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Review

Technological applications of functionalized polymers

AHMED AKELAH
Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

In most of the major applications of polymeric materials their mechanical properties are often of paramount importance. Even in such applications as electrical insulators their stiffness, cut and abrasion resistance will be of importance as well as their low conductivity. Now, polymers containing specific functional groups are being utilized in analytical and many synthetic organic chemical procedures [1–4], in biologically and pharmacologically active systems, in food additives, and in the field of agricultural chemicals [5]. Following their successful applications in the laboratory and industrial processes, the introduction of active functional groups, other than those previously discussed, into polymers will be discussed in the present article. It is meant only to illustrate selected aspects of more general areas of polymers in the technological uses based on their specific active functional groups, in additon to the advantageous properties of the polymeric material.

1. Conductive polymers

Metals are defined as elements which possess certain characteristic chemical properties, such as ease in forming positive ions by chemical processes, and certain characteristic solid state physical properties, such as high electrical conductivity, high reflectivity of light, good thermal conductivity and ductility. In spite of all these collective properties, they have some drawbacks such as high cost of fabrication, poor mechanical properties (stiffness, cut, abrasion resistance) and physical properties (high denisty and weight).

A significant property of many organic polymers is their ability to withstand high electric fields with negligible conduction. This property makes polymeric insulation the material of choice in a wide range of applications. The absence of conductivity is due to large energy differences between localized valence electronic states and the conduction band. However, there is continuing interest in the solid-state chemistry of conducting organic polymers due to their potentially unique applicability to a variety of applications.

1.1. Photoconductive polymers

Photoconductivity of polymers is one of the commercially significant photoresponses of polymeric systems and plays a central role in the development of a generation of organic photoconductors for replacement of selenium based systems, which suffer from the costs and poor mechanical properties associated with metals. Since the first report on photoconductive polymers [6], considerable interest has been focused on these materials by the electrophotography (xerography) as well as a number of related processes [7–10]. The subject of polymer photoconduction has been extensively reviewed in recent years [11–17].

Photoconductivity is defined as a significant increase in the conductivity caused by radiation under illumination. This increase is attributed to an increase in the number of charge carriers (electrons or holes) as a direct result of electronic excitation. The phenomenon of photoconductivity involves two distinctly different steps: (i) the processes of absorption of radiation, photogeneration of charge carriers, and their separation; (ii) transport of charge carriers under the influence of an applied polarizing electric field, their temporary immobilization at sites known as trapping sites, release from traps and finally their recombination. For a polymer to be photoconductive the absorption of a photon must lead to the formation of a mobile charge carrier, followed by energy transfer processes. The accepted mechanisms for photogeneration of charge carriers in photoconductive polymers involves localization of migrating excitation energy at a trapping site, followed by electron transfer to a neighbouring group. The resulting charged geminate pair may then separate and either the positive charge or electron or both may migrate in a polarizing field.

Improved conductivity can be achieved by (i) addition of small molecular dopant; or (ii) chemical modification of the polymer. The dopant is a molecule such that an electron transfer reaction can occur between it and the polymer matrix, for example, rose bengal, methyl violet, methylene blue, pinacyanol. The mechanisms of the dye sensitization process involve both energy transfer from the dye to the polymer and/or electron transfer between the excited state of the dye and the polymer transport matrix leading to the formation of a charge carrier. The direction of electron transfer depends upon the relative energy levels of the dye and the polymer. Electron transfer

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TABLE I Photoconductive polymers

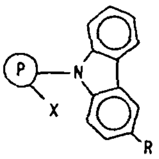
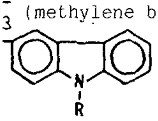
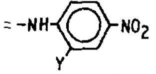
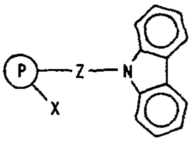
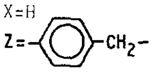
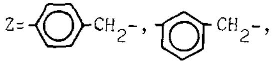
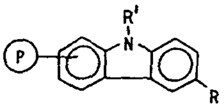
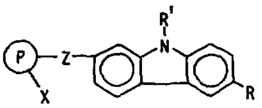
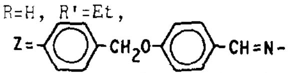
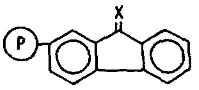
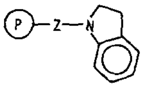
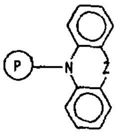
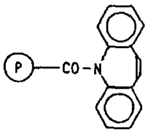
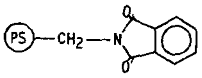
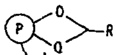
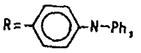
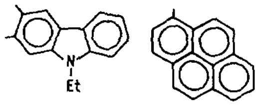
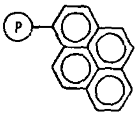
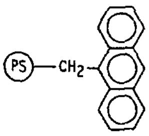
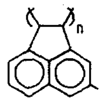
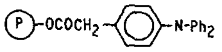
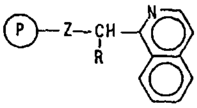
Functional Polymer	Reference
	
(i) X=H	
R=H	[18-60]
=-CHMeEt	[22]
=-C(CN)=C(CN)$_2$	[23]
=Br,I	[24-28]
=NO$_2$	[29,30]
=-SO$_3^-$ (methylene blue)$^+$	[31]
=$^+$C()$_2$ X$^-$	[32]
(ii) R=H	
X=-O-menthyl(-)	[33]
=-COO-menthyl(-)	[34]
= 	[35]
= -O-R^1 (R^1=H,COMe)	[36]
=-COR^2, -CO(CH$_2$)$_2$-R^2, -COO-R^2, -O(CH$_2$)$_2$OCO-R^2, -R^3, -R^4	[36]
	
(i) X=H	
Z= 	[37]
=-(CH$_2$)$_n$- , n=3,4	[38]
=-O(CH$_2$)$_2$-, -CO-	[39,40]
=-CONH-(CH$_2$)$_3$-	[41]
(ii) X=H, Ⓟ=Ⓟ^{a}	
Z=-(CH$_2$)$_n$COO(CH$_2$)$_2$- n=1,2	[42,44]
=-CH$_2$-S-(CH$_2$)$_2$-	[42,43]
(iii) X=-CH$_2$CHMeEt, -O-menthyl, -COO-menthyl,	[45]
Z= 	
-COO(CH$_2$)$_2$-,	
-COO(CH$_2$)$_2$-OCOCH$_2$-	
	
(i) R=H, R'=-CH$_2$CHMeEt	[22]
(ii) R=H, R'=Et	[32]
(iii) R=-C(CN)=C(CN)$_2$, R'=H	[46]
Ⓟ=Ⓟ or Ⓟ^{b}	
	
(i) X=H, Ⓟ=Ⓟ^{a}	
R=-C(CN)=C(CN)$_2$, R'=H, Z=-CONH-	[46]
R=H, R'=Et,	
Z= 	[37]
R=H, R'=Et, Z=-(CH$_2$)$_2$COO-	[48]
(ii) X=-COO(CH$_2$)$_m$OCOR^2, R=H, Z=-COOCH$_2$-, R'=Me, m=2,3	[49-51]
 X=O,=C(CN)$_2$	[52]
 Z= nothing	[53,54]
=-CO-	[55,56]
 Z=S	[53]
=O	[57]
	[58]
	[37]
 R'=H,MeCO	[59,60]
R= 	
	
	[32]
	[61]
 X=NO$_2$	[62,63]
=I,Br	[64-67]
	[60]
(PS)—(CH$_2$)$_m$-N Ph$_2$ m=0,2	[68,69]
Ⓟ—N Ph$_2$	[53,57,70]
	
(i) R=H, Z= 	[71,72]
(ii) R=OCOPh, Z=  ,	[73]

TABLE I *Continued*

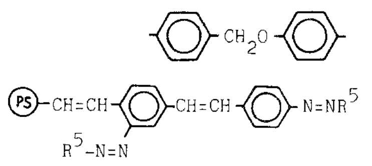
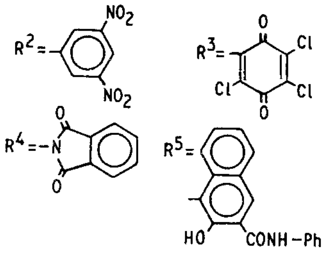
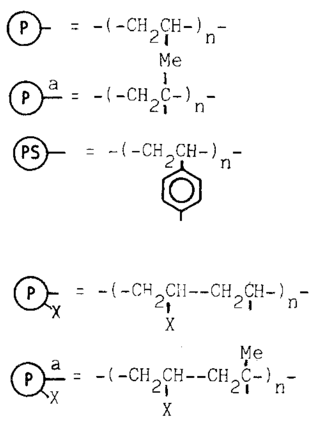
Functional Polymer	Reference
	[74]
	

TABLE I *Continued*

Functional Polymer	Reference
	

from the polymer to the excited dye is the situation usually encountered in practice.

Chemical modification appears to be of general applicability for improving the spectral response and the increase in charge carrier photogeneration efficiency of hole transporting systems. In addition, it has the following advantages: (1) photoconductivity and its component processes, charge generation and transport, can be controlled; (2) the spectral range associated with the charge photogeneration process can be controlled by surface or bulk attachment of dyes or charge acceptors on to the polymer; (3) the charge transport process can be influenced in terms of the sign of the majority carriers and the rate of transport. Introduction of acceptors with low ionization potential, such as carbazole, triarylamine, pyrene, by chemical reaction of the functional polymers can control the sign of the charge carriers and is successful in generating hole (cationic) transporting systems; (4) it is also useful in improving the mechanical properties, particularly solubility, film formation flexibility, and impact resistance of photoconductive polymer systems; (5) it eliminates deleterious reactions with air, water or dopants.

Carbazole-containing polymers are the subject of many investigations with respect to their photoconductive properties [18, 19]. However, by changing the chemical structure while keeping the active group, carbazole, some advantages can be achieved [20]. One idea is the copolymerization of a carbazole-containing monomer with another monomer having the sensitizer (an acceptor group) linked to the double bond through a spacer. The advantages of such a structure are: (i) the possibility of designing donor : acceptor groups ratios and sequences on the side chain; (ii) improvement of film properties; (iii) a relatively large choice of acceptor groups is available, having different electronic affinities and, therefore, exhibiting various charge transfer bands in the visible domain; (iv) relative orientations and interactions of carbazole units in polymers influence the electric absorption, fluorescence, emission, and NMR spectra. Some other photoconductive polymers are listed in Table I.

1.2. Electrically conductive polymers

Interest in electrically conductive polymers stems from the potential for combining in one material the advantageous properties of polymers and the electrical properties of semiconductors or metals [75–85]. The advantageous properties of polymers are their mechanical properties (such as flexibility, stretchability, impact resistance), their ease and low cost of preparation and fabrication. Low density and weight saving is an important advantage of polymeric materials, especially for batteries. The most promising synthetic semiconductors and metals for practical electronic applications are those which can combine solution or melt processibility to thin films, which are environmentally, electrically and mechanically stable and possess high conductivity.

In general, conduction in polymers can be either ionic, e.g. salts of organic polymers, or electronic. Electronic conductivity behaviour of polymers may be achieved by one of three means.

1. Introducing delocalization: a variety of elimination reactions can be employed to generate conjugated polyene structures, i.e. polymers with a high degree of conjugation in the main chain, from a range of functionalized polymers, e.g. polyacetylene, polyphenylene. Electical conductivity appears to be sensitive to the degree of conjugation along the chain backbone, which in turn increases with increasing chain planarity.

2. Introducing electrically active pendant groups, e.g. substituted aromatic amines, large polynuclear aromatic groups with large π-electron systems.

3. Electrochemical doping: doping the polymers, which are normally excellent electrical insulators, with electrically active species of low molecular weight leads to highly electrical conducting materials by charge transfer interaction.

Electronic mobility in polymers is greatly enhanced along a polymer molecule with conjugated bonds, i.e. with delocalized π-orbitals. Instead of the typical insulator value of $< 10^{-14}\,\Omega^{-1}\,\mathrm{cm}^{-1}$, the conductivity may be in the range of 10^{-5} to $10^{-9}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. However, when such a polymer is doped with electron donors (e.g. halogen, AsF_5) or acceptors (e.g. alkaline metal), it becomes semiconducting-to-metal-like in conduction (10^{-6} to $10^4 \Omega^{-1} cm^{-1}$). Doping techniques include exposure of the films to the vapours of dopants such as I_2, H_2SO_4, AsF_5, $SbCl_5$, or to solutions of dopants such as NO_2SbF_6, I_2, sodium naphthalide. The enhanced conductivity may be attributed to the presence of cations and anions formed via electron transfer from the donor species of the acceptor. Transport of the charge may then occur via either cationic (holes) or anionic (electrons) states. The electrical conductivity of a doped polymer may also depend on: (i) the chemical structure of the polymer [86–89]; (ii) the degree of doping; the conductivity can be controlled by the dopant concentration, which increases with increasing dopant concentration; (iii) the nature of the dopant ion; the p- and n-type conductivities depend on the dopant nature, i.e. doping of a polymer with an electron acceptor or an donor gives a p- or n-semiconductor, respectively [90, 91].

2. Polymers in energy

Over recent years, enegy costs have risen rapidly and the supply of available petroleum feed stocks will be exhausted in a few centuries. Thus, the development of new energy sources is a worldwide research subject. Connections between polymers and energy are pervasive and extremely complex. The contributions of polymers to energy can be categorized as: (i) the production and conservation of energy; and (ii) chemical conversion and storage of solar energy.

Excellent electrical and thermal insulating properties of polymeric materials coupled with their ease of fabrication are essential in conventional power-generating equipment which require insulation that permits close windings and freedom from electrical breakdown as well as their use in cables for power distribution. They have also an important contribution to conserve energy, such as their use an insulating materials in homes and other buildings with enormous long-term savings in energy. The use of polymers in solar collectors has also received considerable interest in order to use solar energy economically on a large scale. Although the use of polymers for collection and concentration of the solar energy is economically advantageous because of their light weight, low cost and good mechanical strength, their durability is a major problem associated with this use. Since it is not necessary for the polymer to contain any reactive functional group in these applications, this subject is not discussed in the present section.

The uses of functionalized polymers in conversion and storage of solar energy have recently received much attention to replace the petroleum fuels. Sunlight, when it is converted into a usable form, represents a virtually inexhaustible source of permanent and clean energy with no net consumption of resources [92, 93].

2.1. Conversion of solar energy

Solar spectrum on the earth ranges from 250 to 2400 nm, having its maximum at 500 nm. The visible region between 400 and 800 nm occupies about half of the spectrum and the chemical conversion of this irradiation is therefore important for the direct production of fuel which can be easily stored and transported.

For a fuel, an electron source is needed. Economically viable catalytic photosensitized water splitting as an electron source is the simplest among the chemical conversion systems of solar energy. Since the excited state of a molecule is a better electron acceptor or donor than its ground state, light absorption can drive a redox reaction nonspontaneously. For water oxidation, a redox potential of $E'_0 = 2.33$ V is needed in the first step to abstract one electron from a water molecule (Equation 1). When the intermediate is stabilized on a catalyst and four electrons of two molecules of water are oxidized without isolating the intermediate (four-electron proceess), the

$$H_2O \rightarrow HO^{\bullet} + e^- + H^+ \; (E'_0 = 2.33\,V) \quad (1)$$

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+ \; (E'_0 = 0.82\,V) \quad (2)$$

required redox potential is only 0.82 V (Equation 2). The potential level of the site of oxygen evolution of the photosynthesis ranging around 0.82 V shows that a four-electron process occurs in it. In water photolysis as a model system for photochemical conversion of solar energy, the system is made of a photoreaction centre, two kinds of electron mediators, and reduction as well as oxidation catalysts (C_1 and C_2) in which water should be oxidized at C_2 to give O_2 and protons should be reduced at C_1 to give H_2 (Equations 3 and 4).

$$2H_2O \xrightarrow{C_2} O_2 + 4e^- + 4H^+ \; (E'_0 = 0.82\,V) \quad (3)$$

$$4H^+ \xrightarrow{C_1} 2H_2 \qquad (E'_0 = -0.41\,V) \quad (4)$$

In this system, the potential of C_1 should be lower than -0.41 V and that of C_2 higher than 0.82 V. For the proton reduction, the two-electron process (Equation 4) is much more favourable than the stepwise reaction in which the first step (Equation 5)

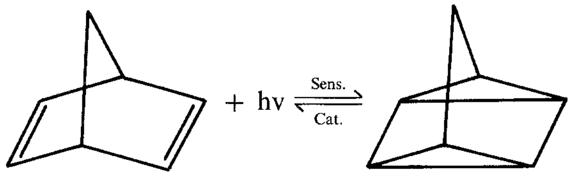
$$H^+ + e^- \rightarrow H^{\bullet} \quad (5)$$

requires -2.52 V. Thus, a multi-electron process is preferable at both the catalyst sites of the water photolysis system.

In the photochemical conversion model, the most serious problem is the undesired back electron transfer when the separated charges combine again to consume the energy as well as side electron transfer. This problem of photoinduced charge separation can be prevented if the reactions are carried out in a heterogeneous conversion system using functionalized polymers. Noble metals are the most potent catalysts to realize a multi-electron catalytic reaction for water photolysis. A functionalized polymer containing a pendant viologen as electron mediator, and platinum as the hydrogen-evolving catalyst [94] and polymer combining viologen units with $Ru(bpy)_3^{2+}$, as photoreaction centre [95] are interesting examples in the field of photochemical solar energy conversions.

2.2. Storage of solar energy

Since the solar irradiation on the earth is intermittent and unstable depending on time, season, weather, and region, storage of the converted energy is required in order to use it on a large scale. The use of photochemical reactions to generate kinetically stable products of high energy content provides an exceedingly attractive fuel source. The photosensitization conversion of norbornadiene (NBD, I) to an energy-rich quadricyclane (QC, II), coupled with reversion of QC to NBD, is the most promising photoisomerization system for storing energy from sunlight. The QC is thermodynamically unstable relative to NBD and a device based on this interconversion as a model system for solar energy storage requires the following two steps: (i) energy storage through the sensitized photolysis of NBD to QC in an endothermic reaction by visible light, and (ii) energy release through the catalysed reconversion of QC to NBD in an exothermic reaction (ΔH = 21 kcal mol^{-1}).



(6)

(I) (NBD) (II) (QC)

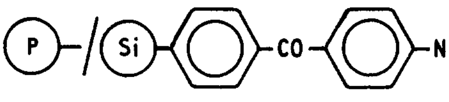
A different kind of sensitizer, which is a catalyst capable of absorbing radiation and transferring the energy to another molecule, is involved in the excitation of molecules in the first step. In general, sensitizers must absorb strongly in the region of available solar energy, be thermally and photochemically stable, and effect efficiently the desired sensitization. Excitation of a sensitizer by solar energy (hv) to the singlet state followed by passing into a longer lived triplet state can activate a molecule (M) and itself return to the ground state:

$$\text{Sens.} + \text{hv} \rightarrow {}^*\text{Sens.} \rightarrow {}^3\text{Sens.} \quad (7)$$

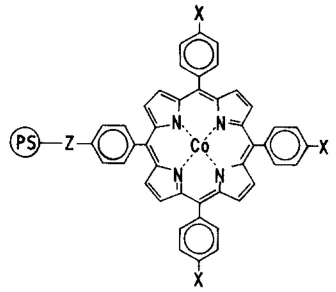
$$^3\text{Sens.} + \text{M} \rightarrow {}^*\text{M} + \text{Sens.} \quad (8)$$

However, an ideal catalyst for the reverse exothermic reaction in the second step must meet several requirements: (i) it should not produce undesirable side reactions; (ii) it should be sufficiently active to evolve heat quantitatively in a rapid conversion; (iii) it should have long-term stability; and (iv) the active species should not be leached by the reaction mixture.

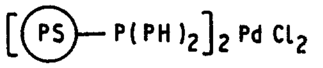
Thus, the immobilization of the sensitizer and catalyst on polymeric supports is especially effective by keeping them apart because contamination of the materials with sensitizer or catalyst markedly lower the efficiency of a solar energy storage system. Hence, the isolation of the catalyst is attractive and important in order to keep the active catalyst away from the photochemical reactor where the conversion reaction of NBD to QC is taking place and to prevent the dispersion of the catalyst throughout the system. The use of functionalized polymers in a storage of energy has been directed toward the development of new polymeric sensitizers for the photochemical process [94–100] as well as the development of polymer bound catalysts for the reversible valence isomerization of solar energy storage system [101–103]. Various polymeric sensitizers, such as III [99], and polymeric catalysts, such as IV [101], V [102] and VI [103], were shown to be active in the NBD-QC solar energy storage system.



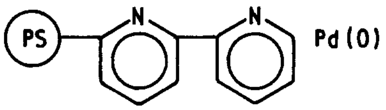
(III)



		Z	X
(IV)	(a)	CO	COOMe
	(b)	NHCO	COOMe
	(c)	NHSO$_2$	SO$_3$Me



(V)



(VI)

3. Polymers in lithographic processes

In semiconductor technology, the manufacture of transistors and integrated circuits, involving microcircuit patterns on a silicon wafer, are required. A large variety of materials and processes are currently employed in the manufacture of hybrid microcircuits. In spite of the precautions taken by the electronic industry, it is often difficult to completely remove the last traces of processing materials through normal cleaning; some being electrostatistically attached to the surface of the circuit, which can cause an electrical short and result in a missile or spacecraft failure.

One of the procedures used in making monolithic integrated circuits to resolve this problem is photolithography based on photoresistance. However, in recent years electron-beam lithography based on electron resistance has been used as an alternative method for cases in which resolution is desired [104, 105]. Resists must be: (i) capable of forming uniform pinhole-free films on a substrate by a simple process, such as spinning, dip-coating or spraying; (ii) of a high degree of purity, i.e. containing low levels of ions to achieve no electrical properties; (iii) easily removed by solvent dissolution; (iv) thermally stable up to 150° C to withstand burn-in temperatures used for hybrid circuits; (v) must produce no stresses on fine-wire bonds and no deleterious effects on active devices, (vi) must be compatible with the devices and wire bonds of high density circuit.

Usually polymers are the only materials which fulfil these requirements. Interaction of organic polymers with energetic electrons or ultraviolet light results in a structural change which may either be broken down to smaller fragments or may link together to form larger molecules. Interaction that causes a break in the main polymer chain and resulting in irradiated material having a lower average molecular weight than unirradiated material allows "positive-working resists" to be formulated. Clearly the successful removal of irradiation degraded polymer without affecting the unirradiated material in the development process will occur if the original polymer has the highest possible molecular weight and irradiated by moderate doses of electron or ultraviolet light. Moreover, the polymer of low glass-transition temperature can be easily deformed and the resolution of fine patterns developed in a film of such a polymer may be easily impaired. Thus, good positive resists should therefore have a glass-transition temperature above the highest temperature to which the resist will be subjected after development of the irradiated pattern in it.

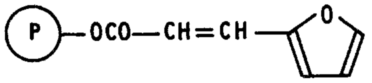
For polymers which link together on irradiation, larger insoluble and infusible molecules are generally formed by a process known as crosslinking. This type of polymer forms the basis of "negative-working resists", where it is possible to dissolve and remove unirradiated material while irradiated material cannot be dissolved away after development. In principle, many polymers are available for use as negative resists; however, the choice may be limited by the sensitivity required, solubility of the resist, etc. [106, 107]. The requirement of a high glass-transition temperature, which is necessary for positive-working resists, does not necessarily apply to negative resists because the resist material in this case is crosslinked during irradiation, which automatically increases its glass-transition temperature.

3.1. Photoresists

Photolithography is generally a coating of a wafer surface with a polymer film containing photosensitive groups and its exposure to the light of a mercury ultraviolet lamp through a photomask. Depending on the type of photoresist, the exposed areas are either crosslinked (negative photoresists) in which the non-exposed areas, i.e. uncrosslinked, are dissolved in a liquid developer, or degraded (positive photoresists) in which they are removed by a solvent under certain developer conditions.

The ideal resist for ultraviolet lithography should: (i) possess good sensitivity to 230 to 280 nm radiation with little or no absorption at longer wavelengths to eliminate the difficult task of filtering the long wavelength radiation present in conventional sources; (ii) be capable of high resolution; (iii) have a reasonable exposure time, and (iv) be compatible with conventional microstructure fabrication processes.

Polymers with pendant cinnamoyl groups are well known as photosensitive polymers and have received considerable industrial application to form a thin lightly hardened film when exposed to light for the preparation of circuits [108, 109]. Polymers with other pendant photosensitive moieties such as α-furylacrylic ester [110] (VII), benzalacetophenone [111], styrylpyridinium [112], α-phenylmaleimide [113] and others, have been reported as photosensitive polymers, as listed in Table II.



(VII)

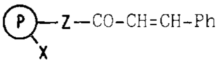
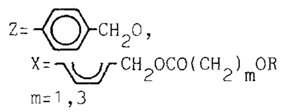
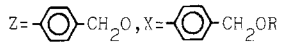
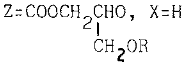
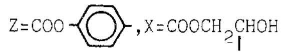
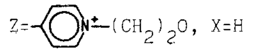
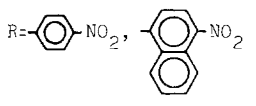
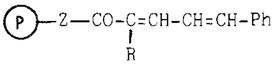
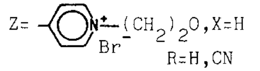
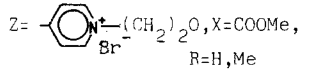
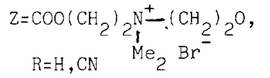
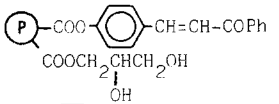
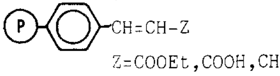
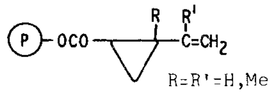
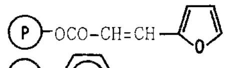
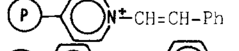
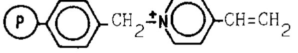
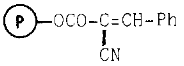
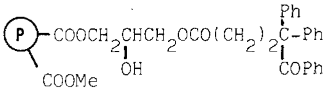
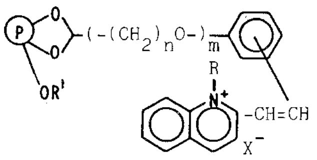
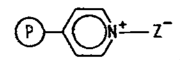
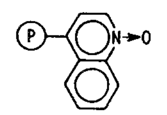
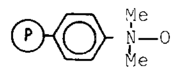
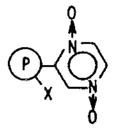
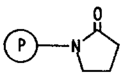
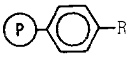
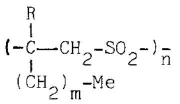
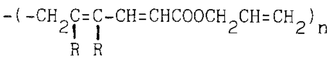
Polymers containing pendant photosensitive, such as cinnamic ester, and photosensitizer moieties have also been prepared either by radical copolymerization of 2-(cinnamoyloxy)ethyl-methacrylate with photosensitizer monomers [114], or by chemical modification of chloromethylated polystyrene containing photosensitizer groups with salts of photosensitive compounds [115]. The photosensitivity, which is used for the determination of the insolubilization of the photoirradiated films, can be measured by the "bismuth photoresistance test" [116, 117] or by the "photoresistance test" [118].

3.2. Electron-beam resists

Electron-beam lithography techniques for defining the pattern have been used as an alternative for the mask and the mercury lamp in photolithographic procedures, in which the wafer is irradiated by electrons [119, 120]. The use of this method in the manufacture of integrated circuits offers the following advantages: (i) the beams used have rather high electron energies (5 to 30 keV) so that diffraction effects are negligible. This allows resolution and accurate definition of details in the range 0.5 to 2 μm which is better than is possible with photolithographic procedures; (ii) it is also feasible to focus electron beams to very small diameters which can allow patterns to be made with detail much smaller than is possible by photolithography; (iii) the ability to make finer detail can lead to an increase in the packing density of the components of integrated circuits with consequent reduction in their size and cost; (iv) smaller components will also reduce power requirements and increase the speed of operation; (v) the ease and precision with which electron beams can be deflected by electric or magnetic fields makes electron-beam techniques relatively amenable to automation; (vi) the energy of the electrons is much greater than that of ultraviolet photons which does not exceed a few electron volts. This broadens the range of polymers from which a choice of a resist can be made.

The radiation chemical yields are a measure of the intrinsic radiation sensitivity of the polymer and are expressed in terms of G-values which are a structure-dependent. G(scission), G(S), equals the number of main chain scissions produced per 100 eV of energy absorbed, and G(crosslinking), G(X), the number of crosslinks formed per 100 eV absorbed. For resist applications, $G(\mathrm{S})/G(\mathrm{X})$ values greater than 4 indicate the system is positive acting whereby there is an

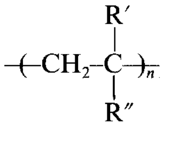
TABLE II Photoresist polymers

Functional Polymer	Reference
	
(a) Z=O, X=H	[108, 109] [131–133]
(b) Z=O(CH$_2$)$_2$O, X=H	[134]
(c) Z=O(CH$_2$)$_2$O, X=O(CH$_2$)$_2$OR	[135,136]
(d) 	[137]
(e) 	[137]
(f) Z=COO(CH$_2$)$_2$O,X=CONH-R	[138]
(g) Z=COO(CH$_2$)$_2$O,X=H,COOEt	[139]
(h)  $\mathrm{Z{=}COOCH_2\underset{\displaystyle CH_2OR}{\underset{\mid}{C}}HO,\ X{=}H}$	[136,140]
(k) 	[111,141]
(l) 	[142]
	
	
(a) Z=O, X=H, R=H	[143]
(b) Z=NH, X=H, R=H,CN	[142,144]
(c) 	[142,144]
(d) 	[144]
(e)  $\mathrm{Z{=}COO(CH_2)_2\underset{\displaystyle Me_2}{\overset{+}{N}}\!\!-\!(CH_2)_2O,\ Br^-}$ R=H,CN	[142,144]
	[111,141]
	[145]
	[146]
	[110]
	[112]
	[147]
	[148]
	[149]
	[150]
R=H,Alk,Aralk, n=1-6, R'=H,Ac, m=0,1	
	
Z=C(CN)$_2$	[151]
Z=O	[116,117,151]
	[151]
	[116,117,151]
 X=H,Ph,COOMe	[152]
	[153,154]
Ⓟ—NHCOOCMe$_3$	[155]
	
R=H	[156]
R=OH	[157]
R=CH$_2$Cl	[158]
Ⓟ-CO—R	
R=Me	[159]
R=OMe	[156,160]
 $\mathrm{(-\overset{\displaystyle R}{\underset{\displaystyle (CH_2)_m-Me}{C}}-CH_2-SO_2-)_{\overline{n}}}$	
R=H, m=1	[128,161,162]
R=Me, m=2	[161,163]
$\mathrm{-(-(CH_2)_4CO-CH_2SO_2-)_{\overline{n}}}$	[161]
 $\mathrm{-(-CH_2\underset{\displaystyle R}{C}=\underset{\displaystyle R}{C}-CH=CHCOOCH_2CH=CH_2)_n}$	[164]
R=H,Me	

increase in solubility of the areas exposed relative to the unexposed regions. $G(S)/G(X)$ ratios less than 4 indicate crosslinking reactions will predominate resulting in an insoluble gel and negative tone formation.

There are many polymeric materials which are available for use as negative electron resists, such as polymers of glycidyl acrylates, polystyrene, polysiloxanes, and epoxidized polybutadiene. Poly(1-alkylvinylpyridinium halides) have also shown to be good negative electron beam resists with sensitivities as high as 5 μC cm^{-2} in a 20 kV electron beam and line widths as low as 0.3 μm [121]. The electron beam sensitivities of these polymers increase with increasing polymer molecular weight and the size of the 1-alkyl group. The use of these polymeric salts eliminates the need to coat the substrate with a metal oxide and the natural electroconductivity of the polymer film prevents a buildup of electrostatic change during exposure with an electron beam [122]. Polystyrene, as a weakly sensitive negative resist, has an excellent combination of properties which are difficult to achieve with positive resists, such as high dry-etching resistance, because of its aromatic content and high resolution of less than 1 μm. However, the sensitivity can be markedly enhanced by substitution on the ring with certain substituents, particularly halogen or halomethyl groups. Poly(chloromethylstyrene)s have been studied as negative electron resists that exhibits very high sensitivity while maintaining the other desirable characteristics of polystyrene [123–127].

Almost all polymers which give good positive electron-beam action should have a high G(S) value and are of the general structure (VIII)



$$-\!\!\left(\mathrm{CH_2}-\overset{\displaystyle \mathrm{R'}}{\underset{\displaystyle \mathrm{R''}}{\mathrm{C}}}\right)\!\!-_n$$

(VIII)

where R′ and R″ are substituents other than H, e.g. polymethylmethacrylate, poly-α-methylstyrene, polyisobutylene, polyvinylidene chloride, polytetrafluoroethylene. However, many of these are unsuitable because their glass-transition temperatures are low, or because they are not easily soluble which makes application of the film and development of irradiation patterns difficult. The only materials which have yet found wide use are polysulphones and modified polymethylmethacrylate [128–130]. The combination of properties which include stability, sensitivity, contrast, adhesion and solubility have kept the improved polymethylmethacrylate as good positive-electron beam. Two directions have been taken towards improving the performance of PMMA without altering the processing characteristics, either by increasing the original molecular weight (e.g. by crosslinking) or by copolymerization with comonomer of a 1,1-disubstituted vinyl type compound containing electron withdrawing substituents such as halogen, cyano, or carboxylic acid groups.

4. Polymeric liquid crystals

Liquid crystals have become an essential part of displays in many electrical and electronic devices. Polymeric liquid crystals, which combine the properties of low molecular weight liquid crystals with those of polymers, have recently received increased interest [165–169]. They are materials with a high degree of molecular orientation and excellent mechanical properties and have the advantages of possessing high modulus, high strength, high impact resistant, high end-use temperature, low melt viscosity, shear rate dependency and low density.

For a polymer to form a liquid crystalline phase, the molecule or a major portion of it should be stiff and rod-like in nature. A flexible chain polymer will not exhibit liquid crystalline behaviour while more rod-like polymers show only lyotropic mesomorphism. Semi-flexible polymers having intermediate chain extensions, i.e. incorporating both a rigid and a flexible segment, exhibit thermotropic mesomorphism. The liquid crystalline states (mesophases) are intermediate between the three-dimensionally ordered crystalline state and disordered isotropic fluid state. The intermediate states are classified with regard to their molecular order into nematic, smectics and cholesteric, and according to the molecular compositions involved into thermotropics and lyotropics. The classification, according to phase behaviour, into lyotropic or thermotropic liquid crystals depends upon whether the mesophase, i.e. the transition from a non-ordered isotropic to an ordered anisotropic liquid crystalline state, is observed by variation of solvent content or by variation of temperture, respectively. Thus, the crystalline, order and hence the properties of the crystalline material, such as the thermal or the mechanical, are strongly dependent on the existence of the long-range order.

In the case of lyotropic mesomorphic polymers, liquid crystal characteristics are found in solution above a critical concentration and are concentration dependent as well as temperature dependent. These polymers are also characterized by a high value of $[(n)/(\eta)]_\infty$ [165] where $[n]$ is the flow birefringence determined from the equation: $[n] = \lim_{g\to 0, c\to 0}(\Delta n/gc\eta_0)$, where Δn is the difference between the two main refractive indices in solution at the concentration, c, and at the flow gradient, g; η_0 is the viscosity of the solvent, and $[\eta]$ is the intrinsic viscosity of solution, and hence by a high optical anisotropy of the molecule. Among the polymer molecules exhibiting lyotropic mesomorphism are synthetic polypeptides, polyalkylisocyanates, cellulose derivatives and p-aromatic polyamides. The chemistry and physics of lyotropic systems have been discussed in the literature [170].

On the other hand, thermotropic systems show liquid crystalline behaviour in the melt and are temperature dependent with respect to mesophase behaviour, the temperature for transition to the thermotropic liquid crystal state depends primarily on the length/diameter ratio and interactions of the rigid molecule. The first reported thermotropic liquid crystal polymer is a copolyester of polyethyleneterephthalate and p-hyroxybenzoic acid which has a stiff, rod-like conformation and is the liquid crystal forming component [171].

Generally, there are two classes of thermotropic liquid crystal polymers in which liquid crystal groups are either in the side chains or in the main chain of the polymer. A considerable amount of work has been performed in this area of polymers in which the liquid crystal order is exhibited primarily by the mesogenic side groups. In this case, the degree of mesomorphism is mainly determined by the length of the side chain rather than by the chain length as a whole, i.e. the order of the main chain is less well defined and the structure of the backbone is only of secondary importance. The direct linkage of rigid mesogenic groups to the polymer backbone restricts transitional and rotational motions of mesogenic moieties which influences their interactions preventing the liquid crystal state. The systematic realization of liquid crystal side chain

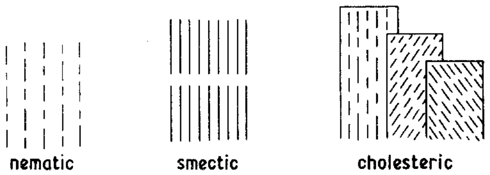


Figure 1 Organization of mesogenic groups.

polymers require a flexible spacer. An increase of the spacer length is associated with less hindered rotation of the mesogenic groups around their molecular axes and the main chain of the polymer does not influence the anisotropic packing of the side chains. The variation of the length of the flexible spacer leads to a change in the character and type of the mesophase as well as the physical properties.

The effects of substituents introduced into mesogenic units are of interest in thermotropic polymers because of high melting temperature of rigid-rod polymers, in which it is desirable to lower the melting temperature for processing. In general, the influence caused by the substituents is complicated by both steric and polar effects. The steric effect results in reducing the thermal stability of the mesophase due to: (i) a decrease in the coplanarity of adjacent units in the mesogenic group because of steric interactions between substituents; (ii) a tendency for the substituents to force apart mesogenic groups in neighbouring polymer chains because of their space requirements. On the other hand, substituents, which impart an increased polarizability and stronger dipolar interactions between the mesogenic groups, can have stronger intermolecular attractions, which would lead to higher thermal stabilities of both crystalline and liquid crystal phases, that is, to higher melting points and clearing temperatures. The presence of substituents may also change the morphology of the mesophase, so that the substituted compounds may form only one mesophase with the lowest degree of molecular order, while the unsubstituted one may have more than one mesophase.

The molecular structure of the liquid crystal phase, i.e. the organization of mesogenic groups, may be of three types as shown in Fig. 1. In the nematic phase, there is order in the direction of the molecules and the long axes of the side groups are oriented parallel to the preferred direction of common axis. In the smectic phase, the molecules lie in planes with defined interlayer spacing and a long range order exists in the preferential orientation of the side groups but in contrast to the nematic phase. The cholesteric phase, is described as a twisted nematic, and the centres of gravity have no long-range order. One approach to create cholesteric type of polymeric liquid crystals is in the synthesis of copolymers that contain monomer units similar to nematic liquid crystals and monomer units with chiral mesogenic groups, such as cholesteryl esters. The cholesteric polymers exist only as copolymer, consisting of (i) nematogenic and chiral monomer units, or (ii) two chiral monomer units, where the polymer shows a cholesteric structure only at a defined composition. However, homopolymerization of chiral cholesteric monomers yield only smectic polymers. Some polymeric liquid crystals containing different mesogenic groups are listed in Table III.

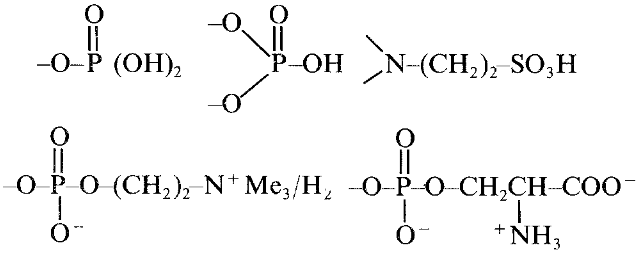
The main application of polymeric liquid crystals has been as a tool for producing high strength fibres from polymers which decompose without melting. The orientation in electric or magnetic fields is the basis of numerous technical applications of these polymers in electro-optical displays and temperature indicators. The covalent attachment of dye molecules and mesogenic units to the same polymer backbone is widely applied in this field of technology.

5. Polymeric surfactants

Vesicles derived from naturally occurring phospholipids (liposomes) are receiving interest as models for biological membranes. However, the use of these aggregates in mechanistic studies and practical applications, especially those based on long-term use, is seriously limited because they are thermodynamically unstable, having relatively short shelf lives.

Recently, growing interest has been shown in the synthesis and characterization of polymerizable surfactants, as shown in Table IV, to build up membranes of enhanced stabilities, controllable sizes, rigidities and permeabilities for utilization in photochemical solar energy conversion and storage, in catalysts for reactivity control, drug delivery, and solid-state device fabrication and operation [232].

Polymeric surfactant aggregates combine the beneficial properties of stable and uniform polymer particles with the fluidities of the aggregate. The structure of these amphiphilic molecules is characterized by the presence of an a hydrophilic head group and hydrophobic alkyl of C_8–C_{18} chains, as well as the polymerizable groups. The hydrophilic head group may be cationic as ammonium halides; anionic as phosphate, sulphonate, carboxylate, ester, hydroxylate; or zwitterionic.



$$-O-\overset{\overset{O}{\|}}{P}(OH)_2 \qquad \rangle N-(CH_2)_2-SO_3H$$

$$-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-(CH_2)_2-N^+Me_3/H_3 \qquad -O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-CH_2\underset{\underset{^+NH_3}{|}}{CH}-COO^-$$

The polymerizable group can be introduced into the surfactant molecules at the hydrophobic alkyl chain, in which there is no influence on the head groups and hence they preserve their physical properties such as charge and charge density, but change the fluidity of the hydrophobic tails. It can also be located at the hydrophilic head group of the surfactants, in which the fluidity is not affected but there is no free choice of the head groups. Molecules containing either diacetylene or acrylate residues have received most attention as polymerizable groups, although a few allyl, styryl, and maleic acid-based species have also been described.

The polymerizable species have been used to produce organized surfactant aggregates mono- and multi-layer films, membranes, micelles (spherical,

TABLE III Polymeric liquid crystals

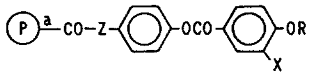
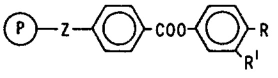
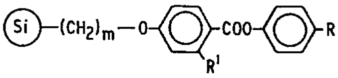
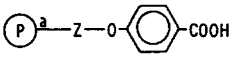
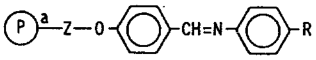
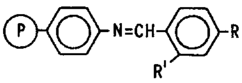
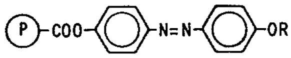
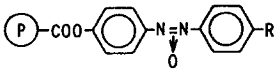
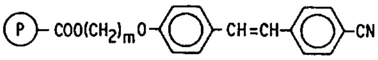
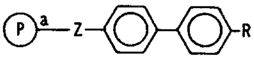
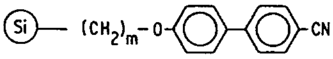
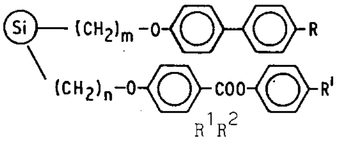
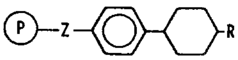
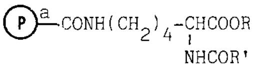
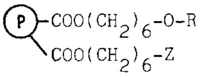
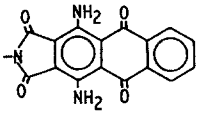
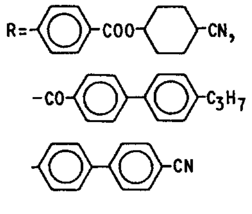
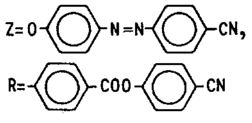
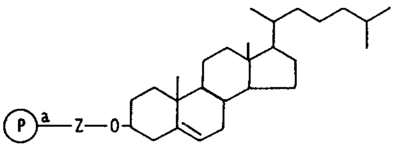
Functional Polymer	Reference
	
(a) Z=O,X=H,NO_2,R=C_3H_7, C_6H_{13},C_9H_{19},$C_{16}H_{33}$	[172-174]
(b) Z=O$(CH_2)_{10}$CO,X=H,R=n-Bu	[172]
(c) Z=NH$(CH_2)_{11}$COO,X=H, R=C_6H_{13}	[175]
	
(a) Z=COO,R'=H,R=-O-c-C_6H_{13}	[176]
(b) Z=COO$(CH_2)_m$O,R'=H R=CN,OBu,OMe	[177-179]
(c) Z=COO$(CH_2)_m$O,R'=H,R=OMe	**[180, 181]**
(d) Z=COO$(CH_2)_5$COO,R'=H,R=OMe	[182]
(e) Z=COO$(CH_2)_m$COO,R'=H,R=OBu m=0,3,10	[183]
(f) Z=$(CH_2)_2$O,R'=Me,R=C_3H_7	[184]
(g) Z=$(CH_2)_6$O,R'=H,R=CN	[185]
	
(a) R'=H,m=3,4,5,R=OMe, CN,OCH_2CHMeEt	[184,186,187]
(b) R'=Me,R=CN, m=6	[184,187]
(c) R'=H,R=OMe,m=5,6	[188,189]
	
(a) Z=CO	[190-193]
(b) Z=CH_2,O$(CH_2)_2$	[194]
	
(a) Z=CH_2,R=n-Bu,OBu	[195]
(b) Z=COO$(CH_2)_m$,R=OH,m=6,11	[196]
(c) Z=COO$(CH_2)_m$,R=CN,m=2-11	[197]
(d) Z=CO,R=alk	[198,199]
R=Oalk	[199,200]
R=COOH/COOalk	[200-202]
R=Br,CN	[198]
R=CH=CHCOOalk	[203]
R=SO_3Na	[200]
R=COMe,NHCOMe,N=NPh	[201]
	
(a) R'=H,R=CN,Oalk	[204-207]
(b) R'=OH,R=Oalk	[208]
 R=Me,Et,n-Bu	[209]
	
(a) R=H,Me,Et,n-Bu	[210,211]
(b) R=OMe,OEt,OBu-n	[212]
 m=5,6,11	[213]
	
(a) Z=COO,R=H	[214,215]
(b) Z=COO$(CH_2)_m$O,R=CN,m=2-11	[182, 197,213,216]
(c) Z=CH_2O,R=CH_2CHMeEt	[184]
(d) Z=$(CH_2)_6$O,R=CN	[185]
 m = 3-6	[184]
	[184]
(a) R=CN,m=5,R'=C_3H_7,n=4,R^1=H, R^2=Me	
(b) R=CH_2CHMeEt,m=3,R'=CN,n=6, R^1=Me, R^2=H	
	
(a) Z=COO, R=H	[217]
(b) Z=$(CH_2)_6$OCO, R=C_3H_7	[185]
Ⓟ—O—$(CH_2)_{15}$-Me	[218]
 $\text{Ⓟ}\overset{a}{—}\text{CONH}(CH_2)_4\text{-}\underset{\text{NHCOR'}}{\text{CHCOOR}}$	[219]
(a) R=H,R'=$C_{13}H_{27}$,$C_{15}H_{31}$, $C_{17}H_{35}$,$C_{21}H_{43}$	
(b) R=Me,R'=$C_{15}H_{31}$	
 Ⓟ-COO$(CH_2)_6$-O-R COO$(CH_2)_6$-Z	[220,221]
(a) Z= 	
	
(b) 	
	
(a) Z=CO	[194,222-229]
(b) Z=-$(CH_2)_2$CO-	[194]

TABLE III *Continued*

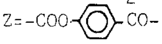
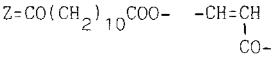
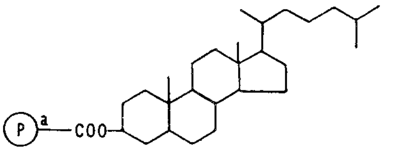
Functional Polymer	Reference
(c) $Z=-COO(CH_2)_2CO-$	[211,230]
(d)  $Z=-COO-C_6H_4-CO-$	[205]
(e)  $Z=CO(CH_2)_{10}COO-\quad -CH=\underset{\substack{\vert\\ CO-}}{CH}$	[194]
(f) $Z=CONH(CH_2)_mCO-$ $m=2,5,6,8,10,11$	[231]
(g) $Z=COO(CH_2)_5CO-$	[182]

TABLE III *Continued*

Functional Polymer	Reference
	[194,205, [223-226]

rod-like, reversed) and vesicles (Fig. 2). Since the formation of monolayers at the gas–water interface is the oldest and most simple of the membrane models, considerable data exist on the ultraviolet polymerization of monolayers and organized multilayers [233–236]. In contrast there are only a few examples on the polymerization of microemulsions [237, 238] and bilayers vesicles [239]. Attention on polymerization of aqueous micelles [240–243] and polymerized vesicles [224–253] have been reported. The vesicles, which are the nearest approach to biomembranes, are closed spherical structures having an aliphatic double chain, aqueous interior and one or several lipid double layers of different sizes depending on the method of formation. There are two methods for the formation of vesicles, either by slow injection of a surfactant

TABLE IV Monomeric surfactants

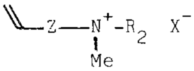
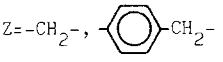
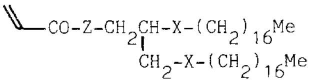
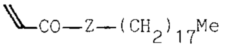
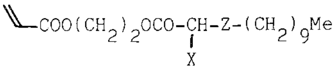
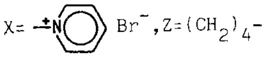
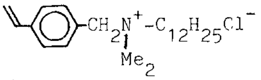
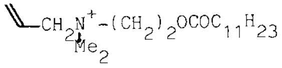
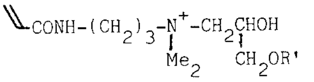
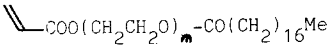
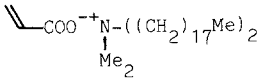
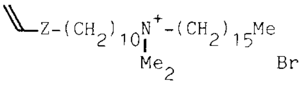
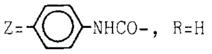
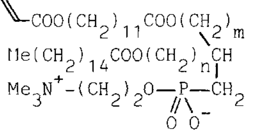
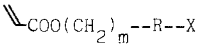
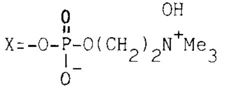
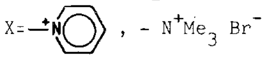
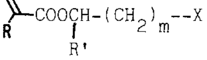
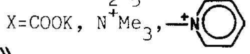
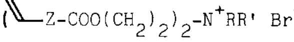
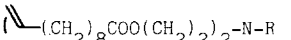
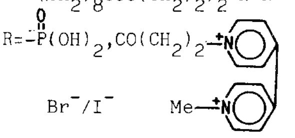
Functionalized monomer	Reference
 $Z-\underset{\substack{\vert\\ Me}}{N^+}-R_2\quad X^-$	
 $Z=-CH_2-,\ -C_6H_4-CH_2-$	[254-258]
$R=-(CH_2)_2OCOC_{11}H_{23},-C_{18}H_{37},$ $-(CH_2)_2OCOC_{15}H_{31}$	
 $CO-Z-CH_2\underset{\substack{\vert\\ CH_2-X-(CH_2)_{16}Me}}{CH}-X-(CH_2)_{16}Me$	
(a) $Z=-O-,\ X=-OCO-$	[251]
(b) $Z=-NH(CH_2)_5COO-,\ X=-OCH_2-$	[251]
(c) $Z=-NH-,\ X=-COOCH_2-$	[244]
 $CO-Z-(CH_2)_{17}Me$	
(a) $Z=-O-$	[259]
(b) $Z=-NH-$	[233]
 $COO(CH_2)_2OCO-\underset{\substack{\vert\\ X}}{CH}-Z-(CH_2)_9Me$	
(a) $X=-N^+Me_3Br^-,Z=-(CH_2)_4-$	[260]
(b)  $Br^-,Z=(CH_2)_4-$	[260]
(c) $X=-CH_2COOK,\ Z=-CH=CH-$	[260]
 $CH_2\underset{\substack{\vert\\ Me_2}}{N^+}-C_{12}H_{25}Cl^-$	[261]
 $CH_2\underset{\substack{\vert\\ Me_2}}{N^+}-(CH_2)_2OCOC_{11}H_{23}$	[258]
 $CONH-(CH_2)_3-\underset{\substack{\vert\\ Me_2}}{N^+}-CH_2\underset{\substack{\vert\\ CH_2OR'}}{CH}OH$ $R'=C_8-C_{20}alk$	[262]
 $COO(CH_2CH_2O)_m-CO(CH_2)_{16}Me$ $m=1-2,\ 8-9$	[260]
 $COO^{-+}\underset{\substack{\vert\\ Me_2}}{N}-((CH_2)_{17}Me)_2$	[255]

TABLE IV *Continued*

Functionalized monomer	Reference
 $Z-(CH_2)_{10}\underset{\substack{\vert\\ Me_2}}{N^+}-(CH_2)_{15}Me\quad Br^-$	
(a)  $Z=-C_6H_4-NHCO-,\ R=H$	[258]
(b) $Z=-COOCH_2-,\ R=Me$	[244,264]
 $COO(CH_2)_{11}COO(CH_2)_m$ $Me(CH_2)_{14}COO(CH_2)_nCH$ $Me_3N^+-(CH_2)_2O-P(O)(O^-)-CH_2$	[250]
(a) $m=0,\ n=1$	
(b) $m=1,\ n=0$	
 $COO(CH_2)_m--R--X$	
(a) $m=11,\ R=COOCH_2\underset{\substack{\vert\\ OH}}{CH}CH_2-,$  $X=-O-\overset{\substack{O\\ \Vert}}{\underset{\substack{\vert\\ O^-}}{P}}-O(CH_2)_2N^+Me_3$	[250]
(b) $m=2,10,\ R=OCO(CH_2)_{10}-,$ $-CH_2-$  $,\ -\ N^+Me_3\ Br^-$	[260]
 $COO\underset{\substack{\vert\\ R'}}{CH}-(CH_2)_m--X$ $m=10,14,\ R=H,Me,$ $R'=H,-(CH_2)_5Me,$  $X=COOK,\ N^+Me_3,$	[260]
 $(\ Z-COO(CH_2)_2)_2-N^+RR'\ Br^-$	
(a) $Z=(CH_2)_8,R=H,Me,$ $R'=Me,(CH_2)_2OH,(CH_2)_2SO_3^-$	[258]
(b) $Z=CONH(CH_2)_{10},R=R'=Me$	[251]
 $(\ (CH_2)_8COO(CH_2)_2)_2-N-R$  $R=-\overset{\substack{O\\ \Vert}}{P}(OH)_2,CO(CH_2)_2-$ Br^-/I^-	[258]

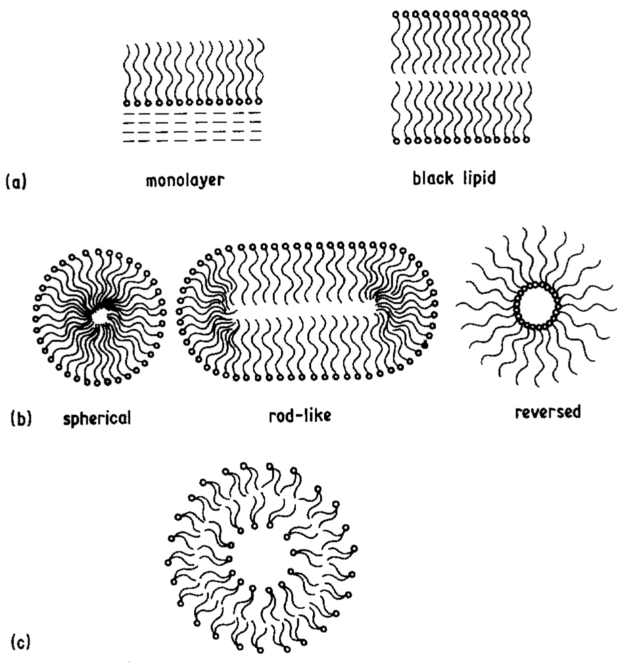


Figure 2 Organized structures formed from surfactants: (a) membranes, (b) micelle, (c) vesicle.

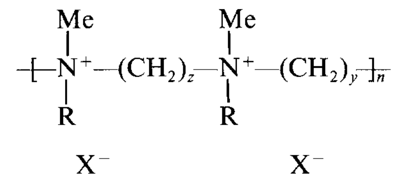
solution in alcohol or ether into thermostated water, or by the ultrasonic dispersal of the surfactant crystal suspensions in water. However, in the ultrasonic method, the type of sonicator, the applied power, and the time and temperature of sonication need to be specified.

Polymerization of vesicles formed by sonicating the surfactant was effectively carried out by direct irradiation by ultraviolet light or by heating the surfactant with a free radical initiator. The extent of polymerization can be monitored by following the disappearance of the polymerizable double bonds either by NMR or ultraviolet absorption spectroscopy [236, 258].

Polymerization of vinyl vesicles in a bimolecular lipid membrane has recently been described in the literature. Depending on the position of the double bonds, vesicles can be linked either across their bilayers or across their head groups. Vesicles having double bonds in their head groups can be polymerized either at their inner *or* outer surfaces or, alternatively be polymerized at *both* their outer and inner surfaces. Irradiation by light results in the complete loss of vinyl protons. Conversely, polymerization by external addition of an initiator to already sonicated vesicles causes only 60% loss of the vinyl protons.

6. Ionomers

Ionomers are synthetic organic polymers that have an ion content of up to 10 to 15 mol% and are thus generally insoluble in water [265–270]. In contrast, polyelectrolytes have much higher ion contents and are insoluble in organic solvents. Thus, an ionomer can be defined as an ionized copolymer whose major component is a nonionic backbone, usually hydrocarbon, and whose minor component consists of ionic comonomers with associated counterions, such as carboxylate, sulphonate, phosphonates, and quaternary ammonium salts, e.g. IX [271–275]. The ionic groups may be introduced either by modifying



$$\left[\overset{\text{Me}}{\underset{\text{R}}{\text{N}^+}} - (\text{CH}_2)_z - \overset{\text{Me}}{\underset{\text{R}}{\text{N}^+}} - (\text{CH}_2)_y \right]_n \qquad \text{X}^- \qquad \text{X}^-$$

(IX) (a) R = dodecyl, $z = y = 3.5$

(b) R = octadecyl, $z = y = 5$

a nonionic polymer through appropriate chemical techniques or by copolymerization with the major components.

The reason for the great interest in ionomers as important industrial potential lies in the often profound changes in structure and properties caused by the introduction of ionic groups into nonionic organic polymers. For example, Nafion, as an ionomer, has found extensive applications as an electrochemical separator. The extent to which the properties are altered depends on a number of factors, such as the dielectric constant of the backbone, the position and type of ionic group, the counter ion type, ion concentration, and degree of neutralization. The major effects of the ions on properties of polymer are: (i) static and dynamic mechanical properties; and (ii) melt rheology – the increase in ion content in the polymer raises T_g, melt strength and melt viscosities, and the modulus at temperatures beyond the glassy plateau and broadens the transition regions. Owing to the great difference in polarity between the ionic functionality and the hydrophobic repeat units of the polymer backbone, the hydrophilic ionic groups leads to microphase separation, which results in the coexistence of two types of ionic aggregates: (i) multiplets are small aggregates with tight, isolated groups, and contain no organic material and are dispersed in the matrix. Consisting of a few ions or ion pairs, they act as moderately strong, temporary, ionic crosslinks; (ii) clusters are larger aggregates, more loosely interacting, contain a relatively large amount of ion pairs and some organic material, and act as crosslinks and as a strongly reinforcing filler. Cluster formation has the most dramatic effects on the polymer properties such as the greatest changes observed in polymers having a low dielectric constant and containing small ions, since such a situation provides the greatest incompatibility between the ionic and nonionic regions of the system. The position of the ions on the chains as well as the nature of the ionic group has an influence on the state of aggregation.

7. Polymeric stabilizers

The growing use of polymers in place of traditional materials, such as metals, glass, wood and stone in building and construction applications, has intensified the search for improving durability where resistance to the outdoor environment degradation or to catastrophic combustion is important.

Polymer degradation can be utilized positively in several areas such as: (i) recycling for conversion of polymers to a useful chemical after their initial use so that they do not become an ecological waste problem, e.g. hydrolysis of waste packing materials or automotive foams to monomers; (ii) agrochemical or drug delivery systems based on chemical erosion of a polymer; (iii) controlled degradation for determining the structure of the natural polymer, e.g. protein, or for obtaining valuable low molecular substances from them, e.g. glucose from cellulose.

However, polymers under weathering conditions are susceptible to deterioration, which restrict their use in outdoor applications. The departed chemical and physical properties of the polymers from the initial optimum may result in changed appearance as discoloration and a transparent material becomes opaque, or damaging mechanical properties which make them technologically so useful. The flaking of paint and perishing of rubber are regrettably well-known examples of the deterioration suffered by most organic polymers after prolonged exposure to air and light. Hence, the protection of polymers against atmospheric ageing and degradation is a prerequisite for their successful technological development and applications. The most important destructive agents for polymers are the environmental factors as well as the aggressive conditions of processing or service especially in the presence of other additives in the polymer itself, added either for a specific purpose or present as an impurity. The applications of functionalized polymers as stabilizers in the field of chain-breaking antioxidants, ultraviolet and flame retardants, have recently received considerable interest [276–285].

7.1. Polymeric antioxidants

The basic oxidative chain reactions occurring in polymers subjected to weathering conditions or high-temperature processing is a chain reaction mechanism which occurs by a sequence of reactions leading to the formation of hydroperoxide groups. The first step in the oxidation cycle is the generation of a free radical at some points on the polymer hydrocarbon chain,

$$\text{polymer} \rightarrow R^{\bullet} \qquad (9)$$

A hydrocarbon radical could arise from a variety of applied stresses, such as heating or mechanical damage when the polymer is stretched, flexed, or milled. Once generated, the radical could undergo further reactions resulting in breaking or in crosslinking of the polymer chain, or it could combine with another radical to form inactive products. The radical can also react with a ground-state diradical oxygen molecule to give a peroxy radical,

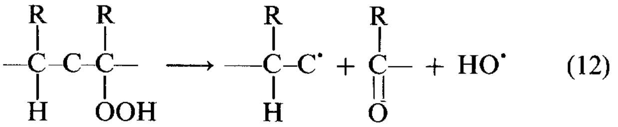
$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \qquad (10)$$

followed by a hydrogen abstraction reaction

$$RO_2^{\bullet} + R\text{–}H \rightarrow R\text{–}OOH + R^{\bullet} \qquad (11)$$

The autoxidation reaction is therefore autocatalytic in character as a result of both the chain reaction behaviour and the formation of large amounts of labile hydroperoxide groups which are potential free-radical initiators.

The loss of desirable mechanical, physical, chemical and electrical properties brought about by oxidation is due to the change in molecular weight distribution of the polymer via decomposition or crossliking. Chain scission which causes a decrease in chain length has been shown to occur by the decomposition of the formed hydroperoxide groups [303],



$$-\overset{R}{\underset{H}{C}}-C-\overset{R}{\underset{OOH}{C}}- \longrightarrow -\overset{R}{\underset{H}{C}}-C^{\bullet} + \overset{R}{\underset{O}{\overset{|}{\underset{\|}{C}}}}- + HO^{\bullet} \qquad (12)$$

Crosslinking occurs as a result of either the combination reaction between two of the parent radicals involved in the oxidation mechanism or by the attack of one of the radicals on an unsaturated point of a chain.

Thus, antioxidants are needed for fabrication and long-term use of most polymers to prevent the initiation of the chain or to interrupt the chain propagation step of the autoxidation reaction. However, the protection given by conventional antioxidants against deterioration is often short-lived under some service conditions due to their loss, either by volatilization or by leaching processes and, thus, a relatively high concentration of antioxidants are required.

Recently, many attempts have been carried out to increase the inhibition efficiency of small molecule antioxidants by producing high molecular weight antioxidants or by chemically combining them with the polymers they are protecting. Polymeric antioxidants have great potential because they do not readily migrate out of the polymer system and give solvent and detergent resistant polymers. The most important classes of antioxidants which have been incorporated into polymers are the phenol and aniline derivatives [304], as shown in Table V.

7.2. Polymeric ultraviolet-stabilizers

Polymers in outdoor applications are usually exposed to damaging sunlight radiations and hence they are susceptible to photodeterioration. The most damaging part of the solar radiation is at $\simeq 33\,000\,\text{cm}^{-1}$ (300 nm) in the near ultraviolet while the shorter wavelength radiations, below 300 nm, are absorbed by the ozone layer of the outer atmosphere which protects the Earth's surface from this harmful solar radiation. The spectral composition and intensity of solar radiation at the Earth's surface varies with the time of day, location and weather conditions due to changes in the thickness of the ozone layer.

Photoinitiation may be attributed to the chromophoric groups present as impurities or created during processes. Absorbed ultraviolet radiation leads to the excitation of the polymer or it returns to the electronic ground state with the reemission of the energy in a non-harmful form. Photochemical reactions are chain cleavage and lead to the formation of functional groups, which may be starting points for degradation, or lead to autoxidation in the presence of oxygen. Thus, it is of considerable practical importance that polymers should be protected against the effects of the solar radiation to increase their durability [286–302]. However, the solubility of a conventional stabilizer in the matrix is often less than the minimum effective

TABLE V Monomeric and polymeric stabilizers

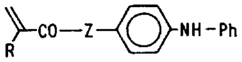
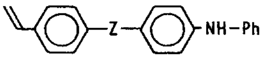
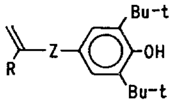
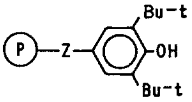
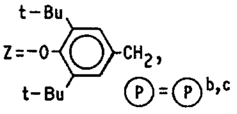
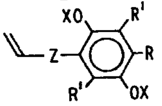
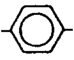
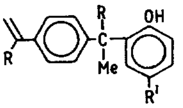
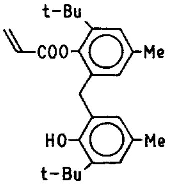
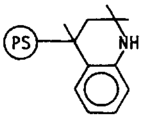
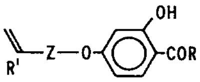
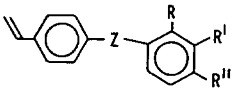
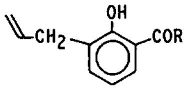
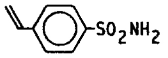
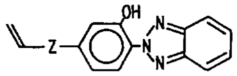
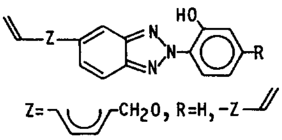
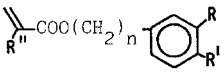
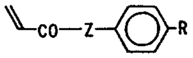
A Monomeric and Polymeric Antioxidants	Reference
	
(a) Z=NH, R=Me	[308-315]
(b) Z=O, R=H,Me	[316,317]
(c) $Z=SO_2NH$, R=H	[318,319]
(d) $Z=CH_2SO_2NH$, R=H	[318,319]
(e) $Z=OCH_2CH(OH)CH_2N(R')-$, R=Me	[320-323]
	
(a) $Z=CH_2NH-$,	[318,319]
(b) $Z=CH_2O-$,	[318,319]
(c) $Z=SO_2NH-$,	[318,319]
(d) Z=NH-CS-NH-	[324]
	
(a) Z=nothing, R=H	[325]
(b) Z=COO, R=H,Me	[326,327]
(c) $Z=COOCH_2$, R=H,Me	[328,329]
(d) $Z=COOCH_2CMe_2CH_2$,R=H,Me	[330-332]
(e) $Z=COO(CH_2)_2OCH_2$,R=H,Me	[333,334]
(f) $Z=COO(CH_2CH_2O)_mCO$,R=H	[335-337]
(g) $Z=COS(CH_2)_m$,R=H,Me m=1,2,3	[338]
(h) Z=CONH, R=H	[339]
(k) $Z=CONHCH_2OCH_2$,R=H,Me	[329]
(l) $Z=OCO(CH_2)_2$, R=H	[340,341]
(m) $Z=O(CH_2)_2OCO$,R=H	[342,343]
	
(a) $Z=-CH_2-$, Ⓟ = Ⓟ^{a}	[345]
(b) 	[344]
(c) $Z=COO(CH_2)_2N(Me)CO(CH_2)_2$	[346,347]
Ⓟ=Ⓟ^{a} 	
(a) Z=nothing,X=H,Ac, R=R'=alk	[348]
(b) **$Z=CONHCH_2$,X=H, R=R'=Me**	**[349-351]**
(c) Z=,X=H,R=Me,R'=H	[352,353]
 R=H,Me, R'=Me	**[354]**
	[355,356]
	[357]
B Monomeric ultraviolet absorbers	
 R'=H,Me	
(a) Z=CO, R=Ph	[358-366]
(b) Z=CO, R=Me	[358-363]
(c) $Z=COOCH_2CH(OH)CH_2$,R=Ph	[367-369]
(d) $Z=(CH_2)_nOCH_2CH(OH)CH_2$, R=Ph, n=1,2	[370,371]
(e) $Z=COO(CH_2)_2$, R=Ph	[372]
	
(a) $Z=CH_2O$,R=H,R'=OH, R''=COPh	[373,374]
(b) $Z=CH_2O$,R=COPh,R'=R''=H	[373]
(c) Z=CO,R=R''=OH,R'=H	[375]
(d) Z=CO,R=OMe,R'=R''=H	[376,377]
 R=Me,Ph	[378]
	[379]
	[380-382]
	[380-382]
	
(a) n=1,R=COOPh,R'=OH	[383]
(b) n=0,R=COOPh,R'=OH	[383-386]
(c) n=0,R=OH,R'=COOMe	[387]
	
(a) Z=NH, R=COOEt	[388]
(b) Z=O, $R=NMe_2$	[389-391]

TABLE V *Continued*

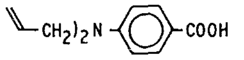
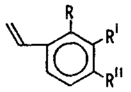
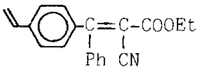
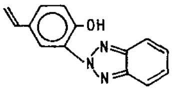
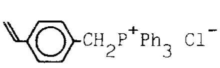
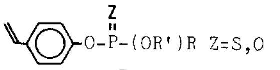
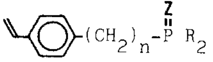
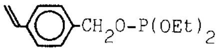
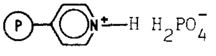
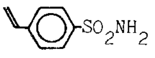
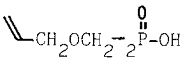
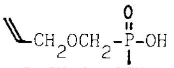
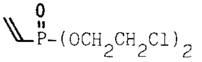
A Monomeric and Polymeric Antioxidants	Reference
	[392]
	
(a) R=H, R'=COOalk,R''=Oalk	[393]
(b) R=Oalk,R'=COOalk,R''=H	[394]
(c) R=H,R'=Oalk,R''=COOalk	[395]
	[396]
	[397-399,408]
C Monomeric and polymeric flame retardants	
	[400]

TABLE V *Continued*

A Monomeric and Polymeric Antioxidants	Reference
	[401,402]
	
(a) n=0, Z=S,O, R=Ph	[403]
(b) n=1, Z=O, R=NH_2	[404]
(c) n=1, Z=O, R=Oalk	[405]
	[405]
	[406]
	[407]
	[409]
	[409]
	[410]

concentration, leading to loss of significant amounts of absorbers from polymers by physical means through exudation, volatilization or through solvent extraction during fabrication and end use. Moreover, blended-in ultraviolet-absorbing additives tend to aggregate in spots within the film and therefore cannot provide full protection. These problems are particularly acute in the stabilization of thin films and coatings. Recent attention with stabilizers grafted on to polymers has shown that these disadvantages decreased with an increase in stabilizer molecular weight. Polymeric ultraviolet absorbers have been prepared through polymerization of the polymerizable vinyl group directly attached to the absorbers, as shown in Table V. For example, vinylbenzyl monomers having *o*-hydroxy-benzophenone substituents have been copolymerized with styrene and other monomers to give a polymer composition (0.5 to 10%) having good ultraviolet stability in plastic articles, films, lacquers, oil-base varnishes, etc.

Polymeric ultraviolet stabilizers are more resistant to solvent extraction, volatilization during high-temperature processing and exudation from plastics, than low molecular weight stabilizers. Thus, over a long period of time or in the presence of solvents, polymeric stabilizers appear to be more permanent and superior to conventional additives.

7.3. Polymeric flame retardants

A rapid increase has occurred in replacing conventional materials with synthetic polymers; very large amounts are used in the construction and decorative finishing as paints and other coatings of buildings. The increasing use of polymers has increased fire hazards resulting in damage to structures and death or incapacitation of occupants of buildings. Thus, the flammability characteristics of polymers are a barrier to their increased use in buildings because they: (i) make a major contribution to the rate of fire growth, i.e. increase fire load; (ii) generate dense smoke and toxic fumes as a result of burning, which make problems for fire fighters due to limiting visibility and the use of breathing apparatus; and (iii) rapidly lose their property due to combustion.

Thus, the problems involved in reducing the fire hazards associated with the use of synthetic polymeric materials are very complex from ecomonic and social points of view. The nature of the combustion process, which occurs when a fire starts, may be represented as shown in Fig. 3. The initial stage of a fire is a source of ignition which decomposes the polymeric materials to inflammable volatile products. Thus, for continuous burning to occur, (i) the application of heat must be sufficient to decompose the polymer, (ii) the temperature must be sufficient to ignite the products

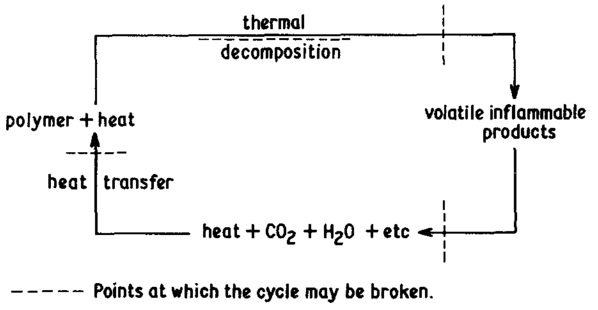


Figure 3 The combustion process cycle. (– – –) points at which the cycle may be broken.

of decomposition and (ii) the amount of heat transferred from the flame back to the polymer must be sufficient to maintain the cycle.

Hence, to reduce flame spread once ignition has taken place, i.e. to make the polymer fire-retardant, it is necessary to break the cycle, which may be done in one of three general ways: (i) by modifying the polymer so that the initial mode of the thermal degradation process is changed, resulting in the evolution of less flammable products; (ii) by inhibiting burning or quenching the flame; or (iii) by reducing the feed-back of heat from the flame to the decomposing polymer so that transfered heat is not sufficient to cause evolution of flammable gases.

The production of fire-retardant grades of commercial polymeric materials can be made by use of appropriate additives which have a dual purpose; to ensure that polymeric material does not present a fire hazard and to enable the hazard of the other flammable materials to be reduced. Many halogen and phosphorus-containing compounds possess an outstanding position in this respect. Unfortunately, conventional flame-retardant additives usually induce the formation of greater volumes of more toxic fumes and volatilize before they perform their action. Recently, the introduction of flame-retardant substances chemically bonded to the polymeric materials has been introduced via monomeric flame retardants, as shown in Table V, to overcome the problems of volatility of conventional retardants [305–307].

8. Polymeric corrosion inhibitors

Recent years have seen a considerable increase in the size of merchant ships, particularly tankers and bulk carriers. The cost of these vessels and their operation (interest, capital repayment, insurance, etc.) are correspondingly high. These charges continue whether the ship is in service or out of service undergoing maintenance or repairs, hence it is necessary to extend the effective life of the protective paint systems and to minimize time out of service when maintenance does become necessary.

At present the factor limiting the intervals between dry dockings is the performance of the antifouling composition applied to the underwater hull to prevent attachment and growth of marine plants and animals [5].

The coatings applied to protect steel hulls against corrosion were capable of providing even longer periods of maintenance-free service [411]. The corrosion of steel requires moisture and oxygen, and is an electrochemical process. Potential differences on the surface of steel arise from a variety of causes, including: (i) the presence or absence of millscale (the oxide film formed on steel when it is hot rolled); (ii) local differences in the composition of the steel; (iii) local variations in heat-treatment of the steel. The electrochemical corrosion cell is set-up at a break in millscale on steel immersed in seawater, in which the potential difference is between the scale-free areas that become anodic and the scale-covered areas that become cathodic. Millscale is a major cause of corrosion in seawater, there being a potential difference of about 0.3 V between the scale-free and the scale-covered areas. The anodic and cathodic reactions are as follows:

$$\text{Anode} \quad 4Fe \rightarrow 4Fe^{2+} + 8e^- \qquad (13)$$

$$\text{Cathode} \quad 8e^- + 4H_2O + 2O_2 \rightarrow 8OH^- \qquad (14)$$

The initial anodic (Equation 13) and cathodic (Equation 14), products – ferrous ions and hydroxyl ions – diffuse from the surface and react to form ferrous hydroxide (Equation 15), which in turn is oxidized by dissolved oxygen to hydrated ferric oxide, rust (Equation 16),

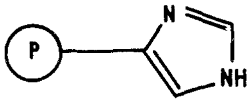
$$4Fe^{2+} + 8OH^- \rightarrow 4Fe(OH)_2 \qquad (15)$$

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 \cdot H_2O + 2H_2O \qquad (16)$$

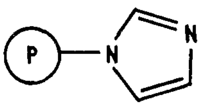
It should be noted that: (i) the ferrous hydroxide is not precipitated in contact with either the anodic or cathodic areas but at some intermediate point, and hence does not stifle the corrosion reaction; (ii) conditions at cathodic areas become alkaline, requiring protective paints to have good alkali resistance.

Corrosion can be prevented by stopping the flow of corrosion currents in the cells, which is possible by: (i) anodic inhibition: the anode reaction (Equation 13) can be suppressed by paints that supply electrons to the metal surface; or paints that reinforce the naturally occurring oxide film on the surface; (ii) cathodic inhibition: suppression of the cathodic reaction (Equation 14) is in general not practicable because paint films of normal thickness are so permeable to water and oxygen that the reaction proceeds almost unhindered; (iii) resistance inhibition: preventing the flow of corrosion currents by impeding the movement of ions in the electrolyte surrounding the metal, i.e. by interposing a high resistance in the electrolytic path of the cells, is the most general mechanism of protection by paints. The resistance of a paint film is affected by (1) the presence of electrolytes in the film, hence water-soluble impurities in pigments must be kept to a minimum, (2) the presence of electrolytes beneath the film, hence the importance of surface cleanliness prior to paint application, (3) penetration of the film by water and electrolytes from the outside, highly crosslinked films being in general more resistant to such penetration, and (4) its thickness, hence the practical importance of applying thick films. Thus, based on these considerations, it is clear that the essential requirements for protective paint coatings on ships bottoms are that they should be (a) applied to a clean steel surface free from millscale, rust or other contaminants, (b) provide a high electrical resistance between the metal and seawater, and (c) withstand alkaline conditions.

Poly(4-vinylpyridine) and its derivatives, including quaternary alkyl halide salts and betaines, such as those prepared from sodium chloroacetate, function as effective inhibitors for preventing corrosion of metals, including iron, aluminium, magnesium and brass, in non-oxidizing acid solutions [412–414]. Sodium poly(styrene-sulphonate) also forms a protective coating on phosphated mild steel which prevents rusting [415]. Polyvinylimidazoles, (X) and (XI), are



(X)



(XI)

effective anticorrosion for copper at elevated temperature environments through the complex formation between copper and nitrogen atoms which inhibit oxygen adsorption on the copper surface [416].

9. Polymers in stone preservation

Natural building stone is often associated with a sense of permanence and durability. However, some types of stone are subjected to relatively rapid decay that may result in the deterioration of carved work, i.e. lead to the loss of works of high artistic value. Thus, it is important to preserve our ancient monuments by the treatment of stone to prevent its decay.

The causes of stone decay are either physical or chemical:

1. Physical processes: they involve two types of damage: (i) Frost damage is due to the expansion of water upon freezing and occurs only in those features of a building that are frequently frozen while wet. The frost susceptibility of a stone is governed by its pore size distribution, because the pore structure governs the natural degree of saturation, and because it governs the magnitude of the stresses that may be generated upon freezing; (ii) crystallization damage is the crystallization of salts within the pores of a stone that causes a powdering or a blistering of the surface, or leads to the formation of deep cavities. Sulphur dioxide in the atmosphere leads to the formation of $CaSO_4$ from limestones and to both $CaSO_4$ and $MgSO_4$ from magnesium limestones. Other common sources of salts include the soil, seawater, and unsuitable cleaning materials. The resistance of a limestone to this type of damage is dependent on its pore-size distribution and the durability decreasing as the proportion of fine pores increases.

2. Chemical attack: the chemical reaction of $CaCO_3$ with SO_2 and CO_2 dissolved in rain water cause rapid deterioration in the case of calcareous sandstones, which consist of grains of silica bound solely by a matrix of $CaCO_3$.

Since water is involved in almost every type of stone decay, water-repellent surface treatments were used as promising preservatives. Many water repellents have been described for the preservation of stone [417], e.g. the deposition of barium salts within the pores of calcareous stones, in which $BaSO_4$ causes less crystallization damage than $CaSO_4$ in view of its lower solubility [418, 419]. Impregnation of stone with molten wax immobilizes soluble salts but it may increase the rate at which the stone picks up dirt and it is also difficult to achieve practical adequate penetration of immersion. Such treatments have no long-term preservative effect and may even accelerate decay due to absorption of rain or ground water at some unprotected point, its evaporation from behind the water-repellent layer, and any salts in solution crystallize there, lead to spalling of the treated surface.

However, the important factors that govern the selection of a treatment are the cost and the effectiveness, i.e. the relative lifetimes, of the various treatments, and the quantity of material that is required to treat a given area depends on the porosity of the stone. An impregnation treatment should consolidate friable stone and prevent further deterioration caused by salt crystallization, either by making the salts inaccessible to water or by making the stone more resistant to crystallization damage. Increased resistance to crystallization damage could be achieved by an increase in the stone's tensile strength or by a modification of its pore structure. In order to achieve adequate penetration the treatment should have a high surface tension, a low contact angle and very low viscosity at the time of application.

From the Young equation

$$\cos\theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \tag{17}$$

where θ is the contact angle, γ_{SA} and γ_{LA} are the surface-free energies of the solid and the liquid, and γ_{SL} is the interfacial energy. For wetting, θ must be minimized; for perfect wetting $\theta = 0$. Hence, for good wetting, large γ_{LA} is needed, and $\gamma_{SA}-\gamma_{SL}$ should be small but must be positive.

The choice of treatment may be further restricted by considerations of such properties as flammability, toxicity, vapour pressure, water miscibility, and elastic modulus upon curing. The viscosity requirement is usually the governing factor which is met in one of two approaches.

1. By dissolving a resin in a solvent of low viscosity, but this approach suffers from a number of disadvantages: (i) the possible migration of the resin back to the surface as the solvent evaporates [420]; (ii) large polymer molecules may be too big to enter the smallest pores of the stone.

2. The impregnation of monomers followed by *in situ* polymerization of functionalized vinyl monomers, alkoxysilanes or epoxide. For example, the radical polymerization of methacrylate esters with trimethylopropane trimethacrylate as crosslinker has been investigated [421, 422]. However, the disadvantages of this are the inhibition of the polymerization by oxygen, and the viscosity increases as the polymerization commences on mixing, which inhibits penetration.

Curing polymerizations of a alkoxysilanes (XII), which depend on the hydrolysis and on the loss of alcohol by evaporation, have received most attention [423]. However, the main limitation of this system is that the loss of alcohol makes it impossible to achieve a complete pore filling, which can be solved by replacing the methyl groups by some larger groups. Compounds containing two expoxide groups and have a low viscosity, such as 1:2-, 3:4-diepoxybutane, diglycidyl ether, 1,4-butanediol diglycidyl ether, diluted with tetramethoxysilane, to decrease the viscosity, have cured with 1,8-diamine-*p*-methane [424]. The drawback of this system is the white efflorescence that may be produced by reaction of the hardener with CO_2.

$$(R'O)_3Si{-}R$$

(XII)

(a) $R' = Et; R = OEt$
(b) $R' = Et; R = Me$
(c) $R' = Me; R = Me$

10. Miscellaneous

10.1. Polymers in improving fibres properties

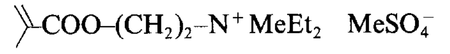
Although the use of synthetic fibres has expanded and their commercial importance grown, many of these polymeric materials have some disadvantages. These drawbacks include: (i) poor dyeability due to the unreactive structure; (ii) the collection of static electricity on fabrics; and (iii) the obviousness of deposited dirt (soil).

For a fibre to be dyeable, some physical or chemical interaction must take place between the dye and the fibre, so that the dye is not removed by subsequent processing, e.g. washing. For example, polymeric fibres, such as polyacrylonitrile, polypropylene, have little affinity for dyestuffs due to their unreactive structure. Functionalized polymers can be used to provide active sites to improve the dyeability of fibres. This improvement of dyeability can be achieved by using comonomers selected to confer affinity for dyestuffs on the resulting copolymers either by copolymerization, grafting, or blending technique. The most common modified fibres contain either acidic or basic groups which can be dyed with conventional anionic or cationic dyestuffs, respectively. Both types of dyestuffs become anchored within the fibre by salt-like bonds.

Copolymerization of a fibre-forming monomer, acrylonitrile, with *p*-dimethylaminomethylstyrene (2 to 10%) [425] or vinylbenzylmethyl ether of diethylene glycol [426] give fibres with relatively hydrophilic composition and which are strongly receptive to acid dye. In another modification process, a graft copolymer formed, e.g. by the reaction of a vinylbenzylmethyl ether of diethylene glycol with a copolymer of an *N*-vinylpyrrolidone and *N*-vinyl-5-methyloxazolidinone (70 : 30) is used to confer dyeability of polyacrylonitrile. The dye-receptive polymer is mechanically trapped between the fibrils of the strand when it is subjected to irreversible drying. The product has excellent dyeability with acid and direct dyes [427]. The graft copolymerization of vinylbenzyl chloride on polypropylene fibres by ionizing radiation gives a product which has directly, or after treatment with a nucleophile, excellent receptivity to acid and direct dyes [428].

An interesting third method of achieving dyeability consits of physical impregnation of the fibre with the suitable functionalized monomer followed by polymerization *in situ* by X-radiation. For example, molten polypropylene, from which the fibre is spun, may be admixed with poly(vinylpyridine) or a copolymer of *N*-vinyl-pyrrolidone and dimethylaminoethyl methacrylate; the fibres can then be dyed with conventional acid dyes.

The build up of electric charge on polymeric fibres attracts dust and dirt particles and thus the fibres become soiled. Thus, the problems of antistatic and antisoiling are coupled. The successful solution for preventing the build up of electrostatic charge and soiling is the copolymerization with monomeric quaternary salts, e.g. methacrylatoethyldiethylmethylammonium methosulphate (XIII), and polyoxyethylene compounds (XIV), as an antistatic agent. The resultant copolymers were less soluble than the original and these agents were not easily removed by washing and were active for quite long periods. Success in preventing soiling in wear is based on: (i) coating fibrics with low energy surfaces which will avoid adherence of soil. For example, fluorochemicals such as (XV), which have a low surface tension and are not readily wetted at all even by mineral and vegetable oils, are used; (ii) application of hydrophilic polymeric finishes to the fabric will repel oils and greasy soils and ensure ready wetting of the fabric surface by aqueous detergents.



(XIII)

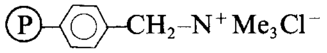
(XIV) $m = 3$ to 10

(XV)

10.2. Polymeric flocculating agents

By flocculating the finely divided solid particles into free-draining agglomerates, most intractable colloidal suspensions may be quickly filtered. The settling rate of slurries can be greatly increased when treated with a solution of polymers having good flocculating properties. An interesting application of polymeric flocculating agents is the filtration and decoloration of various types of slurries, such as bentonite, corn starch, and uranium ore [432].

In decoloration, which can be followed by the significant improvement of light transmission, normally soluble colour bodies are rendered insoluble by association with the flocculating polymer. For example, poly(vinylbenzyltrimethylammonium chloride), (XVI), was used for the decoloration of blackstrap molasses, in which the colour bodies were precipitated as a brown floc [429, 430]. Another important application of this polymer is the treatment of filter aid, such as diatomaceous earth, to yield a material having excellent ability to remove bacteria and viruses from a solution [431]. Some other functionalized polymers which have been applied as flocculating agents are listed in Table VI.

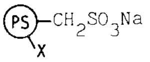
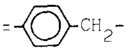
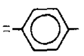
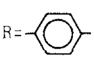
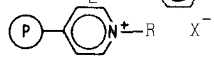


(XVI)

11. Conclusions

On the basis of the above information, the uses of functionalized polymers in technological applications is reviewed in an attempt to report the possible

TABLE VI Polymeric flocculating agents

Functionalized polymer	Application	Reference
$(PS)-CH_2N^+Me_3\ X^-$ $X = Cl^-$	Decoloration of blackstrap molasses	[429,430]
	Filtration to remove bacteria and viruses from solutions	[431]
	To flocculate slurries such as bentonite, corn starch, uranium ore	[432]
	To flocculate negatively charged colloids	[433]
	Filtration of sewage sludges	[434]
$X = Cl^- \cdot SO_2$	Flocculation of Kaolin slurry	[435]
$(PS)-CH_2S^+Me_2\ Cl^-$	Flocculation of taconite slurry	[436]
 $(PS)(X)-CH_2SO_3Na$		
X=H, R= 	Flocculation of uranium ore slurry	[437]
X=H, R= 	As flocculant	[438-444]
	As hardener for gelatin	[445]
	As emulsifier	[446,447]
$X=CONH_2$, R= 	As flocculant	[448,449]
	As flocculant	[450-453]

contributions of polymer science to the development of a number of new polymeric materials for a broad area of utilization. Accordingly, the application of functionalized polymers is broken down into ten main areas, (i) conductive polymers, (ii) polymers in energy, (iii) polymers in lithiographic processes, (iv) polymeric liquid crystals, (v) polymeric surfactants, (vi) ionomers, (vii) polymeric stabilizers, (viii) polymeric corrosion inhibitors, (xi) polymers in stone preservation, and (x) miscellaneous. Emphasis is placed upon the correlation of polymer-supported active groups into specific applications, and in particular six extensive tables list the functional polymers which have been synthesized along with the particular uses for which they have proved useful. This particular format is aimed as a convenient method of reference for those specialists already in the field, and also for chemists who might feel that a functional polymer may solve a particular problem which they might have.

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