Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

History of Heat-Resistant Polymers

Patrick E. Cassidy[a]
[a] Department of Chemistry, Southwest Texas State University, San Marcos, Texas

To cite this Article Cassidy, Patrick E.(1981) 'History of Heat-Resistant Polymers', Journal of Macromolecular Science, Part A, 15: 7, 1435 — 1460
To link to this Article: DOI: 10.1080/00222338108056792
URL: http://dx.doi.org/10.1080/00222338108056792

J. MACROMOL. SCI.–CHEM., A15(7), pp. 1435-1460 (1981)

History of Heat-Resistant Polymers

PATRICK E. CASSIDY

Department of Chemistry
Southwest Texas State University
San Marcos, Texas 78666

ABSTRACT

Thermally stable polymers can be traced back to the late 1950s when structures were first synthesized which could exist above 300°C in air. Perhaps the first two types of polymers most significant here were aromatic polyamides and polybenzimidazoles. The latter was important because its discovery opened the field of polyheterocycles as heat-resistant backbone functions. The impetus for this field of study was originally aerospace technology (ablation shields, coatings, and adhesives). Since that time, however, other needs have been filled with these types of polymers: high modulus fibers, flame-proof clothing, and reverse osmosis membranes. These new, unexpected advantages have provided the need for further research to replace the decrease in aerospace efforts. Research has continued, not to find a material which is more thermally stable, but to enable better processing of the polymers at hand. This change is due to a plateau seen in thermal stability (up to 600°C in air and up to 800°C in nitrogen by TGA) and to the poor tractibility observed for early heat-resistant polymers. Inorganic polymers have not been investigated in depth for these applications.

INTRODUCTION

In the late 1950s the topic of thermally stable polymers was first recognized by the discovery of heterocyclic and aromatic amide polymers which had the ability to withstand extreme temperatures. A fortuitous discovery, as it were, because it preceded the large aerospace effort of the 1960s. And it is no secret that need begets dollars which beget discoveries. The inverse of this has since occurred to prove the bilateral nature of the relationship. Needs, hence funds, hence discoveries have since declined in that order. When speaking of needs now, it is meant political needs or at least those as perceived in the political process and not those determined by scientists.

There are two graphical representations which can be made and are interesting regarding heat-resistant polymers. The first is a plot of the range thermal stabilities of newly discovered polymers against the year of their discovery (Fig. 1).

Note on Fig. 1 that little significant change has occurred since the very early discovery of these types of polymers. This lack of any great improvement upholds the contention of many of today's researchers (including Professor C. S. Marvel, one of the pioneers in this field) that we are at the limit of thermal stability for organic backbones. The next innovation required for an increase thermal stability is in the area of inorganic polymer chemistry where little work has been done.

What is not shown in Fig. 1 are, of course, data other than merely thermal stability. Several serendipitous discoveries have been made in this field of high temperature polymers. The uses originally envisioned were coatings, ablation shields, adhesives, electronic protection (wire coverings, encapsulations, circuit boards, etc.), insulations, clothing, flame resistant cloth, drogue parachutes and lines, etc. These have been met in most cases; however, other unanticipated uses such as high modulus fibers, liquid crystals, and reverse osmosis membranes also have appeared. Furthermore, new techniques arose from necessity, such as fiber spinning under unusual conditions, curing with no off-gas, and precipitation of high strength films.

Also not shown in Fig. 1 is the new approach to the syntheses of these types of polymers. That is, the emphasis in later years was not to discover new backbones but to make known polymers soluble, moldable, tractable, and processable in general. Therefore, the more recent nemesis of the high-temperature polymer chemist has not been the synthesis of thermally stable materials, but has become the overcoming of the "brick dust syndrome" or the inverse relationship between stability and tractability. The trade-off between thermal stability and processability is always present.

Several approaches were taken to introduce processability without loss of stability. First functional groups were placed in the backbone

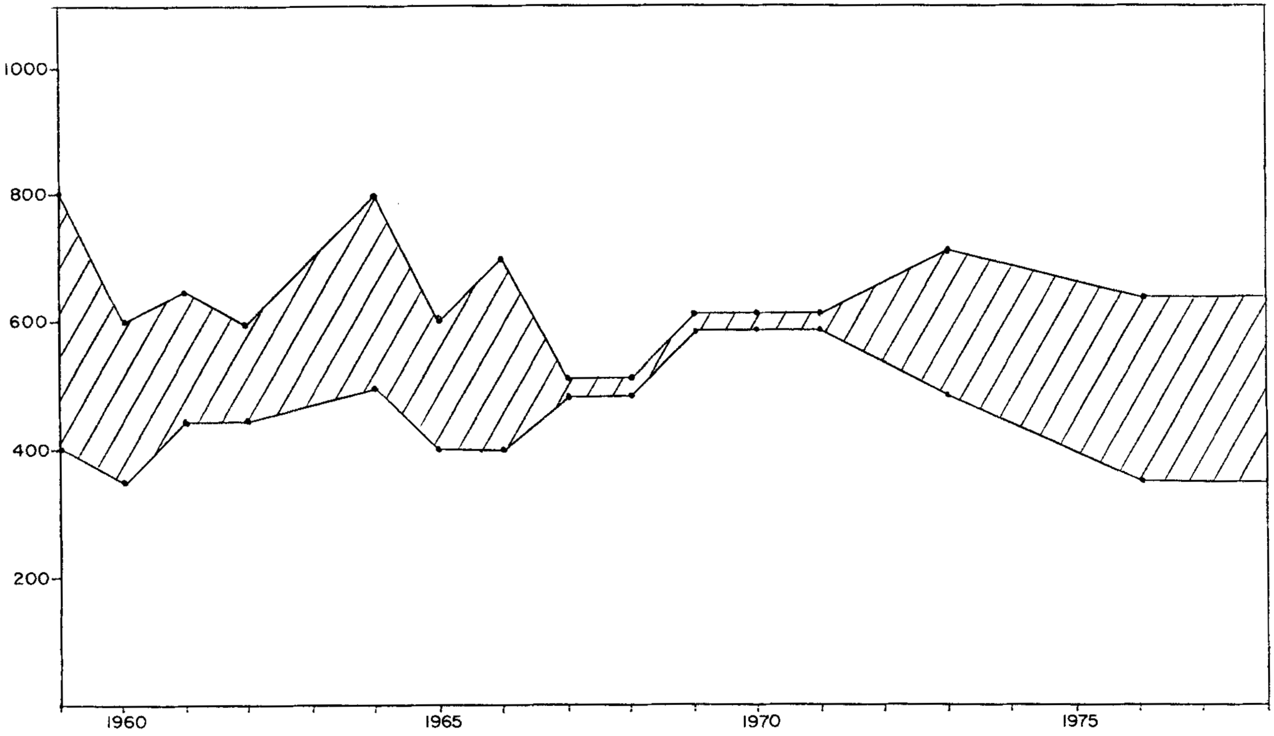


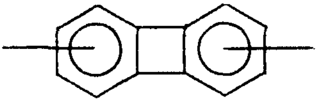
FIG. 1. Thermal stabilities of newly discovered polymers. Ordinate: Thermal stability by TGA (°C). Abscissa: Year of discovery.

to induce flexibility and solubility without the sacrifice in thermal stability. Some of these were ether, sulfone, and thioether.

The second idea was to place bulky yet stable groups such as phenyl pendant to the backbone. This serves to decrease the crystallinity and dense packing of the solid polymer and thereby render it more soluble. The approach was first demonstrated for the polyquinoxalines (PQs) which were made as polyphenylquinoxalines (PPQs) and for the polyphenylenes which were produced as phenylated polyphenylenes. In all cases phenylated versions were much more soluble than their parent structures.

A third and simplest idea was to seek new solvent systems. As a result, several obscure liquids now are readily available such as hexamethylphosphoramide (HMPA) (caution—possible carcinogen). Also the discovery was made that salts such as LiCl in DMF enhanced the solubility considerably; the reason proposed again is the ability of such a solvent system to overcome crystalline forces.

A fourth and most recent approach to the solubility problem was to not produce high molecular weight polymers but instead to synthesize oligomers which could subsequently be cross-linked. This cross-linking must of course take place without an off-gas; that is, without a volatile by-product which would produce bubbles and voids in an adhesive bond or a molded piece. Several methods have proven successful. One is the incorporation of unsaturated end or pendant groups which can trimerize (acetylene or cyano). Other unsaturated functions (norbornenyl) can be incorporated into an addition-type cross-linking reaction. One of the most recent cross-linkable functions to be used is biphenylene which is incorporated into the midst of the backbone:



With heat, one of the two phenylene bonds is broken and reacts with others to provide an interbackbone bond.

A calendar or chronological list can be composed of discoveries in thermally stable polymers. This is given in Table 1 which shows the year in which several syntheses, techniques, and uses were made known. The number of discoveries per year can again be related to funding as discussed earlier. Also noticeable is the fact that in more recent years the number of new polymers reported has decreased, but instead new techniques or modifications of known polymers to improve tractibility and processing are the main points of many publications.

The definition of thermal stability and the way it has been determined and what it means has progressed over the last 20 years during

TABLE 1. Significant Dates in High-Temperature Polymers

1944	Polythiazoles isolated but not characterized
1950-1956	Polyacrylonitrile ladder polymers isolated but not fully cyclized
1955	Poly(p-xylylene)
1957	Low molecular weight polyphenylenes
1958	*(a) Polyoxadiazoles first recognized *(b) Aromatic polyamides patented
1959	*Polyphenylenes of high molecular weight (through 1967)
1960	(a) Polythiazoles (b) Polyperfluoroalkyltriazine elastomers
1961	*(a) Polybenzimidazole, first significant aromatic polyheterocycle *(b) Polyoxadiazoles (c) Poly-bisthiazoles (d) Polytriazoles
1962	Polyborobenzimidazoline
1963	(a) Fibers produced from polyoxadiazoles and polytriazoles (b) Processable polytriazoles
1964	(a) Polytetraazopyrene *(b) Polyquinoxalines (c) Ladder polyaromatic heterocycles suggested (d) Ordered aromatic copolyamides
1965	(a) Polypyrrazoles (b) Poly(ether-quinoxalines) (c) Copoly(benzimidazole-oxadiazole) (d) Polybenzimidazole fibers produced *(e) Pyrrolone ladders—first good ladder system (f) Polybenzthiazoles *(g) Polybenzoxazoles
1966	(a) Regular cyclized ladder from polyacrylonitrile (b) Polyisoxazoles *(c) BBB and BBL (polybisbenzimidazophenanthroline ladders) (d) Poly(pyrazine quinoxaline) ladders (e) Poly(pyrenequinoxaline) ladders (f) Ordered aramid fibers (aromatic polyamides)
1967	(a) Polythiadiazoles (b) Polyetherpyrrones and biphenylpyrrones *(c) Linear polyphenylquinoxaline

(continued)

TABLE 1 (continued)

1968	Experimental polyimide fibers revealed
1969	Pyrazine polyimides (no hydrogen in structure)
1971	*(a) Poly(carborane-siloxanes) (b) Ladder polymers produced from aromatic dianhydrides and tetraaminoanthraquinone
1972	Reverse osmosis properties published
1973	(a) Poly(pyrazine pyrrolones) (b) Adhesives developments
1976	*Polyimidines and poly(benzodipyrolediones)

*Those discussed herein.

which time this field has become known. Without a long discussion here of techniques, the general trend has been to rely more on static methods (isothermal gravimetric analysis, IGA) than on dynamic ones (thermogravimetric analysis, TGA), even though the latter is easier in the academic laboratory. The reason of course is that IGA is more realistic for the anticipated applications.

Of course other methods have come into play, methods which elucidate engineering properties. These techniques (torsional braid analysis, TBA; thermomechanical analysis, TMA; adhesive strength; etc.) are to be expected to be applied more to thermally stable polymers as engineering uses develop.

During early periods in thermally stable polymer work, good thermal stability was defined as above 300°C by TGA in air. Usually this meant that at this temperature the polymer would retain 7-10% of its original weight. More recently maintenance of physical properties for long times at 250°C in air by IGA is more readily accepted as the standard.

Now one sees yet new applications for these high-temperature polymers, generally thought of as polymers for unusual service conditions. A natural extension of these was into geothermal energy applications. Unfortunately, all background data used to select candidates for this new technology were from aerospace research, and geothermal exposure provides an entirely new environment, a reductive, hydrolytic one rather than an oxidative one. Therefore the surprise should have been anticipated (but wasn't) when siloxanes, carboranes, and phosphazene polymers collapsed dramatically in geothermal fluid (CO_2, H_2O, H_2S, CO, and salt) at 200-300°C. Here, thermally stable polymers are hydrocarbons and fluorinated hydrocarbons rather than the sophisticated heterocyclic and inorganic compositions. It is interesting that no definitive screening of backbone types has been made for geothermal stability.

Yet another area from which little has been heard for thermally stable polymers is solar energy equipment. The question is: Can one expect a whole new set of problems here?

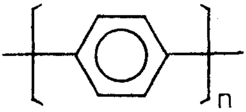
The cost of thermally stable polymers has shown the typical relationship to need and availability. That is, when the need is great and the availability is not, then price is no object. Two examples illustrate this. When Boeing was in production of the SST, the wing panel adhesive (PPQs to replace rivets) was purchased for $450 a pound. Also, O-rings for geothermal drill bits can be made for economical use from a starting material which costs $2000 per pound.

So, it is difficult for the polymer scientist to overcome his frugality in economics to allow him to consider what may seem to be outrageously priced products.

SPECIFIC POLYMERS

Not all polymers which have been shown to be thermally stable can be discussed here. Several examples are given which were unique in structure, stability, historical importance, techniques of synthesis or processing. Some general references which are comprehensive and relatively recent are given here. [6B, 16, 18, 48, 51, 77, 100, 116, 118, 123, 141, 161]. The most recent, a survey by C. Arnold [6B], is particularly interesting in comparing the stability of heterocyclic backbones.

Polyphenylene



The selection of polyphenylene was a natural because of its wholly aromatic, and therefore, stable structure. Much early work was done on this backbone including efforts to render it tractible. Several different synthetic routes yielded a black, friable, insoluble powder. Only when phenyl substituents were placed on the backbone did the polymer become light in color and readily soluble.

The coupling of benzene by a Lewis acid catalyst in Kovacic's laboratory provided the first significant mass of polyphenylene in 1962 [84]. Simple substitution of benzene on itself was accomplished earlier by electrolytic methods [132, 134] and by the reactions of dihalobenzenes or Grignard methods [137]; however, only low molecular weights and small yields were possible.

A partially soluble, branched form was produced by the coupling of benzidine tetrazonium chloride [108]. This polymer had a molecular weight of 20,000 but demonstrated a thermal stability inferior to similar materials from other routes.

The next approach appeared in 1964 from Professor Marvel's laboratory, that of polymerization of 1,4-cyclohexadiene with subsequent aromatization [22]. This product was reacted further to a sulfonated and then hydroxylated version which was cross-linked [23]. The desired result of a significantly improved stability was partially realized.

Finally, a light-colored, soluble polyphenylene was synthesized via a Diels-Alder reaction nearly simultaneously in Stille's laboratory in 1967 [104] and by Reid and Freitag in 1966 [124]. This route provided a means to attach phenyl groups to the backbone by using phenyl-substituted diene adducts [145, 155]. This was one of the first demonstrations of the use of pendant phenyls to decrease crystallinity. Fortunately, the thermal stability of these phenylated polyphenylenes was equal to the simple unsubstituted backbone, 550°C in air or nitrogen (a 10% weight loss by TGA) where the loss of pendant phenyl groups occurs.

Harris and co-workers produced a polyphenylene with pendant carboethoxy and phenyl groups by the Diels-Alder route [54]. This was done in an effort to improve solubility, adhesion, and other mechanical properties.

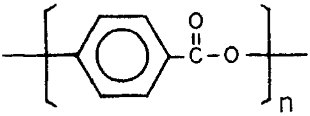
Some of the recent synthetic work has encompassed the diradical coupling of biphenylene units from 4,4'-biphenylene diazonium salts [57] and thermal cross-linking of acetylene-substituted oligomeric polyphenylenes [45].

The structures of polyphenylenes from different syntheses were studied by dilute solution properties [160]. This work served to elucidate the catenation of the backbone units.

Fabrication of the brick dust polymers was accomplished by powder metallurgy techniques to provide a respectable tensile strength (5000 psi or 35 Mpa) [46].

A phenomenon dubbed "ablapaction" was shown to occur with polyphenylene but not with several other analogous systems [47]. This term refers to the extreme shrinkage (20-80%) resulting from controlled ablation (590°C, 1 h in 2000 atm of hydrogen) of polyphenylene.

Polyester

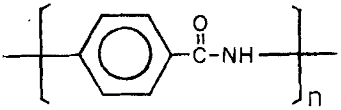


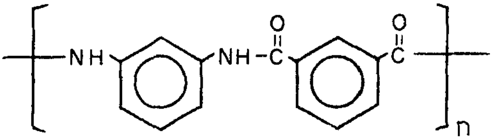
In 1970 Economy, Nowak, and Cottis revealed an aromatic polyester with outstanding properties (Ekonol, Carborundum Co.) [35]. This poly(p-hydroxybenzoic acid) is rated for continual use at 325°C.

Two routes, from p-acetoxybenzoic acid or phenyl p-hydroxybenzoate, yielded the insoluble high-temperature thermoplastic [165]. It displayed high flexural strengths (11,000 psi) and elastic modulus (10^6 psi) but was degraded by bases. By the use of a device known to improve processability of aromatic polyamides, namely the use of ortho- and para-catenation and ordered comonomers, aromatic ester polymers were also synthesized by Mulvaney in 1972 [166]. As expected, however, as solubility increases in analogous polymers the softening point and thermal stability suffer (349 and 380°C in nitrogen, respectively).

Work on Ekonol has continued and is focused on polymer conformation (a double helix crystal) and processing (high-temperature compression sintering or plasma spray coating). A plasticizer for this polymer was found to be poly(tetrafluoroethylene).

Aromatic Polyamides





Following the success of nylons the aromatic analogs were pursued with similar results, even to the point of having the Federal Trade Commission in 1974 designate the term "aramid" as a polyamide with at least 85% of its amide groups adjacent to aromatic rings.

The materials were pursued commercially to give Nomex, Fiber B or Kevlar (DuPont), X-500 (Monsanto), and Exten (Goodyear). These products are in fiber form and are used for heat- or flame-resistant fabric and for high modulus reinforcement, uses which have been reviewed [118]. Most recently the investigation of aramids as liquid crystals has been addressed by Morgan [164], one of the most significant contributors to this class of polymers.

The properties/structure relationship has been well documented in work on aramids [102]. Nomex has a use temperature of 370°C, but the higher modulus para-oriented analog is less tractible and has a higher melting point.

With the advent of ordered copolyamides an easy reference indicator was needed to quickly designate type. Thus "A" referred to carboxylic acid and "B" was amine. Therefore an "A-B" polymer was the result of the condensation of an amino-acid. Whereas an "AA-BB" polymer originated from a diacid and a diammine. One can also envision "A-B/AA-BB" polymers, which indeed are synthesized to decrease backbone order.

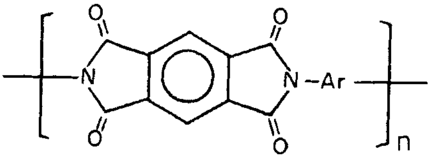
Only interfacial and solution polymerizations are used to prepare aramids. The latter provides a more readily used product, because once the aramid is solidified, resolution is quite difficult. These polymers are soluble in N,N-dimethylacetamide which contains 6.4% lithium chloride (a spinning solution at 19.85% concentration of aramid). The concept of using salts, particularly lithium chloride, in polar, aprotic solvents has proved quite helpful for several polymer types. The reason for this increased solubility has been said to be due to the ability of the salt to interact with crystalline portions of the polymer.

A very recent innovation in aramid chemistry was noted in 1977 by Ogata and Harada [109]. A solution (N-methylpyrrolidone) polymerization is conducted in the presence of arylphosphites [$(C_6H_5O)_3P$], tertiary amines (pyridine), and metal salts (lithium or calcium chloride). High yields (95-100%) of high molecular weight (inherent viscosities 1.05-1.48 dL/g) polymers are obtained except when terephthalic acid is a monomer.

Finally, a third approach to polyamides was shown possible via a formamidinium salt with the elimination of DMF [139].

Numerous references on aramids continue to appear which include structure-property relationships, cross-linkable structures, liquid crystals, processing thermal and photodegradation, and rheological and optical properties.

Polyimides



Another early recognized and now commercial polymer was the polyimide system. Some of those products are H-Film or Kapton (DuPont), P 13 N (TRW), QX-12 (ICI), Kinel or Kerimide 601 (Rhodia, Rhone-Poulenc), and an amide-imide copolymer Amoco A-I (American Oil Co.). They are available as films, fibers, enamels, adhesives, and resins for composite materials and are generally gold or yellow. Polyimides were one of the thermally stable materials which were found to be good reverse osmosis membranes [148, 157]. The physical properties of polyimide films are retained at 185° C for 20,000 h or 235° C for 10,000 h.

The synthesis of polyimides is accomplished by the two-step condensation of a tetraacid dianhydride with a diamine. The intermediate, an amic-acid prepolymer, is soluble and moldable. The second, cyclization step after formation of the desired design, causes the loss of 2 moles of water per repeating unit and results in the insoluble final polyimide. Numerous papers continue to appear which report new syntheses and structures.

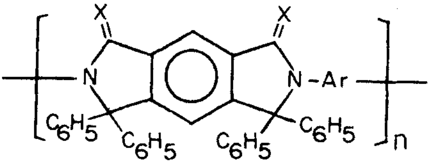
A large number of papers discuss the uses of various acids and amines and their effects on synthesis and properties, the most common system being pyromellitic acid and 4,4'-diaminodiphenyl ether. Several functions (ether, sulfone, alkylene, and bipyridyl) have been sought as ways to induce flexibility [91].

The principal drawback to polyimides is the fact that they have an off-gas, water, upon curing. This by-product causes voids in finished products unless removed during the final cure. Therefore, the use of polyimides as an adhesive is precluded unless the cure reaction is modified. This was accomplished by capping soluble imide oligomers with unsaturated end-groups (maleimide). The final cure then can be an addition-type process with no by-product [29, 70, 91].

Although polyimides are resistant to water at low temperatures (150° C), their high-temperature stability is affected adversely by the presence of water. Even so, these polymers are favored in aerospace use.

An interesting recent datum is that only a 50-85% cyclization can be expected in polyimides due to bound solvent residues [71]. This is important in considering reactions in thermal degradations.

Polyimidines



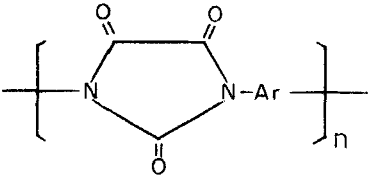
One of the newest types of polymers, first appearing in print in 1976 [20, 25], is polyimidine. Being a fused lactam it could be thought of as being a hybrid of polyimides and polyamides.

The polyimidines as first synthesized incorporated, indeed could not excape incorporating, pendant phenyl groups, four per repeating unit. This undoubtedly was a factor in the ready solubility of these polymers, even when fully cyclized, in common solvents. The synthesis of polyimidines is by the condensation of bis-phthalides or their thio analogs with diamines. Several backbones have been made from oxo and thio and cis and trans forms of tetraphenylpyromellitide [21, 41, 93]. The trans-thio system was found to be the most satisfactory both in terms of ease of preparation, solubility, and thermal stability.

Modification of polyimidine backbones has been by the use of the bisphthalide from BTDA (benzophenone tetracarboxylic acid dianhydride) [17, 19, 96]. Numerous diamines have also been used with this monomer. Further, two aminophthalides have been synthesized and self-condensed [42, 95]. Again, the most stable polymers are the wholly aromatic, but these have poorest solubility.

Thermal stability of these materials ranges from 350° C in air to 650° C in nitrogen, depending on composition.

Polyparabanic Acid

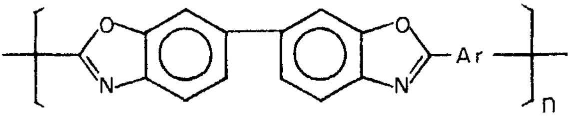


One of the most recent commercial products to arrive out of thermally stable polymer research was wrought by Patton and coworkers at Exxon Chemical [111, 112]. A plant is now being brought on stream to produce yellow-gold, transparent films of this polymer, a competitor for Kapton.

Polyparabanic acids [or poly(1,3-imidazolidine-2,4,5-triones)] are actually produced by hydrolysis of the polydione precursor, the synthesis of which requires the reaction of dicyanides with diisocyanates [110-112].

TGA data show stability to 500° C, and softening points from 55 to 300° C, depending on the backbone composition. The final product is soluble in dimethylformamide and dimethylsulfoxide.

Polybenzoxazoles



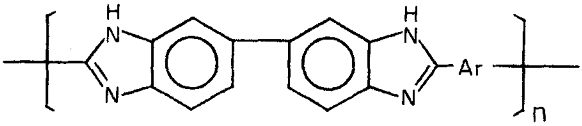
The historical development of this class of polymer was similar to that of its nitrogen analog, polybenzimidazole. In the early 1960s a large number of these polymers were produced [74-76, 90 103] work which has been reviewed by Korshak [82] in 1969. Since that time they have not been investigated perhaps due to poor solubility characteristics (concentrated sulfuric acid). Commercial application has not, therefore, developed even though thermal stability is certainly acceptable (550°C in air by TGA). Hydrolysis resistance for these is not as good as for polybenzimidazoles.

Synthesis of polybenzoxazoles is realized by the two-step condensation of a bis-o-aminophenol with a diamine, done in both solution and melt processes.

The incorporation of oxadiazole functions in the benzoxazole backbone has improved the solubility with no loss of stability [28]. Evers introduced fluoroethers also as a co-backbone function with some sacrifice of stability (400°C), but the product was rubbery (T_g of -31 to 106°C) even after 100 h at 316°C [37-39]. It was soluble in hexafluoro-i-propanol.

Most recently, siloxane benzoxazole copolymers have also been made with improved solubility and retention of stability [14]. However, T_g values were higher (160 to 221°C) than for the fluoroether system.

Polybenzimidazoles



Polybenzimidazoles (PBI), first published in 1961 [156] by Marvel and Vogel, are credited with providing the lead to polyheterocycles as thermally stable materials. Patents on aliphatic systems in 1958 and 1959 gave way to a plethora of papers on aromatic polymers, reviewed by Jones in 1968 [78], and by Levine [94] and Korshak [82] in 1969.

Some interesting side effects have occurred owing to the success of PBI and similar polymers. One is the ready availability of polyfunctional monomers (especially di- and tetraacids and di- and tetraamines). Another is the use of solvents such as concentrated sulfuric acid in fiber spinning processes. Yet a third is the appearance of exotic solvents such as hexamethylphosphoramide and hexafluoroisopropanol.

Again a two-step reaction is envisioned for benzimidazole, through an amic acid intermediate which is soluble and is therefore processed or formed to the desired configuration.

Numerous modifications have been made in the PBI backbone:

incorporation of silane [86], siloxane [14, 105], and oxadiazole and replacement of the amine hydrogen. One of the siloxane copolymers was soluble in pyridine yet retained its stability [14].

A second, better route to PBI by Higgins and Marvel [69] was by the condensation of tetraamines with the bis-bisulfite adduct of isophthaladehyde. Moderate molecular weights were obtained under mild conditions and with short reaction times.

Other routes to PBIs have appeared even more recently. One of these, the condensation of diamines with dinitriles using aluminum chloride followed by cyclization of the resulting amidine, gave oligomers [12]. PBIs with cyano or carboxyl endgroups are possible by this method [13].

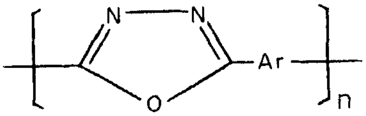
Bisorthoesters also react with tetramines to give PBIs in high yield and molecular weights [34]. Attachment of sulfonic acid pendant groups [152] and phosphorous incorporation [136] with PBI have been accomplished.

Perhaps one of the values of the volumes of data published for PBI is to be able to compare structure-property relationships. These are for PBI, and most others, that stability is lowered and solubility raised when aliphatic, ether, or sulfone groups replace aromatic, or when meta catenation replaces para.

The applications of PBI are numerous and include flame- or heat-resistant clothing, adhesives, ablative shields, parachute lines, reverse osmosis membranes, graphitization, and fuel cell or battery separators, a topic which was well reviewed by Leal in 1975 [92]. Perhaps the most visible application of PBI is in the gold-colored vest prepared for Professor Marvel from this polymer.

Processing of PBI has produced foams as commercial products [159]. A new technique of precipitation has yielded high strength films with PBI as well as with ladder (BBL) (vide infra) and benzoxazole polymers [60]. This discovery could be very important to high-temperature polymer technology.

Poly-1,3,4-oxadiazoles



The oxadiazole ring has been known for some time but not until about 1958 did Huisgen and co-workers [128] begin its detailed exploration. Then in 1961 Abshire and Marvel [1] prepared a long series of the polymers from bis-tetrazoles and diacid chlorides. Finally in 1964 Frazer and Wallenberger [44] developed one of the most popular synthetic routes through the cyclodehydration of polyhydrazides. This last method offered the advantage of soluble and processable intermediate polyhydrazide polymer which can be cast to films, spun to fibers, etc. Once formed, articles are converted by heat treatment to the more thermally stable poly-1,3,4-oxadiazoles.

The subject of polyoxadizoles nearly rivals PBI in the number of articles concerning it. Polyoxadiazoles and analogous polymers have been recently reviewed [18].

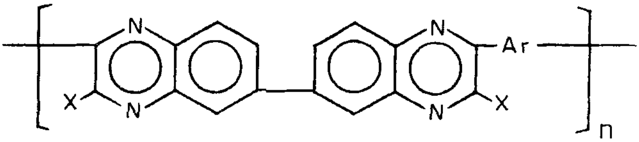
This moiety also lends itself to incorporation with other functions in a backbone such as amide [15, 117], imide [15, 33, 151], carborane [83], siloxane, silane [85-87], and ferrocene [97, 98].

Of the five routes found successful for synthesis of polyoxadiazoles, the most common is polymerization of a diacid derivative with hydrazine followed by a cyclodehydration of the polyhydrazide. The intermediate affords a soluble processable form. A review of this route has been composed by Cotter and Matzner [27].

In general, aromatic polyoxadiazoles are partially crystalline, hydrolytically stable, able to be oriented by drawing, soluble only in concentrated sulfuric or trifluoroacetic acids, and stable to 400-450 °C by TGA.

Fibers and films (yellow to brown) can be formed from polyoxadiazoles. They are candidates for flame-resistant applications, particularly when phosphorus is incorporated into the polymer [162, 163]. A recent development is the production of a porous film by compounding a polyoxadiazole with a thermoplastic resin in sulfuric acid, casting to a film and leaching out the thermoplastic phase [72]. Other applications are composites with glass cloth [26], adhesives to metal [19, 120], cation exchange resin [89], graphitized fibers [40], liquid crystals [36], and high modulus fibers [10, 11].

Polyquinoxalines



Polyquinoxalines have proved to be one of the better high-temperature polymers with respect to both stability and potential application. They are one of the three most highly developed heterocyclic systems, the others being benzimidazoles and oxadiazoles. The interest in the PQs peaked in the late 1960s after the development of the soluble phenylated version (PPQ) and before the demise of the SST (supersonic transport) program. This interest was catalyzed by their ability to act as metal adhesives and by the Boeing Company's desire to have a high-temperature adhesive for the titanium wing panels of the SST. The anticipated weight saving in using an adhesive over rivets was so great that a premium price was no obstacle (said to be $450 a pound at that time). There is still great interest in PQs in spite of the expensive monomers required.

The totally aromatic backbones are derived from the condensation of a tetraamine with a bis-glyoxal and were first synthesized in 1964 concurrently by de Gaudemaris and Sillion in France [31] and by Stille and Williamson [146, 147], and then extended by the latter group with Arnold [142]. In 1967 the phenylated PQ (PPQ) was prepared by Hergenrother and Levine [64, 68]. This material showed significant improvements in solubility, thermal stability, and processability.

Two major difficulties present themselves in the synthesis of high molecular weight PQ: the purity of the tetraamine (very sensitive to air) and the synthesis of the bis-glyoxal, a long, difficult, low yield process, in which improvement is still needed. Solution techniques are used and the final product can be chain extended by a postcure at 375°C.

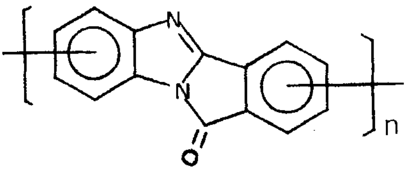
A large number of articles have been written for PQs on structure-property relationships, applications [61, 63, 66, 140], kinetics [53], mechanical properties [9, 62], and characterization [53]. Some applications seen were laminates (with glass [66], boron [67], and graphite fibers [66, 131]) and adhesives (on titanium [61] and stainless steel [66, 67]). The most recent review of PPQs appeared in 1976 by Hergenrother [65].

In general PQs have molecular weights to 300,000, T_g of 133-370°C, inherent viscosities as high as 1.7 dL/g and, for the phenylated version, solubility in chloroform. Tough yellow films of PPQ are cast from cresol solutions.

Several attempts have been made to improve final properties of PQs such as cross-linking of poly(amide-quinoxalines) [9] or of p-tolyl [158] pendant groups or of an acetylenic pendant [59] or end-group [88].

Still another approach to cross-linking was the use of a tris-glyoxal [122]. None of these showed significant changes in thermal stability, although mechanical properties were improved.

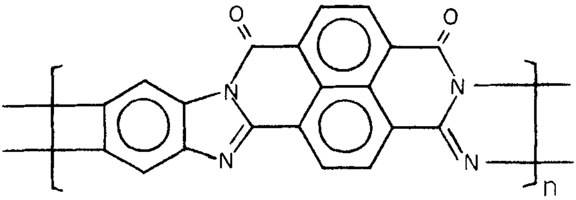
Polypyrrones



Polypyrrones represent one of the first examples of multiple fused rings, a concept which led to the proposal of ladder backbones, a linear chain of fused rings. These polymers, also known as pyrrolones or bisbenzimidazopyrrolones or benzoylenebenzimidazole or benzimidazolimides, were first synthesized in 1965 and most publications and patents occur up to 1969. Very little work is apparent after that time and a review appeared in 1974 [106].

Pyrrone polymers are derived from the solution condensation of tetraacids or their derivatives, with tetraamines, or their salts, via two intermediates which are soluble. There is more off-gas in this reaction than in others in that 4 moles of water are lost from each repeating unit. Therefore the polymerization must be moved through B and C stages so that water can be removed. A rapid polymerization results in a ladder-benzimidazole structure and cross-linking and gelation of the reaction mixture [79].

Phenanthroline Ladder Polymers

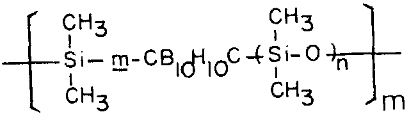


This polymer, one of the best examples of a ladder backbone, developed by van Deusen's group at the Air Force Materials Laboratory in Dayton, Ohio, has been termed a BBL for bisbenzimidazolbenzophenanthroline ladder polymer [7, 154]. A more recent name is imidazoisoquinoline ladders. The purpose and original concept was that a double strand backbone would provide a longer retention of mechanical properties when segments are randomly cleaved. This goal was not realized in that these materials were stable to 450-550°C in air [115], similar to other polyheterocycles. The reason for this probably is due to a high rate of segment degradation once the proper temperature is reached.

As with pyrrones, these ladders are formed by the condensation of the 1,4,5,8-tetraacid of naphthalene, or its anhydride, with a tetraamine. This is accomplished at 150°C in PPA or molten antimony trichloride solutions or at 280°C in the melt.

The preparation of a strong, high modulus film was accomplished recently by the precipitation and vacuum filtration of BBB, a near-ladder backbone [8, 133]. This phenomenon has been said to be due to a supramolecular aggregate with high interchain packing.

Polycarboranes



$$\left[-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\underline{m}\text{-}\mathrm{CB_{10}H_{10}C}\left(-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\right)_n\right]_m$$

Although five- or eight-boron cages are known in polymers, the decaborane ring has been by far most widely exploited. These have been designated as 10-SiB-2 (or 4) types where the 2 or 4 integer is the value of n in the structure. Another designation which has developed is the D_x type, referring to a difunctional silicon link from decaborane. The sub-x refers to the number of siloxane repeating units per carborane. Therefore 10-SiB-2 is equivalent to D_2.

In 1966, reports were first published of the polymers from Princeton University and Olin Matheson. A vinyl-terminated cross-linkable elastomer [129, 130, 138] was developed as a commercial product, Dexsil, by Olin. Its development since has been assumed by Union Carbice as Ucarsil, a very expensive polymer ($2000-4000 per pound). A very recent review has covered this topic [113].

Glass transition temperatures of these polycarboranesiloxanes range from -30 to -60°C; other properties of filled (talc or silica) and unfilled polymers are reported [99, 130]. Data for thermal analysis in air are unusually high and must be regarded with caution. This is owing to the oxidation of carborane beginning at 275°C so that weight is gained during its oxidative decomposition. One must therefore rely on data from an inert atmosphere or actual mechanical property measurements.

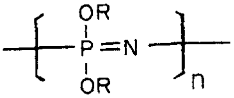
Two syntheses were first possible, both of which involve the condensation of disilanol-capped carborane ring. Lately a third, mild, and fast reaction has been used to give poly(carborane-siloxanes), the condensation of carborane disilanol with bis-ureidosilanes [58].

An attempt to use polycarboranes as elastomeric seals under geothermal conditions served to point out the difference between this application and the usual aerospace uses. The latter are thermo-oxidative while the former are thermoreductive–hydrolytic. Several thermally stable polymers, including this one, showed catastrophic decomposition in this new application [24].

A recent modification was to incorporate a perfluorophenylene group as a bridge between decarboranes in a backbone [6A]. Significantly increased thermal stability was realized, a linear weight loss by TGA in nitrogen to a value of 15% at 1000°C.

Another way to incorporate fluorocarbons is by trifluoropropyl pendant groups [114]. This serves to improve somewhat the solvent resistance but decreases the thermal stability.

Polyphosphazenes



$$\left[-\overset{\displaystyle OR}{\underset{\displaystyle OR}{P}}=N- \right]_n$$

Considerable work by Allcock over 10 years ago at Pennsylvania State University and others at Horizons and then Firestone has resulted in development of broad temperature range, fire-resistant elastomers of polyphosphazenes [125, 126]. Several good reviews are available [2-4, 135], and research on this inorganic rubber is still being actively pursued. The fluorinated commercial product was designated PNF.

The polymer is produced by polymerizing the cyclic dichloro trimer $(Cl_2PN)_3$ in bulk with heat, with or without several catalysts. However, the chlorinated backbone hydrolyzes readily and, therefore, is stabilized by treating with alcohols, phenols, or secondary amines to provide the –OR or –NHR pendant functions.

Among recent publications is the polymerization of the monophenylsubstituted cyclic trimer [5, 126] done to elucidate the reaction mechanism. These products, after alcoholysis, are white, adhesive thermoplastics, soluble in acetone with molecular weights to 300,000.

Alkoxy-substituted backbones have T_g values of -66 to -84°C; aryloxy substituents raise this to +5°C. The latter are also stable in air or argon up to 410°C. Most polyphosphazenes are soluble in common organic solvents such as tetrahydrofuran and chloroform.

Thermal degradation studies of polybis(p-isopropylphenoxy)-phosphazene have shown the process to be by random chain scission rather than depolymerization [49, 153].

Several uses have been proposed and attempted; among these are wire coatings, foam flame retardants [50], biodegradable materials, blood-compatible surgical implants and carriers for slow release drugs [4], and seals [153].

CONCLUSION

In the nearly 20 years of the lifetime of the field of thermally stable polymers, the maximum in stability was reached early. Later work was directed toward improving processability and developing applications and processing techniques.

Many multifunctional compounds (tetraacids and amines) are now commonly available because of the need for them to synthesize more complex molecules. New solvents (hexamethylphosphoramide and hexafluoroisopropanol) and solubilizing agents (lithium chloride) have also appeared.

Techniques to process these stable backbones have been born from necessity: fiber spinning from concentrated sulfuric acid, powder metallurgy operations, and precipitation of high-strength films.

The common uses of these materials can be easily envisioned: fire-resistant fabrics, coatings for electronics, aerospace adhesives, and ablation shields. Several applications have appeared serendipitously, however: biodegradable implants, reverse osmosis membranes, and high-modulus fibers.

Whither now? Perhaps low-cost monomers and processing, better syntheses and characterization, or even inorganic backbones. So far the search has been worth the effort.

ACKNOWLEDGMENTS

The author extends his deepest gratitude to the Robert A. Welch Foundation, Houston, Texas, for their support of some of the original research reported herein and of the author during the preparation of this manuscript. Also the aid of Dr. Newton C. Fawcett is appreciated for his contribution to the sections on polyoxadiazoles and polyparabanic acid. Mr. Richard W. Thomas was also instrumental in the latter and in drawing the structures.

REFERENCES

[1] C. J. Abshire and C. S. Marvel, Makromol. Chem., 44/46, 388 (1961).

[2] H. R. Allcock, Chem. Rev., 72, 315 (1972).

[3] H. R. Allcock, Phosphorous-Nitrogen Compounds, Academic, New York, 1972.

[4] H. R. Allcock, Science, 193, 1214 (1976).

[5] H. R. Allcock and G. Y. Moore, Macromolecules, 8(4), 377 (1975).

[6] (A) C. Arnold, Jr., J. Polym. Sci., Polym. Chem. Ed., 13, 517 (1975). (B) C. Arnold, Jr., Ibid., 14, 265-378 (1979).

[7] F. E. Arnold, Polym. Prepr., 16(2), 251 (1975).

[8] F. E. Arnold and R. L. Van Deusen, Macromolecules, 2, 497 (1969).

[9] J. M. Augl, J. V. Duffy, and S. E. Wentworth, J. Polym. Sci., Polym. Chem. Ed., 12(5), 1023 (1974).

[10] H. C. Bach, F. Dobinson, K. R. Lea, and J. H. Saunders, J. Appl. Polym. Sci., 23, 2125 (1979).

[11] H. C. Bach, F. Dobinson, K. R. Lea, and J. H. Saunders, Ibid., 23, 2189 (1979).

[12] R. A. Brand, M. Bruma, R. Kellam, and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 16, 2275 (1978).

[13] R. A. Brand, R. J. Swedo, and C. S. Marvel, J. Polym. Sci., A-3, 1553 (1965).

[14] L. W. Breed, and J. C. Wiley, J. Polym. Sci., Polym. Chem. Ed., 14, 183 (1976).

[15] M. Bruma, L. Stoicescu-Crivetz, and I Zugravescu, Rev. Roum. Chim., 16(10), 1591 (1971).

[16] P. E. Cassidy, Thermally Stable Polymers: Synthesis and Properties, Dekker, New York, 1980.

[17] P. E. Cassidy and S. V. Doctor, J. Polym. Sci., Polym. Chem. Ed., 18(1), 69 (1980).

[18] P. E. Cassidy and N. C. Fawcett, J. Macromol. Sci.–Rev. Macromol. Chem., C17, 209-266 (1979).

[19] P. E. Cassidy and A. Kutac, J. Polym. Sci., Polym. Chem. Ed., In Press.

[20] P. E. Cassidy and F. W. C. Lee, Ibid., 14, 1519 (1976).

[21] P. E. Cassidy, J. C. Lin, and N. C. Fawcett, Ibid., 17(5), 1309-1315 (1979).

[22] P. E. Cassidy and C. S. Marvel, in Macromolecular Synthesis, Vol. 4 (W. J. Bailey, ed.), Wiley, New York, 1972, pp. 7-8.

[23] P. E. Cassidy, C. S. Marvel, and S. Ray, J. Polym. Sci., A-3, 1553 (1965).

[24] P. E. Cassidy and G. C. Rolls, "Polymeric Materials in Geothermal Energy Recovery," in Proceedings of Materials Sciences Workshop on Polymers, Case-Western Reserve University, Cleveland, Ohio, June 27-29, 1978.

[25] P. E. Cassidy and A. R. Syrinek, J. Polym. Sci., Polym. Chem. Ed., 14, 1485 (1976).

[26] A. Y. Chernikhob, L. A. Rodivilova, E. I., Kraevskay, L. I. Golubenkova, B. M. Kovarskaya, S. N. Nikonova, V. N. Tsuetkov, L. D. Pertsov, and G. V. Bogachev, Plast. Massy, 4, 24 (1973).

[27] R. J. Cotter and M. Matzner, Ring-Forming Polymerizations, Part B-1, Academic, New York, 1972, Chapters 2 and 3.

[28] B. Culbertson and R. Murphy, J. Polym. Sci., Part B, 4, 249 (1966).

[29] F. D. Darmory, Org. Coat. Plast. Chem. Prepr., 34(1), 181 (1974).

[30] F. Dawans and C. S. Marvel, J. Polymer Sci., A-3, 3549 (1965).

[31] G. P. de Gaudermaris and B. J. Sillion, J. Polym. Sci., Part B, 2, 203 (1964).

[32] N. Dogoshi, S. Toyama, K. Ikeda, M. Kurihara, and N. Yoda, Japanese Patent 69, 20,111 (August 1969).

[33] N. Dogoshi, S. Toyama, M. Kurihara, I. K. Masaru, and N. Yoda, Japanese Patent 69, 20,113.

[34] C. D. Dudgeon and O. Vogl, J. Polym. Sci., Polym. Chem. Ed., 16, 1831 (1978).

[35] J. Economy, B. E. Nowak, and S. G. Cottis, SAMPE J., 6, 6 (1970).

[36] S. G. Efimova, N. P. Okromchedlidze, A. V. Volokhina, and M. M. Iovleva, Vysokomol. Soedin., Ser. B, 19(1), 67 (1977); Chem. Abstr., 86(14), 107153 (1977).

[37] R. C. Evers, Polym. Prepr., 15(1), 685 (1974).

[38] R. C. Evers, J. Polym. Sci., Polym. Chem. Ed., 16, 2817 (1978).

[39] R. C. Evers, Ibid., 16, 2833 (1978).

[40] H. M. Ezekiel, Org. Coat. Plast. Chem. Prepr., 31(1), 415 (1971).

[41] N. C. Fawcett, P. E. Cassidy, and J. C. Lin, J. Org. Chem., 42(17), 2929 (1977).

[42] N. C. Fawcett, R. A. Lohr, and P. E. Cassidy, J. Polym. Sci., Polym. Chem. Ed., 17, 3009 (1979).

[43] A. H. Frazer, High Temperature Resistant Polymers, Wiley-Interscience, New York, 1968.

[44] A. H. Frazer and F. T. Wallenberger, J. Polym. Sci., A-2, 1137, 1147, 1157 (1964).

[45] J. E. French, Org. Coat. Plast. Chem. Prepr., 35(2), 72 (1975).

[46] D. M. Gale, J. Appl. Polym. Sci., 22, 1955 (1978).

[47] D. M. Gale, J. Polym. Sci., Polym. Lett. Ed., 15(7), 439 (1977).

[48] A. H. Gerber and E. F. McInerney, Survey of Inorganic Polymers, Horizons Research, Cleveland, Ohio, Document NASA CR-159563, HRI-396, under NASA contract NAS3-21369, June 1979.

[49] L. Goldfarb, N. D. Hann, R. L. Dieck, and D. C. Messersmith, J. Polym. Sci., Polym. Chem. Ed., 16, 1505 (1978).

[50] R. E. Goldsberry, M. J. Adamson, and R. F. Reinisch, Ibid., 11(10), 2401 (1973).

[51] M. A. Golub and J. A. Parker, "Polymeric Materials for Unusual Service Conditions," Appl. Polym. Symp., 22 (1973).

[52] W. F. Gorham, R. S. Gregovian, and J. M. Hoyt, J. Am. Chem. Soc., 82, 5218 (1960).

[53] G. L. Hagnaver and G. D. Mulligan, Macromolecules, 6(4), 477 (1973).

[54] F. W. Harris and B. A. Reinhardt, Polym. Prepr., 15(1), 691 (1974).

[55] F. W. Harris, W. A. Field, and L. H. Lanier, Ibid., 17(2), 353 (1976).

[56] S. Hayama and S. Niino, J. Polym. Sci., Polym. Chem. Ed., 12, 357 (1974).

[57] S. Hayama, S. Niino, and A. Sakamoto, Ibid., 15, 1585 (1977).

[58] E. Hedaya, J. H. Kawakami, P. W. Kopf, G. T. Kwiatkowski, D. W. McNeil, D. A. Owen, E. N. Peters, and R. W. Tulis, Ibid., 15, 2229 (1977).

[59] F. L. Hedberg and F. E. Arnold, Ibid., 14(11), 2607 (1976).

[60] T. E. Helminiak, F. E. Arnold, and C. L. Benner, Polym. Prepr., 16(2), 659 (1975).

[61] P. M. Hergenrother, Org. Coat. Plast. Chem. Prepr., 35(2), 166 (1975).

[62] P. M. Hergenrother, J. Appl. Polym. Sci., 18(6), 1779 (1974).

[63] P. M. Hergenrother, J. Macromol. Sci.–Rev. Macromol. Chem., C6(1), 1-28 (1971).

[64] P. M. Hergenrother, J. Polym. Sci., Part A-1, 6, 3170 (1968).

[65] P. M. Hergenrother, Polym. Eng. Sci., 16(5), 303 (1976).
[66] P. M. Hergenrother, Report D1-82-0969, Boeing Scientific Research Laboratories, Seattle, Washington, May 1970.
[67] P. M. Hergenrother and H. H. Levine, J. Appl. Polym. Sci., 14(4), 1037 (1970).
[68] P. M. Hergenrother and H. H. Levine, J. Polym. Sci., Part A-1, 5, 1453 (1967).
[69] J. Higgins and C. S. Marvel, Ibid., 8(1), 171 (1970).
[70] S. S. Hirsch and S. L. Kaplan, Org. Coat. Plast. Chem. Prepr., 34(1), 162 (1974).
[71] J. H. Hodgkin, J. Appl. Polym. Sci., 20, 2339 (1976).
[72] K. Hosoda, H. Sekiguchi, and K. Sadamitsu, Japanese Patent 73, 00,178.
[73] R. Hisgen, Angew. Chem., 91, 531 (1958).
[74] Y. Imai, J. Taoka, K. Uno, and Y. Iwakura, Makromol. Chem., 83, 167 (1965).
[75] Y. Imai, K. Uno, and Y. Iwakura, Ibid., 83, 179 (1965).
[76] Y. Iwakura, K. Uno, and Y. Imai, Ibid., 77, 33 (1964).
[77] J. I. Jones, Chem. Br., 6(6), 251-259 (1970).
[78] J. I. Jones, J. Macromol. Sci., C2, 303 (1968).
[79] N. J. Johnson, J. Polym. Sci., Polym. Chem. Ed., 19(9), 2727 (1972).
[80] B. Ke, Thermal Analysis of High Polymers, Wiley-Interscience, New York, 1964.
[81] R. E. Kesting, K. F. Jackson, and S. M. Newman, J. Appl. Polym. Sci., 15, 1527 (1971).
[82] V. V. Korshak, Heat Resistance Polymers, Moscow, 1969; pp. 244-248 in Israli translation, 1971.
[83] V. V. Korshak, S. V. Vinogradova, L. A. Glivka, P. M. Valetskii, and V. I. Stanko, Vysokomol. Soedin., Ser. A, 15(7), 1495 (1973).
[84] P. Kovacic and A. Kyriakis, Tetrahedron Lett., p. 467 (1962).
[85] H. N. Kovacs, A. D. Delman, and B. B. Simms, J. Polym. Sci., Part A-1, 6, 2103 (1968).
[86] H. N. Kovacs, A. D. Delman, and B. B. Simms, Ibid., 8(4), 869 (1970).
[87] H. N. Kovacs, A. D. Delman, and B. B. Simms, U.S. Patent 3,567,698 (1971).
[88] R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, Polym. Prepr., 16(2), 246 (1975).
[89] T. V. Kravchenko, M. N. Bogdanov, G. I. Kudryavtsev, and N. P. Okromchedlidge, Vysokomol. Soedin., Ser. B., 15(9), 667 (1973).
[90] T. Kubota and R. Nakanishi, J. Polym. Sci., Part B, 2, 655 (1964).
[91] M. Kurihara and N. Yoda, Bull. Chem. Soc. Jpn., 40, 2429 (1967).
[92] J. R. Leal, Mod. Plast., p. 60 (August 1975).
[93] F. W. C. Lee, P. E. Cassidy, and N. C. Fawcett, "Poly(hexamethylenetetraphenyldithiopyromellitimidine," in Macromolecular Syntheses, Vol. 6, Wiley, New York, In Press.

[94] H. H. Levine, in Encyclopedia of Polymer Science and Technology, Vol. 11, 1969, p. 188.

[95] R. A. Lohr and P. E. Cassidy, Makromol. Chem., 181, 1375 (1980).

[96] R. A. Lohr, P. E. Cassidy, N. C. Fawcett, and A. Kutac, J. Chem. Eng. Data, 24(2), 156-157 (1979).

[97] H. J. Lorkowski and R. Pannier, J. Prakt. Chem., 311, 958 (1969).

[98] H. J. Lorkowski, R. Pannier, and A. Wende, Ibid., 35, 149 (1967).

[99] M. Maienthal, M. Hellman, C. P. Haber, L. A. Lymo, S. Carpenter, and A. J. Carr, J. Am. Chem. Soc., 76, 6392 (1954).

[100] C. S. Marvel, Polym. Prepr., 17(1), 239 (1976).

[101] M. Minami, Japanese Patent 69, 19,878 (August 1969).

[102] G. Montaudo, P. Finocchiaro, and S. Caccamese, J. Polym. Sci., Part A-1, 9, 3627 (1971).

[103] W. W. Moyer, C. Cole, and T. Anyos, J. Polym. Sci., Part A, 3, 2107 (1965).

[104] H. Mukamol, F. W. Harris, and J. K. Stille, J. Polym. Sci., 5, 2721 (1967).

[105] T. Nakajima and C. S. Marvel, J. Polym. Sci., Part A-1, 7, 1295 (1969).

[106] B. Nartississov, J. Macromol. Sci.–Rev. Macromol. Chem., C11(1), 143-176 (1974).

[107] E. W. Neuse, G. Horlbeck, H. Siesler, and K. Yannakow, Polymer, 17(5), 423 (1976).

[108] S. Niino, K. Tsubaki, and S. Hayama, J. Polym. Sci., Polym. Chem. Ed., 11, 683 (1973).

[109] N. Ogata and M. Harada, J. Polym. Sci., Polym. Lett. Ed., 15, 551 (1977).

[110] A. Oku, M. Okano, and R. Oda, Makromol. Chem., 78, 186 (1964).

[111] T. L. Patton, Polym. Prepr., 12(1), 162 (1971).

[112] T. L. Patton, U.S. Patents 3,547,897 (1970), 3,591,562 (1971), 3,635,905 (1972), 3,661,859 (1972), and 3,684,773 (1972).

[113] E. N. Peters, J. Macromol. Sci.–Rev. Macromol. Chem., C17(2), 173-208 (1979).

[114] E. N. Peters, D. D. Stewart, J. J. Bohan, R. Moffit, C. D. Beard, G. T. Kwiatkowski, and E. Hedaya, J. Polym. Sci., Polym. Chem. Ed., 15, 973 (1977).

[115] J. W. Powell and R. P. Chartoff, J. Appl. Polym. Sci., 18(1), 83 (1974).

[116] J. Preston, in Encyclopedia of Polymer Science and Technology, Supplement Vol. 2, 1977, pp. 84-112.

[117] J. Preston and W. B. Black, Macromol. Synth., 3, 93 (1968).

[118] J. Preston and J. Economy, "High Temperature and Flame Resistant Fibers," Appl. Polym. Symp., 21 (1973).

[119] G. Pruckmayr, U.S. Patent 3,376,367 (1968).

[120] G. Pruckmayr, U.S. Patent 3,410,834 (1968).

[121] R. T. Rafter and E. S. Harrison, Org. Coat. Plast. Chem. Prepr., 35(2), 204 (1975).

[122] R. T. Rafter and E. S. Harrison, Polym. Eng. Sci., 16(5), 318 (1976).

[123] N. H. Ray, Inorganic Polymers, Academic, New York, 1979, 173 pp.

[124] W. Reid and D. Freitag, Naturwissenschaften, 53, 306 (1966).

[125] (A) K. A. Reynard, A. H. Gerber, and S. H. Rose, Synthesis of Phosphonitrilic Elastomers and Plastics for Marine Applications, Horizons, Cleveland, Ohio, Naval Ship Engineering, Center, AMMRC CTR 72-29, December 1972 (AD 755188).
(B) K. A. Reynard, R. W. Sicka, J. E. Thompson, and S. H. Rose, Poly(aryloxyphosphazene) Foams and Wire Coverings," Horizons, Cleveland, Ohio, Naval Ship Engineering Center Contract No., N00024-73-5474, March 1975.

[126] R. J. Ritchie, P. J. Harris, and H. R. Allcock, Macromolecules, 12(5), 1014 (1979).

[127] R. Sandler and W. Karo, Polymer Synthesis, Vol. 1, Academic, New York, 1974, p. 258.

[128] J. Sauer, R. Huisgen, and H. J. Sturm, Tetrahedron, 11, 241 (1960).

[129] H. A. Schroeder, R. P. Alexander, T. B. Larchar, and O. G. Schaffling, Report on Contract No. bs-94273, Olin Mathieson Chemical Corp., July 31, 1967.

[130] H. Schroeder, O. G. Schaffling, T. B. Larchar, F. F. Frulla, and T. L. Haying, Rubber Chem. Technol., 39(4), Part 2, 1184 (1966).

[131] T. T. Serafina, P. Delvigs, and R. D. Vannuccim, J. Appl. Polym. Sci., 17(10), 3235 (1973).

[132] A. F. Shepard and B. F. Donnels, J. Polym. Sci., 4, 511 (1966).

[133] A. J. Sicree, F. E. Arnold, and R. L. Van Deusen, J. Polym. Sci., Polym. Chem. Ed., 12, 265 (1974).

[134] C. Simonsev, N. Asandei, and F. Denes, Romanian Patent 50,976 (1968); Chem. Abstr., 70, 20527 (1969).

[135] R. E. Singler, N. S. Schneider, and G. L. Hagnauer, Polym. Eng. Sci., 15(5), 321 (1975).

[136] H. Sivriev and G. Borissov, Eur. Polym. J., 13, (1977).

[137] J. G. Speight, P. Kovacic, and F. W. Koch, J. Macromol. Sci.–Rev. Macromol. Chem., 5(2), 295-386 (1971).

[138] L. H. Sperling, S. L. Cooper, and A. V. Tobolsky, J. Appl. Polym. Sci., 10, 1725 (1966).

[139] J. Spiewak, J. Polym. Sci., Polym. Chem. Ed., 16, 2303 (1978).

[140] J. K. Stille, in Encyclopedia of Polymer Science and Technology, Vol. 11, 1969, p. 389.

[141] J. K. Stille, Polym. Prepr., 17(1), 96 (1976).

[142] J. K. Stille and F. E. Arnold, J. Polym. Sci., B-4, 333 (1966).

[143] J. K. Stille, P. E. Cassidy, and L. Plummer, J. Am. Chem. Soc., 85, 1318 (1963).

[144] J. K. Stille, F. W. Harris, H. Mukanol, R. O. Rakutis, C. L. Schilling, G. K. Noren, and J. A. Reeds, Adv. Chem. Ser., 91, 628 (1969).

[145] J. K. Stille and G. K. Noren, J. Polym. Sci., Part B, 7, 525 (1969).

[146] J. K. Stille and J. R. Williamson, J. Polym. Sci., Part A, 2, 3867 (1964).

[147] J. K. Stille and J. R. Williamson, J. Polym. Sci., Part B, 2, 209 (1964).

[148] S. Strathmann, W. Schumann, and P. E. Gruber, Org. Coat. Plast. Chem. Prepr., 34(1), 487 (1975).

[149] M. Suzuki, E. Hosokawa, S. Hirata, and T. Hoshino, Japanese Patent 69, 26,310 (November 1969).

[150] R. J. Swedo and C. S. Marvel, J. Poly. Sci., Polym. Lett. Ed., 15(11), 683 (1977).

[151] S. Toyama, N. Dokoshi, K. Ikeda, M. Kurihara, N. Yoda, R. Nakanishi, and M. Watanabe, Japanese Patent 69 23,107.

[152] K. Uno, K. Niume, Y. Iwata, F. Toda, and Y. Iwakura, J. Polym. Sci., Polym. Chem. Ed., 15, 1309 (1977).

[153] J. K. Valaitis and G. S. Kyker, J. Appl. Polym. Sci., 23, 765 (1979).

[154] R. L. Van Deusen, O. K. Goins, and A. S. Sicree, J. Polym. Sci., Part A-1, 6, 1777 (1968).

[155] H. F. Vankerckhomven, Y. K. Gilliams, and J. K. Stille, Macromolecules, 5(5), 541 (1972).

[156] H. Vogel and C. S. Marvel, J. Polym. Sci., 50, 511 (1961).

[157] A. Walch, H. Lukas, A. Klimmer, and W. Pusch, J. Polym. Sci., Polym. Lett. Ed., 12, 697 (1974).

[158] S. E. Wentworth and G. D. Mulligan, Polym. Prepr., 15(1), 697 (1974).

[159] Whittaker Corp. product bulletin, Imdite Foam Compounds, San Diego, 1967.

[160] J. L. Work, G. C. Berry, E. F. Casassa, and J. R. Stille, J. Polym. Sci., Polym. Symp., 65, 125 (1978).

[161] W. Wrasidlo, Thermal Analysis of Polymers (Advances in Polymer Science, Vol. 13), Springler, New York, 1974.

[162] M. Yokoyama, Japanese Patent 74 02,198.

[163] T. Yoshida, S. Konya, and M. Yokoyama, Kogyo Kagaku Zasshi, 74(9), 1945 (1971).

[164] P. W. Morgan, J. Polym. Sci., Polym. Symp., 65, 1 (1978).

[165] J. Economy, R. S. Storm, V. I. Matkovich, S. G. Corris, and B. E. Nowak, J. Polym. Sci., Polym. Chem. Ed., 17, 2207 (1979).

[166] D. R. Stevenson and J. E. Mulvaney, Ibid., 10, 2713 (1972).