Kirk-Othmer Encyclopedia of Chemical Technology.

POLYETHERS, AROMATIC

Aromatic polyethers are best characterized by their thermal and chemical stabilities and mechanical properties. The aromatic portion of the polyether contributes to the thermal stability and mechanical properties, and the ether functionality facilitates processing but still possesses both oxidative and thermal stability. With these characteristic properties as well as the ability to be processed as molding materials, many of the aromatic polyethers can be classified as engineering thermoplastics (see Engineering plastics).

One class of aromatic polyethers consists of polymers with only aromatic rings and ether linkages in the backbone; poly(phenylene oxide)s are examples and are the principal emphasis of this article. A second type contains a wide variety of other functional groups in the backbone, in addition to the aromatic units and ether linkages. Many of these polymers are covered in other articles, based on the other functionality (see Polymers containing sulfur, polysulfones).

1. Poly(phenylene oxide)s

The poly(phenylene oxide)s are also referred to as polyoxyphenylenes and poly(phenylene ether)s. Variations in the configuration of the ether group, ie, ortho, meta, or para, and in the extent and type of substitution, eg, alkyl, halo, etc, on the aromatic backbone give rise to a large number of possible homo- and copolymers. The polymers with para-oriented ethers have been studied most extensively and several have significant utility. Poly(2,6-dimethyl-1,4-phenylene oxide) [25134-01-4] (DMPPO), prepared by General Electric by the oxidative coupling polymerization of 2,6-dimethylphenol, is marketed as PPO resin. Blends of DMPPO with polystyrene and additives is marketed under the trade name of Noryl thermoplastic resin. Blends of DMPPO with nylon plus additives are sold as Noryl GTX resin. Other poly(phenylene oxide)s are also of commercial interest. For example, low molecular weight, unsubstituted poly(phenylene oxide)s are of use as heat-transfer fluids and liquid phases for gas chromatography. Poly(2,6-diphenyl-1,4-phenylene oxide) is sold as a gas absorbent and for gas chromatography.

Many newer poly(phenylene oxide)s have been reported in the early 1990s. For example, a number of poly(2,6-diphenyl-1,4-phenylene oxide)s were prepared with substituents in the 4-positions of the pendent phenyl groups. Of particular interest is the 4-fluoro substituent, which imparts a lower melting point, enhanced solubility, and a lesser tendency to crystallize than has been found for the parent material (1).

1.1. Physical Properties

The glass-transition temperatures and melting points of a variety of poly(1,4-phenylene oxide)s are summarized in Table 1. The very high glass-transition temperatures of DMPPO and poly(2,6-dichloro-1,4-phenylene oxide) relative to their melting points provide polymers with excellent high temperature physical properties. Crystallization of several polymers can be induced with certain liquids, eg, α-pinene, decalin, and toluene for DMPPO, and tetrachloroethane for poly(2,6-diphenyl-1,4-phenylene oxide) (2). Although DMPPO dissolves

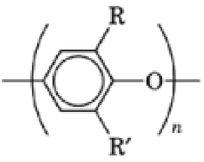


Table 1. Thermal Properties of Poly(Phenylene Oxides)s

Name	CAS Registry Number	R	R′	T_g, °C	Ref.
poly(1,4-phenylene oxide)[a]	[25667-40-7]	H	H	82	5
poly(2,6-dimethyl-1,4-phenylene oxide)[b]	[25134-01-4]	CH_3	CH_3	211	6
poly(2-methyl-6-phenyl-1,4-phenylene oxide)	[25805-39-4]	CH_3	C_6H_5	169	7
poly(2-benzyl-6-methyl-1,4-phenylene oxide)	[26545-37-9]	$C_6H_5CH_2$	CH_3	99	8
poly(2-isopropyl-6-methyl-1,4-phenylene oxide)	[31985-12-3]	$(CH_3)_2CH$	CH_3	144	9
poly(2,6-dimethoxy-1,4-phenylene oxide)	[25667-13-4]	CH_3O	CH_3O	167	10
poly(2,6-dichloro-1,4-phenylene oxide)[c]	[26023-26-7]	Cl	Cl	228	11
poly(2,6-diphenyl-1,4-phenylene oxide)[d]	[24938-68-9]	C_6H_5	C_6H_5	230	12
poly(2-*m*-tolyl-6-phenyl-1,4-phenylene oxide)	[79569-12-3]	*m*-tolyl	C_6H_5	219	13
poly(2-*p*-tolyl-6-phenyl-1,4-phenylene oxide)	[79569-09-8]	*p*-tolyl	C_6H_5	218	13
poly[2-(4-*t*-butyl)phenyl-6-phenyl-1,4-phenylene oxide]	[79569-10-1]	4-*t*-butylphenyl	C_6H_5	240	13
poly(2-naphthyl-6-phenyl-1,4-phenylene oxide)	[79569-11-2]	2-naphthyl	C_6H_5	234	13

[a] Mp = 298°C.
[b] Mp = 268°C.
[c] Mp = 269°C.
[d] Mp = 480°C.

Table 2. Properties of DMPPO[a]

Property	Value
tensile yield (at 23°C), MPa[b]	80
tensile modulus, MPa[b]	2,690
flexural strength, MPa[b]	114
flexural modulus, MPa[b]	2,590
Izod impact (notched), J/m[c]	64–96
oxygen index	28–29
density, g/cm^3	1.06
dielectric constant (at 60 Hz)	2.54
dielectric strength (thickness, 3.18 mm), V/mm	20,000

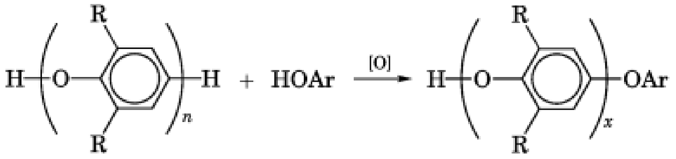
[a] Ref. 14.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J/m to ft·lb/in., divide by 53.38 (ASTM D256).

readily in methylene chloride, a complex of polymer and methylene chloride soon precipitates from the solution (3). Although precipitation of the polymer as the complex can be quantitative, the complex is unstable when separated from the liquid methylene chloride phase and dissociates rapidly to leave the pure polymer. Low molecular weight polymers with very narrow molecular weight distribution ($M_w/M_n = 1.1$) can be prepared by cooling an equilibrating mixture of low molecular weight oligomers in methylene chloride. As the molecular weights of some of the oligomers increase owing to redistribution, these oligomers reach the critical size for complexation and precipitate from solution. The molecular weight at which this occurs is approximately 2000 (4).

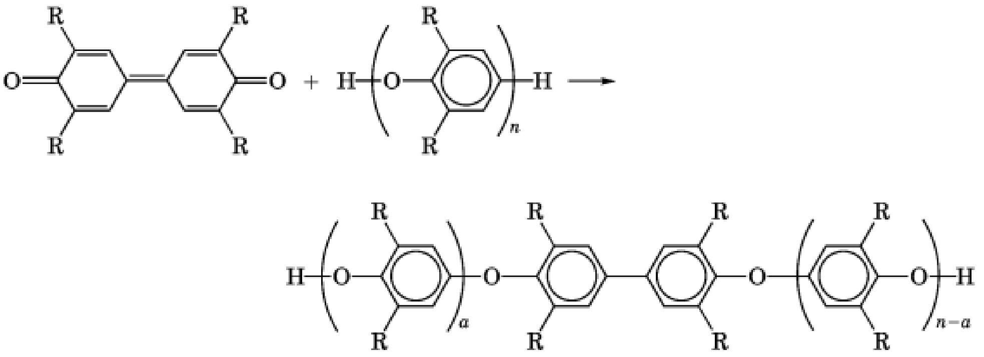
Mechanical and electrical properties for DMPPO are given in Table 2.

1.2. Chemical Properties

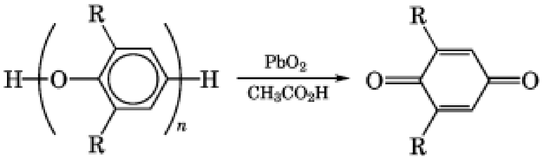
The phenolic end groups in poly(phenylene oxides)s react with oxidizing agents in a variety of ways; the type of product depends in part on other reagents that may be present. Thus, in the presence of other phenols, a catalytic amount of oxidizing agent generates aroxy radicals and the ensuing coredistribution produces low molecular weight products (eq. **1**, where $x = 1, 2, 3 \cdots$) (15). In the absence of the phenol HOAr, and with an equivalent of tetrasubstituted diphenoquinone as an oxidizing agent, biphenyl units are introduced into the polymer at the terminal position and then, through redistribution, internally (16) (eq. **2**, where $a = 0, 1, 2, 3$, etc). Under acidic conditions with excess oxidizing agent, benzoquinones are generated (eq. **3**) (17).



(1)



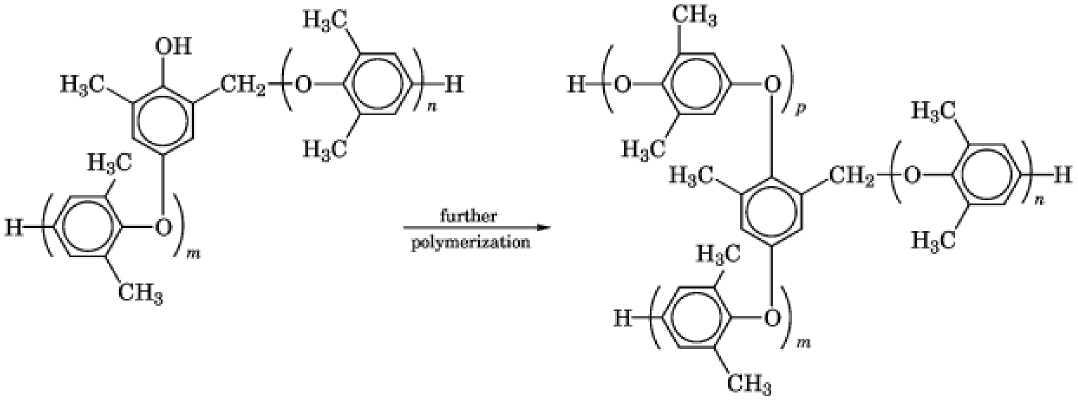
(2)



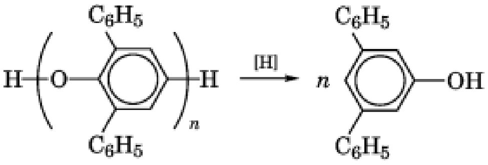
(3)

The preceding reactions do not occur if the terminal hydroxyl group in the polymer is no longer present, eg, if it has been end-capped by acetylation.

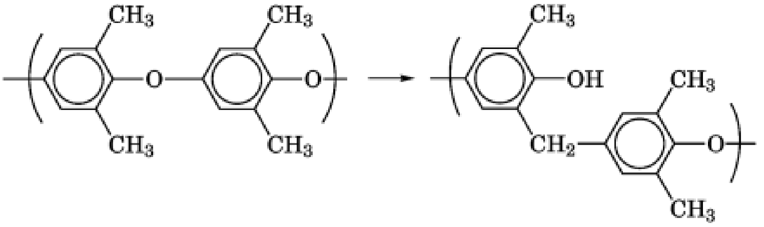
Side reactions during polymerization can lead to abnormal end-group formation and branching. For example, when secondary amines are present during a copper-catalyzed polymerization, they are often covalently bound to the methyl group of a head end group (18). With a manganese catalyst system, secondary amines are bound to the polymer analogously if they are present, but if they are absent polymer chains are bound at this site through the oxygen of a head end group to form a benzyl ether linkage. Additional polymerization attaches more units to produce a branched molecule (19), as follows.



The backbone of poly(phenylene oxide)s is cleaved under certain extreme reaction conditions. Lithium biphenyl reduces DMPPO to low molecular weight products in the dimer and trimer molecular weight range (20) and converts poly(2,6-diphenyl-1,4-phenylene oxide) to 3,5-diphenylphenol in 85% yield (21) (eq. **4**).


(4)

At temperatures near 370°C, DMPPO undergoes a rearrangement (eq. **5**).


(5)

This appears from model studies to be a radical-chain process (22). Abstraction of a hydrogen from a methyl group, followed by migration of the adjacent phenyl group, generates a phenoxy radical that continues the chain process by abstracting a hydrogen from another methyl group.

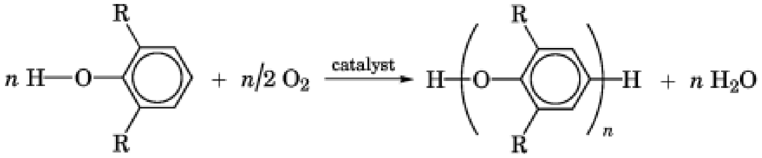
Ultraviolet radiation causes cleavage of the aryl ether linkage (23). DMPPO undergoes oxidation when exposed to ultraviolet light and oxygen by direct attack on the aromatic ring to produce a variety of ring-cleaved and quinoidal structures (24).

Poly(phenylene oxide)s undergo many substitution reactions (25). Reactions involving the aromatic rings and the methyl groups of DMPPO include bromination (26), displacement of the resultant bromine with phosphorus or amines (27), lithiation (28), and maleic anhydride grafting (29). Additional reactions at the open 3-position on the ring include nitration, alkylation (30), and amidation with isocyanates (31).

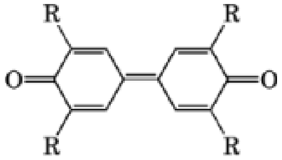
1.3. Synthesis

1.3.1. Oxidative Coupling

Many poly(1,4-phenylene oxide)s have been prepared in a one-step polymerization of 2,6-disubstituted phenols by oxidative coupling (32). The scope and mechanism of polymerization has been studied in detail by many investigators (33). For the preparation of DMPPO, oxygen is passed through a vigorously stirred solution of 2,6-dimethylphenol and a catalyst at ca 25–50°C. A typical catalyst is composed of a copper halide and one or more aliphatic amines or pyridine. If the catalyst is susceptible to hydrolysis, a desiccant, eg, anhydrous magnesium sulfate, is added to remove the water coproduct. With an amine such as dibutylamine, the drying agent is not required. The polymerization is exothermic and often requires cooling to maintain catalytic activity and attain a high molecular weight product. Catalysts based on manganese and cobalt salts also are effective (34). Noncatalytic oxidizing agents, eg, silver oxide, lead dioxide, and manganese dioxide, when used in excess of the stoichiometric amount, also polymerize many 2,6-disubstituted phenols (35).



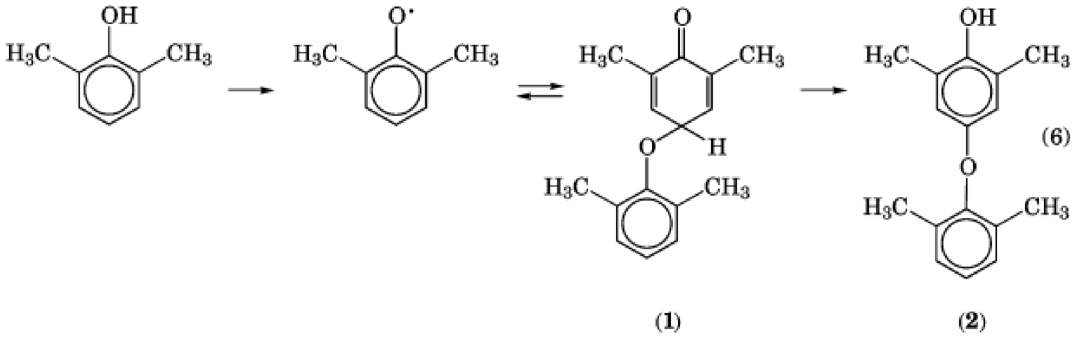
Oxidative coupling polymerizations represent a general reaction for the preparation of high molecular weight linear polymers from many 2,6-di- and 2,3,6-trisubstituted phenols. When the ortho substituents on the phenols are relatively unhindered alkyl or aryl groups, the poly(phenylene oxide) is the chief product (36, 37). Bulky ortho substituents, eg, *tert*-butyl, lead to the formation of the 3,3′,5,5′-tetrasubstituted 4,4′-diphenoquinone (36).



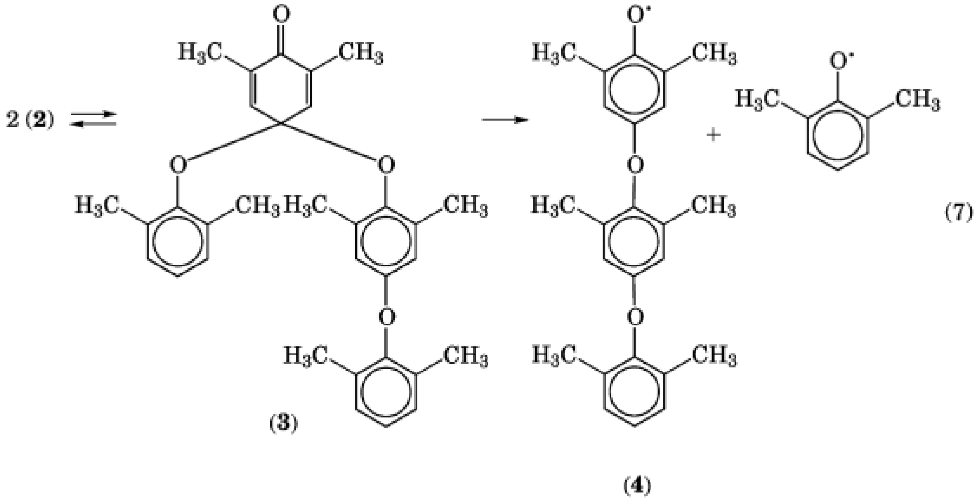
Significant quantities of the diphenoquinone are also produced if the ortho substituents are methoxy groups (36). Phenols with less than two ortho substituents produce branched and colored products from the reactions that occur at the open ortho sites. It is possible to minimize such side reactions in the case of *o*-cresol oxidation by using a bulky ligand on the copper catalyst to block the open ortho position (38).

The selectivity of the oxidation of 2,6-disubstituted phenols depends on the type of oxidizing agent. For example, with a series of cobalt-containing catalysts of the salcomine type, oxidation of 2,6-dimethylphenol produces three products: the poly(phenylene oxide), the diphenoquinone, and 2,6-dimethylbenzoquinone. The product ratio changes with variation in the nature of the ligands (39). The formation of the benzoquinone suggests that ionic processes as well as free-radical reactions take place. Oxidations with reagents that proceed mainly through ionic pathways produce such nonpolymeric products as benzoquinones and cyclohexadienones. Thus, 2,6-dimethylbenzoquinone and its 3-substituted derivatives form when 2,6-dimethylphenol is oxidized with peracids or metal-catalyzed hydrogen peroxide, whereas dimers of 6-hydroxy-2,6-dimethyl-2,4-cyclohexadien-1-one are produced from periodate oxidations (40).

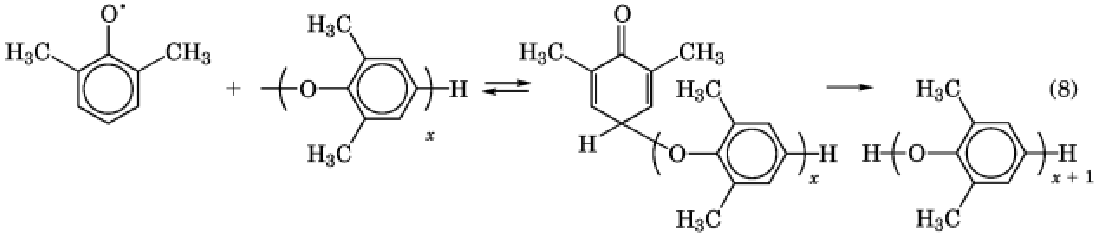
1.3.1.1. Polymerization Mechanism. The mechanism that accounts for the experimental observations of oxidative coupling of 2,6-disubstituted phenols involves an initial formation of aryloxy radicals from oxidation of the phenol with the oxidized form of the copper–amine complex or other catalytic agent. The aryloxy radicals couple to form cyclohexadienones, which undergo enolization and redistribution steps (32). The initial steps of the polymerization scheme for 2,6-dimethylphenol are as in equation **6**.



In equation **6**, the dimer (**2**) is formed by enolization of the quinol ether (**1**). Oxidation of the dimer produces the dimer radical, which can couple with other radicals that are present. If it couples with a 2,6-dimethylphenoxy radical to form a quinol ether, enolization can produce the trimer in a reaction analogous to equation **6**. Similarly, oxidation of the trimer followed by coupling with a 2,6-dimethylphenoxy radical and enolization produces tetramer. By this process, each oligomeric product can form the next higher oligomer, and eventually high molecular weights are attained. However, the polymerization does not proceed only by addition of one unit at a time to the growing chain, because coupling also can occur between other combinations of oligomers. Thus, this is a step-growth polymerization rather than a chain-growth polymerization. As an example, dimer radical also can couple with another dimer radical to form a quinone ketal (**3**) (eq. **7**) or with a larger oligomeric radical to form an analogous ketal. The reaction proceeds further by dissociation of the ketal to form new oligomeric radicals.

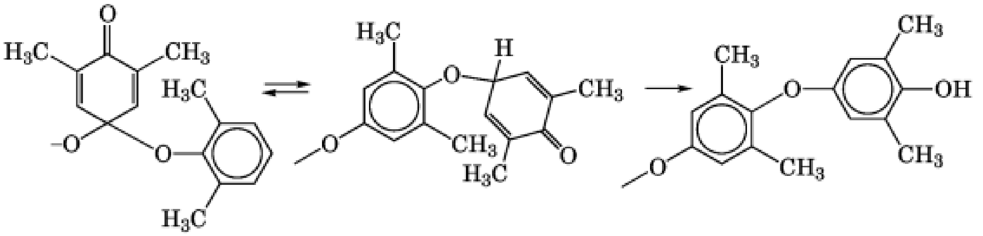


In equation **7**, trimer radical (**4**) is produced when (**3**) dissociates. Whenever (**4**) couples with the other product of equation **7**, ie, the 2,6-dimethylphenoxy radical, the tetramer is produced as described. These redistribution reactions of oligomers that proceed by ketal formation and subsequent dissociation ultimately generate terminal quinol ethers which enolize to the more stable terminal phenol (eq. **8**).


(8)

The enolization aids the attainment of high molecular weights by providing the driving force for the coupling of two oligomeric radicals to form a phenol-terminated oligomer of higher molecular weight, and by generating a phenolic group that can be oxidized to generate a new aryloxy radical which can enter the redistribution–enolization scheme. The overall effect of this combination of oxidation, radical coupling, dissociation, and enolization is to increase the average molecular weight.

A second process that occurs concurrently with the dissociation– redistribution process is an intermolecular rearrangement by which cyclohexadienone groups move along a polymer chain. The reaction may be represented as two electrocyclic reactions analogous to a double Fries rearrangement. When the cyclohexadienone reaches a terminal position, the intermediate is the same as in equation **8**, and enolization converts it to the phenol (eq. **9**).

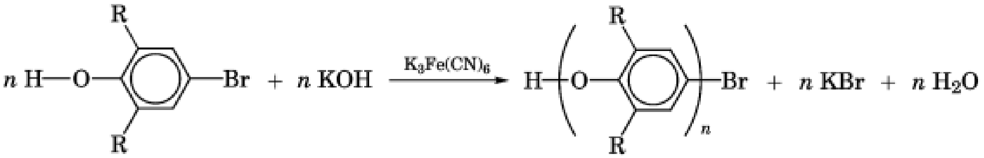

(9)

This process, which predominates at low temperatures, causes migration of internal ketal structures along a chain but does not involve the dissociation to separate aryloxy radicals that occurs during the redistribution process.

Considerable evidence supports these routes and rules out several alternative mechanisms (15, 41–47).

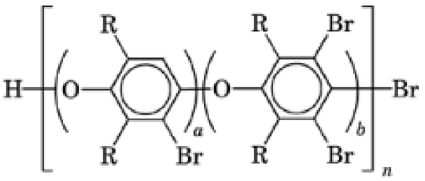
1.3.2. Halogen Displacement

Poly(phenylene oxide)s can also be prepared from 4-halo-2,6-disubstituted phenols by displacement of the halogen to form the ether linkage (48). A trace of an oxidizing agent or free radical initiates the displacement reaction. With 4-bromo-2,6-dimethylphenol, the reaction can be represented as in equation **10**:

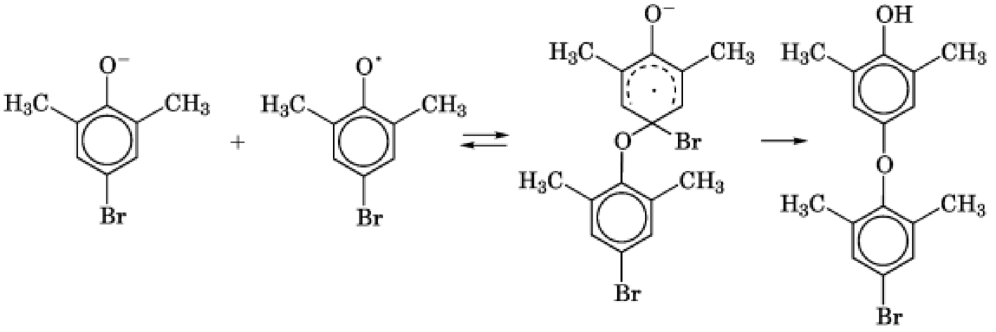

(10)

High molecular weight DMPPO is formed in high yield at room temperature. The reaction is applicable to certain 2,3,5-tri- and 2,3,5,6-tetrasubstituted-4-halophenols. When such compounds have halogens in the 3,4- or 3,4,5-positions only the one in the 4-position is displaced. When a mixture of 3,4-dibromo-2,6-dimethylphenol and 3,4,5-tribromo-2,6-dimethylphenol is polymerized, a random copolymer is formed, where $b = 1, 2$, etc

(49). The two homopolymers from polymerization of these phenols by themselves are sufficiently insoluble in halogenated and aromatic solvents that they precipitate from the reaction mixture with low molecular weight. The copolymer made from an equimolar mixture of the two monomers is soluble and can be prepared with high molecular weight.

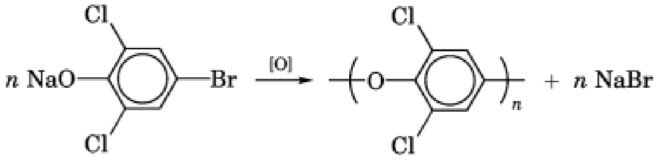


The halogen displacement polymerization proceeds by a combination of the redistribution steps described for oxidative coupling polymerization and a sequence in which a phenoxide ion couples with a phenoxy radical (eq. **11**) and then expels a bromide ion. The resultant phenoxy radical can couple with another phenoxide in a manner that is analogous to equation **11** or it can redistribute with other aryloxy radicals in a process analogous to equations **7** and **8**.

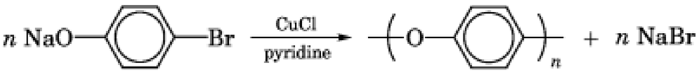


(11)

2,4,6-Trihalophenols can be converted to poly(dihalophenylene oxide)s by a reaction that resembles radical-initiated displacement polymerization. In one procedure, either a copper or silver complex of the phenol is heated to produce a branched product (50). In another procedure, a catalytic quantity of an oxidizing agent and the dry sodium salt in dimethyl sulfoxide produces linear poly(2,6-dichloro-1,4-polyphenylene oxide) (51). The polymer can also be prepared by direct oxidation with a copper–amine catalyst, although branching in the ortho positions is indicated by chlorine analyses (52).



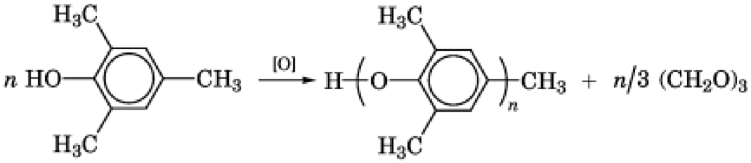
4-Halophenols without 2,6-disubstitution do not polymerize under oxidative displacement conditions. Oxidative side reactions at the ortho position may consume the initiator or interrupt the propagation step of the chain process. To prepare poly(phenylene oxide)s from unsubstituted 4-halophenols, it is necessary to employ the more drastic conditions of the Ullmann ether synthesis. A cuprous chloride–pyridine complex in 1,4-dimethoxybenzene at 200°C converts the sodium salt of 4-bromophenol to poly(phenylene oxide) (1):



Low molecular weight poly(1,3-phenylene oxide) [25190-64-1] has been prepared from the sodium salt of *m*-chlorophenol with copper as a catalyst (53).

1.3.3. 2,4,6-Trimethylphenol Polymerization

An unusual aspect of the oxidative coupling of substituted phenols is the formation of DMPPO from 2,4,6-trimethylphenol. Oxidative cleavage of the 4-methyl group produces paraformaldehyde and relatively low molecular weight ($M_n = 1000 - 3000$) DMPPO with manganese dioxide (54). DMPPO can also be prepared from 2,4,6-trimethylphenol with oxygen as the oxidizing agent and a catalytic amount of copper halide and an amine (55).



1.3.4. Copolymers

Copolymers of poly(phenylene oxide)s can be prepared in several ways. Oxidative coupling of mixtures of phenols, eg, combinations of 2,6-dimethylphenol, and 2-methyl-6-phenylphenol usually provide random copolymers. With a pair of phenols that have different oxidation potentials or that coredistribute at different rates, such as a mixture of 2,6-dimethylphenol and 2,6-diphenylphenol, block copolymers can form (56). Another route is the oxidation of mixed dimers which forms random copolymers (57). Copolymers can also be produced by allowing only some of the rings to undergo reaction in a substitution reaction, eg, bromination of only a fraction of the aromatic rings in DMPPO converts normal units to 3-bromo units (26). Block copolymers have been prepared by condensing the phenolic end groups of DMPPO with other polymers bearing reactive leaving groups on their end groups. For example, block copolymers were formed from aromatic polyesters with α,ω-bis(chloroformyl) end groups by using a phase-transfer catalyst and sodium hydroxide to effect the displacement of the halogen (58). These reactions can be carried out with high yields, thereby enabling the formation of ABA types of block copolymers. In the case of low molecular weight di- or triacyl halides, coupled linear or branched polymers with double or triple the original molecular weight are formed.

1.4. Polyether Blends

DMPPO and polystyrene form compatible blends. The two components are miscible in all proportions (59). Reported dynamic–mechanical results that indicate the presence of two phases in some blends apparently are caused by incomplete mixing (60). Transition behavior of thoroughly mixed blends indicates that the polymers are truly compatible on a segmental level (61). Compatibility may be attributed to a $\pi - \pi$ interaction between the aromatic rings of the two polymers sufficient to produce a negative heat of mixing. However, the forces are very small, ie, ΔH_{mix} = ca40 J/mol (9.6 cal/g), and any change in the substitution pattern of either polymer usually makes them incompatible (62). Tensile strength and modulus of blends of DMPPO and crystal polystyrene reach a maximum with a composition containing about 80 wt % DMPPO, but most properties of blends are close to the weighted average for the two polymers (63). Blends with rubber-modified polystyrene, ie, high impact polystyrene (HIPS), also have intermediate property values, but the ductile PPO matrix is toughened more effectively by rubber than is the brittle polystyrene. Therefore, blends of DMPPO with HIPS have much higher impact strength than either material alone (64). This characteristic makes it possible to prepare a family of tough plastics or modified poly(phenylene oxide)s in which some of the high temperature capability of the DMPPO is combined with the easy processibility of polystyrene.

Blends with good mechanical properties can be made from DMPPO and polymers with which DMPPO is incompatible if an appropriate additive, compatibilizing agent, or treatment is used to increase the dispersion of the two phases. Such blends include mixtures of DMPPO with nylon, polycarbonate, polyester, ABS, and poly(phenylene sulfide).

Sulfonation has been used to change some characteristics of blends. Poly(2,6-diphenyl-1,4-phenylene oxide) and polystyrene are immiscible. However, when the polymers were functionalized by sulfonation, even though they remained immiscible when blended, the functionalization increased interfacial interactions and resulted in improved properties (65). In the case of DMPPO and poly(ethyl acrylate) the originally immiscible blends showed increased miscibility with sulfonation (66).

Blends have also been prepared by dissolving DMPPO in a monomer and then polymerizing the monomer. An example is an epoxy–DMPPO blend prepared by curing a solution of DMPPO in Epon 828 at 85°C with an aluminum–tetramethylguanidine catalyst. Some copolymer formation is observed. The solutions can be applied to glass cloth before curing to produce prepregs for composites in applications such as printed circuit boards (67).

Interpenetrating networks of DMPPO and polymers such as polystyrene, polybutadiene, poly(urethane acrylate), and poly(methyl methacrylate) have been prepared by cross-linking solutions of DMPPO containing bromomethyl groups with ethylenediamine in the presence of the other polymer (68).

1.4.1. Noryl

Noryl engineering thermoplastics are polymer blends formed by melt-blending DMPPO and HIPS or other polymers such as nylon with proprietary stabilizers, flame retardants, impact modifiers, and other additives (69). Because the rubber characteristics that are required for optimum performance in DMPPO–polystyrene blends are not the same as for polystyrene alone, most of the HIPS that is used in DMPPO blends is designed specifically for this use (70). Noryl is produced as sheet and for vacuum forming, but by far the greatest use is in pellets for injection molding.

Noryl is a rigid dimensionally stable material. Dimensional stability results from a combination of low mold shrinkage, low coefficient of thermal expansion (5.9×10^{-5} per°C), good creep resistance (0.6–0.8% in 300 h at 13.8 MPa (2000 psi)), and the lowest water absorption rate of any of the engineering thermoplastics (0.07% in 24 h at room temperature). Noryl resins are completely stable to hydrolysis. They are not affected by aqueous acids or bases and have good resistance to some organic solvents, but they are attacked by aromatic or chlorinated aliphatic compounds.

Noryl has good impact strength in unfilled grades: Gardner impact strength of 200 to $>$400 J ($150 - 300$ ft·lbf), and notched Izod 0.27–0.53 J/mm ($5 - 10$ ftlb·f/in) at room temperature and 0.13 J/mm (2.5 ftlb·f/in.) at 140°C. Other mechanical properties are typical of amorphous engineering thermoplastics: tensile strength 50–70 MPa (8,000–11,000 psi), flexural strength 60–100 MPa (8,000–15,000 psi), and flexural modulus ca 2500 MPa (350,000 psi). Glass- or mineral-filled products have flexural moduli as high as 7600 MPa (1.1×10^6 psi). Dielectric properties are good: dielectric constant is 2.64, dielectric strength is 22 kV/mm at a thickness of 3.18 mm, and it is insensitive to changes in temperature or humidity and to frequencies of $60–10^6$ Hz.

DMPPO–polystyrene blends, because of the inherent flame resistance of the DMPPO component (oxygen index ca 29.5), can be made flame retardant without the use of halogenated additives that tend to lower impact strength and melt stability in other polymers. Approximately one-half of total Noryl sales volume is in flame-retarded grades, ie, V0 or V1 in a 1.6-mm section (UL-94).

Properties of DMPPO–polystyrene blends, especially flammability, deflection temperature under load (DTUL) (ASTM D648), and melt viscosity, can be varied over a wide range by changing the ratio of DMPPO to HIPS, the amount and type of additives, and the characteristics of the HIPS. Noryl originally was introduced to fill a price–performance gap between ABS and polycarbonate, but the property range has been extended steadily and 50 standard grades are available with heat-distortion temperatures of 88–150°C; these include products specially designed for foaming, profile extrusion, and electroplating. In addition to the regular grades, approximately equal numbers of special products are available and each is designed primarily for a single application, eg, an easy-flow V0 product for television cabinets, a high heat Noryl for electrical connectors and food packaging for microwave reheating, Noryl GTX blends for automobile parts, etc.

Principal application areas are in water distribution, electrical–electronic applications, business machines, and automobiles. Water distribution applications include pump housings, impellers and filters, shower heads, faucets, valve handles, and other plumbing fixtures. Among the applications in the electrical–electronic areas are cabinets and internal television and radio parts, lighting fixtures, connectors, junction boxes, wiring ducts, cable covers, protective devices, and motor housings. Noryl is used in many small appliances and personal care products, especially those involving exposure to heat and moisture (food processors, hair dryers, steam irons, hot combs, etc) and in console and decorative trim in dryers, washing machines, and other large appliances. Frames, bases and supports for copiers, display stations, computers, typewriters, printers, and other business machines are commonly made of Noryl. The low temperature impact strength of Noryl and Noryl GTX contribute to its use in a variety of external automotive applications (wheel covers, grilles, fenders, mirror housings steering-column shrouds), instrument panels, electrical connectors, and filler panels.

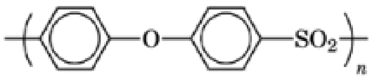
General Electric is the only U.S. producer of Noryl resin and also has facilities in Japan and Europe. DMPPO is also produced in Japan by Ashahi, Mitsubishi Gas Chemical, and Sumitomo.

1.4.2. Health and Safety Factors

Animal-feeding studies of DMPPO itself have shown it to be nontoxic on ingestion. The solvents, catalyst, and monomers that are used to prepare the polymers, however, should be handled with caution. For example, for the preparation of DMPPO, the amines used as part of the catalyst are flammable; toxic on ingestion, absorption, and inhalation; and are also severe skin and respiratory irritants (see Amines). Toluene, a solvent for DMPPO, is not a highly toxic material in inhalation testing; the TLV (71) is set at 375 mg/m^3, and the lowest toxic concentration is reported to be 100–200 ppm (72). Toxicity of 2,6-dimethylphenol is typical of alkylphenols (qv), eg, for mice, the acute dermal toxicity is LD$_{50}$, 4000 mg/kg, whereas the acute oral toxicity is LD$_{50}$, 980 mg/kg (73). The Noryl blends of DMPPO and polystyrene have FDA approval for reuse food applications.

2. Polyethersulfones

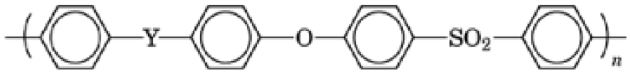
The aromatic sulfone polymers are a group of high performance plastics, many of which have relatively closely related structures and similar properties (see Polymers containing sulfur, polysulfones). Chemically, all are polyethersulfones, ie, they have both aryl ether (ArOAr) and aryl sulfone (ArSO$_2$Ar) linkages in the polymer backbone. The simplest polyethersulfone (**5**) consists of aromatic rings linked alternately by ether and sulfone groups.



(**5**)

2.1. Effect of Structure on Properties

The effect of structure on chain flexibility in the series of polymers having the following common structure has been studied by varying the linking group Y (74). The glass-transition temperature changes in a predictable manner with the nature of Y. For example, when Y is a flexible ether, thio, or methylene group, the glass-transition temperature is ca 180°C. Replacement of the hydrogens of the methylene group by alkyl or aryl groups decreases the flexibility and increases the glass-transition temperature; the larger the substituent, the higher the value of T_g. Polar groups, eg, carbonyl and sulfonyl, that are capable of conjugation with the aromatic ring increase the glass-transition temperature, eg, to 245°C for the sulfonyl group, as in (**5**).



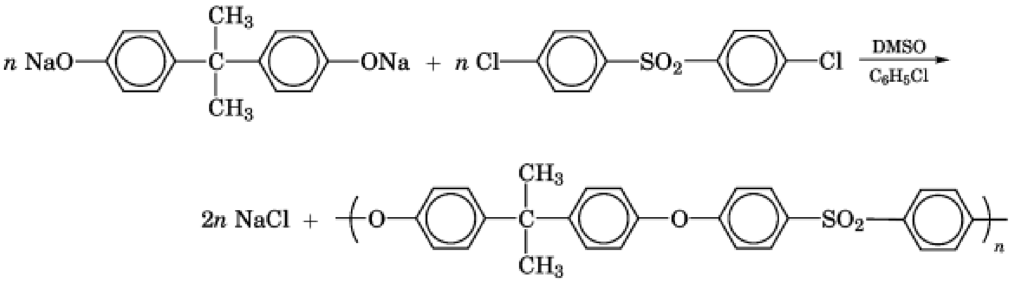
2.2. Synthesis

Aromatic polyethersulfones can be prepared by two different routes. In polyetherification, the sulfone group is present in one of the monomers and the ether linkage is formed in the polymerization step. In polysulfonation, the alternative approach is used and the aryl ethers are coupled through a reaction that forms the sulfone linkage. Both processes have been developed commercially. Unlike oxidative coupling polymerization, the mechanisms of both reactions are relatively straightforward, ie, both are polycondensations corresponding to types of reactions that are well-established in organic chemistry. In general, the two processes are used to produce different types of polymers but some structures, including the basic structure (**5**), are available by either route. Polyetherification and polysulfonation have been reviewed extensively (74, 75).

2.2.1. Polyetherification

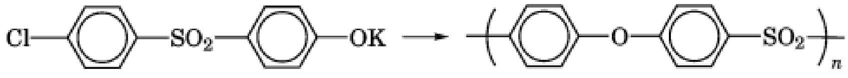
Aromatic polyethersulfones are formed by reaction of the salts of dihydroxyaromatic compounds with di(haloaryl)sulfones. Reactions of this type, ie, nucleophilic aromatic displacement of halogen in aromatic compounds activated by sulfonyl or other strongly electron-withdrawing groups, are familiar in organic chemistry, but successful application to formation of high molecular weight polymers depends on the accelerating effects of certain dipolar aprotic solvents, which are believed to solvate the cations selectively, thus increasing the reactivity of the phenolate anions. The polar compounds must be stable under the conditions of the reaction and be capable of dissolving both the reactants and the polymer. Dimethyl sulfoxide (DMSO) is commonly employed, and other solvents, eg, tetramethylene sulfone (sulfolane), sometimes are useful when high temperatures are required (74).

The first aromatic sulfone polymer produced commercially was introduced as Bakelite polysulfone but now is sold by Union Carbide under the trade name Udel. It is made by reaction of the disodium salt of bisphenol A (BPA) with 4,4′-dichlorodiphenyl sulfone in a mixed solvent of chlorobenzene and dimethyl sulfoxide (eq. **12**).



(12)

Polyetherification is similar to a polycondensation process: formation of high molecular weight polymer requires precise adjustment of composition to approximately 1:1 ratio of bisphenol to dihalosulfone. Trace amounts of water greatly reduce the molecular weight attainable owing to side reactions that unbalance the stoichiometry (76). The reactivity of the halosulfone is in the order expected for two-step nucleophilic aromatic displacement reactions: $F > Cl > Br$. In addition to being the most reactive of the halides, fluorosulfones are the least affected by traces of water. For economic reasons, only the chlorosulfone is used commercially. The reactivity of bisphenols in polyetherification decreases with increasing acidity of the phenol, but aromatic polyethersulfones can be prepared from almost all dihydric phenols under sufficiently vigorous conditions. The hydroxyl group and the active halogen can be combined in the same molecule; for example, (**5**) is produced by the self-condensation of 4-chlorophenyl-4′-hydroxyphenyl sulfone (77). The dichlorosulfone in equation **12** may be replaced by other dihalogen compounds having strongly electron-withdrawing groups ortho or para to the halogens, such as carbonyl, azo, sulfamido, and nitro groups (78).



(**5**)

2.2.2. Copolymers

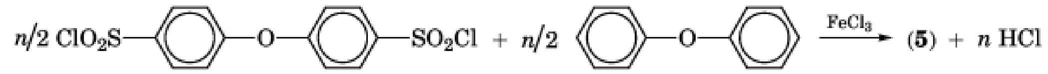
Copolymers from mixtures of different bisphenols or from mixtures of dichlorosulfone and dichlorobenzophenone have been reported in the patent literature. Bifunctional hydroxyl-terminated polyethersulfone oligomers are prepared readily by the polyetherification reaction simply by providing a suitable excess of the bisphenol. Block copolymers are obtained by reaction of the oligomers with other polymers having end groups capable of reacting with the phenol. Multiblock copolymers of BPA-polysulfone with polysiloxane have been made in this way by reaction with dimethylamino-terminated polydimethylsiloxane; the products are effective impact modifiers for the polyethersulfone (79). Block copolymers with nylon-6 are obtained when chlorine-terminated oligomers, which are prepared by polyetherification with excess dihalosulfone, are used as initiators for polymerization of caprolactam (80).

2.2.3. Polysulfonylation

The polysulfonylation route to aromatic sulfone polymers was developed independently by Minnesota Mining and Manufacturing (3M) and by Imperial Chemical Industries (ICI) at about the same time (81). In the polymerization step, sulfone links are formed by reaction of an aromatic sulfonyl chloride with a second aromatic ring. The reaction is similar to the Friedel-Crafts acylation reaction. The key to development of sulfonylation as a polymerization process was the discovery that, unlike the acylation reaction which requires equimolar amounts of aluminum chloride or other strong Lewis acids, sulfonylation can be accomplished with only catalytic amounts of certain halides, eg, $FeCl_3$, $SbCl_5$, and $InCl_3$. The reaction is a typical electrophilic substitution by an arylsulfonium cation (eq. 13).

$$ArSO_2Cl + MCl_n \rightleftarrows ArSO_2^+M\,(Cl)_{n+1} \xrightarrow[-MCl_n]{Ar'H} ArSO_2Ar' + HCl \qquad (13)$$

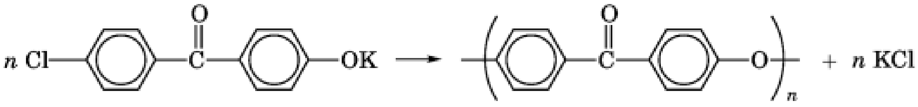
Reaction of bis(sulfonyl chloride)s with diaryl ether produces polyethersulfones. For example, condensation of diphenyl ether with the disulfonylchloride of diphenyl ether yields polyethersulfone (**5**):



The reaction is carried out either in the melt or in a suitable inert solvent such as acetonitrile; ferric chloride is a preferred catalyst. Successful application of the polysulfonylation reaction to polymer synthesis requires a high degree of para coupling. Chain branching or any substantial degree of ortho coupling without branching results in brittle products. Specificity is improved if the sulfonyl group and the reactive ring are in the same molecule. The process described results in 10–20% of ortho coupling, but self-coupling of the monosulfonyl chloride is without detectable ortho coupling and the product is identical with that obtained by polyetherification. The polysulfonylation reaction is not limited to aryl ethers; it can be applied to most compounds having two or more independent aromatic rings, eg, biphenyl, terphenyl, and naphthalene, but the products are not polyethersulfones unless at least one of the reactants contains the ether linkage. Copolymers of (**5**) in which some of the diphenyl ether units are replaced by other groups are readily available by the sulfonation reaction. Incorporation of rigid biphenyl units by copolymerization of the sulfonyl chlorides of biphenyl and diphenyl ether increases the glass-transition temperature of the polyethersulfones; the Astrel polyethersulfones are of this type (82).

3. Polyetherketones

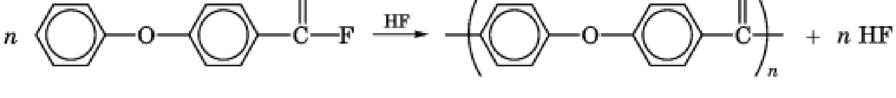
The polyetherification route to polyethersulfones can be adapted to the synthesis of polyethers containing strongly electron-withdrawing groups other than sulfone groups. Poly(1,4-oxyphenylenecarbonyl-1,4-phenylene) [27380-27-4] (**6**) is produced by condensation of 4,4′-dihydroxybenzophenone or by the self-condensation of 4-chloro-4′-hydroxybenzophenone. It has a melting point of 367°C and a glass-transition temperature of 154°C (83).



(**6**)

A polyetheretherketone (PEEK) (**7**) was introduced by Imperial Chemical Industries on a developmental scale in 1978. It is crystalline with a melting point of 334°C and a glass-transition temperature of ca 145°C (84). PEEK can be molded and is used in applications such as liquid chromatography fittings. It is also used for coatings, in electrical insulation for high temperature service, and in composites. Care must be taken on molding composites since the surface of the mold can affect the surface properties of the composite (85). Differential scanning calorimetry and microscopic techniques have been used to determine the morphology of molded PEEK graphite composites (86).

Stilan 1000, introduced by RayChem in 1974 and later withdrawn, is a polyetherketone made by a different route:



Cyclic aryl ether ketones have been prepared from 1,2-bis(4-fluorobenzoyl)benzene and bisphenols under pseudo high dilution conditions. These materials undergo ring-opening polymerization in the presence of an anionic catalyst (87).

Table 3. Selected Properties of Kapton[a]

Property	Value
CAS Registry Number	[25036-53-7]
heat deflection temperature, °C	360
tensile yield (at 23°C), MPa[b]	86
tensile modulus, MPa[b]	3110
flexural strength, MPa[b]	131
flexural modulus, MPa[b]	3110
oxygen index	36.5
density, g/cm^3	1.43
dielectric strength, V/m	58

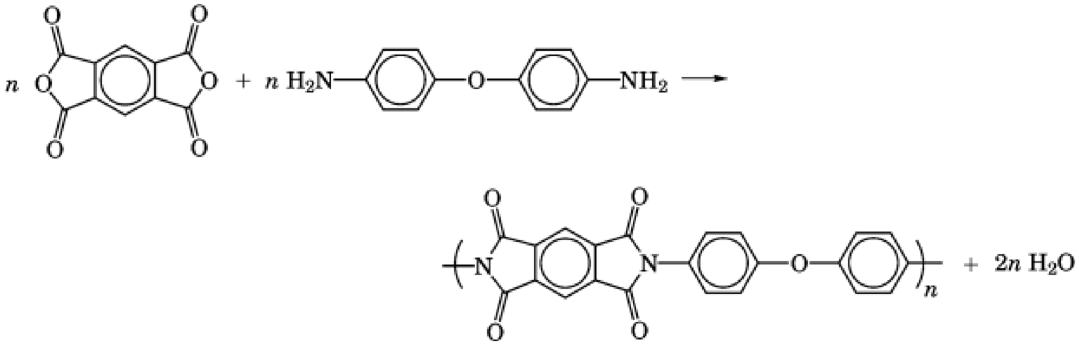
[a] Ref. 83.

[b] To convert MPa to psi, multiply by 145.

4. Polyetherimides

A variety of polyetherimides have been described in reviews on polyimides (qv) (88). Many more recent materials have additional heterocyclic units such as quinoxaline and benzimidazole units, besides the ether and imide functionalities (89).

An all aromatic polyetherimide is made by Du Pont from reaction of pyromellitic dianhydride and 4,4′-oxydianiline and is sold as Kapton. It possesses excellent thermal stability, mechanical characteristics, and electrical properties, as indicated in Table 3. The high heat-deflection temperature of the resin limits its processibility. Kapton is available as general-purpose film and used in applications such as washers and gaskets. Often the resin is not used directly; rather, the more tractable polyamide acid intermediate is applied in solution to a surface and then is thermally imidized as the solvent evaporates.



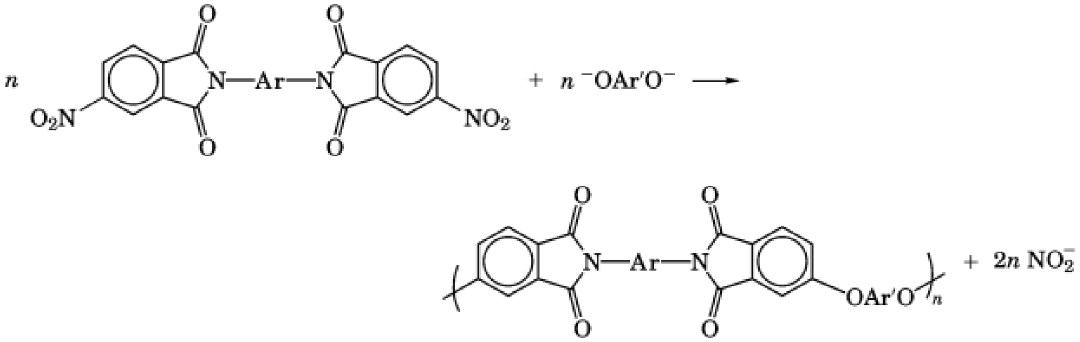
Not all polyetherimides are limited by their tractability, however. Certain aromatic polyetherimides are characterized by a combination of properties that makes them potential engineering thermoplastics (90). One of these polymers contains an isopropylidene unit in the backbone to enhance the solubility. It is a molding material introduced by General Electric in 1981 and sold as Ultem resin. Attractive features include high temperature stability, flame resistance without added halogen or phosphorus, high strength, solvent resistance, hydrolytic stability, and injection moldability.

4.1. Syntheses

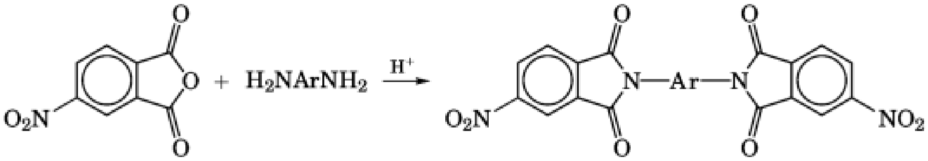
The presence of the ether and imide functionalities provides two general approaches for synthesis. Polyetherimides can be prepared by a nucleophilic displacement polymerization similar to the halide displacement in polysulfone synthesis or by a condensation of dianhydrides and diamines that is similar to normal polyimide synthesis (see Polyimides).

4.1.1. Nitro-Displacement Polymerization

The facile nucleophilic displacement of a nitro group on a phthalimide by an oxyanion has been used to prepare polyetherimides by heating bisphenoxides with bisnitrophthalimides (91). For example with 4,4′-dinitro monomers, a polymer with the Ultem backbone is prepared as follows (92). Because of the high reactivity of the nitro phthalimides, the polymerization can be carried out at temperatures below 75°C. Relative reactivities are nitro compounds over halogens, *N*-aryl imides over *N*-alkyl imides, and 3-substituents over 4-substituents. Solvents are usually dipolar aprotic liquids such as dimethyl sulfoxide, and sometimes an aromatic liquid is used, in addition.

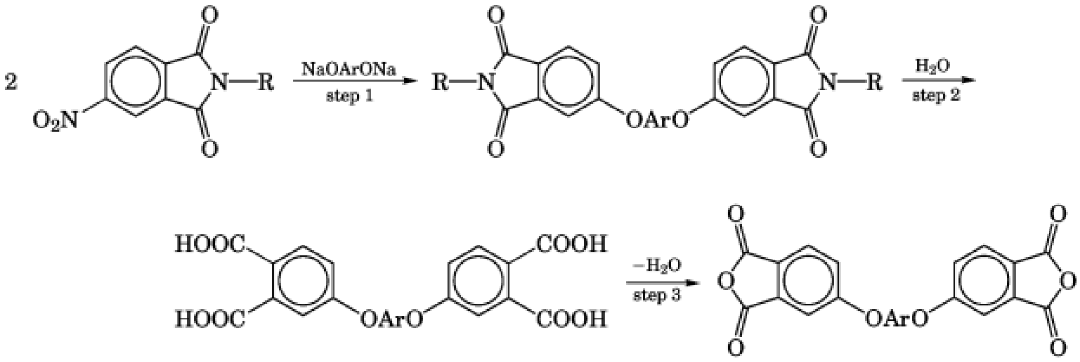


Bisnitrophthalimides can be prepared in high yields and high purity from nitrophthalic anhydrides and diamines under acidic conditions (93).



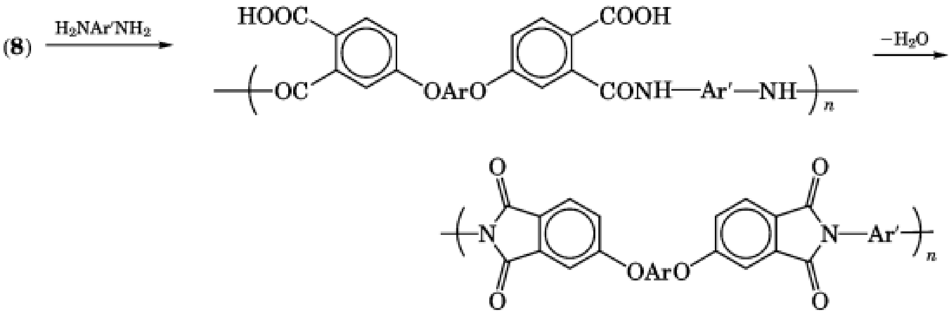
4.1.2. Condensation of Dianhydrides with Diamines

The preparation of polyetherimides by the reaction of a diamine with a dianhydride has advantages over nitro-displacement polymerization: sodium nitrite is not a by-product and thus does not have to be removed from the polymer, and a dipolar aprotic solvent is not required, which makes solvent-free melt polymerization a possibility. Aromatic dianhydride monomers (**8**) can be prepared from *N*-substituted nitrophthalimides by a three-step sequence that utilizes the nitro-displacement reaction in the first step, followed by hydrolysis and then ring closure. For the 4-nitro compounds, the procedure is as follows.



(8)

Polymerization of the dianhydride and diamine proceeds through an intermediate poly(amide acid) stage before ring closure converts the adjacent acid and amide groups to the polyetherimide (94). The polymerization can be carried directly to the polyetherimide as a single-step process, or first to an amide–acid-containing prepolymer, which can be isolated, and then to the polyetherimide.



4.2. Properties

The mechanical properties and oxygen index of Ultem polyetherimide are listed in Table 4. In flammability testing, the oxygen index of many polyetherimides is high and they are self-extinguishing (V-0), nondripping, and generate little smoke (95). Many polyetherimides with additional chemical functional groups have been reported. Such materials and a variety of polyetherheterocyclics have received only limited commercial attention.

Ultem polyetherimides have applications in areas where high strength, dimensional stability, creep resistance, and chemical stability at elevated temperatures are important. Uses include electrical connectors, wave guides and printed circuit boards for electronic equipment, food applications (microwaveable containers, utensils, and films), aircraft interior materials, and sterilizable medical equipment.

A large variety of newer poly(ether imide)s has been described. Included among these are perfluorinated polymers (96), poly(ester ether imide)s (97), poly(ether imide)s derived from *N,N′*-diamino-1,4,5,8-naphthalenetetracarboxylic bisimide (98), and poly(arylene ether imide ketone)s (99). In addition, many other heterocylic groups have been introduced into polyether systems, eg, poly(pyrazole ether)s (100) and poly(aryl ether phenylquinoxaline)s (101); poly(aryl ether oxazole)s with trifluoromethyl groups (102); and polyethers with other heterolinkages, eg, poly(arylether azine)s (103).

Table 4. Ultem Polyetherimide Properties

Property	Value
glass-transition temperature, °C	217
heat-distortion temperature, °C	ca 200
tensile yield (at 23°C), MPa[a]	103
tensile modulus, MPa[a]	3000
flexural strength, MPa[a]	145
flexural modulus, MPa[a]	3300
oxygen index	47
density, g/cm^3	1.28

[a] To convert MPa to psi, multiply by 145.

BIBLIOGRAPHY

"Phenolic Ethers" in *ECT* 1st ed., Vol. 10, pp. 325–334, by W. R. Brookes, Chemical Division, General Electric Co.; in *ECT* 2nd ed., Vol. 15, pp. 165–175, by J. E. Cantrill, General Electric Co.; "Polyethers–Aromatic Polyethers" in *ECT* 3rd ed., Vol. 18, pp. 594–615, by D. M. White and G. D. Cooper, General Electric Co.

Cited Publications

1. H. Yang and A. S. Hay, *J. Polym. Sci. Polym. Chem. Ed.* **31**, 1261, 2015 (1993).
2. W. A. Butte, C. C. Price, and R. E. Hughes, *J. Polym. Sci.* **61**, 528 (1961) S. Horikiri, *J. Polym. Sci., Part A-2* **10**, 1167 (1972) A. R. Schultz, and C. R. McCullough, *J. Polym. Sci., Part A-2* **10**, 307 (1972) D. M. Koehen, C. A. Smolders and M. Gordon, *J. Poly Sci. Polym. Symp.* **61**, 93 (1977) E. Turski and H. Janeczed, *Polymer* **19**, 81 (1978).
3. A. Factor, D. E. Heinsohn, and L. H. Vogt, *Polym. Lett.* **7**, 205 (1969).
4. D. M. White, *Macromolecules* **12**, 1008 (1979).
5. H. M. van Dort and co-workers, *Eur. Polym. J.* **4**, 275 (1968).
6. A. R. Schultz and B. M. Gendron, *J. Appl. Polym. Sci.* **16**, 461 (1972).
7. D. M. White and H. J. Klopfer, *J. Polym. Sci., Part A-1* **10**, 1565 (1972).
8. A. R. Schultz and B. M. Gendron, *J. Polym. Sci. Polym. Symp.* **43**, 89 (1973).
9. Technical data, General Electric Co., Selkivk, N.Y., 1976.
10. H. M. van Dort and co-workers, *J. Polym. Sci., Part C* **22**, 431 (1968).
11. G. D. Cooper and A. Katchman, *Addition and Condensation Polymerization Processes, Advances in Chemistry Series No. 91*, American Chemical Society, Washington, D.C., 1969, p. 660.
12. A. S. Hay, *Macromolecules* **2**, 107 (1969).
13. A. S. Hay and R. F. Clark, *Macromolecules* **3**, 533 (1970).
14. *Poly(phenylene oxide)s, Properties Comparison Chart*, General Electric Co., Pittsfield, Mass., 1969.
15. G. D. Cooper, A. R. Gilbert, and H. L. Finkbeiner, *Polym. Prep.* **7**, 166 (1966) D. A. Bolon, *J. Org. Chem.* **32**, 1584 (1967) D. M. White, *J. Org. Chem.* **34**, 297 (1969).
16. D. M. White, *J. Polym. Sci. Polym. Chem. Ed.* **19**, 1008 (1979) U.S. Pat. 4,140,675 (Feb. 20, 1979), D. M. White (to General Electric Co.).
17. H. L. Finkbeiner and A. M. Toothaker, *J. Org. Chem.* **33**, 4347 (1968).
18. D. M. White and S. A. Nye, *Macromolecules* **23**, 1318 (1990).
19. D. M. White and L. A. Socha, *Preprints of the 3rd Pacific Polymer Conference, Gold Coast, Australia*, Dec. 1993.
20. U.S. Pat. 3,442,858 (May 6, 1969), A. S. Hay (to General Electric Co.).
21. P. C. Juliano, J. V. Crivello, and D. E. Floryan, *Polym. Prep.* **15**, 210 (1974).
22. A. Factor, H. Finkbeiner, R. A. Jerussi, and D. M. White, *J. Org. Chem.* **35**, 57 (1970) A. Factor, *J. Polym. Sci., Part A-1* **7**, 363 (1969).
23. H. J. Hageman, W. L. Louwerse, and W. J. Mijs, *Tetrahedron* **26**, 2045 (1970) H. J. Hageman and W. G. B. Huysmans, *Rec. Trav. Chim. Pays-Bas* **91**, 528 (1972).

24. J. E. Pickett, *5th International Conference on Advances in Stabilization and Controlled Degradation of Polymers*, Zurich, Switzerland, 1983 *ACS Symp. Ser* **280**, 313, 1985. J. Peeling and D. T. Clark, *J. Appl. Polym. Sci.* **26**, 3761 (1981) A. Dilks, and D. T. Clark, *J. Polym. Sci. Polym. Chem. Ed.* **19**, 2487 (1981).
25. J. Liska and E. Borsig, *Chem. Listy* **86**(12), 900 (1992). A review of substitution reactions as well as degradation reactions.
26. D. M. White and C. M. Orlando, *Amer. Chem. Soc. Symp. Ser.* **6**, 179 (1975).
27. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Polym. Sci., Part A-1* **12**, 1141 (1974).
28. U.S. Pat. 3,378,505 (Apr. 16, 1968), A. S. Hay (to General Electric Co.).
29. J. H. Glans and M. K. Akkapeddi, *Macromolecules*, **24**, 384 (1991).
30. A. S. Hay and A. J. Chalk, *Polym. Lett.* **6**, 105 (1668) *J. Polym. Sci., Part A-1* **7**, 691 (1969).
31. S. S. Mahajan, B. D. Sarwade, and P. P. Wadgaonkar, *Polym. Bull.* **20**, 153 (1988).
32. A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Amer. Chem. Soc.* **81**, 6335 (1959).
33. H. L. Finkbeiner, A. S. Hay, and D. M. White, in C. E. Schildknecht and I. S. Skeist, eds., *Polymerization Processes, High Polymers*, Vol. **29**, John Wiley & Sons, Inc., New York, 1977, p. 537.
34. U.S. Pat. 3,965,069 (June 22, 1976), W. K. Olander (to General Electric Co.) U.S. Pat. 3,573,257 (Mar. 30, 1971), S. Nakashio and I. Nakagawa (to Sumitomo Chemical Co.).
35. B. O. Lindgren, *Acta Chem. Scand.* **14**, 1203 (1960) E. J. McNelis, *J. Org. Chem.* **31**, 1255 (1966) M. van Dort, *J. Polym. Sci. Part C* **22**, 431 (1968).
36. A. S. Hay, *J. Polym. Sci.* **58**, 581 (1962).
37. D. M. White and H. J. Klopfer, *J. Polym. Sci Part A-1* **8**, 1427 (1970).
38. A. S. Hay and G. F. Endres, *Polym. Lett.* **3**, 887 (1965).
39. L. H. Vogt, J. G. Wirth, and H. L. Finkbeiner, *J. Org. Chem.* **34**, 273 (1969) D. L. Tomaja, L. H. Vogt, and J. G. Wirth, *J. Org. Chem.* **35**, 2029 (1970).
40. J. D. McClure, *J. Org. Chem.* **28**, 69 (1963) R. G. R. Bacon and A. R. Izzat, *J. Chem. Soc. C*, 791 (1966).
41. G. F. Endres and J. Kwiatek, *J. Polym. Sci.* **58**, 593 (1962) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.* **28**, 1300 (1963).
42. G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. L. Finkbeiner, *J. Amer. Chem. Soc.* **87**, 3996 (1965).
43. D. M. White, *Polym. Prepr.* **9**(1), 663 (1967).
44. W. J. Mijs, O. E. van Lohuizen, J. Bussink, and L. Volbracht, *Tetrahedron* **23**, 2253 (1967).
45. D. J. Williams and R. Kreilick, *J. Amer. Chem. Soc.* **89** 3408 (1967) *J. Amer. Chem. Soc.* **90**, 2775 (1968).
46. H. L. Finkbeiner, G. F. Endres, H. S. Blanchard, and J. W. Eustance, *Polym. Prep.* **2**, 340 (1961).
47. G. D. Cooper and J. G. Bennett, *J. Org. Chem.* **37**, 317 (1972).
48. G. D. Staffin and C. C. Price, *J. Amer. Chem. Soc.* **82**, 3632 (1960) U.S. Pat. 3,257,358 (June 21, 1966), G. S. Stamatoff (to E. I. du Pont de Nemours & Co., Inc.).
49. D. M. White, *Polym. Prep.* **15**, 210 (1974) D. M. White and H. J. Klopfer, in E. J. Vandenberg, ed., *Polyethers*, ACS Symposium Series, American Chemical Society, Washington, D.C., 1975, p. 169.
50. H. S. Blanchard, H. L. Finkbeiner, and G. A. Russell, *J. Polym. Sci.* **58**, 469 (1962).
51. U.S. Pat. 3,236,807 (Feb. 22, 1966), G. S. Stamatoff (to E. I. du Pont de Nemours & Co., Inc.).
52. U.S. Pat. 3,431,238 (Mar. 4, 1969), W. Borman (to General Electric Co.).
53. J. H. Beeson and R. E. Pecsar, *Anal. Chem.* **41**, 1678 (1969).
54. E. McNelis, *J. Amer. Chem. Soc.* **88**, 1074 (1968).
55. U.S. Pat. 3,749,693 (July 31, 1973), G. D. Cooper (to General Electric Co.).
56. G. D. Cooper, J. G. Bennett, Jr., and A. Factor, *Polym. Prep.* **13**, 551 (1972).
57. G. D. Cooper, J. G. Bennett, Jr., and A. Factor, *Polymerization Kinetics and Technology, Advances in Chemistry Series*, No. 128, American Chemical Society, Washington, D.C., 1973, p. 230.
58. D. M. White and G. R. Loucks, *Polym. Preprints*, **25**(1), 129 (1984).
59. A. R. Schultz and B. M. Beach, *Macromolecules* **7**, 902 (1974).
60. S. Krause, *J. Macromol. Sci. Rev. Macromol. Chem.* **7**, 251 (972).
61. J. Stoelting, F. E. Karasz, and W. J. McKnight, *Polym. Eng. Sci.* **10**(3), 133 (1970) A. F. Yee, *Polym. Eng. Sci.* **17**, 213 (1977).
62. W. J. McKnight, F. E. Karasz, and J. R. Fried, *Polymer Blends*, Vol. **1**, Academic Press, Inc., New York, 1978, p. 185.
63. L. W. Kleiner, F. E. Karasz, and W. J. McKnight, *Polym. Eng. Sci.* **19**, 519 (1979).

64. U.S. Pat. 3,383,435 (May 14, 1968), E. P. Cizek (to General Electric Co.).
65. D. T. Hseih and D. G. Peiffer, *J. Appl. Polym. Sci.* **44**, 2003 (1992).
66. R. Murali, A. Eisenberg, R. K. Gupta, and F. W. Harris, in D. E. Bergbreiter and C. R. Martin, eds., *Functional Polymers 6th IUCCP Symposium on Functional Polymers*, Plenum Publishing Corp., New York, 1988, p. 37.
67. H. S. Chao and J. M. Whalen, *J. Appl. Polym. Sci.* **49**, 1537 (1993).
68. H. L. Fricsh, D. Klemperner, H. K. Yoon, and K. C. Frisch, *Macromolecules* **13** 1016 (1980) H. L. Frisch and Y. Hua, *Macromolecules* **22**, 91 (1989) P. C. Mengnjoh and H. L. Frisch, *J. Polym. Sci. Polym. Chem. Ed.* **27**, 3363 (1989) P. C. Mengnjoh and H. L. Frisch, *J. Polym. Sci., Part C, Polym. Lett.* **127**, 285 (1989) S. Singh, H. Ghiradella, and H. L. Frisch, *Macromolecules* **23**, 375 (1990).
69. M. Kramer, *Appl. Polym. Symp.* **15**, 227 (1971).
70. G. D. Cooper, G. F. Lee, A. Katchman, and C. P. Shank, *Mater. Technol.* 12 (1981).
71. J. M. Nielsen, *Solvents and Safety*, General Electric Co., Schenectady, N.Y., 1977, p. 31.
72. *Registry of Toxic Effects of Chemical Substances, 1979 Edition*, U.S. Government Printing Office, Washington, D.C., 1980, p. 621.
73. *Ibid.*, p. 709.
74. R. N. Johnson, A. G. Farnham, R. A. Clendenning, W. F. Hale, and C. N. Merriam, *J. Polym. Sci., Part A-1* **5**, 2375 (1967).
75. M. E. A. Cudby, R. G. Feasy, B. E. Jennings, M. E. B. Jones, and J. B. Rose, *Polymer* **6**, 589 (1965) M. E. A. Cudby, R. G. Feasy, S. Gaskin, V. Kendall, and J. B. Rose, *Polymer* **9**, 265 (1968) K. J. Ivin and J. B. Rose, in W. M. Pasika, ed., *Advances in Macromolecular Chemistry*, Vol. **1**, Academic Press, Inc., New York, 1968, p. 366 V. J. Leslie, G. O. Rudkin, Jr., J. B. Rose, and J. Feltzin, *Amer. Chem. Soc. Symp. Ser.* **4**, 63 (1974).
76. R. N. Johnson and A. G. Farnham, *J. Polym. Sci., Part A-1* **7**, 2415 (1967).
77. U.S. Pat. 4,105,636 (Aug. 8, 1978), I. C. Taylor (to Imperial Chemical Industries, Ltd.).
78. U.S. Pat. 4,108,837 (Aug. 22, 1978), R. N. Johnson and A. G. Farnham (to Union Carbide Corp.).
79. A. Noshay, M. Matzner, B. P. Barth, and K. W. Watson, *J. Polym. Sci., Part A 1* **9**, 3147 (1970).
80. S. E. McGrath, L. M. Robeson, and M. Matzner, in L. M. Sperling, ed., *Recent Advances in Polymer Blends, Grafts and Blocks*, Plenum Press, New York, 1974, p. 195.
81. U.S. Pat. 3,321,449 (May 23, 1967), H. A. Vogel (to Minnesota Mining and Mfg. Co.) Brit. Pat. 1,016,245 (1965), M. E. B. Jones (to Imperial Chemical Industries, Ltd.).
82. T. E. Attwood and co-workers, *Polym. Prep.* **20**(1), 191 (1979).
83. *Plastics for Electronics*, Cordura Publications, Cordura, Calif., 1979.
84. *Plast. World*, 11 (May 1980) I. Schmidt and K. J. Binder, *J. Phys. (Paris)* **46**, 1631 (1985).
85. B. R. Prime, *J. Polym. Sci.* **25**, 641, 1986 R. D. McElhaney, D. G. Castner, and B. D. Ratner, in E. Sacher, J. J. Perreaux, and S. P. Kowalczyk, eds., *Metallization of Polymers*, *ACS Symp. Series No. 440*, American Chemical Society, Washington, D.C., 1990, p. 370.
86. A. Lustiger, F. S. Uralil, and F. M. Newaz, *Polym. Composites* **11**, 65, 1990.
87. K. P. Chan, Y. Wang, and A. S. Hay, *Macromolecules* **28**, 653 (1995).
88. T. Takekoshi, *Advances in Polymer Science*, Vol. **94**. Springer-Verlag, Berlin, 1990 C. E. Sroog, *Prog. Polym. Sci.* **16**, 561 (1991).
89. P. M. Hergenrother and S. J. Havens, *Macromolecules* **27**, 4659 (1994).
90. U.S. Pat. 3,838,097 (Sept. 24, 1974), J. G. Wirth and D. R. Heath (to General Electric Co.) U.S. Pat. 3,803,085 (Apr. 9, 1974), T. Takekoshi and J. E. Kochanowski (to General Electric Co.).
91. L. R. Caswell and T. L. Kao, *J. Heterocycl. Chem.* **3**, 333 (1965) F. J. Williams and P. E. Donahue, *J. Org. Chem.* **42**, 3414 (1979).
92. D. M. White and co-workers, *J. Polym. Sci. Polym. Chem. Ed.* **19**, 1635 (1981).
93. T. Takekoshi, J. E. Kochanowski, J. S. Manello, and M. J. Webber, *NASA Contract Report No. CR-145 007*, NASA, Langley, Va., 1976.
94. T. Takekoshi, D. R. Heath, J. E. Kochanowski, J. S. Manello, and M. J. Webber, *Polym. Prep.* **20**(1), 179 (1979).
95. D. E. Floryan and G. L. Nelson, *J. Fire Flammabil.* **11**, 284 (1980).
96. S. Ando, T. Matsuura, and S. Sasaki, *Macromolecules* **25**, 5858 (1992).
97. D. Venkatesan and M. Srinivasan, *J. M. S.—Pure Appl. Chem.* **A30**, 801 (1993).
98. H. Ghassemi and A. S. Hay, *Macromolecules* **27**, 3116 (1994).

99. S. Matsuo and K. Mitsuhashi, *J. Polym. Sci. Polym. Chem. Ed.* **32**, 1969 (1994).
100. J. A. Moore and P. G. Mehta, *Macromolecules* **28**, 444 (1995).
101. J. Hedrick, R. Tweig, T. Matray, and K. Carter, *Macromolecules* **26**, 4833 (1993).
102. G. Maier, R. Hecht, O. Nuyken, K. Borger, and B. Helmreich, *Macromolecules* **26**, 2583 (1993).
103. K. R. Carter and J. L. Hedrick, *Macromolecules* **27**, 3426 (1994).

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