Recent Advances in High Temperature Polymers

P. M. HERGENROTHER

NASA Langley Research Center, Hampton, VA 23665–5225, U.S.A.

ABSTRACT: The chemistry, mechanical and physical properties of several high temperature polyimides, polyarylene ethers and polyphenylquinoxalines are discussed. As examples, new semi-crystalline polyimides containing carbonyl and ether connecting groups exhibited glass transition temperatures (T_gs) of 215 to 247°C, crystalline melt temperatures (T_ms) of 350 to 442°C, and high film properties. Polyarylene ethers derived from 9,9-bis(4-hydroxyphenyl)fluorene had T_gs of 223 to 280°C, number average molecular weights as high as 39,900 g mol^{-1}, and good adhesive properties. Polyphenylquinoxalines containing pendent phenylethynyl groups were used to form adhesive bonds which exhibited good retention of strength to temperatures as high as 316°C.

KEY WORDS   Polyimides / Polyarylene Ethers / Polyphenylquinoxalines / High Temperature Polymers / Films / Adhesives / Composites / Ethynyl Terminated Oligomers /

High temperature polymers are used or considered for use in functional and structural applications in the aerospace, automotive, domestic, and electronics industry. As examples, adhesives and composites that will withstand thousands of hours of use over the temperature range of −54 to 230°C (and shorter times at higher temperatures) are needed for advanced aerospace vehicles. Nonstick interior coatings and decorative exterior coatings are used on cookware and require excellent adhesion to the substrate and long term chemical and thermal stability. Polymeric thin films are needed in microelectronics which will adhere to the substrate during processing cycles where the temperature may reach 400°C in an inert atmosphere. This paper will discuss our recent work on high temperature polymers with the major emphasis on aerospace applications.

The quest for high temperature polymers began in the early 1960s and led to the development of the aromatic heterocyclic polymers such as the polyimides, polybenzimidazoles and the polyquinoxalines. Polymers from each of these three families are commercially available in various forms such as adhesives, coatings, composite matrices, fibers, films and moldings. Some of these material are used in high temperature aerospace functional and structural applications. However, several problems such as high processing temperatures, environmental durability, and the overall cost of a fabricated component must be resolved before high temperature structural resins find extensive use.

In an attempt to develop better high temperature functional and structural resins, research at NASA Langley Research Center has concentrated on polyimides, polyphenylquinoxalines and polyarylene ethers. The results of our recent work on the chemistry, physical and mechanical properties of these polymers are discussed herein.
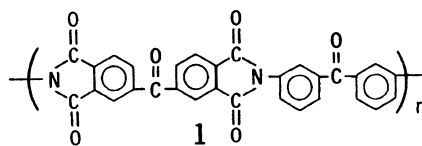
POLYIMIDES

Polyimides constitute the most popular family of high temperature polymers. Because of the availability of the monomers and the

ease of synthesis of new monomers, more structurally different polyimides have been made than all of the other high temperature polymers combined. Polyimides were first reported in the late 1950s and since then, several polyimides such as Kapton®,[1] Upilex,[2] PI-2080,[3] Ultem®,[4] LARC-TPI,[5] Chem-lon,[6] PMR-15,[7] and Thermid 600[8] have become commercially available.* These materials are used in various forms such as adhesives, composite matrices, films, foams, and moldings. The potential market for polyimides is substantial. As a specific example, Du Pont announced a joint venture with Toray in 1984 that provides a worldwide capacity for Kapton® (polyimide film) in excess of 1,132,500 kg/year.[9]

Although several different routes are used to prepare polyimides, the final polymers, if totally aromatic, exhibit good thermooxidative stability and high mechanical properties. The polyimides discussed in this article were prepared from the reaction of aromatic dianhydrides and diamines to form polyamide acids and subsequent conversion of these to the polyimides. The chemical structure of the polyimide can be designed to a large degree with the proper choice of the monomers to provide polymer with a unique combination of properties. In spite of all the work performed on polyimides, these materials still exhibit certain shortcomings such as good processability coupled with high temperature mechanical properties and damage tolerance. Work on polyimides is currently underway in several areas such as improving the processability and high temperature durability, lowering the moisture resistance and dielectric constant, developing transparent and colorless materials, and designing tough polymers with low coefficient of thermal expansion.

In developing polyimides with a better combination of properties, chemical structure/property relationship studies have been perfor-

med. LARC-TPI (Langley Research Center Thermoplastic Polyimide) (structure 1) prepared from the reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzophenone evolved from such a study.[10] The tensile strength, tensile modulus and elongation of thin films of LARC-TPI at 25°C were 135.8 MPa, 3.72 GPa, and 5% respectively.[10,11] Adhesive work with LARC-TPI involved the use of diglyme (diethylene glycol dimethyl ether) as solvent for the polyamide acid because these solutions provided better wetting and significantly higher adhesive strengths than other solutions.[12,13] LARC-TPI as an adhesive to join titanium (Ti, 6Al-4V) to Ti provided tensile shear strengths at 25°C of 42.6 MPa[12] and at 232°C after 32000 h at 232°C in air of 24.8 MPa.[14] LARC-TPI was also found to bond Kapton® to itself as well as to other substrates.[15,16]
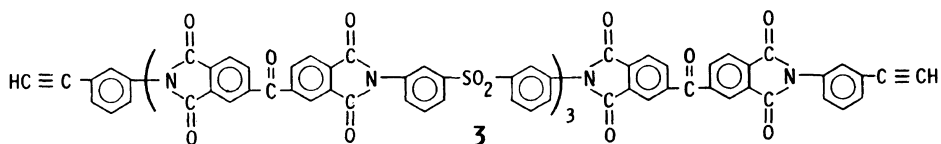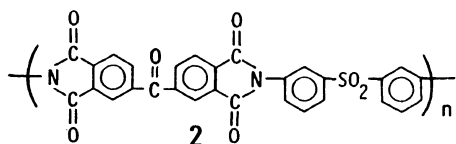
More recent work with LARC-TPI has involved a study on the morphology and evaluation as a composite matrix. LARC-TPI was thought to be an amorphous thermoplastic with a glass transition temperature of 264°C. However, powder samples of LARC-TPI obtained from a commercial source[5] were found to be semi-crystalline.[17,18] The polyamide acid was reportedly cyclodehydrated with acetic anhydride and triethylamine to yield a fine powder of LARC-TPI in a low molecular weight crystalline form (inherent viscosity = 0.23 dl g^{-1} as 0.5% solution in m-cresol at 35°C and crystallinity verified by wide angle X-ray diffraction) with an initial crystalline melt (T_m) of 272°C. The molecular weight of the polymer can be increased by heating, preferably at temperatures >272°C but <330°C.

---

* The use of trade names or manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

For example, a low molecular weight semi-crystalline polymer increased in molecular weight (inherent viscosity $= 0.38$ dl g^{-1}) and transformed into another crystalline form (wide angle X-ray diffractogram different from that of the original powder) with a T_g of 246°C and a T_m of 350°C after heating at 320°C for 1 h. Once the temperature had exceeded 350°C, moderate to high molecular weight polymer became totally amorphous and crystallinity could not be recovered by thermal treatment.

The melt viscosity (10^3 Pa s at 320°C at a strain rate of 0.1 s^{-1})[17] of the semi-crystalline LARC-TPI powder ($T_m = 272$°C) is relatively low, as expected for a low molecular weight polymer. Because of its melt flow properties, it was used in composite fabrication. As an example, two parts (by weight of solids) of LARC-TPI powder were blended with one part of LARC-TPI polyamide acid in diglyme and this slurry was used to impregnate Hercules AS-4 12K carbon fiber to form prepreg. The prepreg was dried at 218°C for 1 h and subsequently was used to fabricate unidirectional composites at 349°C under 2.1 MPa for 1 h. Flexural strength, flexural modulus and short beam shear strengths were 196.4 MPa, 9.7 GPa, and 9.5 MPa at 25°C and 159.9 MPa, 9.0 GPa, and 7.3 MPa at 149°C, respectively.[18]

Another polyimide (structure 2), similar to LARC-TPI, called polyimidesulfone (PISO$_2$) from the reaction of BTDA and 3,3′-diamino-diphenyl sulfone in molded form gave tensile strength and modulus at 25°C of 62.7 MPa and 4.96 GPa, respectively.[19,20] The PISO$_2$ is amorphous with a T_g of 273°C. Unlike LARC-TPI, no crystallinity has been detected in PISO$_2$ even when the polyamide acid was chemically cyclodehydrated to polyimide. Since the melt viscosity of PISO$_2$ at temperatures as high as 371°C was high, semi-crystalline LARC-TPI powder (1 part) was blended with the precursor PISO$_2$ polyamide acid (2 parts by weight of solid) and this slurry was used to make prepreg (Hercules AS-4 12K carbon fiber). Unidirectional composites fabricated at 349°C under 2.1 MPa for 1 h from prepreg dried for 1 h at 218°C gave flexural strength, flexural modulus and short beam shear strength at 25°C of 206.8 MPa, 13.0 GPa, and 12.7 MPa and at 163°C of 147.5 MPa, 10.0 GPa, and 7.7 MPa, respectively.[18]

Another approach under study to improve the processability of high temperature polymers involves blending the high molecular weight polymer with low molecular weight polymer (oligomer) terminated with reactive groups. Upon heating, the terminal groups react to yield a semi-interpenetrating polymer network. For example, an acetylene-terminated imide sulfone oligomer (structure 3) was blended with an equal weight of PISO$_2$. The blend exhibited good processability and provided Ti to Ti tensile shear strengths at 25°C of 24.8 MPa and at 232°C after 1000 h at 232°C in air of 19.3 MPa.[21] This approach is versatile and shows promise of providing structural resins with good processability and mechanical properties.

Semi-crystalline polyimides[24] containing carbonyl and ether connecting groups were prepared (eq 1) because it was known that
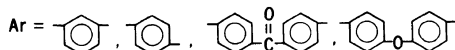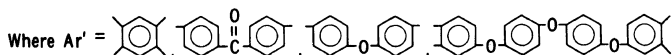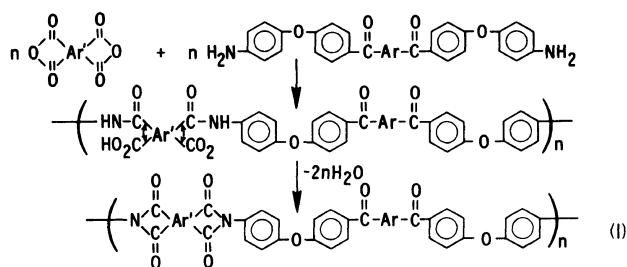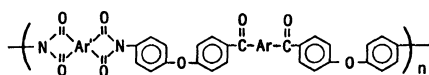

2

3

(1)

Where Ar' = [structures]

Ar = [structures]
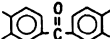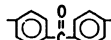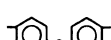
Table I. Polyimides containing carbonyl and ether connecting groups

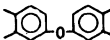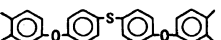| Polymer Designation	Ar'	Ar	Polyamic acid, $\eta_{inh}/dl\,g^{-1}$	Polyimide	
				$T_g/°C$	$T_m/°C$
PMDA/1,3-BABB			1.3	247	442
BTDA/1,3-BABB			0.81	222	350
BTDA/1,4-BABB	''		0.62	233	427
BTDA/4,4'-BABBP	''		0.57	233	422
BTDA/4,4'-BABDE	''		0.52	215	418
ODPA/1,3-BABB			0.65	208	None
BDSDA/1,3-BABB			0.77	192	None

these groups between aromatic rings tend to be so stereochemically similar that there is a strong tendency towards crystalline order.[22] A notable example is polyetheretherketone (PEEK®)[23] which is a readily crystallizable polyarylene ether with a T_g of 143°C and a T_m of 343°C. Carbonyl and ether connecting groups in the semi-crystalline polyimides originated from the diamine monomer. These new diamines were synthesized by the aromatic nucleophilic displacement of fluorine from an activated difluoro compound with 4-amino-

phenol in N,N-dimethylacetamide in the presence of potassium carbonate.

The T_gs and T_ms of several new polyimides are presented in Table I. The last two polyimides in Table I would not crystallize even after annealing for several hours at ~300°C in nitrogen. The differential scanning calorimetric curves in Figure 1 are on a film specimen which had been dried for 1 h at 300°C. A strong melting endotherm is evident at 350°C in run 1. Runs 2, 3, and 4 are consecutive runs on the same sample after

Table II. Thin film properties of semi-crystalline polyimides[a]

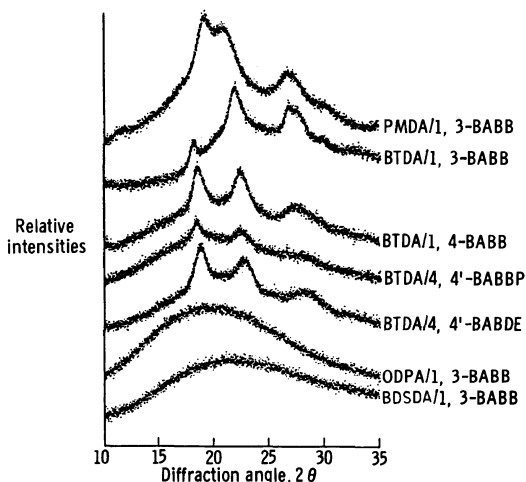| Inherent viscosity of polyamide acid/dl g^{-1}	Test temp	Tensile strength/ MPa (Ksi)	Tensile modulus/ GPa (Ksi)	Elongation
	°C			%
0.81	25	133.7 (19.4)	3.5 (513)	6.5
	177	83.4 (12.1)	3.0 (437)	5.2
	232	31.0 (4.5)	1.4 (206)	74.6
1.16	25	151.7 (22.0)	4.3 (630)	8.3
	177	97.9 (14.2)	3.7 (540)	21.1
	232	35.8 (5.2)	1.7 (245)	76.1

[a] Polyamide acid dried on plate glass through 1 h at 300°C.

Fig. 1. Differential Scanning Calorimetric Curves
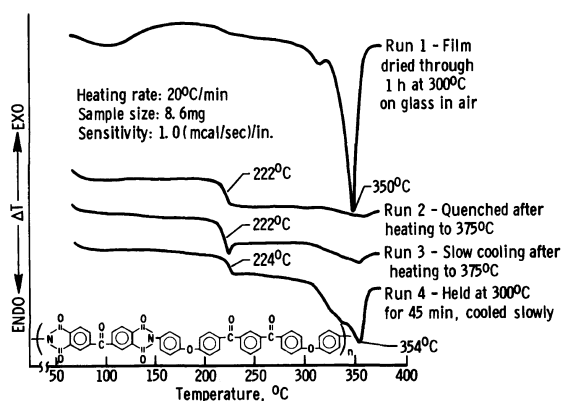
Figure 2. X-Ray diffractograms of polyimide films.

exposure to the conditions indicated. A prominent T_g transition at 222°C is apparent in runs 2 and 3. After annealing the sample from run 3 at 300°C for 45 minutes and slowly cooling, run 4 was obtained and showed a T_g transition at 224°C and a moderately intense endotherm peaking at 354°C. Other polyimides in Table I such as the PMDA/1,3-BABB polymer crystallize more readily than the BTDA/1,3-BABB polymer as expected since the difference between the T_g and T_m is much greater. The X-ray diffractograms of transparent yellow to orange films (dried for 1 h at 300°C) of the polyimides in Table I are shown in Figure 2. Thin film properties of the semi-crystalline BTDA/1,3-BABB polyimide are presented in Table II. Compact tension specimens (essentially amorphous) of the

BTDA/1,3-BABB polyimide prepared by molding at 400°C under 6.9 MPa gave fracture energy (G_{Ic}, critical strain energy release rate) of 6,600 JM^{-2}. The BTDA/1,3-BABB polyimide is currently undergoing evaluation as an adhesive for joining Ti to Ti and as a composite matrix in combination with carbon fibers.

A series of polyimides containing ethylene oxide groups[25,26] have been prepared under NASA-Langley sponsorship. Although these polymers are not true high temperature materials, they exhibit interesting properties worthy of attention. The ethylene oxide group was incorporated into polyimides primarily to
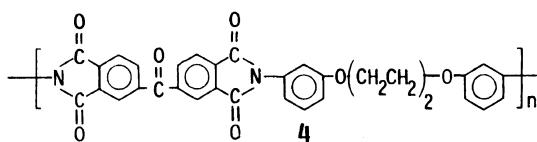
improve the processability, recognizing a sacrifice in the use temperature. As an example, the polyimide of structure 4 was prepared from the reaction of BTDA and bis[2-(3-amino-phenoxy)ethyl]ether. Thermal imidization of the polyamide acid in N-methylpyrrolidone at 200°C provided a semi-crystalline form with a T_g of 155°C and a T_m of 236°C. Once the T_m had been exceeded, the polyimide became amorphous and thermal annealing was unsuccessful in inducing crystallinity. The semi-crystalline polyimide was readily compression molded at 260°C under 6.9 MPa. The melt viscosity of the amorphous polyimide at 210°C was 6×10^5 Pa s at 0.1 radians s^{-1} and 1×10^5 Pa s at 100 radians s^{-1}.[27]

Some of the mechanical properties of the polyimide of structure 4 have been reported.[27] The G_{Ic} at 25°C was 3200 J M^{-2}. Transparent yellow thin films (semi-crystalline) gave tensile strength, tensile modulus and elongation at 25°C of 86.2 MPa, 2.7 GPa and 4% and at 93°C of 64.8 MPa, 2.1 GPa, and 5%, respectively. The most impressive feature of this polyimide was the adhesive strength. Titanium/Ti tensile shear specimens exhibited tensile shear strengths at 25°C of 54.1 MPa and at 93°C of 37.2 MPa. The 25°C strength is probably the highest ever reported for single lap specimens.
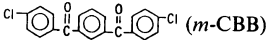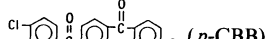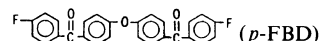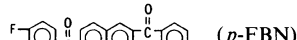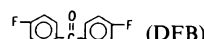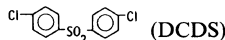
POLYARYLENE ETHERS

Polyarylene ethers are a family of high performance amorphous and semi-crystalline thermoplastics. Since their first report in the late 1950s,[28] several polyarylene ethers such as UDEL® (polysulfone),[29] Kadel® (polyketone),[29] Radel® (polyarylsulfone),[29] PEEK® (polyetheretherketone),[30] and Victrex® PES (polyethersulfone)[30] have become commercially available. These materials are high performance thermoplastics and are used in a variety of applications such as adhesives, coatings, composite matrices, moldings, toughening agents and ultrafiltration membranes. Polyarylene ethers are generally synthesized by nucleophilic substitution reactions or by Friedel–Crafts processes. Our work[31,32] on polyarylene ethers has involved the solution polycondensation of an activated dihalo compound with an aromatic dihydroxy compound in a polar solvent (e.g., N,N-dimethylacetamide) in the presence of a metal base (e.g., sodium hydroxide or potassium carbonate). The impetus for our work on polyarylene ethers is the development of high temperature thermoplastics for use as adhesives and composite matrices on aerospace vehicles. Thermoplastics offer lower cost than thermosets by virtue of indefinite stability under ambient conditions, the ability to be reprocessed to correct minor flaws and the potential of cost effective manufacturing (e.g., short molding time and thermoformability). Other properties such as solvent resistance, damage tolerance, mechanical performance, and long term environmental durability are also required.

The discussion on polyarylene ethers will be confined to polymers based upon the reaction of 9,9-bis(4-hydroxyphenyl)fluorene (BPF) and various activated dihalo monomers as presented in Table III. The cardo fluorene moiety when incorporated in polymers provide materials with relatively high T_gs. All of the polymers were of sufficient molecular weight to melt press transparent flexible films. The fracture toughness (K_{Ic}, critical stress intensity

Table III. Polyarylene ethers based upon 9,9-bis(4-hydroxyphenyl)fluorene

Dihalo monomer	$\eta_{inh}/dl\,g^{-1\,a}$	$\bar{M}_n/g\,mol^{-1\,b}$	$T_g/°C^c$
(m-CBB)	0.95	28,300	223
(p-CBB)	1.27	39,900	243
(p-FBD)	Insoluble	—	231
(p-FBN)	1.29	—	252
(DFB)	1.00	34,000	252
(DCDS)	0.67	26,700	280

[a] Inherent viscosity of 0.5% solution in chloroform at 25°C.
[b] Number average molecular weights ($\bar{M}_n$) by membrane osmometry in chloroform.
[c] Determined by DSC at a heating rate of 20°C min^{-1}.
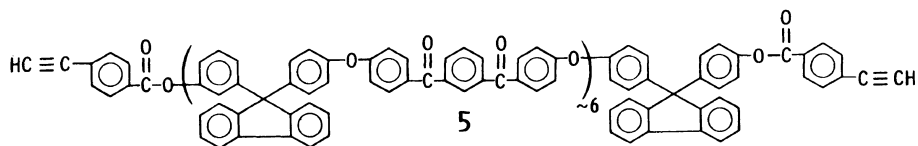
factor) as determined on compact tension specimens of the 1,3-CBB/BPF polymer was 2.64 MN m$^{-3/2}$. Thin transparent yellow films of the 1,3-CBB/BPF polymer gave tensile strength and modulus of 92.7 MPa and 2.6 GPa at 25°C and 47.9 MPa and 2.1 GPa at 150°C, respectively. Titanium/Ti tensile shear strengths of the 1,3-CBB/BPF polymer were 37.6, 31.4, and 24.1 MPa at 25, 93, and 150°C, respectively. The DCDS/BPF polymer gave Ti/Ti tensile shear strengths of 26.5, 22.8, and 19.3 at 25, 177, and 232°C, respectively.

In continuing our work[33-35] with ethynyl terminated arylene ethers, ethynyl groups were placed on the ends of a 1,3-CBB/BPF oligomer by reacting a hydroxy terminated arylene ether of $\bar{M}_n$ of ~4000 g mol^{-1} with 4-ethynylbenzoyl chloride. Upon heating to ~250°C, the ethynyl groups undergo a complex reaction leading to chain extension and crosslinking. The ethynyl terminated arylene ether oligomer (structure 5) was used to fabricate Ti/Ti tensile

shear specimens which gave strengths of 29.6, 29.0, and 26.2 MPa at 25, 93, and 150°C, respectively.[32] The T_g of the cured (0.5 h at 250°C) ethynyl terminated arylene ether oligomer was 231°C, only 8 degrees higher than the corresponding linear 1,3-CBB/BPF polymer. However the ethynyl terminated oligomer exhibited better processability than the corresponding linear 1,3-CBB/BPF polymer. In addition, the solvent resistance of the cured ethynyl terminated oligomer was significantly better than the corresponding linear polymer.

POLYPHENYLQUINOXALINES

Polyphenylquinoxalines (PPQs) like polyimides belong to the class of high performance materials often referred to as polyheterocyclics. The PPQs were first reported in 1967[36] and since then, numerous articles have appeared on their synthesis, mechanical and physical properties. These polymers are gen-

erally prepared by solution polycondensation of an aromatic bis(*o*-diamine) and a bis-(phenyl-1,2-diketone). They are amorphous due to configurational disorder, readily soluble in the fully ring-closed high molecular weight form, and excellent film formers with relatively low equilibrium moisture uptake. The PPQ (structure 6, $T_g = 290°C$) from the reaction of 3,3′,4,4′-tetraaminobiphenyl (TAB) and 4,4′-oxydibenzil (ODB) has been extensively evaluated as a high temperature adhesive for joining titanium to itself and to polyimide glass honeycomb. High strengths were obtained on sandwich specimens, Ti to Ti and Ti to polyimide honeycomb climbing drum peel panels and tensile shear specimens.[37] Other PPQs have also displayed good mechanical properties in adhesive, composite and film form.

Our recent work with high temperature polyphenylquinoxalines has been directed

towards improving the processability and alleviating the high temperature thermoplasticity. This has primarily involved the preparation of new bis(phenyl-1,2-dicarbonyl) compounds and subsequent incorporation into PPQs. For example, 4,4′-bis(phenylglyoxylyl-4-phenoxy)benzophenone (BPGPB) was reacted with TAB to yield a high molecular weight polymer (structure 7) with a T_g of 253°C. A random copolymer from the reaction of TAB and equimolar amounts of ODB and BPGPB exhibited a T_g of 271°C. The copolymer exhibited better processability by compression molding than either of the homopolymers. Titanium to Ti tensile shear specimens of the copolymer gave strengths of 35.2 MPa at 25°C, 26.2 MPa at 203°C, and 21.0 MPa at 232°C.

Work directed towards reducing the high temperature thermoplasticity of PPQ involved a continuation of our past effort[38,39] where pendent phenylethynyl groups were placed along the polymer chain. Upon heating, these groups react to branch and crosslink the molecules. As examples, the linear PPQ in eq 2 had an initial T_g of 257°C and a T_g of 269°C

6

7
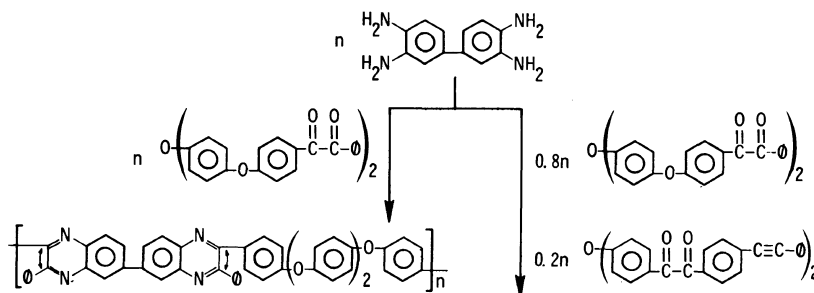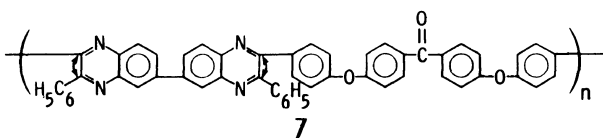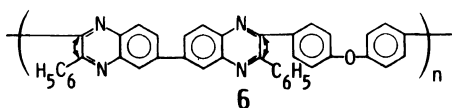
PPQ containing 20 mole % of pendent $-C{\equiv}C-\varnothing$

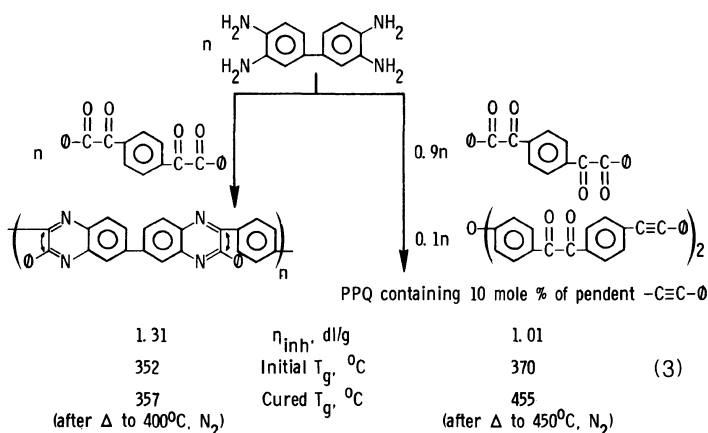|			
0.75	η_{inh}, dl/g	0.64	(2)
257	Initial T_g, °C	267	
269	Cured T_g, °C after Δ to 400°C, N_2	333	

Table IV. PPQ titanium/titanium tensile shear strengths[a]

Polymer (T_g/°C)	Process conditions	Tensile shear strength/MPa (psi)		
		25°C	232°C	316°C[b]
No C≡Cφ (255)	RT→343°C, 100 psi, 0.5 h hold	38.6 (5600)	26.2 (3800)	Thermoplastic
20% C≡Cφ (262)	RT→343°C, 300 psi, 0.5 h hold	30.5 (4430)	22.3 (3240)	5.8 (840)
20% C≡Cφ (278)	RT→343°C, 300 psi, 4 h hold	17.9 (2600)	19.3 (2800)	8.6 (1240)
20% C≡Cφ (283)	RT→343°C, 300 psi, 0.5 h hold; 16 h at 316°C	15.9 (2300)	21.9 (3180)	9.3 (1350)
20% C≡Cφ (272)	RT→343°C, 300 psi, 0.5 h hold; 16 h at 316°C no glass carrier, 30 phr MD105 Al	32.2 (4670)	30.3 (4400)	8.1 (1170)

[a] Ti surface treatment, 10 V chromic acid anodized, 112 glass with A-1100 finish, no filler.
[b] Predominantly thermoplastic failure.

PPQ containing 10 mole % of pendent −C≡C−φ

1.31	n_{inh}, dl/g	1.01	
352	Initial T_g, °C	370	(3)
357 (after Δ to 400°C, N₂)	Cured T_g, °C	455 (after Δ to 450°C, N₂)	

after heating to 400°C in nitrogen. A PPQ of similar chemical structure but with 20 mol% of pendent phenylethynyl groups randomly distributed along the polymer chain exhibited an initial T_g of 267°C and a T_g of 333°C after heating to 400°C in nitrogen. The adhesive properties in Table IV of these two PPQs show that the PPQ containing 20 mol% of C≡Cφ exhibited better strengths (due to higher T_g) at 232 and 316°C than the PPQ with no C≡Cφ. In addition, an unrestrained postcure for 16 h at 316°C and 30 phr of fine aluminum powder

(e.g., particle size: 325 mesh, MD 105 Al) further improved the strength at 316°C.

The synthetic schemes for two other PPQs are shown in eq 3. The linear PPQ had a T_g after heating to 400°C in nitrogen of 357°C. (A PPQ of this chemical structure with a dielectric constant at 25°C of 2.8, low moisture pickup, excellent film forming properties and a T_g of 390°C is commercially available).[40] The PPQ containing 10 mol% of pendent C≡Cφ groups had a T_g initially of 370°C which increased to 421°C after heating at 400°C in nitrogen.

Table V. Thin film properties of phenyl-
quinoxaline polymers[a]

Polymer	Test tempera-ture/°C	Tensile strength/ MPa (Ksi)	Tensile modulus/ GPa (Ksi)	Break elonga-tion/%
No	25	127.5 (18.5)	2.8 (410)	7.1
$C \equiv C\phi$	232	87.6 (12.7)	1.7 (247)	12.9
10%	25	6.9 (17.8)	3.1 (450)	4.8
$C \equiv C\phi$	232	6.7 (14.5)	2.3 (339)	6.2

[a] Film dried through 1 h at 350°C. Average of 3 test specimens.

Tensile properties of transparent orange thin films dried at 350°C in nitrogen of the PPQs in eq 3 are presented in Table V. The film from the PPQ containing 10 mol% of $C \equiv C\phi$ exhibited better retention of properties at 232°C than the linear PPQ (no $C \equiv C\phi$).

SUMMARY

Several new polyimides, polyarylene ethers and polyphenylquinoxalines exhibit good mechanical properties at high temperatures in the form of adhesives, composite matrices, and films.

REFERENCES

1. The du Pont Company, Industrial Films Division, Wilmington, DE, U.S.A.
2. Ube Industries, Ltd., Chiba, Japan.
3. Upjohn Company, CPR Division, Torrance, CA, U.S.A.
4. General Electric Company, Plastics Operation, Pittsfield, MA, U.S.A.
5. Mitsui-Toatsu Chemicals, Inc., New York, N. Y., U.S.A.
6. Chem-tronics, Inc., El Cajon, CA, U.S.A. (discontinued in 1986).
7. Prepreg from various sources such as Fiberite Corporation, Winona, WI, U.S.A.; U.S. Polymeric, Fountain Valley, CA, U.S.A.; Hexcel, Dublin, CA, U.S.A.; and Bristol Composite Materials, Ltd., Bristol, England.
8. National Starch Corporation, Bridgewater, NJ, U.S.A.
9. *SAMPE J.*, **20**, 71 (1984).
10. V. L. Bell, B. L. Stump, and H. Gager, *J. Polym. Sci.,*
11. *Polym. Chem. Ed.*, **14**, 2275 (1975).
11. V. L. Bell, U. S. Patent 4,094,862 (1978) to NASA.
12. D. J. Progar and T. L. St. Clair, *Natl. SAMPE Tech. Conf. Series*, **7**, 53 (1975).
13. D. J. Progar, V. L. Bell, and T. L. St. Clair, U. S. Patent 4,065, 345 (1977) to NASA.
14. C. L. Hendricks and J. N. Hale, "Proceedings of Symposium on Welding, Bonding and Fastening," held at NASA Langley Research Center, Hampton, VA, U.S.A., Oct. 1984, NASA CP 2787, p 351.
15. A. K. St. Clair, W. S. Slemp, and T. L. St. Clair, *Sci. Adv. Natl. Proc. Eng. Series*, **23**, 113 (1978).
16. A. K. St. Clair and T. L. St. Clair, U. S. Patent 4,543,295 (1985) to NASA.
17. H. D. Burks, T. Hou, and T. L. St. Clair, *SAMPE Quarterly*, in press.
18. N. J. Johnston and T. L. St. Clair, *Intl. SAMPE Tech. Conf. Series*, **18**, 53 (1986).
19. T. L. St. Clair and D. A. Yamaki, "Polyimides," Vol. 1, K. L. Mittal, Ed., Plenum Press, New York, N. Y., 1984, p 99.
20. T. L. St. Clair and D. A. Yamaki, U. S. Patent 4,398,021 (1983) and 4,489, 027 (1984) to NASA.
21. A. Hanky and T. L. St. Clair, *SAMPE J.*, July/Aug. issue, 40 (1984).
22. T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose, and P. A. Staniland, *Polymer*, **22**, 1096 (1981).
23. Imperial Chemical Industries, Wilmington, DE, U.S.A.
24. P. M. Hergenrother, N. T. Wakelyn, and S. J. Havens, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
25. F. W. Harris, A. J. Karnavas, C. H. Cucuras, and S. Das, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **26**(2), 287 (1985); F. W. Harris, M. W. Beltz, S. Das, and R. H. Gupta, *ibid.*, **25**(1), 160 (1984).
26. F. W. Harris, A. J. Karnavas, S. Das, C. N. Cucuras, and P. M. Hergenrother, *Polym. Matl. Sci. Eng. Proc.*, **54**, 89 (1986).
27. F. W. Harris, M. W. Beltz, and P. M. Hergenrother, *Intl. SAMPE Tech. Conf. Series*, **18**, 209 (1986).
28. A. Kreuchumas, U. S. Patent 2,822,351 (1958).
29. Amoco Performance Products, Inc., Bound Brook, N.J., U.S.A.
30. ICI Americas, Inc., Wilmington, DE, U.S.A.
31. P. M. Hergenrother, B. J. Jensen, and S. J. Havens, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **26**(2), 174 (1985).
32. P. M. Hergenrother, B. J. Jensen, and S. J. Havens, *Intl. SAMPE Tech. Conf. Series*, **18**, 454 (1986).
33. P. M. Hergenrother, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 3131 (1982).
34. S. J. Havens and P. M. Hergenrother, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 3011 (1984).
35. P. M. Hergenrother, B. J. Jensen, and S. J. Havens, *SAMPE J.*, September/October issue, 18 (1984).
36. P. M. Hergenrother and H. H. Levine, *J. Polym. Sci.,*

A–1, **5**, 1453 (1967).

37. P. M. Hergenrother, *SAMPE Quart.*, **3**, 1 (1971); *Chemtech*, August issue, 496 (1984).

38. P. M. Hergenrother, *Macromolecules*, **14**, 898 (1981).

39. P. M. Hergenrother, *J. Appl. Polym. Sci.*, **28**, 355 (1983).

40. CEMOTA, PBn° 3-69390, Vernaison, France.