

HEAT-RESISTANT POLYMERS

The search for heat-resistant polymers began about 1960 and there is continued growth in the development of these materials that can perform long-term service at elevated temperatures. The intensive interest in these polymers results from new technological processes requiring higher use temperatures for development. Thermally stable or high performance polymers dictate high melting (softening) temperatures, resistance to oxidative degradation at elevated temperatures, resistance to other (nonoxidative) thermolytic processes, and stability to radiation and chemical reagents.

The definition of polymer thermal stability is not simple owing to the number of measurement techniques, desired properties, and factors that affect each (time, heating rate, atmosphere, etc). The easiest evaluation of thermal stability is by the temperature at which a certain weight loss occurs as observed by thermogravimetric analysis (tga). Early work assigned a 7% loss as the point of stability; more recently a 10% value or the extrapolated break in the tga curve has been used. A more realistic view is to compare weight loss vs time at constant temperature, and better yet is to evaluate property retention time at temperature: one set of criteria has been 177°C for 30,000 h, or 240°C for 1000 h, or 538°C for 1 h, or 816°C for 5 min (1).

A number of thermally stable polymers have been synthesized, but in general the types of structures that impart thermal resistance also result in poor processing characteristics. Attempts to overcome this problem have largely been concentrated on the incorporation of flexible groups into the backbone or the attachment of stable pendent groups. Among the class of polymers claimed to be thermally stable only a few have achieved technological importance, some of which are polyamides, polyimides, polyquinoxalines, polyquinolines, and polybenzimidazoles. Of these, polyimides have been the most widely explored.

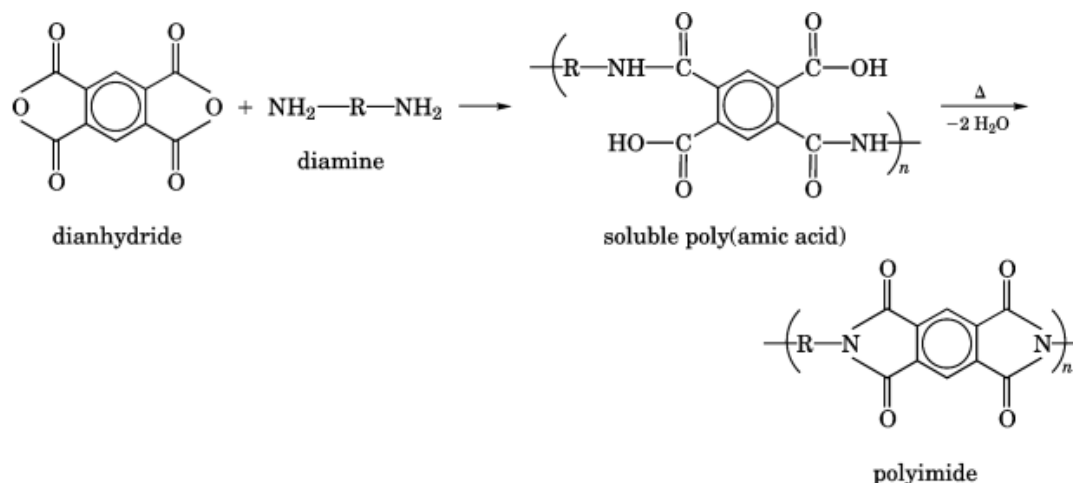
1. Polyimides

Polyimides (PI) were among the earliest candidates in the field of thermally stable polymers. In addition to high temperature property retention, these materials also exhibit chemical resistance and relative ease of synthesis and use. This has led to numerous innovations in the chemistry of synthesis and cure mechanisms, structure variations, and ultimately products and applications. Polyimides (qv) are available as films, fibers, enamels or varnishes, adhesives, matrix resins for composites, and molding powders. They are used in numerous commercial and military aircraft as structural composites, eg, over a ton of polyimide film is presently used on the NASA shuttle orbiter. Work continues on these materials, including the more recent electronic applications.

1.1. Synthesis and Properties

Several methods have been suggested to synthesize polyimides. The predominant one involves a two-step condensation reaction between aromatic diamines and aromatic dianhydrides in polar aprotic solvents (2, 3). In the first step, a soluble, linear poly(amic acid) results, which in the second step undergoes cyclodehydration, leading to an insoluble and infusible PI. Overall yields are generally only 70–80%.

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A viscous solution of poly(amic acid) can be processed into films, fibers, and coatings, and the final product undergoes thermal cyclodehydration.

Numerous diamines and aromatic dianhydrides have been investigated. Wholly aromatic PIs have been structurally modified by incorporating various functional groups, such as ether, carbonyl, sulfide, sulfone, methylene, isopropylidene, perfluoroisopropylidene, bipyridyls, siloxane, methyl phosphine oxide, or various combinations of these, into the polymer backbone to achieve improved properties. The chemistry and applications of PIs have been described in several review articles (4).

PIs commonly have been synthesized from reactions of pyromellitic dianhydride [26265-89-4] (PMDA) or 3,3',4,4'-benzophenone tetracarboxylic dianhydride [2421-28-5] (BTDA) with a number of diamines like 2,2-bis(4-aminophenyl)propane, 2,2-bis(4-amino-3-methylphenyl)propane, 1,1-bis(4-aminophenyl)-1-phenylethane, and 1,1-bis(4-amino-3-methylphenyl)-1-phenylethane (5). The PMDA-based PIs were thermally more stable than the corresponding PIs obtained from BTDA.

A successful synthesis of novel, soluble aromatic PIs involving 3,4-bis-(4-aminophenyl)-2,5-diphenylfuran by polymerization with aromatic tetracarboxylic dianhydrides through the conventional two-step method has been reported (6) (Fig. 1).

The polymers are stable up to 550°C (10% weight loss by tga) in N₂ atmosphere with the glass-transition temperatures, T_g , ranging from 281–344°C. The inherent viscosities of the polymers in H₂SO₄ are up to 0.32 dL/g. Also prepared were aromatic PIs containing triphenylamine units (7). These polymers show a 10% weight loss at 520°C in air, with T_g s in the range 287–331°C. Synthesis of some bismaleimides has been reported from epoxy resins which show thermal stability up to 370°C (8). Thermotropic poly(ester-imides) have been obtained from trimellitic acid with phosphonate or phosphate groups in the main chain (9). These polymers are stable in the range 410–425°C (5% weight loss) in air.

Structurally different PIs have been synthesized with alternating rigid (pyromellitimide) and semiflexible (polymethylene) units along the chain backbone (10). A change in T_g of the polymers obtained with different spacer groups follows the expected trend; that is, as the aliphatic segment increases in length (C-8 to C-12) the T_g decreases (383 to 305°C). Further mixing of aliphatic-type linkages drives the T_g even lower. Polyesterimides are well known for their thermal stability coupled with processing ease. A moderately stable polyesterimide has been synthesized from trimellitic anhydride [552-30-7], bisphenol A [80-05-7], and 4,4'-diaminodiphenyl sulfone [80-08-0] by three different routes (11).

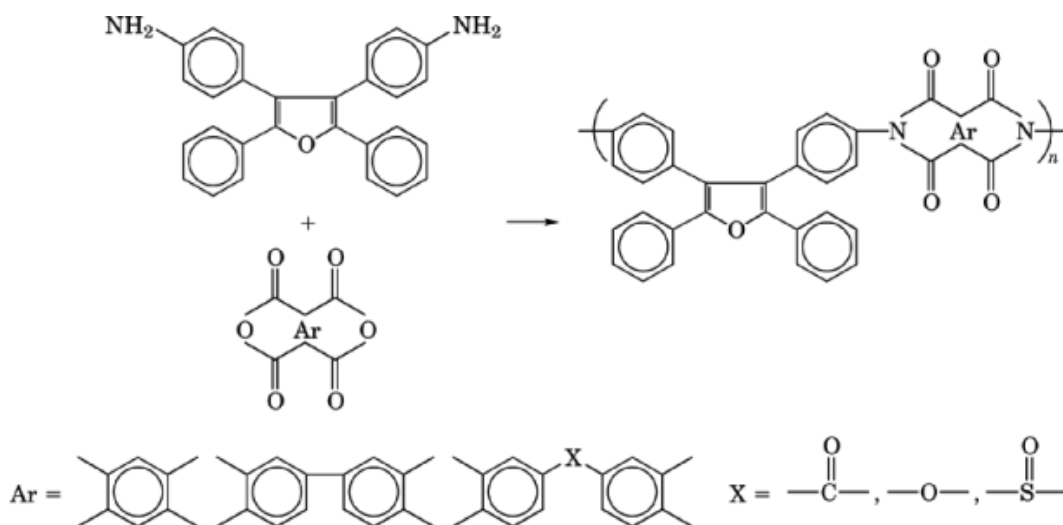
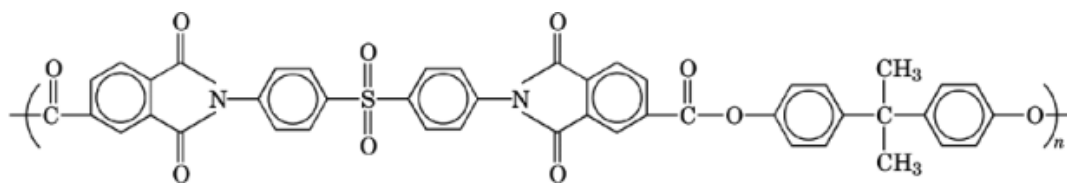


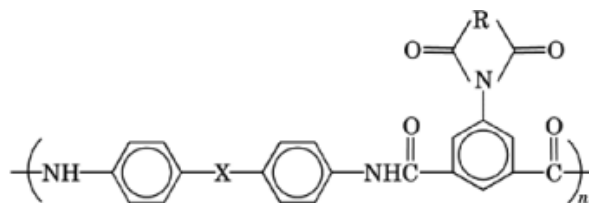
Fig. 1. Wholly aromatic PIs made by conventional methods.



These polymers are soluble in polar solvents and stable up to 290–325°C.

Copoly(amide-imides) comprise an important class of copolyimides that have been developed into a commercial product. Incorporating the amide linkage into the PI makes the polymer more tractable than simple PIs, but involves a loss in thermal stability. However, copoly(amide-imides) still possess quite good thermal stabilities, intermediate between those of polyamides and PIs (12). They are relatively inexpensive to synthesize.

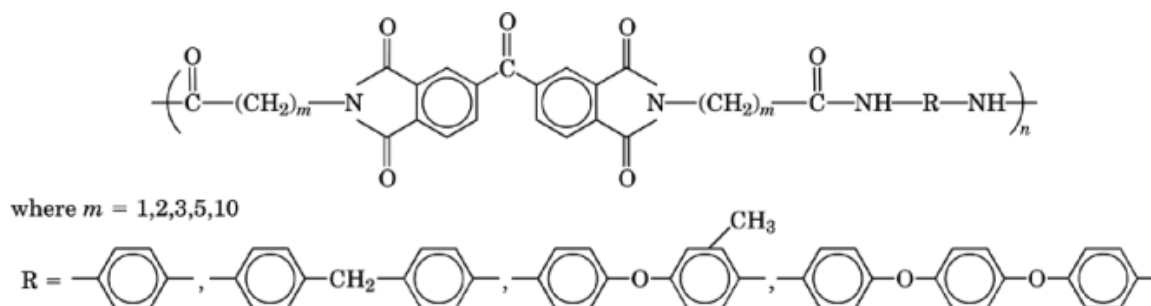
A series of cross-linkable copoly(amide-imides) is known to be possible from aromatic diamines and substituted isophthaloyl chlorides containing unsaturated imide rings as a pendent function (13).



These polymers possess enhanced solubility compared to the aromatic polyamides with no deterioration in thermal stability. Their T_g s vary from 264–311°C depending on the nature of the X group. An additional feature of these polymers is that their tensile strengths increase after heat treatment due to cross-linking.

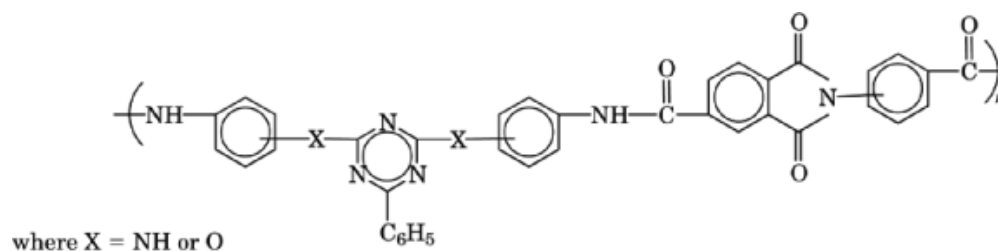
Aliphatic-aromatic poly(amide-imides) based on *N,N'*-bis(carboxyalkyl)-benzophenone-3,3',4,4'-tetracarboxylic diimides have shown a 10% weight loss at 400°C (14).

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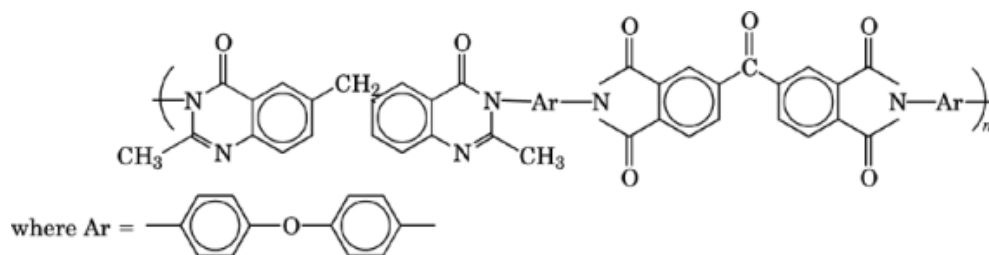
The T_g s of the polymers were in the range 122–250°C, which showed a predictable increase with a decrease in length of the flexible aliphatic chains.

Aromatic copoly(amide-imide)s with *s*-triazine rings in the repeating unit of the backbone are also possible from a diacyl chloride reacting with preformed imide groups and diamines containing *s*-triazine rings (15).



The polymers have been obtained by conventional solution condensation at low temperature using polar organic solvents in N_2 atmosphere and are stable up to 400°C in air (5% weight loss). Their inherent viscosities range from 0.40 to 1.17 dL/g. This method overcomes the disadvantages of PI preparation, ie: (1) a two-step process, and (2) the instability of the intermediate (poly(amic acid)) in the presence of moisture. In another study (16), novel phosphorylated bismaleimides and nonphosphorylated tetramaleimides containing substituted *s*-triazine rings (chain extended by imide, amide, or urea groups) were prepared and polymerized. These polymers were stable up to 312–370°C in air or N_2 .

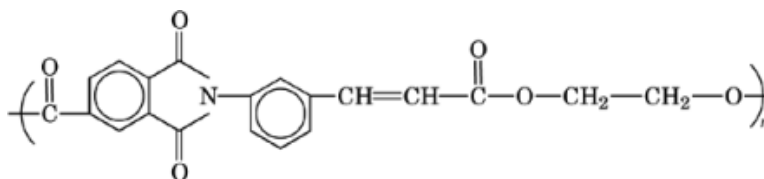
Poly(phenylquinoxaline-amide-imides) are thermally stable up to 430°C and are soluble in polar organic solvents (17). Transparent films of these materials exhibit electrical insulating properties. Quinoxaline-imide copolymer films prepared by polycondensation of 6,6'-methylene bis(2-methyl-3,1-benzoxazine-4-one) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 4,4'-oxydianiline exhibit good chemical etching properties (18). The polymers are soluble, but stable only up to 200–300°C.



Polyetherimide synthesis has been achieved by reaction of a dianhydride containing an ether linkage with a diamine, reaction of a diamine containing an ether linkage with a dianhydride, or nucleophilic displacement of halo or nitro groups of a bisimide by bisphenol dianion (19, 20). Such PIs exhibit good thermal stability and melt processibility.

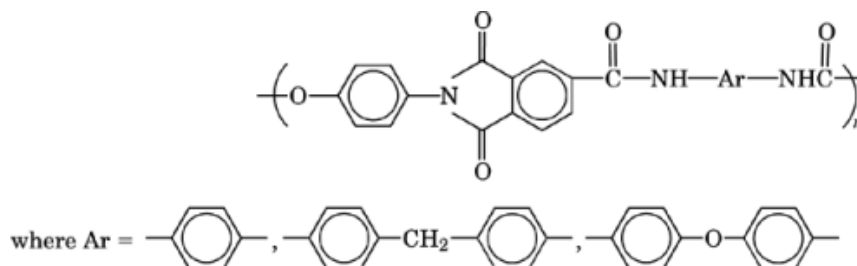
A large variety of bisimides and polymers containing maleimide and citraconimide end groups have also been reported (21–26). Thus polymers based on bisimidobenzoxazoles from the reaction of maleic anhydride and citraconic anhydride with 5-amino-2-(*p*-aminophenyl)benzoxazole and 5-amino-2-(*m*-aminophenyl)benzoxazole are found to be thermally stable up to 500°C in nitrogen.

A cross-linked and crystalline copoly(ester–imide) containing an alkene function was made by reaction of an unsaturated diacid chloride containing a cyclic imido group with ethylene glycol at low temperature (27).



These polymers lost 5% of their weight at 325°C in a nitrogen atmosphere and the T_g of the polymers varied from 230–262°C. The inherent viscosity of the polymers is low (0.13–0.17 dL/g in DMF at 30°C).

Terpoly(amide–imide–urethanes) have been synthesized in yields up to 50–75% by the reaction of 4-carboxy-*N*-(*p*-hydroxyphenyl)phthalimide with diisocyanates in *N*-methyl-2-pyrrolidinone containing 5% lithium chloride (28).



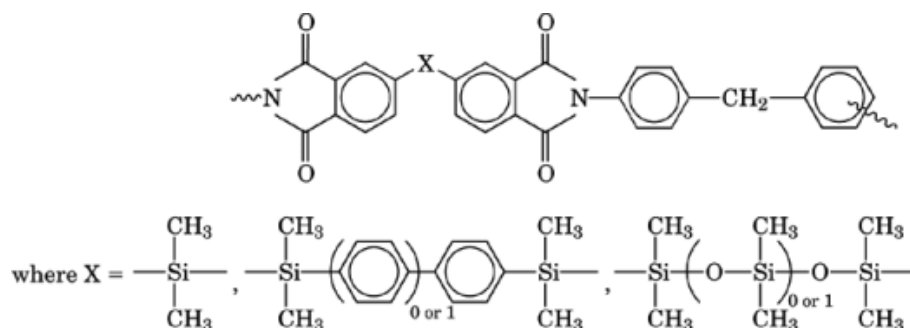
These polymers show thermal stability in the range 300–340°C (10% weight loss) and inherent viscosities of 0.15–0.45 dL/g.

Polypyromellitimide films based on cyclotriphosphazene and bisaspartimide-derived diamines have shown thermal stabilities up to 800°C and char yields of 56–68% in N_2 and 24% in air (29). High strength fire- and heat-resistant imide resins containing cyclotriphosphazene and hexafluoroisopropylidene groups have also been synthesized by the thermally induced melt polymerization of male-imido-phenoxy cyclotriphosphazenes linked by hexafluoroisopropylidenediphthalimide groups (30). The polymers are fire resistant with char yields of 78–80% at 800°C in N_2 and 60–68% in air at 700°C. The laminates have a flexural strength of 490 MPa (71,000 psi) and a modulus of 56,600 MPa (8.2×10^6 psi), demonstrating better properties than those of many other presently used resins.

Some novel copolyimides containing metal phthalocyanines are possible by treating copper, cobalt, nickel, and zinc phthalocyaninetetramines with PMDA and BTDA (31–35). They are self-extinguishing, do not burn when exposed to flame, and oxidize in air at 500–600°C, leaving metal oxides. In nitrogen, degradation occurs at 600–800°C leaving a 75–85% char yield.

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Silicon-containing PIs, useful as insulation and protective materials, demonstrate adhesion to fibers, fabrics, glass, quartz, and carbon (36). The synthetic method used is the reaction of the silicon-containing dianhydride with diamines.



Three important linear aromatic PIs, namely LARC-TPI, LARC-160, and LARC-13 were developed by researchers at NASA-Langley Research Center (37–39) (Fig. 2).

LARC-TPI is a linear thermoplastic PI which can be processed in the imide form to produce large-area, void-free adhesive bonds. Mitsui Toatsu Chemicals, Inc., has obtained license to produce this product commercially for applications such as adhesives, films, molding compounds, etc. These are thermooxidatively stable and show essentially no loss in weight at 300°C in air. Weight loss does not exceed 2–3% after isothermal aging in air at 300°C for 550 h.

LARC-13 is a nadimide-terminated addition-curing adhesive. Because of its high degree of flow during cure, it is autoclave processible. It has been successfully used to bond a high temperature composite to a ceramic for missile applications which achieve several seconds of performance at 595°C. A significant use of this adhesive is in the bonding of honeycomb sandwich structures. PMR-15 polyimides, based on mixtures of reactive components, have also been investigated (40–42) which exhibited thermooxidative stability up to 316°C. PMR is a designation of NASA-Lewis and stands for polymerization of monomeric reactants *in situ*.

Since 1975, numerous polyimide backbones containing hexafluoroacetone or 1hexafluoroisopropoxybenzene groups have been investigated (43, 44). These polymers show greatly enhanced solubility (up to 20% in amide solvents) and significant promise in gas separation research and technology.

1.2. Applications

The excellent chemical, mechanical, and electrical properties of PIs have led to their widespread use and make them attractive as high performance materials. Since the 1980s, there has been an accelerated interest in the use of PIs in a variety of applications ranging from aerospace to microelectronics to medicine. Addition-type PIs have also emerged as state-of-the-art matrix resins for high strength, high temperature-resistant composites for use as structural materials in aerospace applications (45). These low molar mass compounds end capped with reactive imide groups (eg, maleimide or nadimide) can be thermally polymerized to give cross-linked PIs. Their chemical, thermal, and mechanical properties are amenable to a variety of modifications by way of structural changes of the diamine precursor or the reactive imide groups. One of the most recent uses of PIs is as reverse osmosis membranes. The polymers substituted with polar groups such as methoxy show excellent stability toward hydrolytic and bacterial attack (46).

Polyimide films such as Du Pont's Kapton or H-film are used as wire and cable wrap, motor-slot liners, and in transformers and capacitors. These films are excellent choices in applications where high dielectric strength must be retained under thermal stress. Although not yet of commercial significance, several types

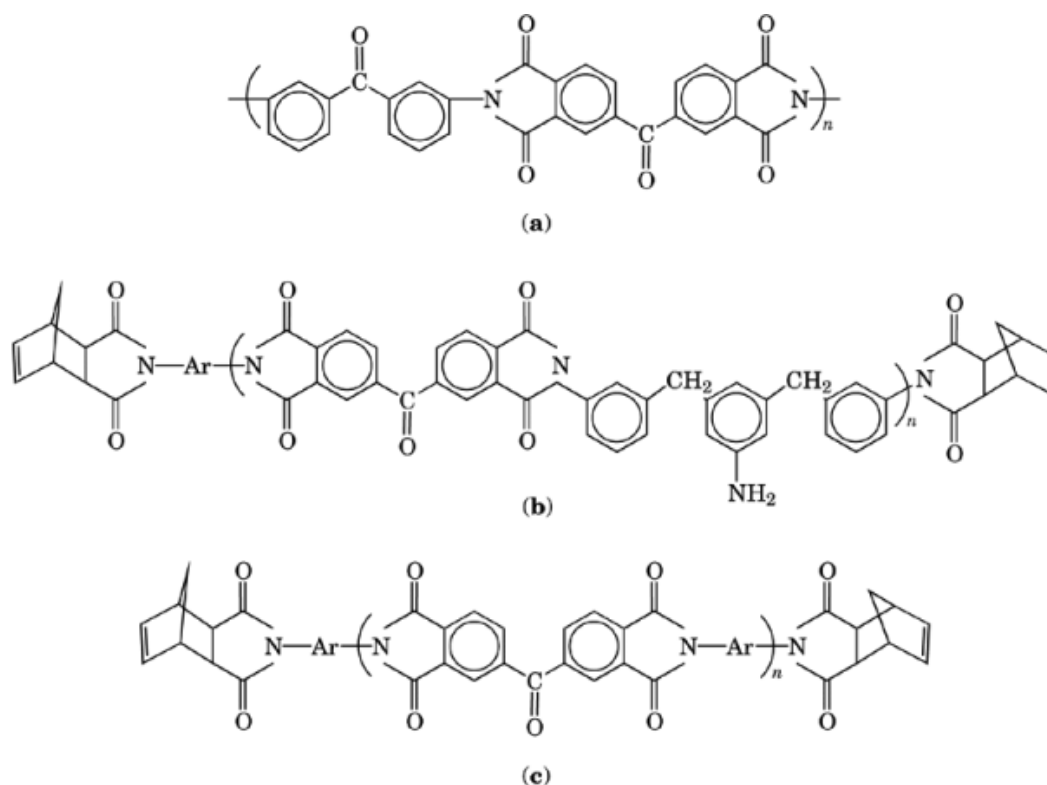
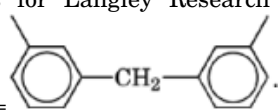


Fig. 2. Fig. 2. LARC polyimides where LARC stands for Langley Research Center. (a), LARC-TPI from 3,3'-

diaminobenzophenone and BTDA; (b), LARC-160, where $\text{Ar} =$ .

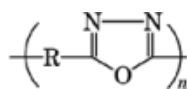
of PIs have been spun into fibers and used in various high technology applications, eg, fire-resistant fabric, thermally stable composites, etc. In silicon dioxide or nitride layers in integrated circuit technology, the PI films are excellent alternative candidates due to their toughness, low conductivity, and ease and reliability of processing (47, 48).

In the electronics industry, PIs find wide applications as a dielectric material for semiconductors due to thermal stability (up to 400°C) and low dielectric constant. PIs are being considered for use in bearings, gears, seals, and prosthetic human joints. The intended part can be machined or molded from the PI, or a film of PI can be applied to a metallic part. Because of their superior adhesion, dielectric integrity, processing compatibility, and lack of biological system impact, PIs have been used in many biological applications with particular success as body implants.

2. Polyoxadiazoles

Poly(1,3,4-oxadiazole) (POD) is a widely used isomer of the oxadiazole family of thermally stable polymers. The general structure of POD is

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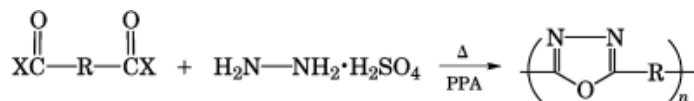


where R is often an aromatic ring, eg, *m*- or *p*-phenylene. The popularity of this particular isomer is attributed to the superior thermal stability it adds to a polymer structure as compared to the 1,2,4- or 1,2,5-isomers. Detailed studies began on this class of polymers in the late 1950s; since then, a large number of PODs have been developed. The literature up to 1979 on polyoxadiazoles has been reviewed (49).

2.1. Synthesis and Properties

Polyoxadiazoles containing aromatic moieties with aliphatic linkages/groups have been widely explored in the literature. The aromatic moieties increase the rigidity of the polymer; the presence of aliphatic groups makes the chain more flexible and processible.

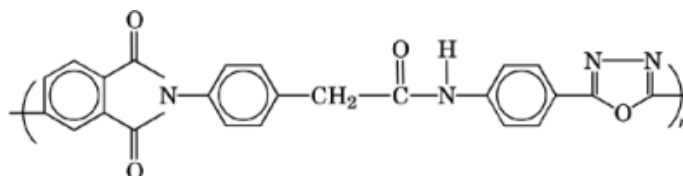
One series of POD has been prepared from the corresponding dicarboxylic acid/acid chlorides and hydrazine sulfate in polyphosphoric acid (PPA) (50, 51), one of the most common techniques for this type of backbone.



where X = OH or Cl, R = C₆H₅, (CH₂)₄, (CH₂)₈, *cis* CH=CH

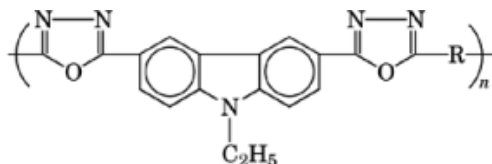
Thermal stability of the polymers ranges from 328 to 390°C in N₂ atmosphere (10% weight loss).

Aromatic PODs containing amide and imide groups have been synthesized by the solution polycondensation method (52).



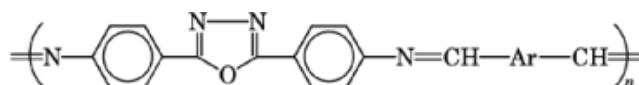
Decomposition temperatures are in the range of 360–375°C and inherent viscosities range from 0.62 to 0.90 dL/g in conc H₂SO₄. The polymers are insoluble in DMAC.

Carbazole-containing PODs have been obtained (53) by cyclodehydration (in the presence of POCl₃) of polyhydrazides prepared by polycondensation of *N*-ethyl-3,6-carbazoledicarbonyl chloride with dihydrazides of the corresponding dicarboxylic acids. Thermal decomposition of the polymers containing aliphatic units occurs at 365–380°C, compared to 400–405°C for polymers containing aromatic units.



where R = (CH₂)₄, (CH₂)₈, *m*-C₆H₄, *p*-C₆H₄, 9-ethylcarbazole-3,6-diyl

Novel 1,3,4-oxadiazole-containing polyazomethines have been synthesized by the polycondensation of diamines, 2,5-bis(*m*-aminophenyl)-1,3,4-oxadiazole and 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole with aromatic dialdehydes, isophthalaldehyde, and terephthalaldehyde (example follows), in *m*-cresol at 20°C (54).



These polymers have reduced viscosities up to 1.13 dL/g and electric conductivity as high as $10^{-11} - 10^{-12}$ S/cm. All the polymers are insoluble in common organic solvents but soluble in conc H_2SO_4 . Thermal degradation begins around 400°C in air and nitrogen according to tga.

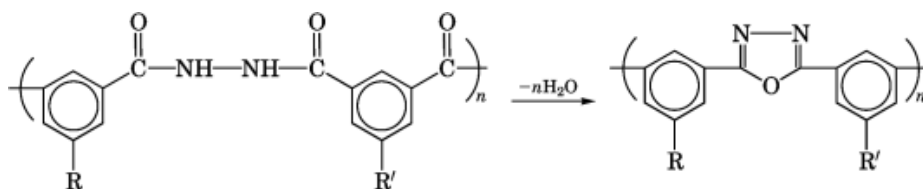
Poly(1,3,4-oxadiazole-2,5-diyl-vinylene) and poly(1,3,4-oxadiazole-2,5-diyl-ethynylene) were synthesized by polycondensation of fumaramide or acetylene-dicarboxamide with hydrazine sulfate in PPA to study the effect of the two repeating units on polymer electronic and thermal properties (55).



Both the polymers are dark in color and exhibit semiconductivity and paramagnetism. The electric conductivity measurements are performed on pellets and on thin films in sandwich and surface cells.

Research activities in the area of PODs containing aromatic groups have been centered around the production of highly processible, soluble, and thermally stable polymers. In this particular class of PODs, the imide-and phenylene-containing backbones have been widely explored.

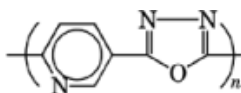
Fully aromatic, thermally (up to 250°C) and hydrolytically resistant films of PODs have been realized from polyhydrazides (56). Films of these polymers are useful as seawater desalination membranes.



where $\text{R} = \text{H}, \text{OCH}_3$; $\text{R}' = \text{H}, \text{OCH}_3, \text{CN}$

Polyoxadiazole-imides containing hexafluoroisopropylidene (HFIP) groups are soluble in common solvents and still retain good mechanical and thermal properties (57). The HFIP- based POD has the best solubility in common solvents of this series of polymers, and its tough, transparent films are the lightest in color. All the PODs show nearly identical thermal stabilities (10% weight loss) at 415–430°C in air and argon by tga. These films exhibit an initial modulus of 296 MPa (42,900 psi), an ultimate strength of 95.6 MPa (13,900 psi), and an ultimate elongation of 32.4%.

Thermally stable POD films containing pyridine rings have potential application as reverse osmosis membranes (58).



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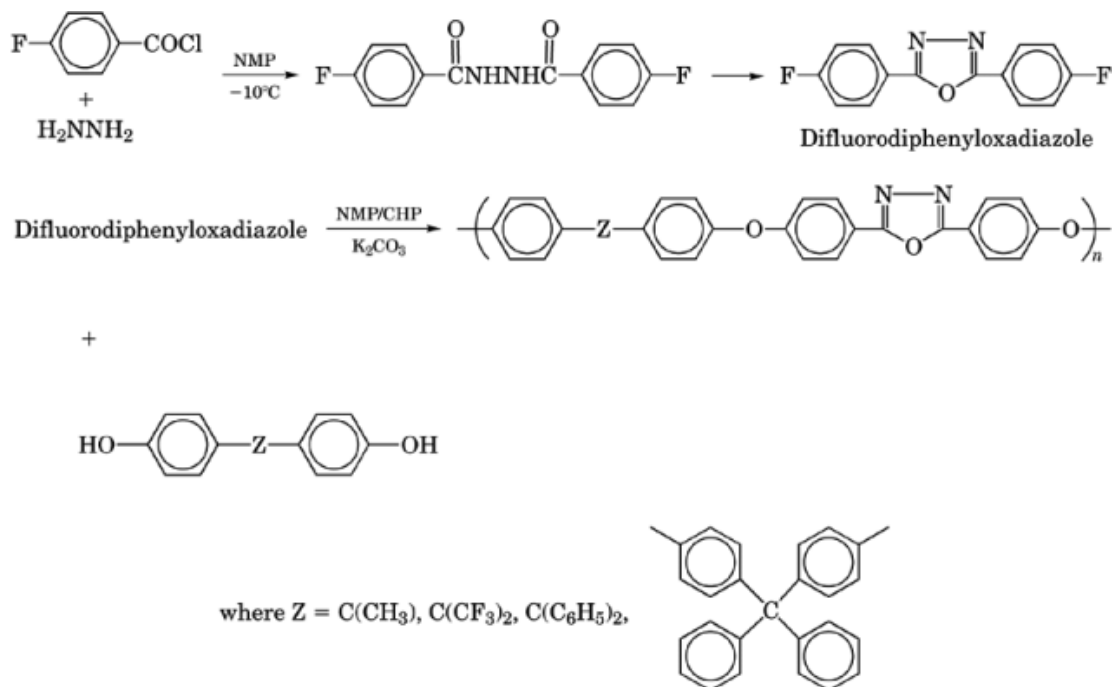
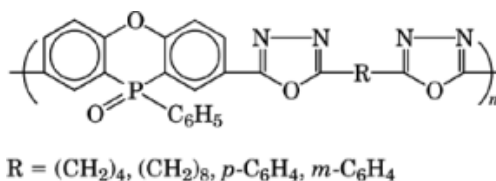


Fig. 3. Preparation of copolyoxadiazoles.

A general method for the preparation of copolyoxadiazoles, ie, poly(aryl ether oxadiazoles), has been developed where the generation of an aryl ether linkage is the polymer-forming reaction (59) (Fig. 3). Synthetic methods are based on either an oxadiazole-activated or an hydrazide-activated halo-displacement with phenoxides. The hydrazide is subsequently thermally dehydrated to the oxadiazole heterocycle. An appropriately substituted diarylfluorooxadiazole is prepared and polymerized with various bisphenols in NMP and *N*-cyclohexyl-2-pyrrolidinone (CHP) mixture in the presence of K_2CO_3 to give the copolyoxadiazole. The inherent viscosities range from 0.44 to 0.76 dL/g in NMP at 25°C and the T_g s from 190 to 210°C . The excellent thermal stability of these materials (polymer decomposition temperatures in excess of 450°C) allow them to be melt processed in spite of their high T_g .

The synthesis of phenoxaphosphine-containing PODs by the cyclodehydration of polyhydrazides obtained from 2,8-dichloroformyl-10-phenylphenoxaphosphine-10-oxide and aliphatic and aromatic dihydrazides has been described (60). All polymers are soluble in formic acid, *m*-cresol, and conc H_2SO_4 , but insoluble or partially soluble in benzene, chloroform, and hexamethylphosphoric triamide.



The PODs obtained from aromatic dihydrazides are partly soluble in dimethyl-acetamide, DMSO, etc; the others dissolve in these solvents. The thermal stabilities (up to 464°C in air and 476°C in nitrogen (10% weight loss)) of the polymers were determined by tga.

2.2. Applications

The uses of PODs have been extensively investigated as evidenced by the large number of patents, but not widely developed into commercial products. The polymers are hydrolytically stable and partially crystalline, and they can be oriented to a high degree of crystallinity by drawing. By far the most widely known uses of this type of polymer are in fibers and films; the films are often transparent yellow or brown with a percent elongation-to-break reported as high as 140, but more commonly in the range of 25 to 75%. Tensile strengths are near 118 MPa (1200 kgf/cm²), and upon weathering or heat aging this value often drops to around 78 MPa (800 kgf/cm²). These polymers are frequently processed from sulfuric acid solution.

The fibers of aromatic PODs are known to have a combination of good properties, such as strength and stiffness, fatigue resistance, and relatively low density, in the range of 1.2 to 1.4 g/cm³. PODs have been used to improve the heat resistance of many synthetic fibers. This is usually done by dissolving the POD in sulfuric acid and then treating the fibers with this solution. Poly(*p*-phenylene-1,3,4-oxadiazole) is the most commonly used commercial polyoxadiazole, and the fiber spun from this polymer is called Oksalon.

Conducting polymers having good thermal resistance are often prepared by heat treating POD alone. The heat-treated POD can be obtained in the form of a strong, flexible film composed of highly ordered graphite crystallites. POD is also used in liquid crystal display cells in which electrode plates are coated with the polymer. A patent has been filed for battery electrodes and batteries fabricated with PODs and other heterocyclic ring system polymers, which reportedly exhibit an open-circuit voltage of 0.75 V after charging from a 2.7 V dry cell for a few minutes.

In other areas, POD has been used to improve the wear resistance of a rubber latex binder by incorporation of 25% of Oksalon fibers. Heat-resistant laminate films, made by coating a polyester film with POD, have been used as electrical insulators and show good resistance to abrasion and are capable of 126% elongation. In some instances, thin sheets of PODs have been used as mold release agents. For this application a resin is placed between the two sheets of POD, which is then pressed in a mold, and the sheets simply peel off from the object and mold after the resin has cured. POD-based membranes exhibit salt rejection properties and hence find potential as reverse osmosis membranes in the purification of seawater. PODs have also been used in the manufacturing of electrophotographic plates as binders between the toner and plate. These improved binders produce sharper images than were possible before.

3. Polyquinoxalines

Polyquinoxalines (PQ) have proven to be one of the better heat-resistant polymers with regard to both stability and potential application. The aromatic backbones are derived from the condensation of a tetramine with a bis-glyoxal, reactions first done in 1964 (61, 62). In 1967, a soluble, phenylated version of this polymer was produced (63). The chemistry and technology of polyquinoxalines has been reviewed (64).

Polyphenylquinoxalines (PPQ) are easier to make than the polyquinoxalines and offer superior solubility, processibility, and thermooxidative stability (65). The PPQs exhibit excellent high temperature adhesive, composite, and film properties. However, to increase the use temperature of PPQs, acetylene groups have been placed on the backbone and subsequently thermally cured (66). In order to raise the T_g of the polymer, attempts were made to introduce the pendent ethynyl and phenylethynyl groups along the PPQ backbone followed by thermal curing (67) and their mechanical and thermal properties have been studied (68, 69). The cured, acetylene-terminated PPQs are less thermooxidatively stable than the parent polymers. The thermooxidative

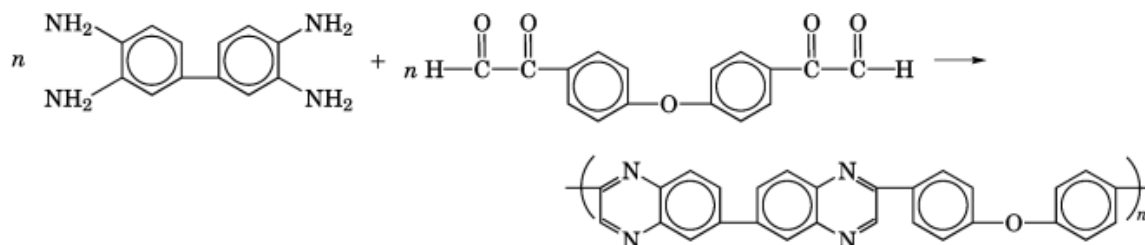
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stability of cured PPQ containing pendent ethynyl or phenylethynyl moieties is lower than that of PPQ without ethynyl moieties. However, introduction of phenylethynyl groups improves the mechanical properties at 232°C as demonstrated on adhesives (70).

3.1. Synthesis and Properties

A number of monomers have been used to prepare PQs and PPQs, including aromatic bis(*o*-diamines) and tetramines, aromatic bis(α -dicarbonyl) monomers (bisglyoxals), bis(phenyl- α -diketones) and α -ketones, bis(phenyl- α -diketones) containing amide, imide, and ester groups between the α -diketones. Significant problems encountered are that the tetraamines are carcinogenic, difficult to purify, and have poor stability, and the bisglyoxals require an arduous synthesis.

Polyquinoxalines are prepared by the solution polymerization of aromatic bis(*o*-diamines) such as 3,3',4,4'-tetraminobiphenyl and aromatic bis(glyoxal hydrates) such as 4,4'-oxybis(phenylglyoxal hydrate):



The aromatic bis(*o*-diamine) is added as a fine powder or slurry to a stirred slurry of the bis(glyoxal hydrate) to form PQ or bis(phenyl- α -diketone) to form PPQ in *m*-cresol at ambient temperature. The reaction temperature is maintained below 40°C because during the early stages of polymerization higher temperatures lead to branching. After the exotherm subsides, the mixture is stirred at ambient temperatures for several hours to give a viscous solution of the polymer. Solutions of high molar mass PPQs can be readily prepared this way without gel formation. High molar mass, linear PQs cannot be prepared by melt polycondensation because the bisglyoxals decompose upon heating. The linear high molar mass PPQs are generally soluble in phenolic and chlorinated solvents but insoluble in polar solvents.

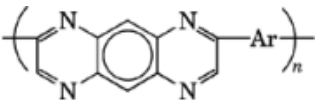

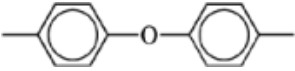
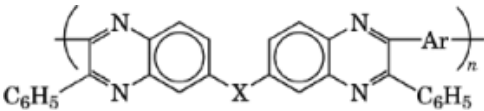

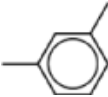
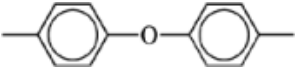
Some representative backbone structures of PQs and PPQs and their T_g data are given in Table 1. As in other amorphous polymers, the T_g s of PQs and PPQs are controlled essentially by the chemical structure, molecular weight, and thermal history. Several synthetic routes have been investigated to increase the T_g and also to improve the processibility of PPQ (71). Some properties of PPQ based on 2,3-di(3,4-diaminophenyl)quinoxaline and those of 1,1-dichloro-2,2-bis(3,4-diaminophenyl)ethylene are summarized in Table 2.

Acetylene-terminated phenylquinoxaline oligomers have been reported for possible adhesives in the aerospace industry (72–74). Several PQs containing 4-substituted phenyl groups on the quinoxaline ring have been prepared and their thermal properties studied (75). However, in an attempt to improve the thermal stability of PQs, poly(phenylquinoxaline-*co*-naphthoylene) benzimidazoles have been synthesized through catalytic copolycondensation of bis(*o*-phenylenediamines) with bis(α -diketones) and bis(naphthalic anhydrides), a number of these having acenaphthylene groups (76).

A rigid-rod polyimide derived from biphenyldianhydride and *p*-phenylene-diamine was modified by the incorporation of diamines containing phenylquinoxaline and aryl ether linkages and the morphology and mechanical properties of the resulting imide–aryl ether–phenylquinoxaline polymers were investigated (77). The films displayed T_g s in the 300°C range, and their thermal stabilities were comparable to that of the parent PI. Quinoxaline-activated poly(aryl ether) synthesis has been demonstrated to be an efficient route for the preparation of poly(aryl ether–phenylquinoxalines) (78, 79).




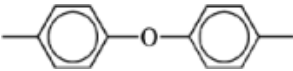
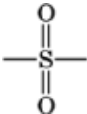

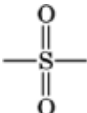
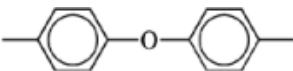
New heat-resistant polymers containing *p*-nitrophenyl-substituted quinoxaline units and imide rings as well as flexible amide groups have been synthesized by polycondensation reaction of a diaminoquinoxaline derivative with diacid dichlorides (80). These polymers are easily soluble in polar aprotic solvents with inherent viscosities in the range of 0.3–0.9 dL/g in NMP at 20°C. All polymers begin to decompose above 370°C.

Table 1. Glass-Transition Temperatures of PQ and PPQ

X	Ar	T_g°, C^a
<i>Polyquinoxalines</i>		
		
—		393
—		354
<i>Polyphenylquinoxalines</i>		
		
—O—		298
—O—		279
—O—		257

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Table 1. *Continued*

X	Ar	T_g , °C ^a
		325
		269
		346
		293

^a T_g is determined by dsc at a heating rate of 20°C/min.

3.2. Applications

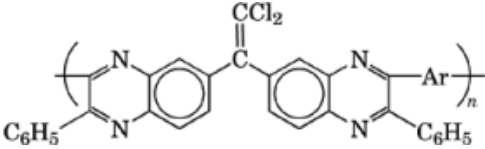
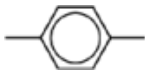
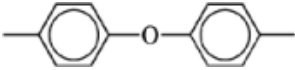
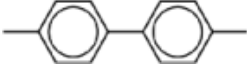
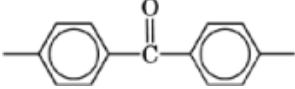
Films of PQs and PPQs can be readily prepared by melt pressing at temperatures above the T_g . Thermally and chemically stable polyquinoxalines find potential applications as films, coatings, adhesives, ultrafiltering materials, and composite matrices that demand stability in harsh environments. PPQs exhibit good stability toward strong acids and bases. Small composite nozzles of PPQ have shown excellent stability upon deep submergence in geothermal energy wells (superheated steam, brine, and sulfur compounds.)

PPQs possess a stepladder structure that combines good thermal stability, electrical insulation, and chemical resistance with good processing characteristics (81). These properties allow unique applications in the aerospace and electronics industries (82, 83). PPQ can be made conductive by the use of an electrochemical oxidation method (84). The conductivities of these films vary from 10^{-7} to 10^{-12} S/cm depending on the dopant anions, thus finding applications in electronics industry. Similarly, some thermally stable PQs with low dielectric constants have been produced for microelectronic applications (85). Thin films of PQs have been used in nonlinear optical applications (86, 87).

4. Polyquinolines

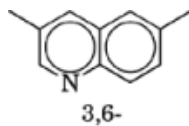
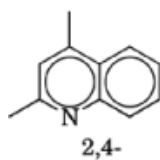
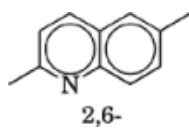
Polyquinolines are some of the most versatile thermally stable polymers; they were developed during the 1970s in response to increasing demand for high temperature resistant materials and are undergoing commercial development (Maxdem, Inc., San Dimas, California). Evidence of their stability is manifested by weight losses

Table 2. Some Properties of PPQs

		
Ar ^a	[η], dL/g	T _g ^o , C
	1.64	330
	0.65	280
	0.40	325
	0.57	290

^a All show a 10% weight loss at 500°C.

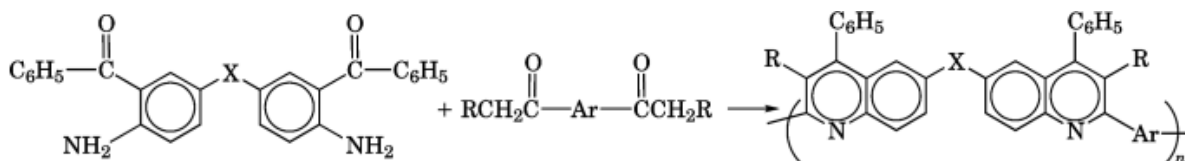
in nitrogen of only 15–30% when heated to 800°C and by demonstration of useful lifetimes in air at 300°C. Polyquinolines are characterized by repeating quinoline units, which display catenation patterns of 2,6-, 2,4-, or 3,6-.



4.1. Synthesis and Properties

Polyquinolines are formed by the step-growth polymerization of *o*-aminophenyl (aryl) ketone monomers and ketone monomers with alpha hydrogens (mostly acetophenone derivatives). Both AA-BB and AB-type polyquinolines are known as well as a number of copolymers. Polyquinolines have often been prepared by the Friedlander reaction (88), which involves either an acid- or a base-catalyzed condensation of an *o*-amino aromatic aldehyde or ketone with a ketomethylene compound, producing quinoline. Surveys of monomers and their syntheses and properties have been published (89–91).

The wide variety of ketomethylene and amino ketone monomers that could be synthesized, and the ability of the quinoline-forming reaction to generate high molar mass polymers under relatively mild conditions, allow the synthesis of a series of polyquinolines with a wide structural variety. Thus polyquinolines with a range of chain stiffness from a semirigid chain to rod-like macromolecules have been synthesized. Polyquinolines are most often prepared by solution polymerization of bis(*o*-amino aryl ketone) and bis(ketomethylene) monomers, where R = H or C₆H₅, in *m*-cresol with di-*m*-cresyl phosphate at 135–140°C for a period of 24–48 h (92).



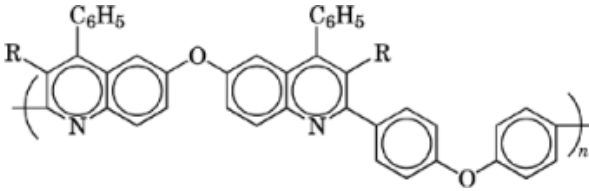
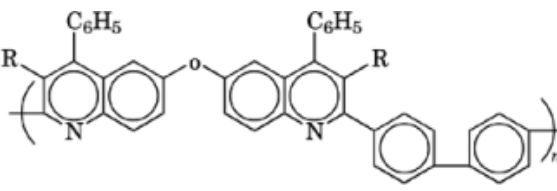
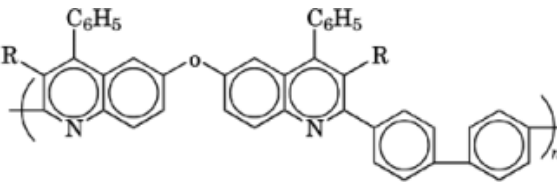
Polyquinolines have also been obtained by a post-polymerization thermal treatment of poly(enamino nitriles) (93). The resulting polymers show excellent thermal stability, with initial weight losses occurring between 500 and 600°C in air (tga); under nitrogen, initial weight loss occurs at about 600°C and there is a 20% weight loss up to 800°C.

In an effort to increase the processibility of polyquinolines, fluoromethylene groups have been successfully incorporated into the chain in place of Ar in the bis(ketomethylene) moiety (94). In fact, a small percentage of perfluorobutylene groups in the polyquinoline chain was sufficient to decrease the T_g significantly while still retaining other desired mechanical and thermal properties. Another approach was to prepare a series of oligomeric polyquinolines containing pendent biphenylenes and capped with either phenyl or biphenylene moieties (95). A representative list of different polyquinoline backbones and their properties appears in Table 3.

The glass-transition temperatures of the polyquinolines are influenced greatly by the catenation pattern, the position of phenyl substitution, and the type of linkage connecting quinoline units in the polymer chain. Although many of the polyquinolines display melt-transition temperatures, x-ray analysis has shown that they are largely amorphous, typically with less than 20% crystallinity; however, rigid polyquinolines can be annealed above the T_g to a high (up to 60%) degree of crystallinity. The thermal stabilities of polyquinolines are excellent both in air and nitrogen. In general, polyquinolines with ether linkages are less stable than their rigid counterparts.

All the flexible polyquinolines are readily soluble in chlorinated hydrocarbons such as methylene chloride and chloroform. Semirigid polyquinolines are soluble in tetrachloroethane or *m*-cresol, but rigid polyquinolines are soluble only in strong acids like sulfuric and trifluoromethane sulfonic acid. Dilute solution properties of polyquinolines have been investigated by techniques such as membrane osmometry, light scattering, viscometry, and gel-permeation chromatography (96, 97).

Table 3. Representative Polyquinolines and their Properties

Polymers	R	T_g , °C	Tga data, °C ^a	
			Air	N ₂
<i>Flexible chains</i>				
	H	266	545	565
	C ₂ H ₅	305	530	555
<i>Rigid chains</i>				
	H	340	570	580
	C ₂ H ₅	360	570	595
<i>Semirigid chains</i>				
	H	308	530	555
	C ₂ H ₅	351	520	570

^a Temperature of 10% weight loss.

4.2. Applications

Most of the stilbene-based polyquinolines display photoresponsive (98) and photomechanical effects as manifested by a contraction in polymer film samples upon irradiation.

Polyquinolines have been used as polymer supports for transition-metal catalyzed reactions. The coordinating ability of polyquinoline ligands for specific transition metals has allowed their use as catalysts in hydroformylation reactions (99) and for the electrochemical oxidation of primary alcohols (100).

Polyquinolines are good electrical insulators as indicated by conductivity values in the order of $10^{-15} - 10^{-12}$ S/cm (101). However, by virtue of their extended conjugation, doped, wholly aromatic polyquinolines offer potential for high conductivity. Rigid polyquinolines display highest values of conductivity, generally on the order of 8–11 S/cm.

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Some biphenylene end-capped polyquinolines have been used to make carbon-fiber reinforced composites (102). However, properties of these composites dropped off significantly when oxidatively aged for 50–100 h at 316°C.

5. Hexafluoroisopropylidene (HFIP)-Containing Polymers

Much attention has been paid to the synthesis of fluorine-containing condensation polymers because of their unique properties (43) and different classes of polymers including polyethers, polyesters, polycarbonates, polyamides, polyurethanes, polyimides, polybenzimidazoles, and epoxy prepolymers containing pendent or backbone-incorporated bis-trifluoromethyl groups have been developed. These polymers exhibit promise as film formers, gas separation membranes, seals, soluble polymers, coatings, adhesives, and in other high temperature applications (103, 104). Such polymers show increased solubility, glass-transition temperature, flame resistance, thermal stability, oxidation and environmental stability, decreased color, crystallinity, dielectric constant, and water absorption.

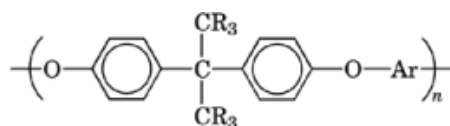
5.1. Synthesis and Properties

In 1972, Du Pont marketed a series of linear aromatic polyimides called NR-150 (105) based on 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and diaminobenzene or 1,5-diaminonaphthalene. These polymers displayed excellent high temperature adhesive properties but were difficult to process because of the presence of condensation volatiles and high boiling solvent residues. Thermoplastic PIs for use as heatseals have been developed by Du Pont by reaction of 6FDA with a variety of diamines (106, 107). Similarly, Hoechst-Celanese Corp. (108) has synthesized a class of fully imidized, soluble PIs based on hexafluoro-2,2-bis(aminophenyl)propanes (4,4'-6FDA and 3,3'-6FDA). These polymers form transparent, colorless, flexible films with good resistance to uv radiation and humidity at elevated temperature. Additionally, they exhibit higher long-term thermooxidative stability and better electrical insulating properties than the conventional PIs.

Polyimides of 6FDA and aliphatic diamines with good low temperature processing and low moisture swelling are known to be useful as hot-melt adhesives (109). Aluminum strips bonded by this polymer (177°C/172 kPa (25 psi) for 15 min) exhibited a lap-shear strength of 53 MPa (7690 psi) at room temperature and 35 MPa (5090 psi) at 100°C. The heat- and moisture-resistant 6F-containing PIs useful in electronic devices are prepared from 1,3-bis[4-(4-aminophenoxy)- α,α -bis-(trifluoromethyl)benzyl]benzene [89444-72-4] and PMDA (110). The T_g of the films (after being annealed at 300°C) is approximately 350°C.

In another study (111), several PIs were synthesized from 6FDA with different diamines. These polymers form tough, clear films with enhanced solubility in amide solvents. Inherent viscosities range from 0.28 to 1.10 dL/g with the number-average molar mass, M_n , from 22,100 to 170,000. Thermal stabilities (temperature of 10% weight loss by tga) are 480 to 530°C. The permeability of hydrogen for these films is roughly four times higher than in cellulose acetate or polysulfone.

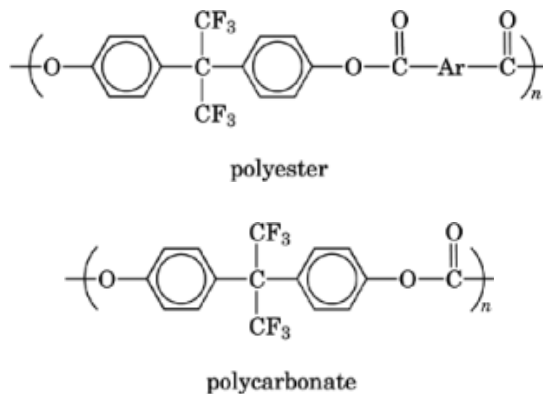
A number of HFIP-derived polyethers are known which exhibit good mechanical, thermal, and electrical properties (112, 113). Aromatic polyethers have been synthesized from bisphenol A ($R = H$) or AF ($R = F$) and fluorinated aromatics ($Ar =$ perfluorophenyl, perfluorobiphenyl, or 2,4-difluorophenyl) (114–116). Polymerization of bisphenol with 1,2,4,5-tetrafluorobenzene was not observed, and with hexafluorobenzene proceeded only if the ratio of potassium carbonate to bisphenol was carefully controlled. The polymer derived from decafluorobiphenyl and bisphenol AF is produced in 77% yield and has an inherent viscosity of 1.07 dL/g. These polymers are highly soluble and thermally stable and exhibit low water uptake (0.3%) and a very low dielectric constant (2.21).



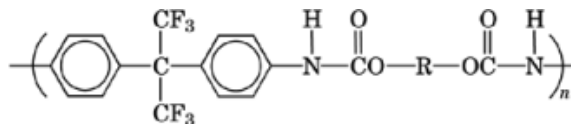
Some amorphous copoly(ether-sulfone) films have been prepared (117) with T_g s around 130°C with no loss in weight up to 400°C in air or N₂. Other backbones investigated in this class of polymers are copoly(ether-amides) (118) and copoly(ether-ketones) (119). These polymers show good mechanical properties, flow characteristics, and abrasion resistance.

A polyester backbone with two HFIP groups (12F aromatic polyester of 12F-APE) was derived by the polycondensation of the diacid chloride of 6FDCA with bisphenol AF or bisphenol A under phase-transfer conditions (120). These polymers show complete solubility in THF, chloroform, benzene, DMAC, DMF, and NMP, and form clear, colorless, tough films; the inherent viscosity in chloroform at 25°C is 0.8 dL/g. A thermal stability of 501°C (10% weight loss in N₂) was observed.

The first HFIP-based polycarbonate was synthesized from bisphenol AF with a nonfluorinated aromatic diol (bisphenol A) and phosgene (121, 122). Incorporation of about 2–6% of bisphenol AF and bisphenol A polycarbonate improved the dimensional stability and heat-distortion properties over bisphenol A homopolycarbonate. Later developments in this area concern the flame-retardant properties of these polymers (123, 124).



High molar mass polyurethanes were obtained from condensation of 4,4'-(hexafluoroisopropylidene)bis(phenylchloroformate) with various diamines (125). These polymers could be cast into transparent, flexible, colorless films or spun into fibers which showed promise as crease-resistant fabrics. Other polyurethanes discovered are good candidates for naval and aerospace applications (126).



5.2. Applications

The applications sought for these polymers include composites, structural plastics, electronics/circuit boards, aircraft/spacecraft coatings, seals, dental and medical prosthetics, and laser window adhesives. However, other

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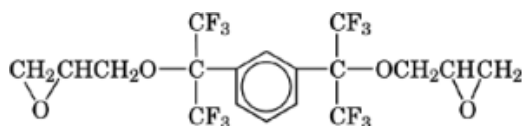
than the early commercialization by Du Pont of the NR-150 B material, little development has occurred. These polymers are quite expensive (\$110 to \$2200 per kg for monomers alone).

6. Hexafluoroisopropoxy (HFIP-O) Group-Containing Polymers

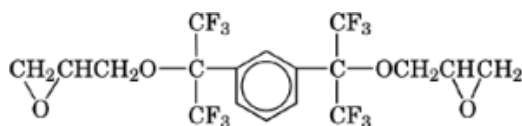
Several classes of polymers containing the HFIP-O group have been reported. These polymers show promise as film formers, gas separation membranes, coatings, seals, and other high temperature applications due to the properties imparted by this function, similar in many ways to the HFIP group.

6.1. Synthesis and Properties

Several polymers containing HFIP-O groups have been investigated, the most common being epoxies and polyurethanes. The development of fluorinated epoxy resins and the basic understanding of their chemistry has been reviewed (127).

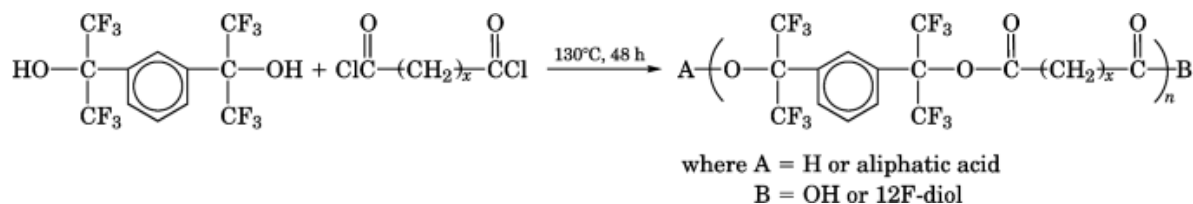


Numerous avenues to produce these materials have been explored (128–138). The synthesis of two new fluorinated bicyclic monomers and the use of these monomers to prepare fluorinated epoxies with improved physical properties and a reduced surface energy have been reported (139, 140). The monomers have been polymerized with the diglycidyl ether of bisphenol A, and the thermal and mechanical properties of the resin have been characterized. The resulting polymer was stable up to 380°C (10% weight loss by tga).



One of the first attempts to produce polyurethane was from the reaction of an intermediate polyol of 1,3- and 1,4-bis(hydroxyhexafluoroisopropyl)benzene (*m*- and *p*-12F-diols) by reaction with epichlorohydrin. This polyol was subsequently allowed to react with a commercial triisocyanate, resulting in a tough, cross-linked polyurethane (129, 135, 139). ASTM and military specification tests on these polyurethanes for weather resistance, corrosion prevention, blister resistance, and ease of cleaning showed them to compare quite favorably with standard resin formulations.

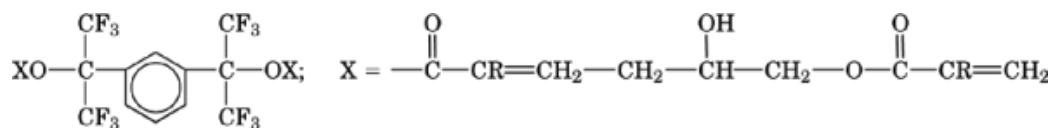
The next approach to incorporate the 12F-diol into a polyurethane matrix was reaction of the *m*-12F-diol with aliphatic diacid chlorides (where $x = 3$ or 4) to give low molar mass polyesters (141):



For OH terminals chain extension leads to polyurethanes, polyesters, etc. For acid terminals, chain extension leads to polyesters, polyamides, etc. Interestingly, a stoichiometric balance between the acid and diol did not yield a high molar mass polyester, and further heating to 150°C resulted in degradation of the product. However, by reaction of a slight excess of the diol or diacid chloride, either an oligomeric ($M_n = 2100 - 2700$) diol or diacid, respectively, was achieved, either of which could then be chain extended to high molecular weights.

Following this work, the *m*-12F-diol was used for the direct reaction with hexamethylene-1,6-diisocyanate in the presence of dibutyltin dilaurate to produce a cross-linked elastomer or a reactive prepolymer which was terminated with either isocyanate or hydroxyl groups, depending on which reactant was in excess (142, 143).

Acrylate or methacrylate resins ($R = H$ or CH_3) have been obtained from 1-3-bis(hexafluoroisopropanolyl)-4-fluoroalkylbenzene (144), where $R_f = -C_nF_{2n-1}$ and $n = 1 - 18$, and X is as shown.



These monomers were mixed with nonfluorinated acrylates and cured conventionally, such as by free-radical mechanism. Similar monomers and their polymers have also been reported (144, 145). Monomer was synthesized by the condensation of acryloyl chloride with a 5-fluoroalkyl-substituted *m*-12F-diol in a chlorofluoroalkane solvent with triethylamine acid acceptor.

6.2. Applications

These polymers have been proposed or evaluated for a number of applications such as structural plastics, special aircraft coatings, aircraft windshield coatings, lubricant barrier films, coatings for ships and ice breakers, and as fillings for teeth or the molding of false teeth. More recent applications of these polymers include laser window adhesives and optical cement. The largest application, however, has been as a chemically resistant coating for storage tanks.

HFIP-O-containing fluoroacrylate polymers have been suggested earlier for biomedical applications such as artificial human organs and dental materials (146). This is largely due to the ability to polymerize monomers containing a suspension of polytetrafluoroethylene. The result is a tough product with low water absorption and a low friction surface. These polymers are also useful as textile impregnants (147). Epoxy resins have potential for use in computer composite circuit boards. The resin with branched ether suggests possible application in blood oxygenators or, eventually, artificial lungs (148).

BIBLIOGRAPHY

"Heat-Resistant Polymers" in *ECT* 3rd ed., Vol. 12, pp. 203-225, by J. Preston, Monsanto Triangle Park Development Center, Inc.

Cited Publications

1. H. H. Levine, *Ind. Eng. Chem.* **54**, 22 (1962).
2. P. E. Cassidy and N. C. Fawcett, *Encycl. Chem. Technol.* **18**, 704 (1982).
3. P. E. Cassidy, *Thermally Stable Polymers-Synthesis and Properties*, Marcel Dekker, Inc., New York, 1980.
4. J. W. Verbicky, Jr., in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. **12**, Wiley-Interscience, New York, 1988, p. 364.
5. N. D. Ghatge, B. M. Shinde, and U. P. Mulik, *J. Macromol. Sci. Chem.* **A22**, 1109 (1985).

6. H. J. Jeong and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **29**, 39 (1991).
7. Y. Oishi and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 1027 (1992).
8. J. O. Park and S. H. Jang, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 723 (1992).
9. H. R. Kricheldorf and R. Huner, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 337 (1992).
10. J. R. Evans, R. A. Orwall, and S. S. Tang, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 3559 (1984).
11. S. K. Dolui, D. Pal, and S. Maiti, *J. Appl. Polym. Sci.* **30**, 3867 (1985).
12. J. F. Dezern, *J. Polym. Sci., Polym. Chem. Ed.* **26**, 2157 (1988).
13. F. J. Serna, J. D. Abajo, and J. G. De la Campa, *J. Appl. Polym. Sci.* **30**, 61 (1985).
14. S. H. Hsiao and C. P. Yang, *J. Polym. Sci., Polym. Chem. Ed.* **29**, 447 (1991).
15. E. Butuc and G. Gherasim, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 503 (1984).
16. J. A. Mikroyannidis and A. P. Melissaris, *J. Polym. Sci., Polym. Chem. Ed.* **26**, 1405 (1988).
17. V. V. Korshak and co-workers, *Acta Polym.* **39**, 8 (1988).
18. S. Kubota and T. Ando, *J. Appl. Polym. Sci.* **35**, 695 (1988).
19. R. O. Johnson and H. S. Burlhis, *J. Polym. Sci., Polym. Symp.* **70**, 129 (1983).
20. B. K. Mandal and S. Maiti, *J. Polym. Sci., Polym. Lett. Ed.* **23**, 317 (1985).
21. I. K. Varma, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.* **20**, 283 (1982).
22. A. V. Galanti and D. A. Scola, *J. Polym. Sci., Polym. Chem. Ed.* **19**, 451 (1981).
23. C. P. R. Nair and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **24**, 1109 (1986).
24. B. S. Rao, *J. Polym. Sci., Polym. Letts.* **26**, 3 (1988).
25. I. K. Varma, S. P. Gupta, and D. S. Varma, *Die Angew. Makromol. Chem.* **153**, 15 (1987).
26. K. N. Ninan and co-workers, *J. Appl. Polym. Sci.* **37**, 127 (1989).
27. S. Maiti and A. Ray, *Makromol. Chem.* **183**, 2949 (1982).
28. K. Kurita and H. Murakoshi, *Polym. Commun.* **26**, 179 (1985).
29. D. Kumar, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 3439 (1984).
30. D. Kumar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 927 (1984).
31. B. N. Achar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.* **20**, 773 (1982).
32. B. N. Achar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.* **20**, 2781 (1982).
33. B. N. Achar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.* **21**, 3063 (1983).
34. B. N. Achar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 319 (1984).
35. B. N. Achar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.* **23**, 1677 (1985).
36. G. N. Babu, in K. L. Mittal, ed., *Polyimides, Syntheses, Characterization and Applications*, Vol. 1, Plenum Press, New York, 1984, p. 51.
37. A. K. St. Clair and T. L. St. Clair, in Ref. 36, Vol. 2, p. 977.
38. H. D. Burks and T. L. St. Clair, in Ref. 36, p. 117.
39. H. D. Burks and T. L. St. Clair, *J. Appl. Polym. Sci.* **30**, 2401 (1985).
40. G. D. Roberts and R. W. Lauver, *J. Appl. Sci.* **33**, 2893 (1987).
41. D. Wilson, *Brit. Polym. J.* **20**, 405 (1988).
42. D. Garcia and T. T. Sarafini, *J. Polym. Sci., Polym. Phys. Ed.* **25**, 2275 (1987).
43. P. E. Cassidy, T. M. Aminabhavi, and J. M. Farley, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **C29**, 365 (1989).
44. P. E. Cassidy and co-workers, *European Polymer J.* (in press).
45. J. Malinge, J. Garapon, and B. Sillion, *Brit. Polym. J.* **20**, 431 (1988).
46. K. Taguchi, *J. Polym. Sci., Polym. Lett. Ed.* **18**, 525 (1980).
47. G. A. Brown, *Org. Coat. Plast. Prepr.* **43**, 476 (1980).
48. Y. K. Lee and J. D. Craig, *Org. Coat. Plast. Prepr.* **42**, 451 (1980).
49. P. E. Cassidy and N. C. Fawcett, *J. Macromol. Sci., Rev. Macromol. Chem.* **C17**, 209 (1979).
50. I. K. Varma and C. K. Geetha, *Indian J. Chem.* **16A**, 352 (1978).
51. I. K. Varma and C. K. Geetha, *J. Appl. Poly. Sci.* **22**, 411 (1978).
52. S. U. Ahmed and S. I. Ahmed, *Polym. Mater. Sci. Eng.* **59**, 994 (1988).
53. N. D. Negodyaev and T. P. Sokolova, Deposited Doc., VINITI 3390-75, (1975); *Chem. Abstr.* **88**, 74564.
54. Y. Saegusa, T. Koshikawa, and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 1369 (1992).

55. I. Schopov and M. Vodenicharova, *Makromol. Chem.* **179**, 63 (1978).
56. A. Klimmek and J. Krieger, *Angew. Makromol. Chem.* **109/110**, 165 (1982).
57. C. J. Thaemlitz, W. J. Weikel, and P. E. Cassidy, *Polym. Prepr.* **32(2)**, 260 (1991).
58. E. Oikawa and H. Nozawa, *Polym. Bull.* **13**, 481 (1985).
59. J. L. Hedrick, *Polym. Bull.* **25**, 543 (1991).
60. M. Sato and M. Yokoyama, *J. Polym. Sci., Polym. Chem. Ed.* **18**, 275 (1980).
61. G. P. De Gaudemaris and B. J. Sillion, *J. Polym. Sci., Polym. Phys. Ed.* **2**, 2203 (1964).
62. J. K. Stille and J. R. Williamson, *J. Polym. Sci., Polym. Chem. Ed.* **2**, 3867 (1964); and *Polym. Phys. Ed.* **2**, 209 (1964).
63. P. M. Hergenrother and H. H. Levine, *J. Polym. Sci., Polym. Chem. Ed.* **5**, 1453 (1967).
64. P. M. Hergenrother, in P. M. Hergenrother, *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. **13**, Wiley-Interscience, New York, 1988, p. 55.
65. P. M. Hergenrother, *J. Macromol. Sci. Rev. Macromol. Chem.* **6**, 1 (1971).
66. F. L. Hedberg and F. E. Arnold, *J. Polym. Sci., Polym. Chem. Ed.* **14**, 2607 (1976).
67. P. M. Hergenrother, *Macromolecules* **14**, 8918 (1981).
68. P. M. Hergenrother, *Polym. Eng. Sci.* **21**, 1072 (1981).
69. R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, *J. Polym. Sci., Polym. Chem. Ed.* **15**, 1081 (1977).
70. P. M. Hergenrother, *J. Appl. Polym. Sci.* **28**, 355 (1983).
71. N. M. Belomoina and co-workers, in M. J. M. Abadie and B. Silliori, eds., *Polyimides and Other High Temperature Polymers*, Elsevier Science Publishers, Amsterdam, 1991, p. 143.
72. S. Lin and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 1939 (1984).
73. R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, *J. Polym. Sci., Polym. Chem. Ed.* **15**, 1081 (1977).
74. F. L. Hedberg and F. E. Arnold, *J. Appl. Sci.* **24**, 763 (1979).
75. S. Kubota and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **24**, 2047 (1986).
76. V. V. Korshak and co-workers, *Acta Polym.* **39**, 455 (1988).
77. J. L. Hedrick and J. W. Labadie, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 105 (1992).
78. J. L. Hedrick and J. W. Labadie, *Macromolecules* **21**, 1883 (1989).
79. J. W. Labadie, J. L. Hedrick, and S. K. Boyer, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 519 (1992).
80. M. Bruma and co-workers, *Angew. Makromol. Chem.* **193**, 113 (1991).
81. L. Fengcai, W. Baigeng, and C. Jinbao, *Polym. Sci. Technol.* **26**, 261 (1984).
82. L. Y. Chiang and co-workers, *Polym. Mater. Sci. Eng.* **64**, 216 (1991).
83. N. H. Hendricks and co-workers, *Int. SAMPE Electron. [Conf.]* **4**, 544 (1990).
84. Z. Chi, L. Zhugan, and L. Fengcai, *Polymer* **32**, 3075 (1991).
85. N. H. Hendricks and co-workers, *Int. SAMPE Electron. [Conf.]* **5**, 365, (1991).
86. A. K. Agarwal and S. A. Jenekhe, *Chem. Mater.* **4**, 95 (1992).
87. A. K. Agarwal and co-workers, *Polym. Prepr.* **32(3)**, 124 (1991).
88. P. Friedlander, *Chem. Ber.* **15**, 2572 (1882).
89. D. M. Sutherlin, in J. I. Kroschwitz ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. Index, Wiley-Interscience, New York, 1990, p. 279.
90. J. F. Wolfe and J. K. Stille, *Macromolecules* **9**, 489 (1976).
91. J. K. Stille, *Contemp. Top. Polym. Sci.* **5**, 209 (1984).
92. P. D. Sybert and J. K. Stille, *Macromol. Synth.* **9**, 49 (1985).
93. J. A. Moore and D. R. Robello, *Macromolecules* **22**, 1084 (1989).
94. D. T. Clark and co-workers, *Macromolecules* **17**, 1871 (1984).
95. D. M. Sutherlin and J. K. Stille, *Macromolecules* **19**, 251 (1986).
96. P. M. Cotts and G. C. Berry, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **24**, 328 (1983).
97. P. M. Cotts, *J. Polym. Sci., Polym. Phys. Ed.* **24**, 1493 (1986).
98. E. K. Zimmermann and J. K. Stille, *Macromolecules* **18**, 321 (1985).
99. M. Ding and J. K. Stille, *Macromolecules* **16**, 839 (1983).
100. S. J. Stoessel, C. M. Elliott, and J. K. Stille, *Chem. Mat.* **1**, 259 (1989).
101. S. E. Tunney, J. Suenaga, and J. K. Stille, *Macromolecules* **20**, 258 (1987).

24 HEAT-RESISTANT POLYMERS

102. J. P. Droske, J. K. Stille, and W. B. Alston, *Macromolecules* **17**, 14 (1984).
103. W. J. Koros and D. R. B. Walker, *Polym. J.* **23**, 481 (1991).
104. C. J. Thaemlitz, W. J. Weikel, and P. E. Cassidy, *Polymer* **33**, 3278 (1992).
105. H. H. Gibbs, *Proc. 17th Natl. SAMPE Symp.* **17**, 1 (1972).
106. H. H. Gibbs, and C. V. Breder, *Polym. Prepr.* **15**(1), 775 (1974).
107. H. H. Gibbs and C. V. Breder in N. A. J. Platzter, ed., *Copolymers, Polyblends, and Composites, Adv. Chem. Ser., No. 142*, Am. Chem. Soc., Washington, D.C., 1975, p. 442.
108. W. H. Mueller and R. Vora, *Product Data Sheet*, American Hoechst Corp., SPG-Central Research, Rhode Island, 1987.
109. U.S. Pat. 4,569,988 (Feb. 11, 1986), D. A. Scola and R. H. Pater (to United Technologies Corp.).
110. Jpn. Kokai Tokkyo Koho, JP. 58,180,531 (Oct. 22, 1983), (to Hitachi Chem. Co., Ltd.).
111. G. R. Husk, P. E. Cassidy, and K. L. Gebert, *Macromolecules* **21**, 1234 (1988).
112. Fr. Pat. 1,394,897 (Apr. 9, 1965), (to E. I. du Pont de Nemours & Co., Inc.).
113. U.S. Pat. 3,332,909 (July 25, 1967), A. G. Farnham and R. N. Johnson (to Union Carbide Corp.).
114. J. Irvin and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 1675 (1992).
115. F. W. Mercer and co-workers, *J. Polym. Sci., Polym. Chem. Ed.* **30**, 1767 (1992).
116. U.S. Pat. 5,115,082 (May 19, 1992), F. W. Mercer and R. C. Sovish (to Raychem Corp.).
117. M. Shimizu, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.* **25**, 2385 (1987).
118. Jpn. Kokai Tokkyo Koho JP. 58,149,944 (Sept. 6, 1983) (to Hitachi Chem. Co., Ltd.).
119. P. E. Cassidy, G. L. Tullos, and A. K. St. Clair, *Macromolecules* **24**, 6059 (1991).
120. L. S. Wells, P. E. Cassidy, and K. M. Kane, *High Perform. Polym.* **3**, 191 (1991).
121. Eur. Pat. Appl. 29,111 (May 27, 1981), S. Krishnan and A. L. Baron (to Mobay Chemical Corp.).
122. U.S. Pat. 4,346,211 (Aug. 24, 1982), S. Krishnan and A. L. Baron (to Mobay Chemical Corp.).
123. PCT Int. Appl. WO 82 02,402 (July 22, 1982), V. Mark and C. V. Hedges (to General Electric Co.).
124. Jpn. Kokai Tokkyo Koho, JP., 62,141,061 (June 24, 1987), T. Tokuda and K. Furukawa (to Teijin Chemicals Ltd.).
125. U.S. Pat. 3,373,139 (Mar. 12, 1968), P. W. Morgan (to E. I. du Pont de Nemours & Co., Inc.).
126. T. M. Keller, *J. Polym. Sci., Polym. Chem. Ed.* **23**, 2557 (1985).
127. J. R. Griffith, J. G. O'Rear, and S. A. Reines, *Chemtech*, 311 (May 1972).
128. J. R. Griffith and D. E. Field, *NRL Progr. Rep.*, (June 1973).
129. J. G. O'Rear and J. R. Griffith, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Prepr.* **33**(1), 657 (1973).
130. U.S. Pat. 3,879,430 (Apr. 22, 1975), J. G. O'Rear and J. R. Griffith (to U.S. Navy).
131. U.S. Pat. 3,852,222 (Dec. 31, 1974), E. F. Donald, C. V. Falls, and J. R. Griffith (to U. S. Navy).
132. J. R. Griffith, D. E. Field, and J. G. O'Rear, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Prepr.* **34**(1), 709 (1974).
133. Can. Pat. 956,398 (Oct. 15, 1974), J. R. Griffith (to U. S. Navy).
134. D. E. Field and J. R. Griffith, *Ind. Eng. Chem. Prod. Res. Dev.* **14**, 52 (1975).
135. J. R. Griffith, J. G. O'Rear, and J. P. Reardon, *Polym. Sci., Technol. (Adhes. Sci. Technol.)* **9A**, 429 (1975).
136. U.S. Pat. Appl. 329,229 (Mar. 27, 1989), J. R. Griffith (to U. S. Navy).
137. J. R. Griffith and J. G. O'Rear, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Prepr.* **40**, 781 (1979).
138. U.S. Pat. 4,045,408 (Aug. 30, 1977), J. R. Griffith and J. G. O'Rear (to U.S. Navy).
139. R. F. Brady and A. M. Sikes, *Macromolecules* **24**, 688 (1991).
140. A. M. Sikes and R. F. Brady, *Polym. Prepr.* **31**(1), 358 (1990).
141. T. M. Keller, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 2719 (1984).
142. T. M. Keller, *J. Polym. Sci., Polym. Chem. Ed.* **23**, 2557 (1985).
143. B. S. Holmes and T. M. Keller, *Am. Chem. Soc., Div. Polym. Chem. Prepr.* **25**(1), 338 (1984).
144. U.S. Pat. Appl. 237,838 (Aug. 14, 1981), J. R. Griffith and J. G. O'Rear (to U. S. Navy).

145. J. R. Griffith, *Am. Chem. Soc., Div. Polym. Mater. Sci., Eng. Prepr.* **50**, 304 (1984).
146. U.S. Pat. 4,356,296 (Oct. 26, 1982), J. R. Griffith and J. G. O'Rear (to U.S. Navy).
147. U.S. Pat. 3,544,535 (Dec. 1, 1970), E. E. Gilbert (to Allied Chemical Corp.).
148. J. R. Griffith and J. G. O'Rear, *Polym. Mater. Sci. Eng.* **53**, 766 (1985).

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