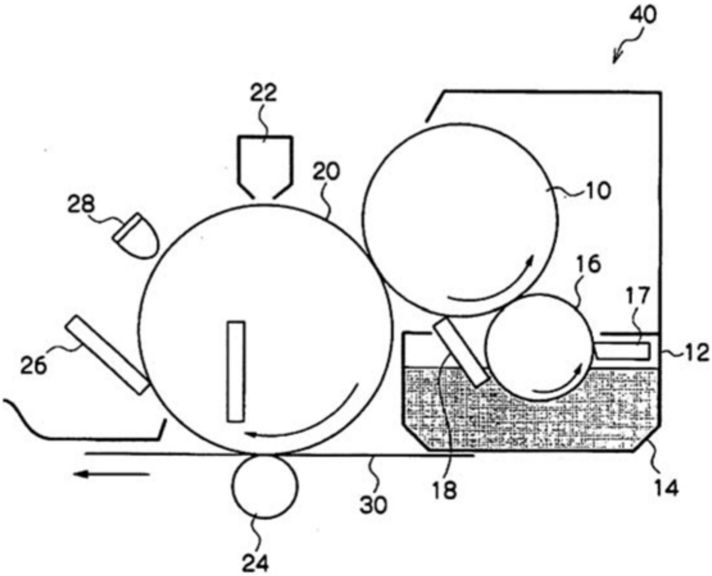


**Figure 9.7** Image-forming apparatus (7).

In the image-forming apparatus, a development roll, a liquid retaining unit, 10, retaining an image-forming recording solution is brought into contact with a magnetic recording drum, 20, to form an image (7). First, on the magnetic recording drum, 20, made mainly of Co–Ni magnetic plating, a magnetic recording head, 22, records a magnetic latent image in response to an image signal, by a line scanning method. Next, the development roll, 10, retaining a recording solution is brought into contact with the magnetic recording drum, 20, so that the magnetic latent image is visualized by the magnetic polymer particles. As the recording solution, the aqueous dispersion according to an exemplary embodiment of the invention is used. The recording solution is supplied to the development roll, 10, by a recording solution coating roll, a liquid supplying unit, 16, part of which comes into contact with the recording solution, 14, stored in a liquid storage container, 12, to retain the recording solution, 14, and another portion of which comes into contact with the development roll, 10, to apply the recording solution, 14, to the development roll, 10. Furthermore, the amount of the solution retained by the recording solution coating roll, 16, is controlled by use of a metering blade, 17. The development roll, 10, the storage tank, 12, the recording solution coating roll, 16, the metering blade, 17, and the like integrally form a cartridge, 40. Next, a visualized image on the magnetic recording drum, 20, is transferred to a portion brought into contact with a transfer roll, 24, and, simultaneously, at a contact portion between the transfer roll, 24, to which a voltage is applied and the magnetic recording drum, 20, a recording medium, 30, is inserted, thereby transferring a visual image formed by the magnetic polymer particles on the recording medium. The transferred visual image formed by the magnetic polymer particles is transported without further treatment, and fixed on the recording medium, 30, under heating and pressure by means of a fixing device (not shown). On the other hand, residual toner on the magnetic recording drum, 20, after the transfer is removed by a blade, 26, and the magnetic latent image on the surface of the magnetic recording drum, 20, is erased by a demagnetizing head, 28. Recording solution remaining on a surface of the development roll 10 after development is scraped off by a cleaning blade, 18, which is pressure contacted with a surface of the development roll, 10, and then collected in the storage tank 12 (7).

### *9.2.3 High Performance Magnetic Toner*

An image-forming apparatus such as copying machines and printers is sought to achieve much higher speed, higher image quality and higher stability (9). For example, printers, which have ever been chiefly used in offices, have come to be used in severe environments, and it has become important for them to promise stable image quality even in such a case.

In a magnetic one-component developing system, the magnetic toner is held by using a toner carrying member, i.e., a so-called developing sleeve, provided in its interior with a magnetic-field generation by means such as a magnet roll, and is transported to a developing zone to perform development. The magnetic toner is also provided with electric charges, chiefly by triboelectric charging, by the rubbing friction between the toner and a triboelectric charge providing member such as the developing sleeve.

In a low-temperature and low-humidity environment, where the magnetic toner tends to be electrostatically charged, a phenomenon called charge-up, in which the toner greatly increases in charge quantity, may, come about to damage developing performance of the toner. That is, any toner having been charged up may remain on the developing sleeve, and this may cause a decrease in image density or may make the whole toner thereon charged nonuniformly to cause image defects such as fog.

In order to resolve such a problem, many methods have been proposed in which conductive fine particles are added as an external additive to toner particles so as to control chargeability required as the toner. However, the presence of conductive fine particles on the toner particle surfaces may on the other hand, be likely to make the toner charged nonuniformly or insufficiently in environments where electric charges tend to leak, e.g., in a high-temperature or a high-humidity environment. Also, the rubbing friction between toner particles themselves or between the toner and a toner layer thickness control member may cause the external additive of the toner to come off or become buried in the toner particles, resulting in a low charging stability.

Studies have revealed that a toner inside the toner particles of which a magnetic material is locally present and on the toner particle surfaces of which any magnetic material is substantially not present, has a high resistance and tends to cause the charge-up, because its particle surfaces are composed of a resin. Also, where the magnetic material is locally present or is agglomerated in the toner particles, the toner may have a nonuniform chargeability. As a result, tone nonuniformity, called a *sleeve ghost*, may occur on images, or low density uniformity may result on solid black images.

In order to resolve these problems, it has been proposed to control the dielectric dissipation factor ($tan\delta$), which is an index of the state of dispersion of a magnetic material in toner particles, so as to make the toner stable against changes in the developing performance resulting from environmental variations.

The toner can be so structured that the magnetic material is present at a relatively high density in the vicinity of the particle surfaces. The presence of the magnetic material in the vicinity of particle surfaces without standing bare makes the material less chargeable. However, since the magnetic material is present at a high density in the vicinity of toner particle surfaces, the particles may agglomerate.

A magnetic toner has been developed that exhibits a superior uniformity in triboelectric charging between the particles themselves of the toner and also a superior charging stability. Further, the toner has a stable developing performance without any dependence on the service environments. The toner does not suffer from any image defects such as fog and ghost (9).

The toner is composed from a binder resin, a magnetic material, and an inorganic fine powder. A magnetic iron oxide may be used as the magnetic material, and may be subjected to a hydrophobic surface treatment with a silicon compound. This is preferable, because the dispersibility of the magnetic material in toner particles is improved. A magnetic iron oxide can be produced as follows (9):

**Preparation 9–1:** In 50 $l$ of an aqueous ferrous sulfate solution containing 2.0 $mol\,l^{-1}$ of $Fe^{2+}$, 55 $l$ of an aqueous 4.0 $mol\,l^{-1}$ NaOH solution was mixed, followed by stirring to obtain an aqueous ferrous salt solution containing ferrous hydroxide colloids. This aqueous solution was kept at 85°C, and oxidation reaction was carried out while air was blown into it at a rate of 20 $l\,min^{-1}$, to obtain a slurry containing core particles. The slurry obtained was filtered with a filter press and washed, and thereafter the core particles were again dispersed in water to make a re-slurry. To this re-slurry solution, sodium silicate was added in an amount providing 0.10 part of silicon per 100 parts of the core particles, and the pH of the slurry solution was adjusted to 6.0, followed by stirring to obtain magnetic iron oxide particles having silicon-rich surfaces.

The slurry obtained was filtered with a filter press and washed, and thereafter re-slurry was made using ion exchanged water. To this re-slurry solution (solid content: 50 $g\,l^{-1}$), 500 g (100% by mass based on the mass of the magnetic iron oxide) of an ion exchange resin SK110 (available from Mitsubishi Chemical Corporation) was introduced, and these were stirred for 2 *h* to carry out the ion exchange. Thereafter, the ion exchange resin was removed by filtration with a mesh. Further, the product obtained was filtered with a filter press and washed, followed by drying and disintegration to obtain a magnetic iron oxide, having a volume average particle diameter of 0.21 $\mu m$.

There are two kinds of possible methods of treating the surface of the magnetic particles, i.e., a wet method and a dry method (10).

In the wet method, the magnetic iron oxide is treated with a silane coupling agent, for example, $C_4H_9Si(OCH_3)_3$, dispersed in an aqueous medium in a high-speed mixer at elevated temperature to allow the condensation reaction of the silane (9).

On the other hand, the dry method involves spraying the silane compound, or a dispersion of the silane compound in water while stirring the magnetic particles in a high-speed stirring machine, such as a Henschel mixer, and condensing the silane compound while drying the magnetic particles at a high temperature to treat the surface of the magnetic particles (10).

The magnetic toner may be mixed with a charge control agent in order to improve the charging performance (9). Negative charge control agents are metal compounds of aromatic carboxylic acids. Positive charge control agents are quaternary ammonium salts or polymeric compounds that bear a quaternary ammonium salt in the side chain.

The toner should have a core-shell structure in order to improve the running developing performance. In the case of shell layers, the magnetic toner can have uniform particle surface properties. This improves the fluidity and uniform charging performance (9).

A specific method for forming the shells is to embed the fine particles for shells in core particles. When the magnetic toner is produced in an aqueous medium, the fine particles for the shells may be made to adhere to the core particles. Also, in the case of solution suspension or suspension polymerization, a hydrophilic resin may be used as the high-molecular material for shells. This enables the shells to be formed by utilizing the hydrophilicity of the resin to make such a high-molecular material localized at interfaces with water, i.e., in the vicinity of the magnetic toner particle surfaces.

Further, the shells may also be formed by a seed polymerization, where a monomer is made to swell on the core particle surfaces and then is polymerized.

As shell-forming resin an amorphous polyester resin is particularly preferable. Possible components of the amorphous polyester resin are summarized in Table 9.6 and are shown in Figure 9.8 and 9.9.

**Table 9.6** Components of an amorphous polyester resin (9).

| Alcohol | Acid |
|---|---|
| Ethylene glycol | Phthalic acid |
| Propylene glycol | Terephthalic acid |
| 1,3-Butanediol | Isophthalic acid |
| 1,4-Butanediol | Phthalic anhydride |
| 2,3-Butanediol | Succinic acid |
| Diethylene glycol | Adipic acid |
| Triethylene glycol | Sebacic acid |
| 1,5-Pentanediol | Azelaic acid |
| 1,6-Hexanediol | Fumaric acid |
| Neopentyl glycol | Maleic acid |
| 2-Ethyl-1,3-hexanediol | Citraconic acid |
| Cyclohexane dimethanol | Itaconic acid |
| Butenediol | |
| Octenediol | |
| Cyclohexene dimethanol | |

As final binder resin homopolymers and copolymers of styrene may be used, such as PS and poly(vinyltoluene), or a styrene-propylene copolymer and styrene-acrylic resins. The polymerization runs as suspension polymerization in an aqueous medium. A suitable composition is shown in Table 9.7.

The composition in Table 9.7 was uniformly dispersed and mixed. This monomer composition was heated to 60°C, and 12.0 parts of Fischer-Tropsch wax was added and mixed to dissolve it. Thereafter, 7.0 parts of dilauroyl peroxide as a polymerization initiator were dissolved to prepare a polymerizable monomer composition. The polymerizable monomer composition was introduced into an aqueous medium, followed by stirring for 10 *min* at 60°C in an atmosphere of nitrogen. Thereafter, the granulated product obtained

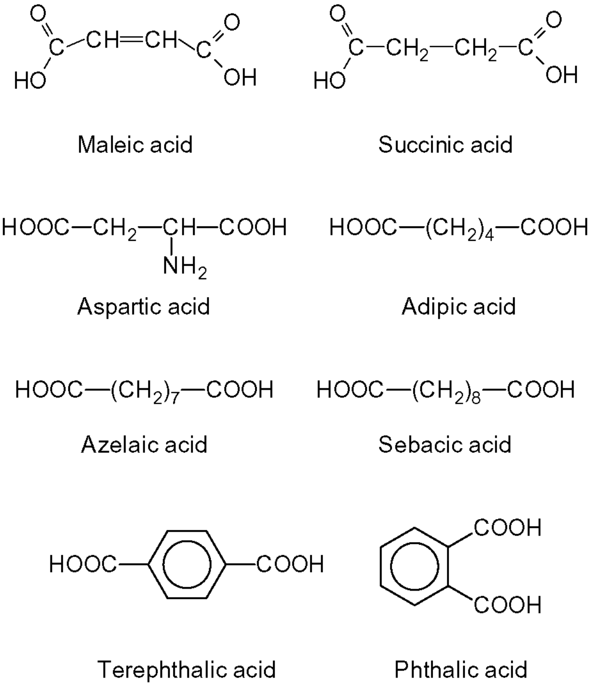


**Figure 9.8** Acids for polyesters.

**Table 9.7** Composition for polymerization (9).

| Component | Amount/[Parts] |
|---|---|
| Styrene | 78.0 |
| *n*-Butyl acrylate | 22.0 |
| Divinylbenzene | 0.6 |
| Iron complex dye | 1.5 |
| Treated magnetic material | 90.0 |
| Saturated polyester resin | 7.0 |

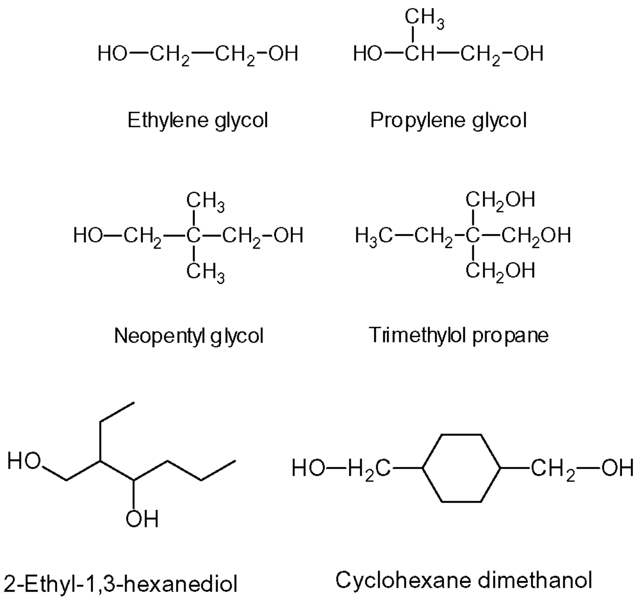


**Figure 9.9** Alcohols for polyesters.

was stirred with a paddle stirring blade, during which the reaction was carried out at 74°C for 6 *h*. After the reaction was completed, the suspension formed was cooled, and hydrochloric acid was added thereto to effect washing, followed by filtration and then drying to obtain the final toner particles.

In the magnetic toner, the dielectric loss factor $\varepsilon$ may be controlled by controlling the presence of the magnetic material in the vicinity of toner particle surfaces. In order to get a high dielectric loss factor $\varepsilon$, the magnetic material should be present at the toner particle surfaces or in the vicinity of the toner particle surfaces. The magnetic material, which has a lower resistance than resins, may be considerably present on toner particle surfaces or in the vicinity of toner particle surfaces. This enables the electric charges to dissipate appropriately. However, making the magnetic material bare to the toner particle surfaces is not preferable because the dielectric loss factor $\varepsilon$ may become so excessively large as to make the electric charges leak conspicuously. In order to satisfy the dielectric loss factor $\varepsilon$, the magnetic material may be made present at particle surface portions without making it bare to the toner particle surfaces. On the other hand, in order to lower the value of the dielectric loss factor $\varepsilon$, the magnetic material may be made present in a small quantity in the toner particle surface layers. The magnetic material may be dispersed throughout the interiors of toner particles (9).

## 9.3 Biotechnology

### 9.3.1 *Alcohol Production by Magnetic Immobilized Yeast*

*Saccharomyces cerevisiae* was immobilized in a calcium alginate gel together with varying concentrations of iron oxide, in the form of magnetite or a colloidal ferrite suspension, Ferrofluid™ (11).

The inclusion of the magnetic material apparently had no adverse effect on the yeast cells as judged from their fermentation capacity, their operational stability as well as their ability to propagate *in-situ* in the presence of nutrients. The usefulness of magnetic preparations in viscous or particle-containing media has been discussed (11).

### 9.3.2 *Solid Acidic Catalysts*

Mesoporous poly(vinylsulfonic-*co*-divinylbenzene) with $CoFe_2O_4$ was prepared and used as solid acidic catalysts to directly transform cellulose into 5-hydroxymethylfurfural (12). The yield of 5-hydroxymethylfurfural can reach as much as 98% from the dehydration of glucose using $CrCl_3 \times 6H_2O$ catalyst in tetrabutylammonium chloride at 120°C for 90 *min*.

The magnetic catalysts can be readily separated from the resulting products in a magnetic field, as well as recycled and reused with a negligible loss in their activity (12).

### 9.3.3 *Supports for Biological Molecules*

Magnetic separation techniques provide a rapid and convenient method of separating certain particles from dilute suspensions, especially those that might block columns or filters (13).

Magnetic supports for immobilized enzymes and bioaffinity adsorbents have been reviewed (14). The magnetic separation of immobilized enzymes or bioaffinity adsorbents allows their selective recovery from liquors containing other suspended solids, and gives easier handling of large numbers of samples in analysis.

Nonporous magnetic supports seem to be more resistant to fouling, diffusional limitation and attrition than conventional porous supports. A variety of magnetic powders and linkage methods have been used in the preparation of supports. Nonporous magnetic supports are attractive for use in liquors containing fouling materials or suspended solids, either for bioaffinity adsorbents or for immobilized enzymes acting on small molecular substrates. Magnetic supports also offer considerable advantages in analysis based on bioaffinity interactions such as immunoassay (14).

The use of magnetic polymers as supports for biological molecules has created much interest (15). The inherent advantages of such preparations are, in particular, the ease of recovery of these polymers by applying a magnetic field. Thus, when used as supports for immobilized enzymes, their easy retrieval from liquors containing colloids or undissolved solids should be of great practical value

Magnetic polymers have recently been tested as an alternative to conventional radioimmunoassay technique, obviating the need for vertical rotation and for the time-consuming, multiple centrifugations required with conventional solid phase procedures (15).

In the established techniques for producing magnetic polymer particles, the attachment of the biomolecules had to follow the preparation of the specific magnetic material; furthermore, most of these preparations have been nonporous, exhibiting rather poor capacity. A general procedure using magnetic fluids which allows the post-magnetization of polymers already substituted with biological molecules has been described. The properties of such preparations have been tested primarily as affinity chromatography gels. These preparations showed unaltered biospecificity when applied in general ligand-affinity chromatography studies. The simplified separation possible due to the magnetic properties of the gels eliminates the usual centrifugation and column chromatography steps. The procedure of post-magnetization seems to be suitable for different polymer particles, both unsubstituted gels and those carrying immobilized ligands as affinity adsorbents or enzymes (15).

### 9.3.3.1 *Chymotrypsin*

Chymotrypsin has been immobilized to several nonporous magnetic materials (16). Nickel particles were considered to be most suitable as immobilized enzyme supports.

Chymotrypsin immobilized to nonporous magnetic supports was not fouled significantly by whole milk or clarified yeast homogenate; aminoethyl-cellulose-chymotrypsin was rapidly fouled by both these materials and chymotrypsin immobilized to acrylic-based ion exchangers was slowly fouled. Immobilized enzyme activity was found to be inverted proportional to particle diameter for nonporous rock magnetite particles. Immobilization by adsorption and then glutaraldehyde crosslinking was used to produce controlled amounts of chymotrypsin on the particles.

The esterolytic activity increased with enzyme loading but caseinolytic activity did not increase. Chymotrypsin is inhibited by metal ions from the magnetic supports. It is partially protected by use of a preliminary protein coating and may be reactivated by incubation with ethylenediamine tetraacetic acid or bovine serum albumin (16).

### 9.3.3.2 *Protein and Polysaccharide*

Magnetic separations are one of the most versatile separation processes in biotechnology as they are able to purify cells, viruses, proteins and nucleic acids directly from crude samples. These fast and gentle processes provide unique advantages over other separation techniques. Magnetic adsorbents can be tailored for the target. The synthesis and the tailoring of magnetic adsorbents for bioseparations as well as their ultimate application have been reviewed (17).

The recovery of immobilized enzymes on iron oxide particles have been described (18). Core shell composite microspheres from $Fe_3O_4$/poly(styrene-*co*-maleic anhydride) are suitable for binding enzymes such as $\alpha$-amylase. The microspheres were prepared using magnetite particles as seeds by the copolymerization of styrene and maleic anhydride (19). The magnetite particles were encapsulated by poly(ethylene glycol) (PEG), The encapsulation improves the affinity between the magnetite particles and the monomers. Thus, the size of the microspheres, the amount of the surface anhydrides, and the magnetite content in the composite are highly dependent on magnetite particles, comonomer ratio, and dispersion medium used in the polymerization. Free $\alpha$-amylase could be immobilized on the microspheres that contain reactive surface-anhydride groups by covalent binding.

## 9.4 Medical Uses

### 9.4.1 *Zero-Valent Nanoparticles*

Magnetic polymer nanoparticles are playing a vital role in various biomedical fields, such as diagnostics, drug delivery, and cancer therapeutics (20). Nowadays, magnetic zero-valent metal polymer nanoparticles are receiving considerable attention in the research field of magnetic nanomaterials due to their improved magnetic properties in comparison to conventional magnetic iron oxide polymer nanoparticles.

Two types of magnetic zero-valent metal polymer nanoparticles, metallic and bimetallic, have been prepared by different techniques, and their selection depends on various factors such as stability, particle size, and application.

The recent developments in the synthesis of such nanoparticle systems have been reviewed (20). Also, future perspectives have been described.

### 9.4.2 *Drug Targeting*

There is currently a considerable interest in the area of drug targeting. The use of magnetic carriers in affinity chromatography has been studied and it became clear that a magnetic material might also be used as support for drugs which could be brought to the target site with the aid of a magnetic field (21).

Interactions with non-target sites, such as a specific location, would allow a high concentration of the drug to be used and would extend the time of exposure at the site.

### 9.4.3 *Stimuli-Responsive Polymers*

There is a continuing interest in stimuli-responsive polymers, in particular in the fields of controlled and self-regulated drug delivery (22).

Delivery systems based on these polymers have been developed that closely resemble the normal physiological process of the diseased state. This issue ensures an optimum drug release according to the physiological need.

These polymers should experience rapid changes in their microstructure, from a hydrophilic to a hydrophobic state, triggered by small changes in the environment. The changes should be reversible.

Therefore, the polymer is capable of returning to its initial state as soon as the triggering effect is removed. Stimuli may occur internally, e.g., by a change in pH in certain organs or diseased states, a change in temperature or the presence of specific enzymes or antigens.

On the other hand, external stimuli include magnetic or electric fields, light, ultrasound, and others (22).

### 9.4.4 *Magnetic Drug Carriers*

The preparation and application of such magnetic drug-carrying materials have been described (21).

Acid-hydrolyzed starch with powdered magnetite was used in magnetic microspheres. The starch carbonyl iron slurry was slowly poured into stirred toluene containing a dissolved emulgator. The active compounds, etanolamine, plasmin, and albumin were covalently coupled to the microspheres.

In animal experiments the uptake, near the ear, was investigated, when a magnetic field was applied and in the case of a zero magnetic field. It was concluded that an enrichment of the drugs near the ear was caused by the magnetic field (21).

Other uses of microspheres for biomedical applications, including fluorescent species, radionuclides and magnetite particles, have been reviewed (23).

### 9.4.4.1 Doxorubicin Loaded Magneto-niosomes

In chemotherapy, magnetic drug-targeting to a specific organ or tissue has been proposed assuming that magnetic fields are harmless to biological systems (24).

Doxorubicin, c.f. Figure 9.10, has been used as a model drug by magneto-niosomes in order to evaluate the physicochemical properties of the formulations and the *in-vitro* release profile.

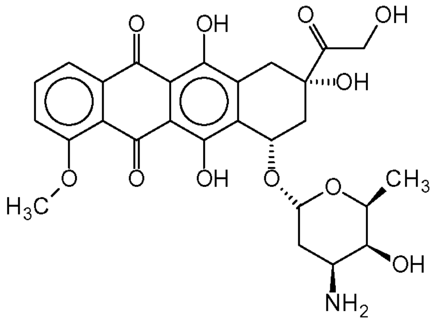


**Figure 9.10** Doxorubicin.

Tween® 60 and Pluronic® L64 have been used as surfactants and the formulation cytotoxicity has been performed by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide and trypan blue dye exclusion tests. These compounds are shown in Figure 9.11.

This test, also addressed as MTT test, is used for assessing cell metabolic activity (25). Some cellular oxidoreductase enzymes can, under defined conditions, reflect the number of viable cells present. These enzymes can reduce the tetrazolium dye 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide to its insoluble formazan, which has a purple color.

The results showed that the niosome dimensions and the doxorubicin entrapment efficiencies are influenced by the composition of the bilayer. The formulations are able to control the delivery and the release of the drug in its active form in a retarded manner. No additional toxicity, due to the encapsulation of the ferrofluid into the niosomes core, has been detected (24).

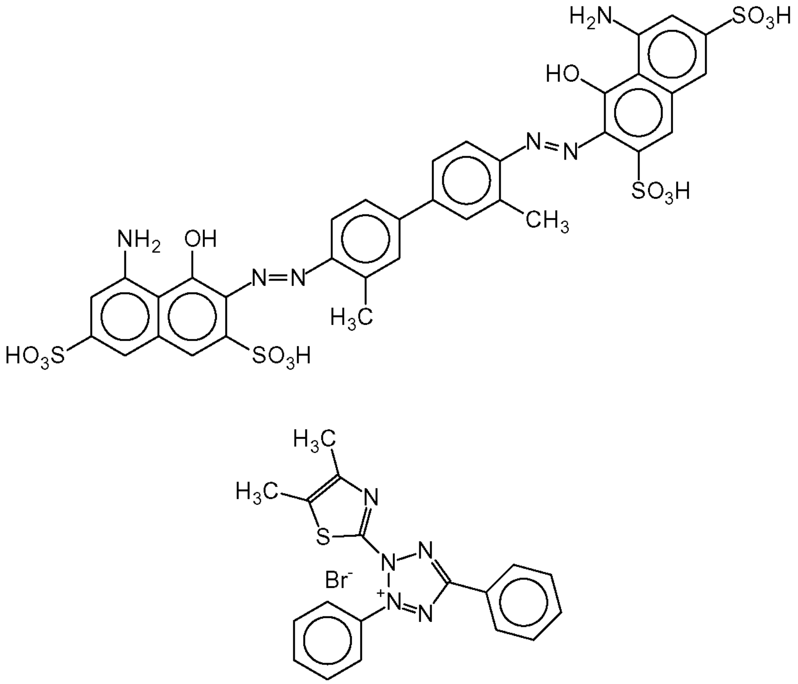


**Figure 9.11** Trypan blue (top), 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (bottom).

### *9.4.4.2 Stimuli-Responsive Polymers*

A magnetic drug-targeting carrier has been developed that consists of magnetic nanoparticles encapsulated with a smart polymer with the characteristics of controlled drug release (26). The carrier is a functionalized magnetite ($Fe_3O_4$) and the therapeutic agent doxorubicin, which is encapsulated with the thermosensitive polymer, dextran-*g*-poly(*N*-isopropylacrylamide-*co*-*N*,*N*-dimethylacrylamide). The surface of magnetite nanoparticles was functionalized by chemical bonding with 3-mercaptopropionic acid hydrazide via Fe–S covalent bonds. 3-Mercaptopropionic acid hydrazide is shown in Figure 9.12.

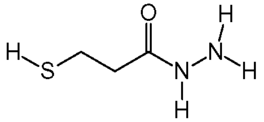


**Figure 9.12** 3-Mercaptopropionic acid hydrazide.

Doxorubicin was attached to the surface of the functionalized magnetic nanoparticles through an acid-labile hydrazone bond, formed by the reaction of the hydrazide group of 3-mercaptopropionic acid hydrazide with the carbonyl group of doxorubicin.

The dextran grafted polymer exhibits a lower critical solution temperature of ca. 38°C, which is representative of a phase transition behavior. This behavior allows for an on-off trigger mechanism.

At an experimental temperature lower than lower critical solution temperature, the drug release was very low. However, at a temperature greater than lower critical solution temperature, there was an initially rapid drug release followed by a controlled release in the second stage, especially in a mild acidic buffer solution of pH 5.3.

The proposed carrier is appropriately suitable for magnetic targeting drug delivery system with longer circulation time, reduced side effects and controlled drug release in response to the change in external temperature (26).

### *9.4.5 Surface Effects*

Due to finite size effects, such as the high surface-to-volume ratio and different crystal structures, magnetic nanoparticles are found to exhibit interesting and considerably different magnetic properties than those found in their corresponding bulk materials (27).

These nanoparticles can be synthesized in several ways with controllable sizes enabling their comparison to biological organisms from cells of 10–100 *μm*, viruses, genes, down to proteins of 3–50 *nm*.

The optimization of the size of the nanoparticles, their size distribution, agglomeration, coating, and shapes, along with their unique magnetic properties, prompted the application of nanoparticles of this type in diverse fields.

Biomedicine is one of those fields where intensive research is currently being conducted. In this review, we will discuss the magnetic properties of nanoparticles which are directly related to their applications in biomedicine.

The surface effects of ferrite nanoparticles, and a diagnostic application of magnetic nanoparticles as magnetic resonance imaging contrast agents, have been detailed (27).

### *9.4.6 Superparamagnetic Iron Oxide Nanoparticles*

Nanoparticles can be used for various biomedical applications, where they facilitate laboratory diagnostics and therapeutics. For drug delivery purposes, the use of nanoparticles is attracting attention due to their unique capabilities and their negligible side effects, not only in cancer therapy but also in the treatment of other ailments (28).

Among all types of nanoparticles, biocompatible superparamagnetic iron oxide nanoparticles with proper surface architecture and conjugated targeting ligands/proteins have attracted a great deal of attention for drug delivery applications.

The state of the art of superparamagnetic iron oxide nanoparticles has been reviewed (28). Also, their possibilities and limitations from fabrication to application in drug delivery have been described.

Further, synthetic routes and surface modification of some superparamagnetic iron oxide nanoparticles for drug delivery purposes have been described (28).

Monodisperse, water-soluble dextran-coated iron oxide nanorods have been synthesized using a facile and scalable method (29,30). A room temperature method utilizes the mixing of an acidic solution of iron salts with a basic solution of ammonium hydroxide to facilitate initial formation of iron oxide crystals. The stability, cystallinity and shape of these nanorods depend on the time of addition of the dextran as well its degree of purity. The so snythesized nanorods exhibit unique magnetic properties, including superparamagnetic behavior and high spin-spin water relaxivity. Additionally, they possess an enhanced peroxidase activity. Therefore, this method for preparation of polymer-coated iron oxide nanorods will expedite their use in applications for magnetic sensors, devices and nanocomposites with magnetic and catalytic properties.

### *9.4.7 Magnetized Scleral Buckle*

Retinal detachment is a leading cause of blindness. A magnetic polymer may be polymerized in living tissues (31). The retinal detachment can be repaired without needing suturing, by using a magnetic fluid with a magnetic scleral buckle.

The magnetic scleral buckle may be polymerized into place in the eye, rather than being preformed outside the eye as has been conventionally done.

Carboxylic acid functional groups bind strongly to magnetite (31). Thus, an approach to preparing magnetic nanoparticles for dispersion into biocompatible poly(dimethylsiloxane) carrier fluids is to (31):

1. Prepare a poly(dimethylsiloxane) surfactant with appropriate binding groups,
2. Bind the new surfactant to magnetite nanoparticle surfaces, and then
3. Disperse these into well-defined poly(dimethylsiloxane) fluids.

Carboxylic acid-functionalized poly(dimethylsiloxane) surfactants have been synthesized for steric stabilization of magnetite nanoparticle dispersions in biocompatible polysiloxane carrier fluids. Trivinylsilyl-terminated poly(dimethylsiloxane) was prepared by a living polymerization method. Then this was reacted with either mercaptoacetic acid or mercaptosuccinic acid using a free radical thiol-ene addition to afford poly(dimethylsiloxane) containing carboxylic acid groups.

The synthesis is shown in Figure 9.13.

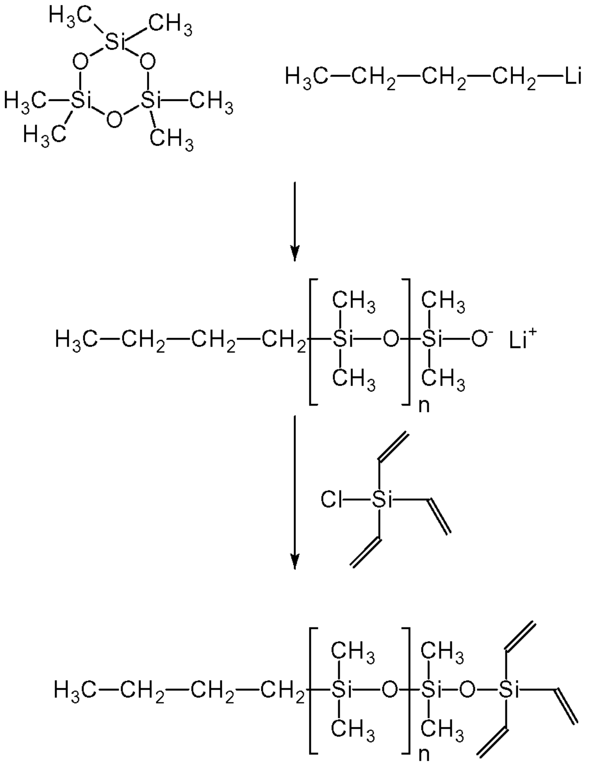


**Figure 9.13** Functionalized poly(dimethylsiloxane).

Magnetite nanoparticles were prepared by chemically co-precipitating $FeCl_2$ and $FeCl_3$ at pH 9–10, then the poly(dimethylsiloxane)-magnetite nanoparticle complexes were prepared via interfacial adsorption of the carboxylate groups of the poly(dimethylsiloxane) stabilizer onto aqueous magnetite particles at a slightly acidic pH (31). Magnetic systems formed internally may also be used in other medical contexts, such as in drug delivery (31).

### 9.4.8 *Magnetic Polymer Carriers*

Magnetic polymer particles are used within several fields of biochemistry and medicine (32,33). They have been tried as carriers for pharmaceutical preparations since, due to their magnetic properties, they are capable of transporting the preparations to the desired location in the body. Magnetic particles also have other practical applications and have been used within diagnostics since it is possible to replace separation of particles by means of centrifugation by the much simpler method of magnetic extraction. Further, magnetic particles have been used for cell separation and as carriers for enzymes.

Several properties are important to make magnetic particles useful in biological and diagnostic systems (34).

1. The particle must possess the necessary biological activity, affinity, or reactive nature, by which it will perform its function.
2. The particles must be suspendable in an aqueous medium for delivery to the biological or reaction system.
3. It may also be desirable that the particle suspension be stable, i.e., not settled out or agglomerated.
4. A small particle size may be desirable so that a suspension of the magnetic particles may be filter sterilized by conventional techniques.

### 9.4.9 *Magnetically-Controllable Delivery System for Therapeutic Agents*

Many drugs developed by the pharmaceutical industry have shown remarkable success during *in-vitro* testing and animal trials, but have yielded undesirable results in clinical trials due to systemic toxicity of the drug to the body. Thus, the ability to deliver large concentrations of drugs locally is of major importance for both the pharmaceutical industry and also for clinicians.

An intravascularly administrable, magnetically localizable biodegradable carrier, comprising microspheres formed from an amino acid polymer matrix containing magnetic particles embedded within the matrix for targeted delivery of chemotherapeutic agents to cancer patients, has been described (35).

Also, microspheres with magnetic particles, which are suggested to enhance binding of a carrier to the receptors of capillary endothelial cells when under the influence of a suitable magnetic field, have been described (36).

A magnetic delivery system for delivering a magnetizable particle to a location in a body has been developed. The device includes a magnetizable object implanted in the body, wherein the magnetizable object includes a plurality of segments distributed throughout the magnetizable object. The segments are configured to provide a magnetic gradient for attracting the magnetizable particle and an external source of a magnetic field capable of (37):

1. Magnetizing the magnetizable particle, and
2. Increasing a degree of magnetization of the magnetizable object and thereby creating the magnetic gradient.

Magnetic cell delivery is accomplished by the use of the two-source method for magnetic drug delivery to magnetizable implantable surfaces (37). Biological cells are loaded with magnetizable particles, e.g., superparamagnetic nanoparticles, thereby forming magnetic cells. The cells can be isolated from the patients themselves or obtained from maintained cell lines. Magnetizable particles provide cells with a large collective magnetic moment in the presence of the uniform fields used within this method to deliver magnetic cells to magnetic implants within the body. The cells are then injected into the body by arterial puncture, catheter release, or intravenous injection. The externally applied magnetic field does not serve to direct the cells to the implant.

It saturates their magnetic moment, along with the magnetic moment of the implanted magnetizable implant. The high local magnetic field gradients of the magnetic moment and geometry of the implant provide the strong magnetic forces necessary to capture the cells from the blood flow. These cells can serve as a delivery vehicle for magnetic particles loaded with therapeutics or biologics, e.g., drugs, radioisotopes, antibodies, retroviruses; or they can be used in promoting healthy tissue growth for endothelialization of an implant, wound healing, or otherwise needed tissue regeneration (37).

Magnetic nanoparticles are delivered by endocytosis into cells, which can then be delivered magnetically to implantable surfaces, e.g., stents. These cells can be used as a vehicle for mass transport of drug-loaded particles, or as a means to deliver various cell types, such as adult or embryonic stem cells, as well as endothelial cells. This method can be used for wound healing, *in-vivo* engineering of new healthy tissues, targeted delivery of cells loaded with magnetic drug for local targeting of pathologies, such as heart disease, cancer, and nervous system disorders, targeting of autologous and allogous cell types for wound healing and in *vivo-tissue* engineering (37).

In the cases where the use of a magnetic carrier comprising microspheres or nanospheres for encapsulation of the therapeutic agent is required, the microspheres or nanospheres preferably comprise a biodegradable polymer, such as poly(lactic acid) (PLA) or poly(lactic-*co*-glycolic acid) which cause minimal inflammatory response upon degradation. Numerous other biodegradable polymers are known, such as poly(3-hydroxybutyrate) and elastomeric poly(ester amide), which may also be used in these microspheres or nanospheres. The ultimate selection of the biodegradable polymer for encapsulation of the drug is based upon the desired degradation times, side effects, and drug conjugation (37).

### *9.4.10 Magnetic Polymer Scaffolds*

The development of sophisticated magnetic polymer scaffolds with aligned structural features have been described (38). Tissue engineered magnetic scaffolds have been prepared by incorporating iron oxide magnetic nanoparticles into a three-dimensional structure of aligned starch and polycaprolactone fibers.

The fibers were fabricated by a rapid prototyping technology. The effect of an externally applied magnetic field has been investigated on the tenogenic differentiation of adipose stem cells. Also, the magnetic scaffolds were implanted in an ectopic rat model. This procedure showed a good biocompatibility and integration within the surrounding tissues.

The results suggest that the effect of the magnetically aligned scaffolds structure combined with magnetic stimulation has a significant potential to impact the field of tendon tissue engineering toward the development of more efficient regeneration therapies (38).

### 9.4.11 *Theranostic Nanoparticles*

A magnetic polymer nanocarrier was developed with folate receptor targeting and pH-sensitive multifunctionalities to carry doxorubicin for the treatment of advanced gastric cancer (39). Folate conjugated, pH-sensitive, amphiphilic poly($\beta$-aminoester) self-assembled with hydrophobic oleic acid-modified iron oxide nanoparticles. The resulting hydrophobic interaction area was demonstrated to be a reservoir for lipophilic doxorubicin. The accumulation of the lipophilic doxorubicin in the tumor site was detected by magnetic resonance imaging. The findings suggest that lipophilic doxorubicin could be a promising theranostic candidate for advanced gastric cancer treatment.

### 9.4.12 *Biodegradable Polymer Composites*

A method for preparing colloidal particles formed by a magnetite nucleus and a biodegradable poly(*D*,*L*-lactide) polymer coating has been described (40).

The method is based on the so-called double-emulsion technique, employed to obtain polymeric spheres loaded with therapeutic drugs, to be used as drug delivery vectors. Colloidal particles that are both magnetic field responsive, and useful as drug delivery systems, can be fabricated.

The studies revealed that this material displays a behavior intermediate between that of magnetite and poly(*D*,*L*-lactide) spheres. Thus, electrophoresis measurements as a function of pH showed that the isoelectric point of a pH of 5.2 of core/shell colloids is in between those of magnetite (isoelectric point of a pH 7) and the polymer (isoelectric point of a pH $< 2$) (40).

### 9.4.13 *Nanoencapsulation Methods*

Nanoencapsulation methods have been developed for the synthesis of polymeric magnetic nanoparticles for use in biomedical applications. The method of making polymeric nanoparticles runs as (41):

1. Providing active agent nanoparticles having an average diameter of 5–100 *nm*,

2. Treating said active agent nanoparticles with an anionic surfactant to form modified active agent nanoparticles,
3. Mixing the modified active agent nanoparticles with a solution of a polymer in a solvent at a first temperature, which is greater than the melting temperature of the polymer and less than the boiling point of the solvent to form a first mixture, said mixing comprising the use of sonication,
4. Mixing a non-solvent with the first mixture to form a second mixture, the non-solvent being a non-solvent for the solvent and for the polymer and having a boiling point greater than the melting temperature of the polymer,
5. Sonicating the second mixture to form an emulsion, and
6. Cooling the emulsion to a second temperature and at a rate effective to precipitate polymeric nanoparticles comprising the polymer with the modified active agent nanoparticles dispersed therein. In one embodiment, the mixing of a non-solvent with the first mixture and the sonicating of the second mixture are conducted in the same step. The method can further comprise isolating the polymeric nanoparticles from the solvent and the non-solvent.

The polymer preferably is a crystalline polymer, and should have a melting temperature of less than about 200°C. The polymer can be selected for from poly(amide)s, poly(carbonate)s, poly(alkene)s, poly(vinyl ether)s, poly(glycolide)s, cellulose ethers, poly(vinyl halide)s, poly(glycolic acid), and PLA. Transmission electron micrographs of poly(ethylene) (PE)/maghemite composite nanoparticles are shown in Figure 9.14.

### *9.4.14 Uniform Field Magnetization*

Therapeutic agents delivered in a conventional or nonspecific manner often are distributed to non-designated areas of the body (42,43). As a consequence, the agent may be metabolized, for example, through first-pass metabolism of the liver, thereby resulting in diminished bioavailability and the possibility for increased dosing at a higher cost and with the risk of adverse side effects. In addition, the nonspecific distribution of therapeutic agents may result in adverse effects and unwanted pharmacological responses in the subject to

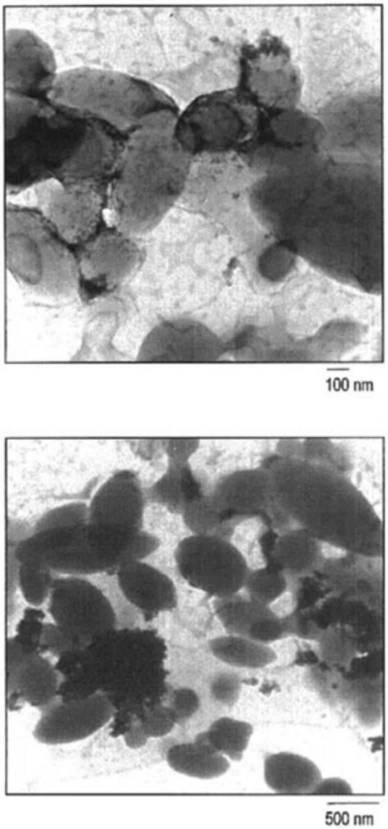


**Figure 9.14** Transmission electron micrographs of nanoparticles (41).

which they are administered. As a result, certain agents may be contraindicated in certain subjects or under certain conditions.

Systems for magnetically targeting therapeutic particles have been developed (43). Methods have been focused for magnetically targeting a therapeutic particle to an implanted device, such as a stent. The methods are further suitable for removing spent particles.

The systems are composed of a particle with a therapeutic agent and a magnetic or magnetizable material, an implantable device such as a stent comprising another magnetic material, and a retrieval system with a third magnetic material capable of being reversibly connected to a subject (43).

Polymeric nanoparticles with incorporated superparamagnetic nanocrystals can be prepared by dispersing the superparamagnetic nanocrystals in an organic solvent, in which the polymer and the therapeutic agent are dissolved, emulsifying the organic phase in water in the presence of a suitable stabilizer, and finally eliminating the solvent to obtain solidified nanoparticles. The conditions of preparation should not be damaging for the therapeutic agent to be attached. Thus, the temperature for the preparation preferably ranges from about 25–37°C. Methods for the preparation are available in the literature (44–46).

Bioresorbable nanoparticles can be rendered magnetic by the inclusion of magnetically responsive nanocrystals in their structure. This can be done by combining a fine suspension of such crystals, i.e., a ferrofluid with the anionic lipid solution prior to the particle formation. Ferrofluids are composed of nanoscale ferromagnetic particles suspended in an aqueous carrier fluid. The preparation of such nanoparticles is a two-step process consisting of (43):

1. Making the fine suspension of magnetic nanocrystals, the ferrofluid in the presence of an anionic lipid, and
2. Forming nanoparticles by controlled precipitation of the anionic lipid with a polyvalent cation in the presence of a stabilizer and a therapeutic agent.

For example, the magnetic nanoparticles are prepared by a controlled aggregation of an oleate-stabilized ferrofluid with $Ca^{+2}$. The preparation of a ferrofluid runs basically as follows (43):

**Preparation 9–2:** In detail, to prepare a ferrofluid, an aqueous solution containing a water soluble ferric $Fe^{+3}$ salt, such as ferric chloride hexahydrate, and a water soluble ferrous salt $Fe^{+2}$, such as ferrous chloride tetrahydrate, is precipitated with a base, such as an aqueous sodium hydroxide solution, to form a magnetite precipitate containing magnetic nanocrystals. A water soluble salt of a fatty acid, such as an aqueous solution of sodium oleate, is added, and the magnetic nanocrystals re-suspended by heating, for example, in an inert atmosphere, such as under argon. A stabilizer such as albumin can be added, along with the therapeutic agent, either to the first aqueous solution, which comprises the magnetic nanocrystals, stabilizer, water soluble salt of a mono-carboxylic fatty acid, and therapeutic agent, or to the second aqueous solution, which comprises the polyvalent biocompatible cation. The second solution is then added to form the magnetic nanoparticles.

Extended circulation time of the particles associated with a therapeutic agent can be achieved by preventing opsonization and clearance by the subject's immune system by coating the particle with a biocompatible hydrophilic polymer such as PEG or dextran, or by coating the particle with albumin to inhibit the binding of opsonins to the particle surface. Opsonins are molecules that enhance the phagocytosis by marking an antigen for an immune response.

A single magnetic field gradient can be used to direct the particles to the implantable device, and then reconfigured to direct extant unused or spent particles to the retrieval system. Alternatively, multiple gradients can be produced and used, with at least one gradient directing particles to the implanted device, and at least one additional gradient directing particles to the retrieval system. The gradient can be generated proximal to the implanted device, and can be generated proximal to the retrieval system (43).

Several procedures to prepare magnetic therapeutic formulations have been explained in detail (43).

### *9.4.15 Nanomagnetic Actuation of Molecular Cell Signaling*

A fundamental principle of cell biology is that complex behaviors such as cell growth, differentiation, motility, and apoptosis are controlled by receptor-mediated signal transduction, which impacts gene expression, protein synthesis, and cell metabolism by triggering a series of molecular-mediated intracellular signaling cascades (47). Receptor-mediated signal transduction allows cells to convert one type of stimulus into a different type of stimulus. The receptor acts as the intermediary in carrying out the conversion. Such transduction is often triggered by the binding of chemical ligands, such as hormones, cytokines, and adhesive macromolecules, to cell surface receptors and propagated by specific binding of different molecules inside the cell. Conventional approaches to transduction-mediated cellular control have relied upon the use of these chemical cues.

A few highly specialized cell types, including neurons and myocytes, have been activated using electrical stimuli, and microelectrode arrays have been developed to influence the activity of these cells in microdevices and in patients. Most cells are not electrically active in this way, however, and switches activated by electrical signals have high power requirements, so this approach may not be generalized for cellular microsystems design. Medical microdevices that require electrical stimulation also often require indwelling wires or transcutaneous electrodes that can lead to medical complications, such as infection.

On the other hand, nanomagnetic interfaces that link to physiological cellular signal transduction mechanisms open a new mechanism to interface living and physical systems. Thus, methods for non-invasively controlling cellular signaling functions have been disclosed (47). These methods transduce magnetic inputs into physiological outputs in living cells.

Magnetic cores can be coated with biocompatible polymers, such as PVA, silica and dextran, that bind readily to biomolecules or specific antibodies (48).

### *9.4.16 Aerosol Therapy*

Aerosols are solid or liquid suspended particles in gases with a diameter of from about 0.0001 $\mu m$ to about 100 $\mu m$. If solid particles are present in the aerosol, such aerosols are typically called smokes or dusts. On the other hand,when liquid particles are present in the aerosol, these aerosols are called mists.

Medicinal aerosols in aerosol therapy are typically inhaled orally or nasally by the patient to be treated. During or after the inhalation of the particles into the lung, a certain proportion of the particles escapes from the flow line of the particles formed by the inhalation or exhalation and thereby comes into contact with the moist surface of the air cavities, e.g., the throat, nasal or pharyngeal cavity, the trachea or the lung tissue. This phenomenon is in general called particle deposition or deposition.

For effective and gentle therapy it is desirable for the pharmaceutical active agents transported by aerosols to be administered in a targeted manner to only defined, diseased regions of the lungs. On the one hand, the dose of the pharmaceutical active agent to be administered can be reduced by this means, and on the other hand, undesirable side effects on the surrounding healthy tissue can be reduced or avoided.

The possibility of a magnet-guided transportation of aerosol particles has been discussed (49). So, aerosols containing magnetic particles and a pharmaceutical active agent can be used for a directed magnetic-field-guided transfer of the active agents in the aerosol therapy (50).

The basic concept of the magnetic field-guided administration of aerosol is shown in Figure 9.15. An aerosol containing magnetic particles is generated with a commercially obtainable nebulizer. The drops of liquid containing magnetic particles formed here are in-

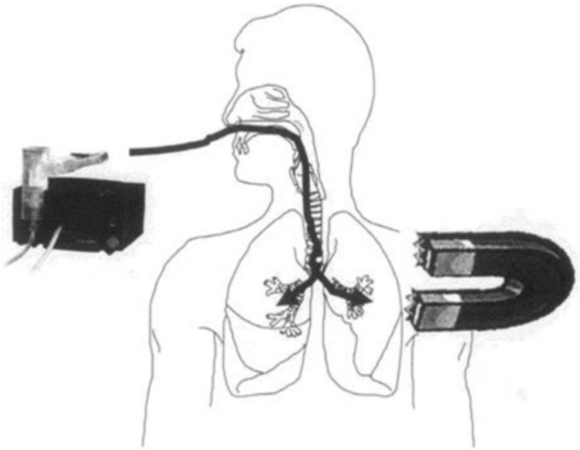


**Figure 9.15** Concept of the magnetic-field-guided administration of aerosol (50).

haled by the patient and guided by the externally applied magnetic field directly into the desired regions of the lung of the patient (50).

The magnetic particles contained in the aerosol can consist of various metals and oxides or hydroxides thereof or contain these. The magnetic particles are typically synthetic magnetic particles, i.e., are not obtainable from a living organism. The magnetic particles should not induce systemic toxic side effects in the organism to which they are administered.

The magnetic particles are coupled to liposomes, hollow colloids or to the pharmaceutical active agents themselves. Processes which can be used for a chemical coupling of the magnetic particles to the pharmaceutical active agents have been described in detail (51).

If the magnetic particles are present in coated form, the coating is preferably selected from positively or negatively charged electrolytes, such as phosphates, citrates or amines, with silanes, fatty acids or polymers, e.g., polysaccharides, proteins or natural or synthetic polymers. The coating serves for the reduction of toxicity and for a coupling of the pharmaceutical active agents to the magnetic particles.

After administration of the aerosol an externally applied magnetic field should be permanently present, in order to direct the aerosol to the desired location (50). The control of the magnetic field can take place dynamically in coordination with the breathing of the patient as a function of the breathing rhythm of the patient, so that during the inhalation and exhalation by the patient no magnetic field is applied in the region to be treated, but in the resting phases a magnetic field is applied there and only then does a deposition of the aerosol on the surface of the respiratory tract take place.

### *9.4.17 Magnetofection*

Magnetic formulations of vectors for nucleic acid delivery and their characterization, mechanisms of magnetofection, and the application of magnetofection in viral and nonviral nucleic acid delivery in cell culture and in animal models have been reviewed (52). The results that have been obtained with using magnetofection have been summarized. Magnetofection is now widely used as a generic term for magnetically guided and enhanced nucleic acid delivery. This occurs under the influence of a magnetic field acting on nucleic acid vectors that are associated with magnetic nanoparticles (53).

Nanoparticles formed from biodegradable polymers have been used to carry active molecules to sites in the body where the therapeutic effect is required (54,55).

Various techniques for the preparation of biodegradable nanoparticles from polymers have been detailed (54). These techniques include emulsification-solvent evaporation, solvent displacement, salting-out, and emulsification diffusion.

Various studies have been conducted to improve the delivery of a biomaterial, such as viruses and plasmid deoxyribonucleic acid (DNA), by only physical techniques, such as an application of a magnetic field to a vector including magnetically responsive solid phases, which are nanometer sized particles (56–59).

The use of a magnetic force in gene therapy was investigated (60, 61). Nanoparticles with both controllable particle size and magnetic properties should enable a magnetically driven gene delivery.

A family of biodegradable polymeric superparamagnetic nanoparticle formulations has been generated. Poly(lactide) magnetic nanoparticles were formulated by a modified emulsification-solvent evaporation methodology with both the incorporation of oleate-coated iron oxide and a poly(ether imide) (PEI) oleate ion-pair surface modification for DNA binding. magnetic nanoparticle size could be controlled by varying the proportion of the tetrahydrofuran cosolvent. The relation of the size of the magnetic nanoparticles with the tetrahydrofuran cosolvent content is shown in Figure 9.16.

The magnetically driven magnetic nanoparticle-mediated gene transfer was studied using a green fluorescent protein reporter plasmid in cultured arterial smooth muscle cells and endothelial cells. Magnetic nanoparticle-DNA internalization and trafficking were examined by confocal microscopy.

The cell growth inhibition after magnetic nanoparticle-mediated adiponectin plasmid transfection was studied as an example of a therapeutic end point. Magnetic nanoparticle-DNA complexes protected the DNA from degradation and efficiently transfected quiescent cells under both low and high serum conditions after a 15 *min* exposure to a magnetic field of 500 G.

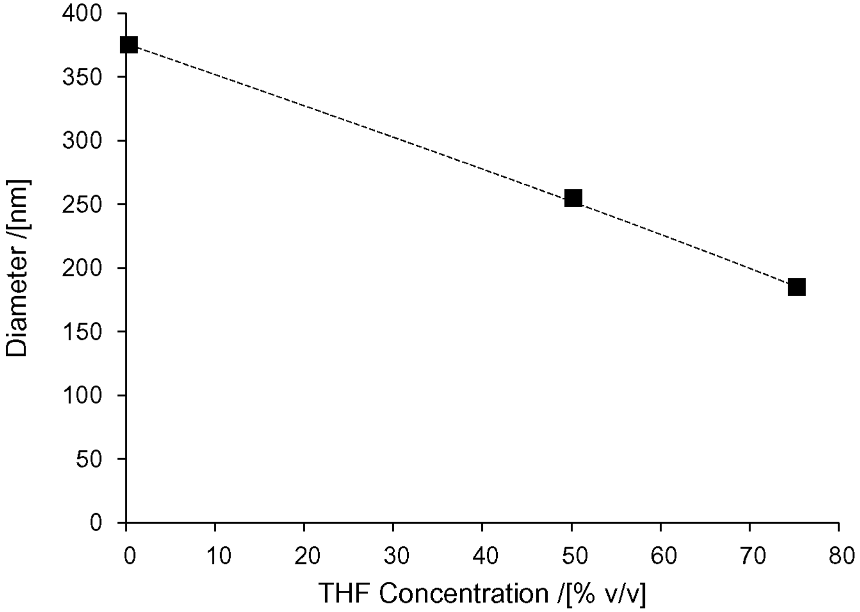


**Figure 9.16** Size of the magnetic nanoparticles with the tetrahydrofuran cosolvent content (61).

There was only a negligible transfection with magnetic nanoparticle in the absence of a magnetic field. Larger sized magnetic nanoparticle (375 *nm* diameter) exhibited higher transfection rates compared with 185 *nm*, and 240 *nm*-sized magnetic nanoparticle. Internalized larger sized magnetic nanoparticle escaped lysosomal localization and released DNA in the perinuclear zone.

Adiponectin plasmid DNA delivery using magnetic nanoparticles resulted in a dose-dependent growth inhibition of the cultured arterial smooth muscle cells.

It has been concluded that magnetically driven plasmid DNA delivery can be achieved using biodegradable magnetic nanoparticles containing oleate-coated magnetite and surface modified with PEI oleate ion-pair complexes that enable DNA binding (60,61).

### *9.4.17.1 Ferrogels*

A magneto-controlled elastic medium has been addressed as a ferrogel. Such magnetic-field-sensitive gels, have been originally prepared by introducing monodomain magnetite particles of colloidal size into chemically crosslinked PVA hydrogels (62).

PVA is a unique synthetic biocompatible polymer that can be chemically crosslinked to form a gel. The synthesis of an aqueous ferrofluid and the preparation of a biocompatible magnetic gel with PVA and glutaraldehyde has been detailed (63).

In such a ferrogel, the influence of a nonuniform external magnetic field on the shape of gel tubes and the possibility to induce elongation and contraction by means of a magnetic field gradient produced by an electromagnet have been demonstrated. Both the concentration of magnetite particles and the crosslinking density of the ferrogels play an essential role in the magneto-elastic behavior.

The deformation of a ferrogel sample in response to an applied uniform magnetic field has been investigated (63).

It has been assumed that the ferrogel is an isotropic linearly magnetizable medium. In a hollow sphere shaped ferrogel, the elongation grows with the diminution of the wall thickness. This is accompanied by the decrease of the internal volume of the vesicule (64).

A vesicule is actually a hollow sphere. A schematic representation of a ferrovesicule, i.e., a hollow sphere made of a ferrogel medium and both surrounded and filled with a nonmagnetic fluid in the field-free and deformed due to a uniform field *H*, is shown in Figure 9.17.

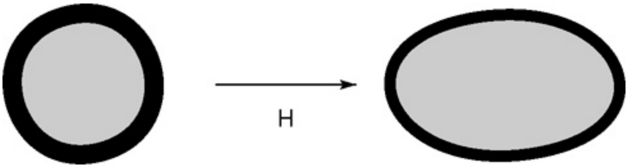


**Figure 9.17** Deformation of a ferrovesicule in a magnetic field (64).

A linear magnetization law has been assumed and from this law elasticity equations for a vesicule have been established. In this way, internal and elongation parameters have been derived (65).

A ferrogel has been prepared by a two-step procedure (66). The first step is the synthesis of the poly(*N*-*tert*-butylacrylamide-*co*-acrylamide) hydrogel. In the course of the second step, $Fe_3O_4$ particles were formed in the hydrogel by the coprecipitation of Fe(II) and Fe(III) ions under alkaline conditions at 70°C.

The thus obtained ferrogel showed a bending degree that depends on the applied magnetic field strength (66).

### 9.4.17.2 *Artificial Muscles*

The application of soft polymer gels suitable for external stimuli as muscle-like soft linear actuators started already in 1997 (67).

Muscles are, from an engineering point of view, soft and wet mechanical transducers. Artificial muscles can be thought of as mechanical actuators. The combination of magnetic and elastic properties leads to a number of striking phenomena that are exhibited in response to impressed magnetic fields. Giant deformational effects, high elasticity, anisotropic properties, temporary reinforcement and quick response to magnetic field are of interest, among others, for artificial muscles, among other applications (68).

Magnetic polymeric gels have been used as materials for intelligent artificial muscles (69). In particular, the mechanical and swelling behavior of magnetic-field-responsives of materials, including flexible polymer networks and gels, have been reviewed (70).

The ability of magnetic-field-sensitive gels to undergo a quick controllable change of shape can be used to create an artificially designed system possessing sensor and actuator functions internally in the gel itself. The peculiar magneto-elastic properties may be used to create a wide range of motion and to control the shape change and movement, that are smooth and gentle, similar to that observed in muscle. Magnetic-field-sensitive gels provide attractive means of actuation as artificial muscle for biomechanics and biomimetic applications (71).

Certain polymer gels can act as mechanical actuators that have the ability to change their elasticity and their swelling (72).

Ferrogels are polymer materials whose properties are controlled by an applied magnetic field. Magneto-elastic properties of ferrogels can be tailored for several potential applications, such as biomembranes for separation, biomedical materials, biosensors, artificial muscles, and as matrices for drug delivery systems (73). The synthesis of a PVA-magnetite ferrogel by freezing-thawing technique has been described in detail (74). The PVA-magnetite ferrogels were prepared by subjecting a PVA/dimethyl sulfoxide (DMSO)/magnetite solution to freeze/thaw cycles. In detail, the preparation is as follows:

**Preparation 9–3:** $FeCl_3 \times 6H2O$, $FeCl_2 \times 4H_2O$, and $NH_4OH$ were used to obtain the magnetite particles by the chemical coprecipitation method (75). To prepare the ferrogels a solution with 2 *g* of PVA was prepared by dissolving PVA in 30 *ml* of DMSO at 85°C. Next, 2 *g* of magnetite powder of size around 12 *nm* was added to the solution and mixed homogenously. The resulted solution was then introduced in a cylindrical PE container and kept for 16 *h* at -25°C and then for 8 *h* at room temperature of 25°C. This cycle was repeated for one, three and five times. After this process, a brown heterogeneous ferrogel was obtained.

The incorporation of the magnetite nanoparticles are modifying the crystallization temperature, as well as the melting temperature of the PVA gel. Thus, the nanoparticles act as nucleation agents during the crystallization process.

#### 9.4.17.3 *Drug Delivery*

#### 9.4.17.4 *Controlled Pulsatile Drug Release*

A ferrogel can be useful for drug release. It has been demonstrated that a controlled pulsatile drug release from a ferrogel can be achieved by a high-frequency magnetic field (76).

#### 9.4.17.5 *Smart Magnetic Hydrogels*

Magnetic hydrogels could be fabricated by a chemical crosslinking of gelatin hydrogels and $Fe_3O_4$ nanoparticles with a sizer of 40–60 *nm*. Genipin was used as the crosslinking agent (77).

The $Fe_3O_4$ nanoparticles were fairly uniformly distributed in the gelatin matrix, as was demonstrated by scanning electron microscope studies. *In-vitro* studies revealed that the drug release profile of the resulting hydrogels can be controlled by switching a magnetic field on or off.

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# 10

# Environmental Issues

In recent years, magnetic nanoparticles have attracted much interest and been widely used as sorbents due to properties such as high surface to volume ratio, short diffusion rate, high dispersibility in water, and exhibition of super magnetic properties. The synthesis and environmental applications of magnetic nanoparticles have been detailed (1).

The use of magnetic nanoparticles and microspheres as separation media in different fields of chemistry, biochemistry, biology, and environmental protection has been reviewed (2). The preparation of the most widely used magnetic iron oxides in appropriate form, their coating or encapsulation in polymer microspheres, and functionalization has been discussed. Also, recent developments in the main application areas of magnetic composite particles for separation and catalytical purposes have been described. These applications are separations and isolations of toxic inorganic and organic ions, proteins, and other biopolymers, cells, and microorganisms.

## 10.1 Analysis Methods

### *10.1.1 Fluoroquinolone Antibiotics in Environmental Water*

The determination of trace amounts of pharmaceutical residues in water, such as antibiotics, is important for environmental monitoring (3). Significant amounts of antibiotics used in human and veterinary medicine are excreted and can arrive in natural water courses (4).

Quinolones are bactericidal drugs that may actively kill bacteria (5). Actually, the majority of quinolones in clinical use are fluoroquinolones, which have a fluorine atom attached to the central ring system,

A simple method based on magnetic separation for selective extraction of fluoroquinolones from environmental water samples has been developed (6). Here, a magnetic molecularly imprinted polymer was used as sorbent. The molecularly imprinted polymer has been prepared using ciprofloxacin as template molecule, methacrylic acid as functional monomer, ethylene glycol dimethacrylate as crosslinking agent and $Fe_3O_4$ magnetite as magnetic component.

The analytes desorbed from the polymers were determined by liquid chromatography-tandem mass spectrometry. The detection limits of the fluoroquinolones are in the range of 3.2–6.2 $ng\,l^{-1}$.

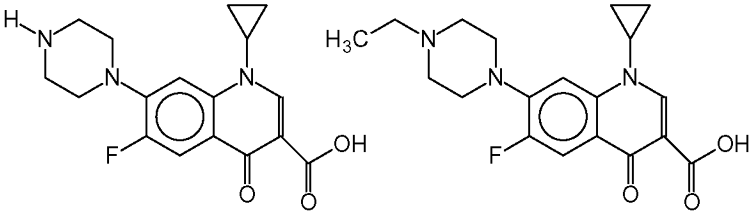
The method could be successfully applied to determine several fluoroquinolones, including ciprofloxacin, enrofloxacin, lomefloxacin, levofloxacin, fleroxacin and sparfloxacin in different water samples such as lake water, river water, primary and final sewage effluent (6).

Fluoroquinolones are shown in Figure 10.1.

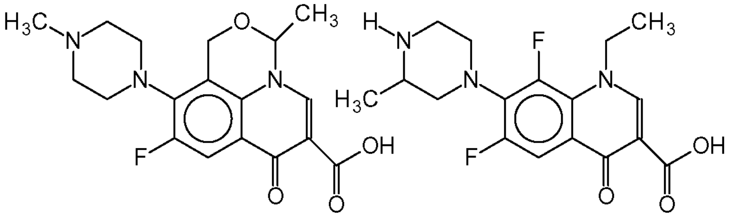
### *10.1.2 Determination of Endocrine-Disrupting Compounds*

In order to improve the practical applied value of molecularly imprinted polymers, a novel concept of uses has been developed. Multiple templates have been used to prepare magnetic molecularly imprinted polymers (7). The magnetic multi-template molecularly imprinted polymers were obtained by selecting silica-coated magnetic nanoparticles as supporters, three endocrine-disrupting compounds, 17-$\beta$-estradiol, estriol, and diethylstilbestrol, as the multitemplate, and two kinds of silane coupling agents, 3-aminopropyltriethoxysilane and phenyltrimethoxysilane, as bifunctional monomers for the simultaneous specific recognition of the endocrine-disrupting compounds.

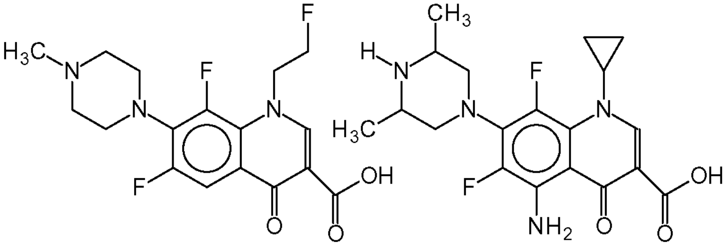
The polymers showed homogeneous imprinting shells, stable crystalline phase, and superparamagnetic properties. Further, the imprinted nanomaterials displayed an extraordinarily fast kinetics, and also a satisfactory adsorption capacity, as well as favorable selectivity (7).



Ciprofloxacin Enrofloxacin



Levofloxacin Lomefloxacin



Fleroxacin Sparfloxacin

**Figure 10.1** Fluoroquinolones.

The imprinted nanoparticles were used as a specific adsorbent coupled with high performance liquid chromatography for the rapid isolation and the simultaneous determination of all three endocrine-disrupting compounds. In addition, the method could be successfully applied for the detection of multiple aimed estrogens in environmental water samples, with satisfactory recoveries in the range of 92.3–98.6% (7).

### *10.1.3 Selective Recognition of Neodymium(III)*

Neodymium ions are used as microadditives in functional materials such as high-temperature superconductors, secondary batteries, luminescence, and magnetic polymers. Thus, these ions may appear in environmental samples.

A method for the selective recognition of $Nd^{3+}$ in aqueous solutions in the presence of various lanthanide ions by molecularly imprinted polymers has been described (8). Molecularly imprinted polymers have been prepared by the suspension polymerization of *N*-methacryloylamido folic acid as functional monomer.

The effects of different variables such as pH, time, and initial $Nd^{3+}$ concentration on the binding characteristics were elucidated. The binding equilibrium time was achieved after 30 *min*. The maximum binding capacity of $Nd^{3+}$ in the polymer was found as 14.6 $mgg^{-1}$. Also, cross effects with other ions, such as $Ce^{3+}$, $La^{3+}$, and $Eu^{3+}$, were investigated and showed a high selectivity to $Nd^{3+}$ (8).

### *10.1.4 Bisphenol A*

A magnetic molecularly imprinted polymer of bisphenol A was prepared by a miniemulsion polymerization method (9).

A method based on molecularly imprinted solid phase extraction assisted by magnetic separation was developed to extract bisphenol A from environmental water and from milk samples. Various parameters, such as the mass of sorbent, the pH of the sample, the extraction time, and desorption conditions, could be optimized.

For water samples, the method exhibited a limit of detection of 14 $ng\,l^{-1}$ and for milk samples, the limit of detection was 0.16 $ng\,l^{-1}$ (9).

### *10.1.5 Sub-ppb Analysis of Dissolved Copper*

For the determination of traces of copper ions in environmental waters, functionalized magnetic nanoparticles were used (10). Cobalt magnetic nanoparticles were functionalized on their surface with iminodiacetic acid. The nanoparticles were evaluated as a nanoparticulate solid phase extraction absorbent for copper ions, i.e., $Cu^{2+}$ from environmental water samples. In the presence of an external magnetic field, the nanoparticles could be separated from the aqueous phase. Then, the adsorbed ions could be decomplexed using dilute $HNO_3$.

The effects of pH, buffer concentration, sample and sorbent volume, extraction equilibrium time, and interfering ion concentration on extraction efficiency were investigated. Under optimum conditions, the limits of detection using a combined extraction and chromatographic method were around 0.1 $ng\, ml^{-1}$. The recovery of $Cu^{2+}$ from rain water, samples was measured as 108.5% (10).

### *10.1.6 Polycyclic Aromatic Hydrocarbons*

Magnetic nanoparticles have been used for the extraction of polycyclic aromatic hydrocarbons from environmental samples. Magnetic nanoparticles from $Fe_3O_4$ with divinylbenzene and sulfonate functionalities could be prepared by thiol-ene click chemistry (11). The thiol-ene reaction is a reaction between a thiol and an alkene to form an alkyl sulfide, as shown in Equation 10.1. The issues of the thiol-ene click chemistry have been reviewed (12).

$$\mathrm{R{-}S{-}H + H_2C{=}CH{-}R' \rightarrow R{-}S{-}HC{=}CH_2} \qquad (10.1)$$

The hydrophobic divinylbenzene moieties were dedicated for the extraction procedure, while the hydrophilic sulfonate groups were designed for dispersing the nanoparticles in the aqueous sample solution. For these reasons, this tailored material could ensure operational convenience and improve the reproducibility during extraction. Under optimized conditions, the extraction showed a satisfactory reproducibility and also low limits of detection, as shown in Table 10.1.

**Table 10.1** Limits of detection for aromatic compounds (11).

| Compound | Limit of detection $[pg\,ml^{-1}]$ |
|---|---|
| Naphthalene | 1.1 |
| Acenaphthene | 0.8 |
| Fluorine | 1.1 |
| Phenanthrene | 1.4 |
| Anthracene | 0.6 |
| Fluoranthene | 2.1 |
| Pyrene | 0.7 |

### *10.1.7 Magnetic Graphene for Phthalate Analysis*

Magnetic graphenes were used for the enrichment and analysis of phthalates in environmental water samples (13). Magnetic graphene poly(dopamine) composites could be fabricated by a solvothermal reaction and self-polymerization of the dopamine.

Graphene is treated with nitric acid to introduce outside carboxylic groups by oxidation. Then, $Fe_3O_4$ microspheres. In the final step dopamine is added under weak alkaline conditions and a polymer is formed, attached to the graphene. This material showed a great potential as a magnetic solid phase extraction sorbent.

Several types of phthalates were selected as target analytes for testing the extraction performance. The detection of limits were found to be in the range of 0.05–5 $\mu g l^{-1}$ (13).

Also, magnetic nanoporous carbon with a high surface area has been used for the extraction of phthalate esters, such as diethyl phthalate, diallyl phthalate, and di-*n*-propyl-phthalate (14). The nanoporous carbon was synthesized from cheap commercial silica gel as template and sucrose as the carbon source. The magnetic nanoporous carbon exhibits a high adsorptive capability toward the target phthalate esters in water and also aloe juice samples. A schematic diagram of the synthesis is shown in Figure 10.2.

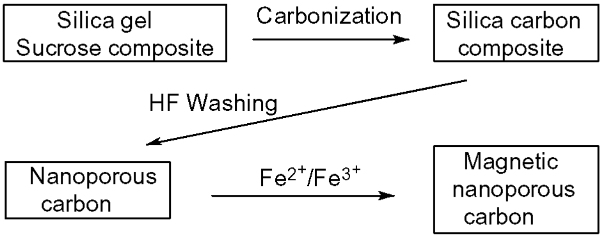


**Figure 10.2** Synthesis of nanoporous carbon (14).

## 10.2 Magnetic Polymers in Water Treatment

Magnetic polymers have been originally prepared for ion exchange processes for a thermally regenerable desalination process. But these types have now been prepared in a variety of configurations for use in a number of water purification procedures. Processes have been devised which employ magnetic polymers in filtration, in oil slick removal, and in the adsorption of metal ions (15).

Suitably shaped particles, when magnetized, can form a filter bed of a high voidage volume. Tests have been run on a variety of turbid waters. The particles give considerably better performance as filter aids than the diatomaceous earth normally used. An extremely important advantage is that the magnetic filter aids can be recovered and reused after washing.

Vesicular forms of magnetic hydrophobic polymers float on water and have application in the removal of oil spills from water surfaces. The oil becomes trapped in the voids between the particles; the resulting mass is readily removed from the water by magnetic means, after which the oil is separated from the particles simply by centrifugation. The particles and residual oil are then recycled.

Magnetic ion exchangers, smaller in size than conventional resins, can be used in continuous contacting systems, such as fluidized and semifluidized beds. In comparison to normal continuous ion exchange systems, the same removal of ions can be accomplished using considerably less resin in a plant which is smaller, simpler, and much cheaper to build up (15).

In recent years, there has been an increasing use of engineered magnetic nanoparticles for remediation and water treatments, leading to elevated public concerns. Thus, it is necessary to enhance the understanding how these magnetic nanoparticles can react with contaminants and interact with the surrounding environment during their applications. The current knowledge of magnetic nanoparticles in environmental applications has been reviewed (16). Also the fabrication methods of the nanocomposites have been discussed (17).

Also, the removal mechanisms of contaminants by magnetic nanoparticles have been detailed, along with the factors that are affecting the ability of contaminant desorption. Factors influencing the recovery of magnetic nanoparticles are outlined, describing the challenges of magnetic particle collection. Further, methods for enhancing the stability have been summarized. Moreover, the toxicological effects owing to magnetic nanoparticles are discussed. It was concluded that magnetic nanoparticles can be applied in a sustainable way after a detailed consideration of the above discussed factors (16).

### *10.2.1 Carbon Dioxide Capturing*

Carbonic anhydrase is the most efficient catalyst for $CO_2$ hydration and dehydration (18). Magnetic polymer microspheres functionalized with epoxy group were prepared, and carbonic anhydrase enzyme was immobilized on the carriers by selective covalent binding.

The thermal stability, storage stability and reusability of the immobilized carbonic anhydrase confirmed that carbonic anhydrase immobilized on the epoxy-functionalized magnetic polymer microspheres has a stable and efficient catalytic ability on $CO_2$ hydration (18).

### *10.2.2 Separation of Metals from Wastewater*

A high potential exists for magnetic particles in the environmental sciences. Several methods have been proposed for the separation of metals from wastewater using either micro-magnetic or nanomagnetic particles (19).

The synthesis of such particles has been reviewed. Also, the possibility of selectivity for metals ions, and radionuclides has been discussed (19).

### *10.2.3 Polymer Support for Nanoscale Inorganic Particles*

Nanoscale inorganic particles and their agglomerates offer excellent opportunities for the selective removal of a wide array of target compounds from contaminated water bodies (20). The high surface area to volume ratio of these nanoscale particles offers favorable sorption or reaction kinetics.

Applications of nanoscale inorganic particles in fixed-bed columns, in situ reactive barriers are not possible due to extremely high pressure drops. Also, the particles are not durable and lack mechanical strength.

However, harnessing these inorganic nanoparticles and their aggregates appropriately within polymeric beads offers new opportunities that are amenable to rapid implementation in the area of environmental separation and control.

The nanoparticles retain their intrinsic sorption/desorption, redox, acid-base or magnetic properties, and the robust polymeric support offers an excellent mechanical strength, durability and favorable hydraulic properties in the flow-through systems.

The preparation, characterization and the environmental applications of two polymer supported nanoparticles has been discussed. These are a hydrated iron oxide dispersed polymeric exchanger and magnetically active polymeric particles. The polymer supported nanoparticles are reusable and can be easily reprocessed over many cycles of operation (20).

### *10.2.4 Selective Extraction of Pb(II) from Environmental Samples*

A magnetic ion-imprinted polymer was synthesized from 3-(2-aminoethylamino)propyltrimethoxysilane as the functional monomer, tetraethylorthosilicate as crosslinking agent and Pb(II) as the template (21). 3-(2-Aminoethylamino)propyltrimethoxysilane is shown in Figure 10.3.

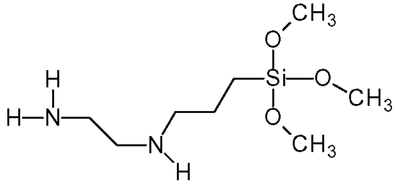


**Figure 10.3** 3-(2-Aminoethylamino)propyltrimethoxysilane.

The imprinted polymer was tested for the selective extraction of Pb(II) from environmental sample by a magnetic solid phase extraction procedure. It was found that the adsorption mechanism is corresponding with the second order adsorption process. The maximum adsorption capacity is 19.61 $mg\,g^{-1}$. In real environmental samples high recoveries of 98.0% could be detected (21).

### *10.2.5 Chromium Removal from Aqueous Solutions*

Magnetic polymer microspheres using glycidyl methacrylate as a functional monomer were synthesized in the presence of $Fe_3O_4$ nanoparticles by a dispersion polymerization technique (22). After polymerization, the magnetic polymer microbeads were modified with ethylenediamine. The functionalized magnetic microspheres showed a spontaneous adsorption of $Cr^{6+}$ from aqueous solutions. A regeneration study demonstrated that the polymer microspheres could be repeatedly utilized with no significant loss of their adsorption efficiency.

### *10.2.6 Magnetic Zeolite-Polymer Composite*

A magnetic zeolite-polymer composite as an adsorbent for the remediation of wastewaters containing vanadium has been prepared (23).

The effects of initial pH, sorbent dosage, adsorption isotherms and the removal efficiency were investigated. Up to 75% removal efficiency was obtained when the pH was 5 and the initial vanadium concentration was 100 $mg\,l^{-1}$. The isotherm data fitted well to a Langmuir isotherm model. The maximum adsorption capacity determined from the Langmuir isotherm was 57.803 $mg\,g^{-1}$ at 25°C.

### 10.2.7 *Binding of Nitrate and Nitrite*

Hydroxyapatite-coated $Fe_2O_3$ nanoparticles have been fabricated. These nanoparticles were used for the adsorption and removal of nitrite and nitrate ions from environmental samples (24). After adsorption of of nitrite or nitrate ions, process, the separation of the nanoparticles from the aqueous solution could be effectively achieved by the application of an external magnetic field.

Variables that are governing the adsorption efficiency are the amount of magnetic hydroxyapatite nanoparticles, sample volume, pH, stirring rate, adsorption time, and temperature. The experimental parameters could be optimized using a Box-Behnken design (25) and a response surface methodology using a Plackett-Burman screening design (26).

Under optimum conditions, the adsorption efficiencies of the magnetic hydroxyapatite nanoparticles toward $NO^{3-}$ and $NO^{2-}$ ions were found to be in the range of 93–101%. Thus, these magnetic hydroxyapatite nanoparticles can be used as a simple, efficient, and cost-effective material for the removal of nitrate and nitrite ions from environmental water and soil samples (24).

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## Acronyms

# Chemicals

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