Imide–Aryl Ether Phenylquinoxaline Block Copolymers

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Received December 11, 1990; Revised Manuscript Received February 26, 1991

ABSTRACT: Imide–aryl ether phenylquinoxaline block copolymers were prepared and their morphology, mechanical properties, and adhesion characteristics investigated. A key feature of the copolymer synthesis was the preparation of bis(amino) aryl ether phenylquinoxaline oligomers (PQE) via a nucleophilic aromatic substitution reaction. The molecular weights of the oligomers were 6200 and 15 500 with T_g's of 230 and 250 °C, respectively. The oligomers were coreacted with 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) diethyl ester diacyl chloride in a *N*-methylpyrrolidone (NMP) *N*-cyclohexylpyrrolidone (CHP) solvent mixture in the presence of *N*-methylmorpholine. The resulting amic ester–aryl ether phenylquinoxaline block copolymers were isolated and given selective solvent rinses, when required, to remove homopolymer contamination. Copolymer compositions, determined by ^{1}H NMR, were close to those predicted by the charge. Solutions of the copolymers were cast and cured (350 °C) to effect imidization, affording clear films with elongations ranging from 30 to 120% and moduli between 2000 and 2600 MPa, approximately 5–20% higher than the PMDA/ODA polyimide values. Multiphase morphologies were observed irrespective of the PQE block lengths, and the phase purity increased with PQE weight. Furthermore, the ordered morphology characteristic of the parent polyimide was retained in the polyimide component of the block copolymer. The autoadhesion characteristics (i.e., adhesion of the polyimide to itself) were also investigated, and significant improvements were observed by the incorporation of the PQE block.

Introduction

High-temperature polymers are important materials for the microelectronics industry and are finding applications as interlayer dielectrics, passivation layers, and structural resins. The polymer properties required for these applications generally include high thermal and dimensional stability, low thermal expansion coefficient and residual stress upon thermal cycling, planarization, low dielectric constant, and good mechanical properties. Aromatic polyimides derived from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) are the most widely used in the microelectronics industry due to their availability, ease of processing [via the soluble poly(amic-acid) precursor], excellent thermal and dimensional stability ($T_g > 400$ °C), and high modulus (2000 MPa) and elongations (>40%). These good mechanical properties and low thermal expansion coefficient can be attributed, in part, to the liquid crystalline or crystalline order exhibited by these materials.[1,2] Although the rigid and semirigid polyimides fulfill many of the material requirements for microelectronic packaging, drawbacks to their ordered morphology and the absence of a T_g result in poor melt processability (planarization) and self- or autoadhesion (i.e., the adhesion of the polyimide to itself). The latter feature is a deterrent in the successful fabrication of multilayer circuitry. Conversely, thermally stable engineering thermoplastics [i.e., poly(ether imide), poly(phenylquinoxaline) (PPQ), poly(aryl ether sulfone) (PSF), etc.] show excellent autoadhesion and melt characteristics, since they are amorphous with moderately high T_g's to provide sufficient mobility at high temperatures to allow interdiffusion. Consequently, it is of interest to combine the desirable characteristics of engineering thermoplastics with those of polyimide in such a way as to produce a material which shows good autoadhesion yet retains the ordered morphology and mechanical properties characteristic of the rigid polyimide.

Mixing two polymers is a convenient means of obtaining materials with properties characteristic of the respective homopolymers. Although it has been demonstrated that engineering thermoplastics such as poly(aryl ether ketones) and poly(aryl ether sulfones) are miscible with selected polyimides, these polyimides are amorphous with low T_g's.[3-7] For the case of rodlike polyimide mixtures with flexible polymers, phase separation generally occurs. Slight nonfavorable interactions between the segments far outweigh the small entropic gains on mixing.[8] There are reports that some mixtures of such rigid rod and flexible polymers form "molecular composites".[9] However, the extent of phase separation is kinetically rather than thermodynamically controlled. These reports include mixtures of rigid and flexible polyimides prepared by the respective poly(amic acid) precursors. However, Feger[10] and Ree et al.[11] have shown that the poly(amic acid) precursors often undergo transamidization leading to block and random copolymers. By nature of the connectivity of the segments and blocks miscibility is promoted. Alternatively, Yoon and co-workers[12] have demonstrated the formation of molecular composites of polyimide/polyimide mixtures where at least one of the polyimide precursors was in the stable alkyl ester form which is not prone to transamidization reactions. Even here, however, the desired level of phase separation was kinetically controlled. The subsequent molecular composites showed enhanced autoadhesion with the retention of many of the desirable characteristics of the rigid rod polyimide.

Recently, another approach in the modification of the autoadhesion characteristics of rigid and semirigid polyimides has been described. Imide–aryl ether phenylquinoxaline and imide–aryl ether benzoxazole statistical or random copolymers have been prepared and their morphology and adhesion characteristics investigated.[13,14] In each case, the incorporation of the *co*-diamine containing either a preformed phenylquinoxaline or benzoxazole moiety resulted in significantly improved autoadhesion. However, wide-angle X-ray diffraction measurements showed that the "liquid crystalline" like ordering observed in the PMDA/ODA polyimide persists in the copolymers, where the phenylquinoxaline or benzoxazole compositions were less than 50 wt %. At higher concentrations the ordering vanishes due to hindrance of interchain packing and, hence, a disruption of the ordering. Coincident with

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this loss in ordering is the clear development of a T_g and loss of the high-temperature dimensional stability. Thus, these copolymers show improved adhesion with the retention of the ordered morphology over a very narrow composition range.

This paper will describe another approach in modifying the adhesion characteristics of polyimide without sacrificing the ordered morphology and properties associated with this morphology. This approach involves the preparation of multiblock copolymers derived from polyimide and amorphous engineering thermoplastics. The use of block copolymers offers numerous advantages over polymer/polymer mixtures and random copolymers since the molecular architecture, block lengths, and composition can be designed to produce materials with a wide range of properties and morphologies. Furthermore, since the two dissimilar materials are covalently bonded, miscibility is enhanced and phase separation, when it occurs, is restricted to dimensions on the order of 200–400 Å. Polyimides, as a class of materials, have received little attention as a component in the synthesis of block and segmented copolymers,[15,16] and among these examples the imide–siloxane copolymers have been the most widely studied.[16,17] The general synthetic methodology used for the imide–siloxane copolymers utilized a monomers–oligomers approach via the poly(amic acid) precursor to the polyimide.[16] Bis(amino)siloxane oligomers of various molecular weights were coreacted with either a dianhydride or a mixture of a dianhydride and a diamine to yield poly(amic acid) solutions, which were cast and cured to imidize the polymers producing a multiblock microstructure.

We have used an alternative synthetic procedure for the preparation of imide-containing copolymers based on a poly(amic alkyl ester) intermediate to the polyimide.[18,19] Using a poly(amic alkyl ester) precursor offers more synthetic flexibility due to improved solubility and greater structural variety in both the polyimide backbone and the coblock. The hydrolytically stable precursors may be isolated, characterized, and purified. Furthermore, since imidization occurs at substantially higher temperatures, molecular mobility is attained before imidization, thus minimizing the control of the resultant morphology by kinetic factors.

This work focuses on the preparation of imide–aryl ether phenylquinoxaline block copolymers, since poly(aryl ether phenylquinoxalines) (PQE) are tough engineering thermoplastics which have the required thermal stability for most microelectronic fabrication processes.[20] PQE's are amorphous with moderate T_g's (~250 °C) which allow molecular interdiffusion for autoadhesion and good melt processability. Such block copolymers have not been reported previously since most poly(phenylquinoxaline) and related structures are not soluble in common aprotic dipolar solvents [i.e., *N*-methylpyrrolidone (NMP), dimethylacetamide (DMAC), etc.] used for the preparation of poly(amic acid) precursors to polymide.[21] We have demonstrated a new synthetic route to the preparation of NMP-soluble poly(aryl ether phenylquinoxalines) via a heterocyclic activated displacement in which an aryl ether linkage is generated as the polymer forming reaction.[20,22] Herein, the details of the synthesis of these block copolymers and the structure–property relationships are described.

Experimental Section

Materials. 4-Fluoro-*o*-phenylenediamine (ICN), 4-aminophenol (Aldrich), and 3-aminophenol (Aldrich) were sublimed prior to use. 1,4-Bis(phenylglyoxalyl)benzene (BPGB) (IFP Enterprises), 4,4′-oxydianiline (ODA) (Davos Chemical Corp.), and pyromellitic dianhydride (PMDA) (Chriskev Co.) were obtained as polymer grade monomers and used without further purification. 2,3-Diphenyl-6-fluoroquinoxaline, referred to as I, and 1,4-bis(6-fluoro-3-phenyl-2-quinoxalinyl)benzene, referred to as III, were prepared according to literature procedure.[20] *N*-Methyl-2-pyrrolidone (NMP) was vacuum distilled from P_2O_5.

6-(3-Aminophenoxy)-2,3-diphenylquinoxaline (II). A three-neck 25-mL flask fitted with a Dean-Stark trap was charged with 580 mg (5.30 mmol) of 3-aminophenol, 212 mg (5.30 mmol) of a 23.85 wt % solution of aqueous sodium hydroxide, 5 mL of NMP, and 10 mL of toluene. The reaction mixture was heated at the reflux temperature for several hours to remove the water generated from phenate formation. The mixture was cooled to room temperature, 1.50 g (5.00 mmol) of I in 2 mL of NMP was added, and the reaction was heated at 160 °C for 16 h. The reaction mixture was partitioned between ether and water, washed three times with water, dried ($MgSO_4$), and concentrated under reduced pressure. The resulting yellow solid was purified by flash chromatography (silica gel, 1% methanol/methylene chloride) to afford 1.90 g (97% yield) of II as a pale yellow solid: mp 184–185 °C; IR (KBr) cm^{-1} 3453, 1613, 1594, 1566, 1467, 1340, 1220, 1193, 1168; ^1H NMR (DMSO-d_6) δ 5.4 (s, 2 H, NH), 6.3 (M, 1 H), 6.4 (s, 1 H), 6.5 (M, 1 H), 7.2–7.4 (M, 11 H), 7.6 (M, 1 H), 7.6 (M, 1 H), 8.1 (d, 1 H, $J = 4$ Hz); ^{13}C NMR (DMSO-d_6) δ 1502, 1070, 110.8, 112.5, 123.8, 128.2, 128.8, 129.0, 129.9, 130.6, 130.7, 137.3, 138.9, 139.0, 141.7, 151.1, 151.5, 153.4, 156.4, 159.2. Anal. Calcd for $C_{26}H_{19}N_3O$: C, 80.18; H, 4.92; N, 10.79. Found: C, 80.19; H, 5.12; N, 10.61.

Diethyl Pyromellitate Diacyl Chloride. Pyromellitic dianhydride (PMDA) (50.0 g, 0.230 mol) was suspended in 250 mL of dry ethanol and refluxed for 3 h, yielding a clear solution.[18,19] Evaporation of the ethanol followed by vacuum drying at 50 °C for 24 h gave diethyl dihydrogen pyromellitate (mixed isomers) in quantitative yield. The material was then suspended in ca. 200 mL of dry ethyl acetate in a 500-mL three-neck flask equipped with a magnetic stirrer, reflux condenser, and N_2 bubbler. Next, oxaloyl chloride (75 g, 0.591 mol) was added in three portions over a period of 8–10 h, each addition being followed by 1–2 drops of dimethylformamide (DMF). The DMF allowed the reaction to proceed at ambient temperature as evidenced by vigorous gas evolution. Stirring was continued overnight, and the reaction was then heated to ca. 60 °C in a water bath for an additional 6 h (total run time was ca. 28 h). The ethyl acetate was then stripped, and the residue was dried under vacuum at room temperature overnight. The product was recrystallized twice from approximately 150 mL of hexane and vacuum dried. The yield was approximately 75% with a slight enrichment of the para isomer to a meta/para ratio of ca. 45/55: ^1H NMR ($CDCl_3$) δ 8.30 and 7.92 (d, 1 H_1, *m*-Ar H), 8.10 (s, 1 H, *p*-Ar H) 4.50–4.38 (q, 4 H, methylene), 1.39–1.36 (t, 6 H, methyl).

Oligomer Synthesis. A standard synthesis of a poly(aryl ether phenylquinoxaline) oligomer was conducted in a three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean-Stark trap, and condenser.[20,23] A detailed synthetic procedure designed to prepare an oligomer of 7000 molecular weight is provided. The flask was charged with III (5.7442 g, 0.0100 mol), Bisphenol AF (IV) (2.95889 g, 0.088 mol), and 3-aminophenol (0.2619 g, 0.0024 mol) and carefully washed down with 32 mL of NMP. Toluene (20 mL) and K_2CO_3 (1.25 g, 9.06 mmol) were then added. Note that the K_2CO_3 was used in 40–50% excess. The reaction mixture was then heated until the toluene began to reflux. An optimum reflux temperature range was achieved when the oil bath was maintained between 140 and 150 °C. Toluene was periodically removed from the Dean-Stark trap and replaced with deoxygenated, dry toluene to ensure dehydration. The reaction mixture was maintained at 140 °C until the presence of water was no longer observed in the Dean-Stark trap. This usually took between 4 and 8 h, and during this stage of the reaction several color changes were observed. For example, during the initial formation of the phenoxide, a yellow-brown color developed, and as the refluxing proceeded, the color eventually changed to dark brown. Upon dehydration the temperature was slowly increased to 180 °C and the toluene was removed through the Dean-Stark trap. The polymerization was maintained at 180 °C for approximately 20 h to effect the displacement reaction. Completion or near completion was estimated as the point at which the viscosity increased. The oligomer solution was diluted with 50 mL of NMP and filtered hot to remove the inorganic salts. The polymer solution was then coagulated in an approximately 10× volume of methanol and then boiled in deoxygenated water to remove any trapped salts. The polymer (V) was then dried in a vacuum oven (80 °C) to a constant weight. In each oligomer synthesis, the yield was essentially quantitative.

Copolymer Synthesis. The amic ester–aryl ether phenylquinoxaline copolymers were prepared by the coreaction of the PQE oligomers with ODA and PMDA diethyl ether diacyl chloride in a CHP/NMP solvent mixture (50/50) in the presence of *N*-methylmorpholine. A detailed procedure designed to prepare an amic esther–aryl ether phenylquinoxaline copolymer with a PQE oligomer of 6200 molecular weight and 25 wt % PQE composition is provided. A three-neck flask equipped with an overhead stirrer and addition funnel was charged with V (1.000 g, 0.00016 mol) and ODA (1.0062 g, 0.0050 mol) and carefully rinsed with 8 mL of a CHP/NMP solvent mixture. Throughout the polymerization N_2 was passed through the system. The solution was then cooled to −5 °C, and *N*-methylmorpholine (1.0489 g, 0.0100 mol) was added and rinsed with the solvent mixture. PMDA diethyl ester diacyl chloride (1.8000 g, 0.0050 mol) was added to the addition funnel and dissolved in approximately 25 mL of methylene chloride. This solution was added in 125-mL increments over a 2-h period so as to slowly approach the stoichiometric endpoint. The polymerization was allowed to proceed overnight, and then the polymer was isolated in an excess methanol/water mixture, rinsed with water (to remove excess salts), rinsed with chloroform to remove homopolymer contaminations, and dried in a vacuum oven.

Measurements. Films for thermal and mechanical analysis were cast from a NMP/CHP solvent mixture and heated to 350 °C (5 °C/min heating rate) and held for 30 min. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a Du Pont DSC 1090 instrument with a heating rate of 10 °C/min in the tension mode. Isothermal and ramped temperature (5 °C/min, heating rate) thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer Model TGA-7. Mechanical property measurements were performed on an Instron tensile tester at a strain rate of 10 mm/min.

The number-average molecular weights, $\langle M_n \rangle$, of the oligomers were determined by ^{1}H NMR after derivatization of the end groups with 3-(trimethylsilyl)propionyl chloride.[24] Integration of the resonance assigned to the trimethylsilyl groups associated with the oligomer endgroups were compared to the integration of the aromatic protons, and the ratio of the integrated area per proton gave the degree of polymerization from which $\langle M_n \rangle$ was calculated.

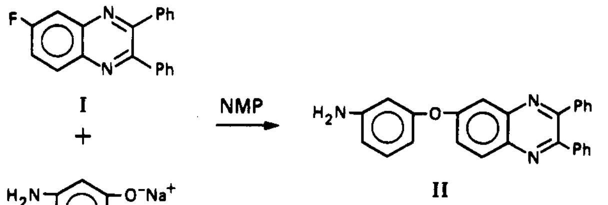
Samples for adhesion testing were prepared by doctor blade coating poly(amic acid) solutions onto glass slides and curing them at 80 (1 h) and 400 °C (1 h). An adhesion inhibitor was added to the ends of the films to generate the initial peel strips for testing. A second layer of polymer solution was applied and cured in an analogous fashion. Specimens were sliced with a razor blade to remove from the glass substrate. Peel strengths were determined by using the T-peel test, where the layers are pulled 180° apart.[25] Tests were performed on an Instron Model 1120 material tester with a crosshead speed of 0.1 mm/min. The data reported were averages of five or more specimens tested.

Wide-angle diffraction measurements were performed in both reflection and transmission geometries by using a sealed-tube X-ray source with the incident radiation at a 1.54 Å. The diffracted X-rays were detected with a scintillation counter mounted behind an analyzer crystal that was step scanned over the angular range in interest.

Results and Discussion

Poly(phenylquinoxalines) (PPQ) are generally prepared by the polycondensation of an aromatic bis(*o*-diamine) with a bis(phenyl-α-dicarbonyl) compound in either an *m*-cresol or an *m*-cresol/xylene solvent mixture.[21] The interfacial nature of these polymerizations generates high molecular weight polymer in the early stages of the reaction, making synthesis of well-defined oligomers of controlled molecular weight and endgroup functionality difficult. Furthermore, rigid PPQ's are soluble only in *m*-cresol and selected chlorinated solvents, which are not viable solvents for polyimide polymerizations. We have recently reported the synthesis of poly(aryl ether phenylquinoxalines) by a fluoro displacement polymerization of appropriately substituted fluorophenylquinoxaline monomers with bisphenols, using conventional condensation polymerization techniques.[20,22] Facile displacement of aryl fluorides activated by the phenylquinoxaline ring system was demonstrated, and polymerization of fluoro-substituted bis(quinoxalines) with bisphenols yielded high polymer. These polymers were soluble in NMP, an important consideration for polyimide copolymerizations. This general route for the preparation of poly(aryl ether phenylquinoxalines) has been extended to the preparation of functional oligomers which are amenable to conventional polyimide syntheses.

Scheme I



The synthetic methodology used for the preparation of bis(amino) PQE oligomers was based on the the use of 3-aminophenol, an amine-substituted monofunctional monomer, which controls both molecular weight and endgroup functionality as described by Jurak and McGrath.[26] To demonstrate the feasibility of this route in preparing bis(amino) PQE oligomers, a model reaction between 3-aminophenol and I was investigated in a NMP/toluene solvent mixture using sodium hydroxide as the base (Scheme I). Toluene was used to azeotrope the water generated upon phenoxide formation (150 °C). Upon dehydration, the toluene was removed through the Dean-Stark trap and the reaction was heated to 180 °C to effect the displacement reaction (16 h). Quantitative conversion of I was observed with the formation of a single product peak. The expected phenylquinoxaline substituted ether, II, was isolated in high yield. It is important to note that side reactions involving nucleophilic attack of the aromatic amine with the quinoxaline-activated fluoride were not observed. Therefore, the model reaction clearly demonstrates that the fluoroquinoxaline is cleanly displaced by 3-aminophenol and that this transformation is suitable for controlling both the molecular weight and the endgroup functionality of the PQE oligomers.

Bis(amino) aryl ether phenylquinoxaline oligomers of various molecular weights were prepared by the reaction of III, IV, and 3-aminophenol in an NMP/toluene solvent mixture in the presence of K_2CO_3 (Scheme II).[20,23,26] As is the case for most polyether syntheses, the solids composition was maintained between 20 and 25 wt %. The water generated by bisphenoxide formation during the initial stages of the polymerization was removed as an azeotrope with toluene. This solvent mixture gave an optimum reflux temperature between 140 and 150 °C. In an effort to maintain a dry system, toluene was periodically removed through the Dean-Stark trap and replaced with deoxygenated toluene. Upon completion of bisphenoxide formation and dehydration, 4–6 h, the polymerization mixture was heated to 180–190 °C to effect the displacement reaction. In each case, oligomer was obtained within

Scheme II

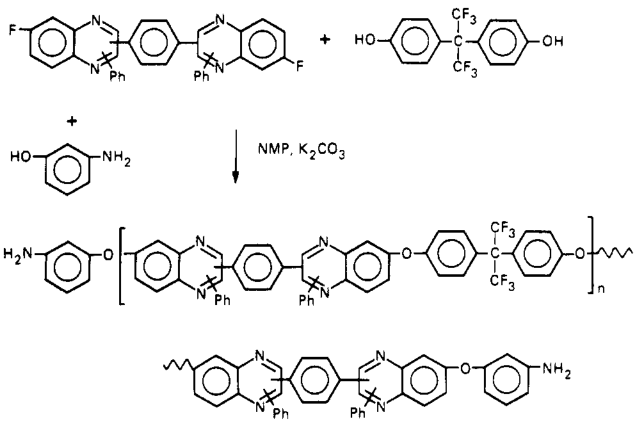


Table I
Characteristics of Amine-Terminated Aryl Ether Phenylquinoxaline Oligomers

sample no.	M_n predicted	M_n measured	T_g, °C
V	7000	6200	225
VI	15000	15500	235
poly(aryl ether phenylquinoxaline)			255

24 h as judged by the increase in viscosity. The resulting polymerization dopes were filtered to remove inorganic salts and isolated in excess methanol as yellow powders.

The Carothers equation was used to determine the quantity of 3-aminophenol required to control both the molecular weight and the chain end functionality of the oligomers. Table I contains the characteristics of the oligomers prepared. The number-average molecular weights, determined by ^{1}H NMR[24] were 6200 and 15 500 for oligomers V and VI, respectively. The T_g's of the oligomers increased with increasing molecular weight (Table I).

The imide–aryl ether phenylquinoxaline copolymers were prepared via the poly(amic alkyl ester) route.[18,19,27–31] This intermediate route to polyimide is believed to be more versatile than the poly(amic acid) analogue due to its enhanced solubility. Volksen[18] reported that up to 75% of a cosolvent could be used along with NMP, which is an important consideration in copolymerization of chemically dissimilar block copolymers. Furthermore, the poly(amic alkyl ester) precursor to the polyimide can be isolated, characterized, and subjected to selective solvent rinses to remove homopolymer contamination. Through the judicious choice of the ester moiety, further synthetic flexibility is possible in both imidization temperature and solubility. In our work we have primarily used the poly(amic ethyl ester) precursor to polyimide since it is soluble in a variety of solvents and solvent mixtures and imidization occurs at a significantly higher temperature than for the poly(amic acid) analogue, preventing vitrification prior to solvent loss.[18] The copolymer synthesis involved the incremental addition of PMDA diethyl ester diacyl chloride in methylene chloride to a solution of the PQE oligomer and ODA in an NMP/CHP solvent mixture in the presence of N-methylmorpholine (Scheme III). Although both the poly(amic ethyl ester) and PQE homopolymers are soluble in NMP, mixtures of the two polymers in NMP formed cloudy solutions, and subsequent copolymers formed cloudy films. The addition of CHP (50%) to the NMP produced clear solutions and minimized homopolymer contamination observed after copolymerization. The solids content for the copolymerizations was maintained between 12 and 13 wt %. N-Methylmorpholine was used as the acid acceptor since the subsequent salt, N-methylmorpholium hydrochloride, precipitated from the reaction mixture. This is believed to be important since other acid acceptors such a triethylamine form salts which remain in solution and may adversely affect the solubility of the oligomer(s) or subsequent copolymer, leading to homopolymer contamination. High molecular weight polymers were readily achieved as judged by the dramatic increase in viscosities, which is characteristic of most condensation polymerizations. The resulting amic ester–aryl ether phenylquinoxaline copolymers were precipitated in water and rinsed with methanol to remove salts formed during polymerization.

Scheme III

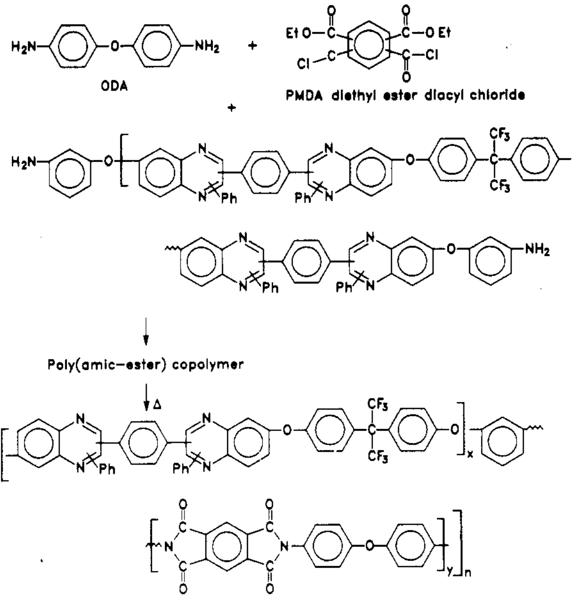


Table II contains the characteristics of the amic ester–aryl ether phenylquinoxaline copolymers. Two series of copolymers were prepared (VIIa–d and VIIIa–c) in which oligomer V or VI was coreacted with various compositions of ODA and PMDA diethyl ester diacyl chloride, respectively. The PQE compositions varied from approximately 10 to 50 wt % (denoted a–d) so as to vary the microphase-separated morphology of the copolymer. The composition of PQE in the copolymers, as determined by ^{1}H NMR, was similar to that calculated from the charge of either V or VI (Table II). The viscosity measurements, also shown in Table II, were high and comparable to that of a high molecular weight poly(amic ethyl ester) homopolymer. In some cases, a chloroform solvent rinse was required to remove PQE homopolymer contamination. It should also be pointed out that both the powder and solution forms of the poly(amic ethyl ester) copolymers are stable and do not undergo transamidization reactions or viscosity loss with time.

Solutions of copolymer series VIIa–d and VIIIa–c were cast and heated to 350 °C to imidize the copolymers, yielding polymer series IXa–d and Xa–c, respectively (Scheme III). In each case, clear tough films were obtained, indicating minimal homopolymer contamination. The thermal analyses for copolymer series IX and X are shown in Table III together with that of a polyimide homopolymer for comparison. It is important to note that the PQE composition increased after imidization due to the loss of ethanol in the imidization process. No detectable T_g was observed for the polyimide homopolymer or for either of the copolymer series IX or X. Thus, the calorimetric

Table II
Characteristics of Poly(amic ester–aryl ether phenylquinoxaline) Multiblock Copolymers

sample no.	PPQ block length, g/mol	PPQ comp, wt % charged	PPQ comp, wt % incorporated	$[\eta]^{25°C}_{NMP}$, dL/g
VII-a	6200	8	10	0.43
VII-b	6200	13	15	0.47
VII-c	6200	25	28	0.53
VII-d	6200	50	49	0.43
VIII-a	15500	13	12	0.41
VIII-b	15500	25	28	0.43
VIII-c	15500	50	52	0.46
poly(amic ester) homopolymer (control)				0.35

Table III
Characteristics of Imide–Aryl Ether Phenylquinoxaline Multiblock Copolymers

sample no.	PPQ block length, g/mol	PPQ comp, wt %	T_g, °C	isothermal wt loss, 400 °C (N_2)	decomp temp, °C	TEC,[a] 200 °C, ppm
IX-a	6200	12		0.04	480	
IX-b	6200	18		0.04	480	
IX-c	6200	32		0.03	490	19
IX-d	6200	54	270	0.04	490	
X-a	15500	16		0.03	480	
X-b	15500	29		0.02	480	15
X-c	15500	55	260	0.04	480	
PMDA/ODA polyimide				0.04	480	35–40

[a] TEC, thermal expansion coefficient.

measurements provided no insight as to the morphology of the block copolymers. Table III also contains the thermal stability, as determined by the polymer decomposition temperature (PDT) and weight loss upon isothermal aging at 400 °C, for the block copolymers and polyimide. The PDT's for the copolymers are comparable to that of the polyimide (~480 °C) as was the weight loss upon isothermal aging. This is not entirely unexpected since the PQE homopolymer is thermally stable. Interestingly, the thermal expansion coefficients (TEC), also included in Table III, for the copolymers containing low PQE compositions were significantly lower than that of the parent polyimide. However, at higher PQE compositions the TEC's were comparable to that of the parent polyimide.

The morphology of block or segmented copolymers is dependent on a number of factors including sequencing and molecular weights of the blocks and the segmental interaction parameter. This synthetic route utilized a preformed oligomer–monomer(s) synthetic approach producing an $A–B_n$ multiblock where blocks of varying length are randomly placed along the chain. In such a case, the equilibrium morphology based on the volume fraction of the components is difficult to achieve. The average molecular weight of the PQE block is identical with that of the preformed oligomer, whereas the average molecular weight of the polyimide block is controlled by the stoichiometric imbalance between the ODA and PMDA diethyl ester diacyl chloride. This is dictated by the PQE block length and composition, where low PQE block lengths and high PQE compositions generate a larger imbalance between the ODA and PMDA diethyl ester diacyl chloride and, consequently, a lower polyimide block length. This may be very important, since the polyimide block length may control, to a large extent, the phase purity in the subsequent block copolymers.

Figures 1 and 2 contain the dynamic mechanical analysis for both copolymer series containing the various PQE compositions IXa–d and Za–c, respectively. Two transitions were observed indicative of a microphase-separated morphology. The first transition was in the 250 °C range, resulting from the T_g of the PQE, and the second was approximately 350 °C, which is identical with the transition observed in the dynamic mechanical spectra of the polyimide homopolymer. The PQE transition in the copolymer series containing the 6200 g/mol PQE block length is somewhat higher (~20 °C) than that of the oligomer used in copolymerization. This may result from polyimide contamination in the PQE phase (phase mixing) or, alternatively, from the restriction of the PQE chain ends since the degree of polymerization in this oligomer is relatively low. Moreover, the region between the tran-

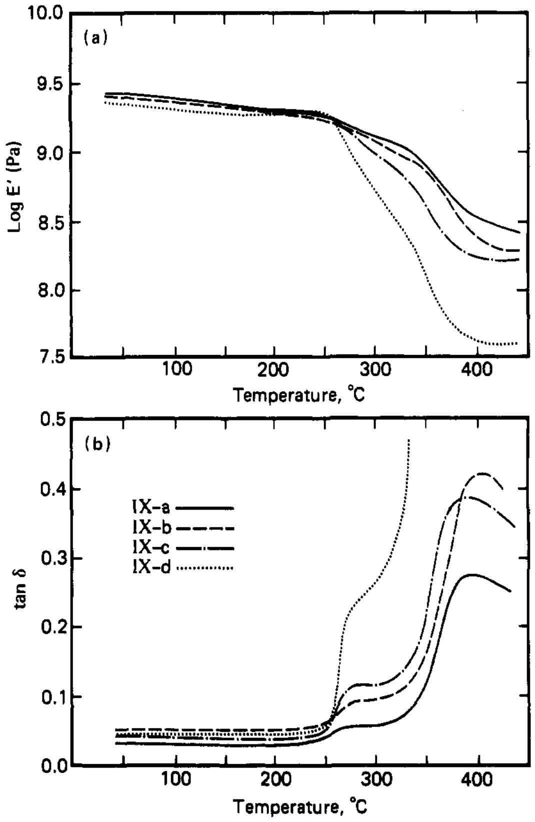


Figure 1. Dynamic mechanical behavior for copolymer series IX: (a) modulus vs temperature; (b) tan δ vs temperature.

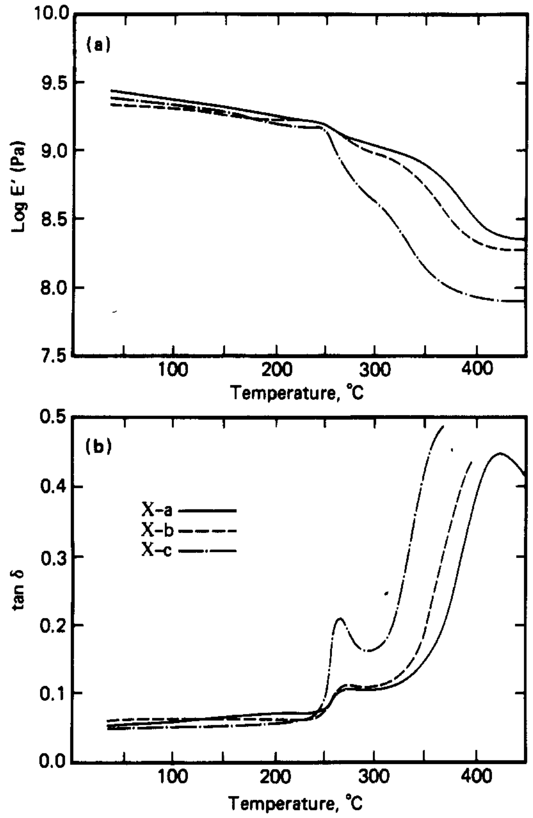


Figure 2. Dynamic mechanical behavior for copolymer series X: (a) modulus vs temperature; (b) tan δ vs temperature.

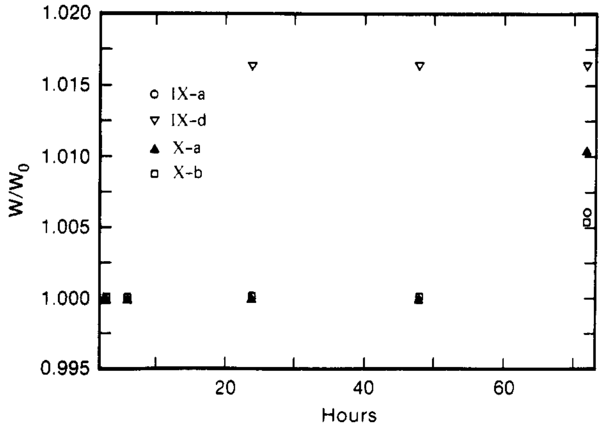


Figure 3. Swelling behavior in NMP/CHP solvent mixture.

sitions, in both the storage modulus and damping, is broad, suggesting a large diffuse interfacial region between the respective domains. Likewise, multiphase morphologies were also observed for copolymer series X composed of a PQE block length of 15 500 g/mol for each of the compositions which range from 8 to 52 wt % PQE (Xa–c) (Figure 2). Two transitions were observed; the first was in the 250 °C range, corresponding to the PQE transition, and the second transition was in the 350 °C range, which is identical with the transition observed for the parent polyimide. In this copolymer series, the PQE transition in the copolymer is the same as that observed in the oligomer used in the copolymerization, consistent with either improved phase purity or minimized chain end effects. The latter feature is not unexpected since the degree of polymerization in oligomer VI is significantly higher than in V. However, as in the previous case (copolymer series IX), the transitions are not sharp, indicative of a diffuse region between the phases.

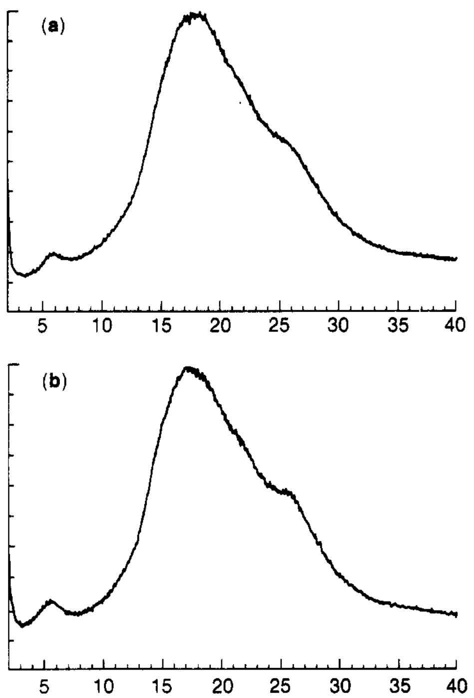


Figure 4. X-ray diffraction profile for (a) copolymer IX-a and (b) copolymer X-a in the reflection mode.

The incorporation of PQE into the PMDA/ODA chain markedly alters the swelling behavior of the films. Typically, PMDA/ODA imidized at 350 °C has, approximately, a 30% weight gain after immersion in solvents like NMP. Due to the orientation of the molecules parallel to the surface of the films, the swelling occurs in only one direction, normal to the film surface. By the incorporation of only 13% of the PQE, however, the maximum weight uptake is ~1.5%. The swelling results in a NMP/CHP solvent mixture for the two different PQE molecular weights and for different compositions are shown in Figure 3. In essence, the films do not swell. This result is very surprising since the PQE is soluble in the NMP/CHP solvent mixture and the PMDA/ODA portion swells with NMP.

The swelling of PMDA/ODA depends upon both the extent of ordering and the orientation. In general, the higher the imidization temperature, the more ordered the polymers will be and the less the PMDA/ODA will swell. The imidization of the PMDA/ODA on a substrate causes an orientation of the molecules parallel to the film surface.[2,32] As mentioned, such films swell. However, imidization of PMDA/ODA in a free-standing state, i.e., off the substrate, produces a film where the ordered regions are randomly oriented in space. Such films do not swell with solvents like NMP or DMSO.[33] For the copolymers studied here, neither of these explanations can be the origin of the reduced swelling. This can be easily seen by examination of the X-ray diffraction profiles of the copolymers. Shown in parts a and b of Figure 4 are the diffraction profiles of copolymers containing 8 and 13% PQE with molecular weights of 6200 and 15 500, respectively. The diffraction profiles were determined in a reflection geometry, and consequently, the diffraction vector is oriented normal to the surface of the film. The two diffraction profiles are virtually identical with that of the parent PMDA/ODA. At ~6° a reflection is seen characteristic of the 15.8-Å spacing associated with the projection of the length of the monomer unit onto the chain axis, i.e., the (002) reflection. At ~18° and ~26° very diffuse reflections are seen characterizing the dis-

Table IV
Autoadhesion Characteristics of Imide–Aryl Ether Phenylquinoxaline $[A-B]_n$ Block Copolymers

sample no.	PPQ block length, g/mol	PPQ comp, wt %	T_1, °C	T_2, °C	peel strength, g/mm
IX-a	6200	12	400	400	57
IX-b	6200	18	400	400	61
IX-c	6200	32	400	400	laminate
IX-d	6200	54	400	400	laminate
X-a	15500	16	400	400	laminate
X-b	15500	29	400	400	laminate
X-c	15500	55	400	400	laminate

Table V
Mechanical Properties of Imide–Aryl Ether Phenylquinoxaline $[A-B]_n$ Block Copolymers

sample no.	PPQ block mol wt	PPQ compn, wt %	modulus, MPa	tensile strength, MPa	elongation, %
IX-a	6200	12	2300	200	92
IX-b	6200	18	2000	150	90
IX-c	6200	32	2600	120	25
IX-d	6200	54	2300	115	40
X-a	15500	16	2100	200	120
X-b	15500	29	2400	110	30
X-c	15500	55	2500	170	110
	PMDA/ODApolyimide		2000	120	45

tances between adjacent PMDA/ODA chains. Thus, at least in terms of the ordering of the PMDA/ODA chains, the introduction of the PQE segments has not caused a major perturbation. In addition, the reflection at 6° for both the copolymers and the parent PMDA/ODA is weak in the reflection geometry and of approximately equal intensity. In a transmission geometry, however, this reflection is much more intense. Consequently, the molecular orientation is not altered markedly by the introduction of the PQE.

The only reasonable means by which the reduced swelling of the copolymers can be explained is by the phase separation of the PQE segments. Small-angle X-ray was used to estimate the size of the PQE domains. However, insufficient contrast between the PMDA/ODA and PQE phases along with scattering present from the original PMDA/ODA precluded quantitative assessment of the morphology. At best it can be said that the transparency of the films, provided the refractive index difference between the PMDA/ODA and PQE is large enough, indicates that the phases are at most on the order of several hundred angstroms or less. Provided the phase separation is complete, a situation exists where the matrix component, polyimide, can be swollen with NMP but the PQE domain is not soluble in NMP. This latter statement can be made due to the opacity of the homopolymer mixtures and copolymer solutions in NMP. CHP, on the other hand, does not swell the PMDA/ODA but will solubilize the PQE. Thus, the tendency would be for the NMP to penetrate into the PMDA/ODA, but significant swelling is not seen since the PQE domains act as effective cross-links prohibiting swelling. The CHP, on the other hand, cannot penetrate into the PQE domains since the PMDA/ODA matrix acts as a diffusion barrier. This explanation is, however, only speculative, but it is the only rational explanation of the observed swelling behavior given the fact that both the ordering and the orientation of the PMDA/ODA remain unchanged by the addition of the PQE.

The adhesion of polyimide to itself (self or autoadhesion) is important in the fabrication of multilayer structures. It has been demonstrated that the interfacial strength of polyimide layers sequentially cast and cured depends on the interdiffusion between layers, which in turn depends on the cure time and temperature for both the first layer (T_1) and the combined first and second layers (T_2).[25] In this work it was shown that unusually high diffusion distances (~200 nm) were required to achieve bulk strength.[25] For $T_2 \geq T_1$, the adhesion decreased with increasing T. However, for $T_2 < T_1$ with T_1 ~400 °C the adhesion between the layers was poor irrespective of T_2. The adhesion characteristics of the imide–aryl ether phenylquinoxaline block copolymers and, for comparison, PMDA/ODA polyimide are shown in Table IV. The peel strength for polyimide under these cure conditions is minimal ($T_1 = T_2 = 400$ °C). The block copolymers, on the other hand, showed markedly different behavior. Copolymers IXa and IXb with the low PQE block lengths and low PQE compositions showed significantly enhanced adhesion with peel strengths of 57 and 61 g/mm, respectively. Peel strengths between 60 and 100 g/mm are considered excellent. As the PQE composition increased to 32 and 54 wt%, further improvements in the adhesion were realized. In fact, after the T_2 cure cycle, sequentially cast and cured films were indistinguishable, and the adhesion was characterized as a laminate. Copolymer series X showed similar dramatic improvement over the PMDA/ODA by the incorporation of the PQE block irrespective of the PQE composition (Table IV).

The mechanical properties for the imide–aryl ether phenylquinoxaline block copolymers are shown in Table V. Poly(aryl ether phenylquinoxalines) are tough ductile engineering thermoplastics which undergo large-scale plastic deformation, as evidenced by necking and drawing. It is expected that the incorporation of the PQE into polyimide should favorably modify its mechanical properties. Interestingly, the moduli of the block copolymers are somewhat higher than those of either of the respective homopolymers, and this increase was more pronounced for the higher PQE compositions. Likewise, the tensile strengths of the copolymers increased, reflective of both higher moduli and elongations. For most of the block copolymers the elongations to break were substantially higher than that of PMDA/ODA polyimide (Table V). The shape of the polyimide stress–strain curve is similar to that of a "work-hardened" metal with no distinguishable yield point characteristic of small-scale or local plastic deformation.[34] The incorporation of PQE, particularly at the high compositions irrespective of the block lengths used, resulted in a stress–strain curve which appeared more as an engineering thermoplastic with a small, yet distinguishable, yield point and necking and drawing. This is characteristic of a larger scale of plastic deformation.

Summary

Imide–aryl ether phenylquinoxaline block copolymers were successfully prepared, and their thermal, mechanical, and adhesion characteristics and morphology were investigated. Bis(amino) aryl ether phenylquinoxaline oligomers of various molecular weights were prepared via a novel nucleophilic aromatic substitution polymerization. The oligomers were coreacted with ODA and PMDA diethyl ester diacyl chloride in an NMP/CHP solvent mixture. The poly(amic ethyl ester) intermediate to the polyimide was found to be more versatile than the poly(amic acid) analogue since it could be isolated and characterized prior to imidization. Copolymer compositions, determined by NMR, were close to those predicted by the charge and ranged from ~8 to 54 wt % PQE. Solutions of the copolymers were cast and cured (350 °C) to effect imidization and to produce clear films with mechanical properties comparable to those of PMDA/ODA polyimide. Multiphase morphologies were observed for each of the PQE blocks investigated at all compositions. The ordered morphology associated with the PMDA/ODA homopolymer was retained in the polyimide component in the block copolymer. Significant improvement in the autoadhesion characteristics was also observed by the incorporation of the PQE block.

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