Imide–aryl ether phenylquinoxaline random copolymers

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Novel imide–aryl ether phenylquinoxaline copolymers were prepared and their morphology and mechanical properties investigated. A key feature of these copolymers is the incorporation of an aryl ether phenylquinoxaline linkage into a semi-rigid polyimide backbone based on 4,4′-oxydianiline (ODA) and pyromellic dianhydride (PMDA) by the use of either 1,4-bis[6-(3-aminophenoxyl)-3-phenyl-2-quinoxalinyl] benzene or 1,4-bis[6-(4-aminophenyoxyl)-3-phenyl-2-quinoxalinyl]benzene as co-diamines. These monomers were prepared by a novel nucleophilic aromatic substitution reaction of 1,4-(6-fluoro-3-phenyl-2-quinoxalinyl) benzene with 4- or 3-aminophenol in the presence of K_2CO_3. These diamines were used as co-monomers with PMDA and ODA to synthesize poly(amic-acids). Films were cast and cured (350°C) to effect imidization, affording films which showed high elongations and moduli. The copolymers with high phenylquinoxaline compositions displayed T_g values in the 300°C range. The thermal stability of the copolymers was comparable to that of the parent polyimide with decomposition temperatures between 470 and 530°C. The morphology of the copolymers was investigated by dynamic mechanical, wide angle X-ray diffraction (WAXD) and swelling measurements.

(Keywords: Imide–aryl ether phenylquinoxaline copolymers; morphology; mechanical properties; WAXD; swelling measurements)

INTRODUCTION

High temperature polymers are becoming increasingly important as materials for microelectronics fabrication and are finding applications as interlayer dielectrics, passivation layers and structural resins. Aromatic polyimides are the most widely used due to their availability, ease of processing, excellent thermal and dimensional stability ($T_g > 400$°C), and good mechanical properties[1]. These properties can be attributed in part to the liquid crystalline or crystalline order exhibited by these materials[2,3]. However, drawbacks associated with the retention of this ordered structure to high temperatures and the absence of a T_g are poor melt processibility and poor self- or auto-adhesion. Conversely, poly(phenylquinoxalines) (PPQ) have glass transition temperatures ranging from 280 to 400°C depending upon the polymer structure[4], and their amorphous morphology results from the mixture of constitutional isomers present in the polymer backbone[5]. PPQ in the fully cyclized form is soluble in selected chlorinated solvents and *m*-cresol, but the toxicity of these solvents limits the use of PPQ in many applications. Consequently, it is of interest to combine the desirable characteristics of PPQ with the aromatic polyimide to afford a material which can be processed in acceptable solvents and show good auto-adhesion.

A number of reports have appeared in the literature dealing with the preparation and characterization of phenylquinoxaline–imide copolymers[6–8]. Duffy and co-workers[6,7] reported the synthesis of such copolymers in which the quinoxaline ring formation was the polymer forming reaction. A bis(dicarbonyl) monomer containing a preformed imide linkage, prepared by the reaction of aminobenzil with the appropriate dianhydride, was reacted with various bis(*o*-diamines). More recently, Korshak *et al.*[8] have reported imide–phenylquinoxaline copolymers which were prepared by the melt polycondensation of bis(aminophenyl)-quinoxaline with 1,4,5,8-naphthalenetetracarboxylic dianhydride. These materials displayed excellent thermal stability and could be melt fabricated.

We have recently reported the synthesis of imide–aryl ether phenylquinoxaline statistical copolymers by the co-reaction of PMDA with various compositions of ODA and a bis(amino) monomer with preformed phenylquinoxaline moieties, 1,4-bis[6-(3-aminophenoxy)-3-phenyl-2-quinoxalinyl]benzene[9]. This diamine was synthesized by a novel halo-displacement reaction of an appropriately substituted halophenylquinoxaline with 3-aminophenol in the presence of K_2CO_3 (ref. 10). Facile displacement of the halide was demonstrated, affording the desired diamine in high yield. In this paper, a detailed synthesis and characterization of these copolymers is described.

EXPERIMENTAL

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 Corporation), and pyromellitic dianhydride, PMDA (Chriskey Company), were obtained as polymer grade monomers and used without further purification. 2,3-Diphenyl-6-fluoro-quinoxaline, referred to as **1**, and 1,4-bis(6-fluoro-3-phenyl-2-quinoxalinyl)benzene, referred to as **3**, were prepared according to literature

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procedure[10]. *N*-methyl-2-pyrrolidone (NMP) was vacuum distilled from P_2O_5.

6-(3-Aminophenoxy)-2,3-diphenylquinoxaline, **2**

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 23.85 wt% solution 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 phenoxide formation. The mixture was cooled to room temperature, 1.50 g (5.00 mmol) of **1** in 2 ml 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 **2** as a pale yellow solid: m.p. = 184–185°C; i.r. (KBr) cm^{-1} 3453, 1613, 1594, 1566, 1467, 1340, 1220, 1193, 1168. ^1H n.m.r. (d^6-DMSO) δ 5.4 (s, 2H, NH), 6.3 (M, 1H), 6.4 (s, 1H), 6.5 (M, 1H), 7.1 (M, 1H), 7.2–7.4 (M, 1H), 7.6 (M, 1H), 7.6 (M, 1H), 8.1 (d, 1H, J = 4 Hz). ^{13}C n.m.r. (d^6-DMSO) 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.

1,4-Bis[6-(3-aminophenoxy)-3-phenyl-2-quinoxalinyl]-benzene, **4**

A three-neck flask equipped with a nitrogen inlet, overhead stirrer and Dean–Stark trap was charged with 6.000 g (0.01148 mol) of **3** and 3.133 g (0.02870 mol) of 3-aminophenol which were carefully rinsed in the flask with 40 ml of NMP and 25 ml of toluene. Finally, 2.9 g (0.021 mol) of K_2CO_3 was added to the flask. It is important to note that K_2CO_3 was used in excess[11]. The reaction was heated at the reflux temperature (≈140–150°C) to dehydrate the system (6 h). The temperature was increased to 180°C (20 h) to effect the displacement reaction and toluene was removed through the Dean–Stark trap. The product was then cooled and dissolved in 250 ml of chloroform, washed with dilute acid and water, dried ($MgSO_4$) and concentrated under reduced pressure. The product was isolated and recrystallized (chloroform/methanol) to yield a crystalline yellow powder: m.p. = 260–264°C: i.r. (KBr) cm^{-1} 3359, 1697, 1508, 1491. Anal. calcd. for $C_{46}H_{32}N_6O_2$: C, 78.84; H, 4.60; N, 11.99. Found: C, 78.88, H; 4.43; N, 11.67.

1,4-Bis[6-(4-aminophenoxy)-3-phenyl-2-quinoxalinyl]-benzene, **5**

A three-neck flask equipped with a nitrogen inlet, overhead stirrer and Dean–Stark trap was charged with 6.000 g (0.01148 mol) of **3** and 3.133 g (0.0287 mol) of 4-aminophenol and rinsed in the flask with 40 ml of NMP and 25 ml of toluene. Approximately 3 g of K_2CO_3 was added to the flask and the reaction mixture was heated to the reflux temperature (~140–150°C) to dehydrate the system (6 h). Toluene was then removed through the Dean–Stark trap and the temperature was increased to 180°C (20 h) to effect the displacement reaction. The product was cooled and dissolved in 250 ml of chloroform, washed with dilute acid and water and dried ($MgSO_4$) and concentrated under reduced pressure. The product was isolated and recrystallized (chloroform/methanol) yielding a yellow crystalline powder: m.p. = 325–328°C; i.r. (KBr) cm^{-1} 3359, 1690, 1510, 1492. Anal. calcd. for $C_{46}H_{32}N_6O_2$: C, 78.84; H, 4.60; N_1, 11.99. Found: C, 78.82; H, 4.44; N_1, 11.60.

The copolymers were prepared according to a published literature procedure[12]. A three-neck flask equipped with an overhead stirrer and nitrogen outlets was charged with the diamines (ODA and **4** or **5**), which were rinsed, washed in with NMP and cooled to −10°C under a strong nitrogen flow. To this solution, solid PMDA was added with slow stirring, and the reaction mixture was allowed to return to room temperature affording a viscous polymer solution (24 h). The solution was filtered (0.5 μm) and stored cold until used.

Films for thermal and mechanical analysis were cast from NMP and heated to 350°C (5°C min^{-1} heating rate) and held for 30 min. Glass transition temperatures, taken as the mid point of the change in slope of the baseline, were measured on a DuPont d.s.c. 1090 instrument with a heating rate of 10°C min^{-1}. The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at Hz and a heating rate of 10°C min^{-1}, in the tension mode. Isothermal and variable temperature (5°C min^{-1} heating rate) thermal gravimetric analysis (t.g.a.) 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^{-1}.

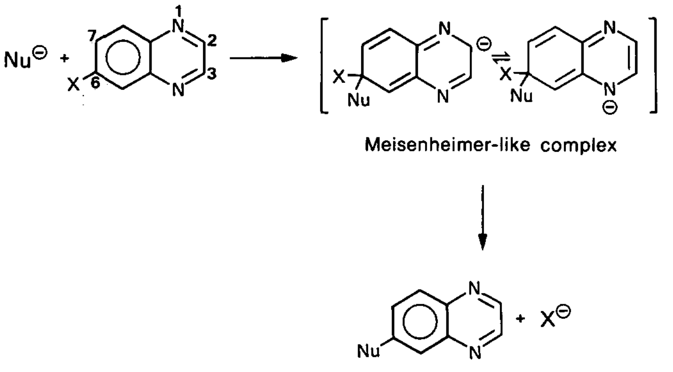
Samples for adhesion testing were prepared by doctor blading the poly(amic-acid) solutions onto a glass slide and curing them at 80°C (1 h) and 400°C (1 h). An adhesion inhibitor was added to the ends of the films to generate the initial peel strips for testing. The second layer of polymer solution was applied and cured in an analogous fashion. Specimens were sliced with a razor blade to initiate removal from the glass substrate without assistance of water. Peel strengths were determined using the T-peel test where the layers are pulled 80 degrees apart. Tests were performed using an Instron Model 1120 Material tester with a crosshead speed of 0.1 mm min^{-1}. The data reported were averages of five or more specimens tested.

Wide angle diffraction measurements were performed in both reflection and transmission geometries using a sealed tube X-ray source where the incident radiation was 1.542 Å. The diffracted X-rays were detected with a scintillation counter mounted behind an analyser crystal that was step scanned over the angular range of interest.

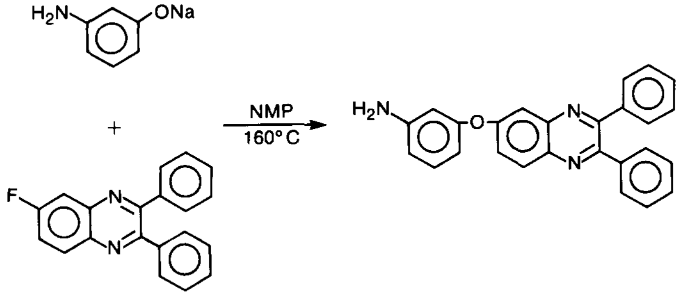
RESULTS AND DISCUSSION

The synthetic approach used for the preparation of the bis(amino)phenylquinoxaline was based on a quinoxaline activated fluoro-displacement by either 3- or 4-aminophenol. It has been shown that 6-fluoro-quinoxalines undergo a facile fluoro displacement with phenoxides, and high molecular weight poly(aryl ether-phenylquinoxalines) were synthesized using this reaction[10]. The rationale for facile nucleophilic aromatic substitution from the benzo ring of a quinoxaline was twofold: the electron poor pyrazine ring would have the effect of an electron withdrawing group[13], and due to the resonance of the negative charge in the pyrazine ring, a Meisenheimer-like complex would form as a stable intermediate (and/or transition state) during the transformation (*Scheme 1*). The synthesis of a variety of quinoxaline based diamines should be possible via the reaction of bis(6-fluoroquinoxaline) compounds with two equivalents of an aminophenol. This synthetic approach is analogous to the sulphone- and ketone-based diamines previously reported by Kawakami *et al.*[14] and Hergenrother *et al.*[15], respectively.

To demonstrate that aminophenol would react cleanly with fluoroquinoxalines, a model reaction between **1** and the sodium salt of 3-aminophenol was investigated (*Scheme 2*). The reaction was carried out at 160°C in NMP. Quantitative conversion of **1** was observed yielding **2** as the sole product (97% yield). The results of the model reaction demonstrated the feasibility of this synthetic method for the preparation of bis(amino)-quinoxalines.



Scheme 1



Scheme 2

The monomers 1,4-bis[6-(3-aminophenoxy)-3-phenyl-2-quinoxalinyl]benzene, **4**, and 1,4-bis[6-(4-aminophenoxy)-3-phenyl-2-quinoxalinyl]benzene, **5**, were synthesized by the reaction of **3** with either 1,3- or 1,4-aminophenol, respectively, in NMP (170°C) in the presence of K_2CO_3 (*Scheme 3*)[11]. As in the case of the model reaction, quantitative conversion of **3** was observed with the formation of a single product peak in each case. The resulting monomers, **4** and **5**, were isolated in 90% yield and recrystallized (methanol/chloroform) to produce polymer grade monomers. The i.r. spectrum for **5** is shown in *Figure 1*, and the important features are pointed out including the absorption due to the aryl ether linkage which is generated in the monomer forming reaction. Due to the non-selectivity of the quinoxaline ring formation in the synthesis of **3**, three constitutional isomers are possible[4,5]. These isomers are retained in **4** and **5** and may influence the solid state properties of the subsequent copolymers.

The imide–aryl ether phenylquinoxaline copolymers were prepared via the amic-acid route in NMP. Mono-

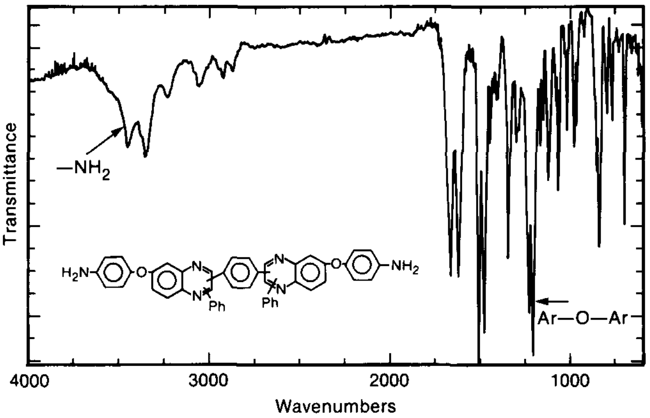
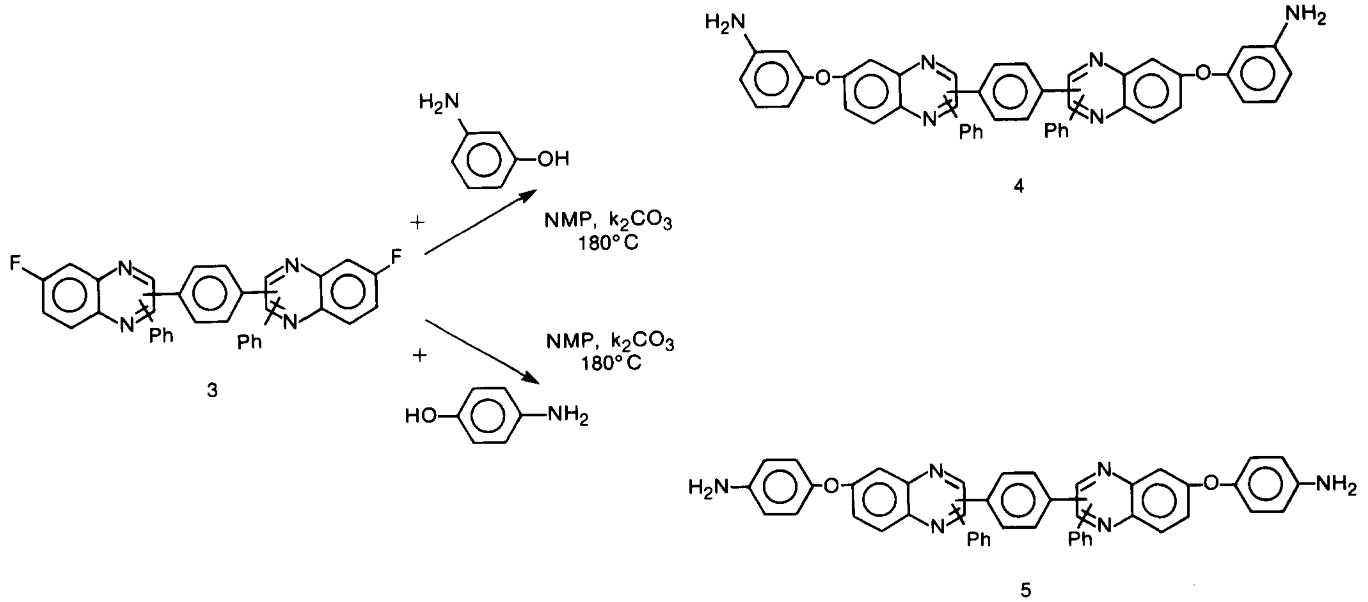
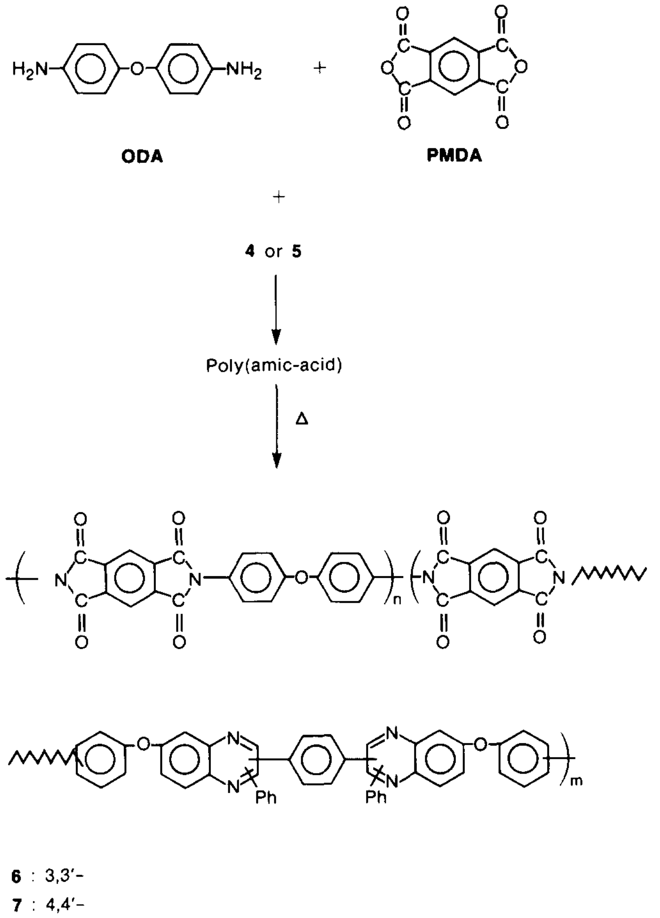


Figure 1 I.r. spectrum for compound **5**



Scheme 3



Scheme 4

mers **4** or **5** were co-reacted with various compositions of PMDA and ODA to afford copolymer series **6a–e** and **7a–d**, respectively (*Scheme 4*). The copolymer synthesis involved the incremental addition of PMDA to a solution of ODA and either **4** or **5** (−10°C) in NMP. The solids composition was generally maintained at approximately ten percent. PMDA is only marginally soluble in NMP at low temperatures, and upon dissolution, near perfect stoichiometry is generated with the diamines affording high molecular weight polymer early in the polymerization somewhat similar to an interfacial synthesis[12]. The polymerizations were allowed to return to room temperature and stirred for 24 h. High molecular weight poly(amic-acid) solutions were obtained as judged by the dramatic increase in viscosity. It is interesting to note that the incorporation of the phenylquinoxaline containing diamines produced lower viscosity solutions than typically encountered in polyimide syntheses, allowing many of the polymerizations to be performed in solutions with solid contents as high as 20% (w/v). This is not entirely unexpected because NMP is a non-solvent for many PPQ homopolymers.

Copolymer compositions were prepared so as to vary the weight percent of **4** or **5** (denoted as **a**–**e** in each copolymer series), the phenylquinoxaline component, relative to the total weight of ODA and PMDA, the polyimide component. The phenylquinoxaline compositions ranged from 10 to approximately 75 wt%, with the latter sample being **4** or **5** chain extended with PMDA (copolymers **6e** and **7d**) (*Table 1*). A blocky chain microstructure is avoided in these copolymerizations since poly(amic acid) solutions are known to undergo transimidization yielding random or statistical copolymers[12]. The copolymer solutions were filtered and cured (350°C) to effect imide formation.

Table 1 contains the thermal analysis for copolymer series **6** and **7** and a PMDA/ODA polyimide control for comparison. No detectable T_g was observed for the polyimide homopolymer or the copolymers containing the high polyimide compositions (samples **6a–c** and **7a** and **b**). However, the copolymers with the high phenylquinoxaline compositions (**6d** and **e** and **7c** and **d**) displayed T_g values in the 320°C range, and as expected, copolymers derived from the *meta*-linked **4** (copolymer series **6**) were somewhat lower. Presumably the manifestation of a T_g in these copolymers results from the presence of the constitutional isomers and ether linkages associated with the phenylquinoxaline diamines (**4** and **5**). In addition, series **6** copolymers derived from **4** containing meta-linkages which may also influence the solid state morphology and subsequent melt behaviour.

Table 1 also contains the thermal stability for copolymer series **6** and **7** together with the parent polyimide. The thermal stability was assessed by the weight loss on isothermal aging at 400°C (N_2 atmosphere) and by the polymer decomposition temperature (PDT) obtained from the variable temperature thermogram (N_2 atmosphere). The thermal stability of the copolymers is comparable to that of PMDA/ODA polyimide with a weight loss of 0.04 wt% h^{-1} upon aging at 400°C and PDT values over 470°C. The incorporation of the

Table 1 Thermal characteristics of imide–aryl ether phenylquinoxaline copolymers based on PMDA/ODA polyimide

Sample No.	Wt% PPQ	T_g °C	PDT °C	ITGA (400°C) weight loss, % h^{-1}	TEC ppm (100–200°C)
6a	10	[a]	500	0.02	38
6b	25	[a]	480	0.04	40
6c	45	[a]	470	0.04	42
6d	65	315	475	0.04	50
6e	76	300	475	0.04	50
7a	10	[a]	500	0.01	35
7b	25	[a]	510	0.04	40
7c	45	348	490	0.04	42
7d	65	340	500	0.04	45
PMDA/ODA polyimide	0	[a]	480	0.04	40

[a] No detectable T_g

phenylquinoxaline containing diamines into polyimide is not deleterious to the thermal stability as measured by these techniques.

The incorporation of **4** and **5** into PMDA/ODA polyimide did not result in significant changes in thermal expansion coefficient (TEC) (*Table 1*). The copolymers containing the high phenylquinoxaline compositions (**6c** and **d**), on the other hand, have somewhat higher TEC values ($\approx$50 ppm). Likewise, the TEC values in copolymer series **7** are similar to polyimide ($\approx$40 ppm) (*Table 1*).

Many of the drawbacks related to the aromatic polyimides (i.e. poor adhesion, planarization and melt processibility) result from the retention of the ordered morphology to high temperatures together with the absence of a T_g. PPQ, however, has a T_g in the 370°C range thereby overcoming the problem associated with processing and adhesion. These homopolymers can best be compared by their dynamic mechanical behaviour (*Figure 2*). The PMDA/ODA polyimide shows only a small drop in modulus at $\approx$350°C, reflecting the absence of a T_g and the retention of the ordered structure, whereas, PPQ shows a modulus invariance up to the T_g at which point the modulus falls dramatically characteristic of an amorphous melt. The dynamic mechanical results for copolymer series **6** and **7** are shown in *Figures 3* and *4* and are consistent with the calorimetry results. The effect of having the phenylquinoxaline containing comonomers in polyimide is clearly illustrated. The copolymers with the high imide compositions (**6a** and **b** and **7a** and **b**) show only a minimal drop in modulus at high temperatures, indicating both the absence of a T_g and the retention of the morphology characteristic of the parent polyimide. However, the copolymers containing ~50 wt% phenylquinoxaline compositions (**6c** and **7c**) show significantly different behaviour. A large, broad drop in modulus is observed at ~340°C. The copolymers with the highest phenylquinoxaline compositions (**6d** and **e** and **7d**) show T_g values in the 320°C range, which decrease with increasing phenylquinoxaline content.

The introduction of PPQ into the PMDA/ODA chain markedly alters the swelling behaviour of the

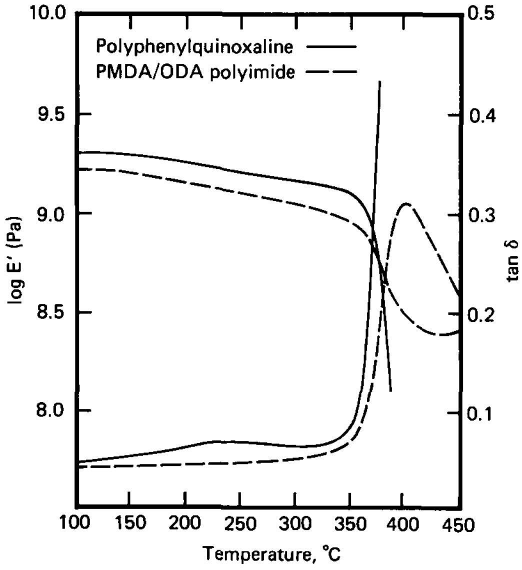


Figure 2 Storage modulus and tan δ *versus* temperature for PMDA/ODA polyimide and PPQ

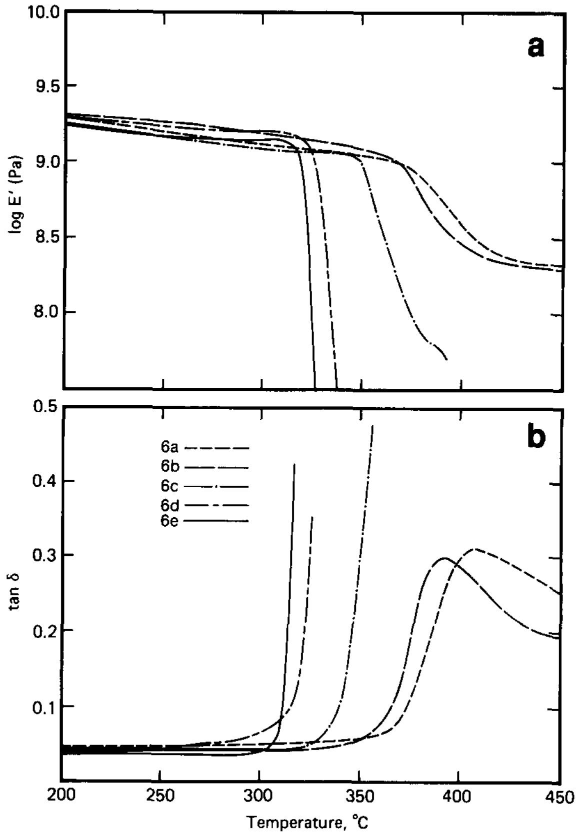


Figure 3 (a) Storage modulus *versus* temperature and (b) tan δ *versus* temperature for series **6** copolymers

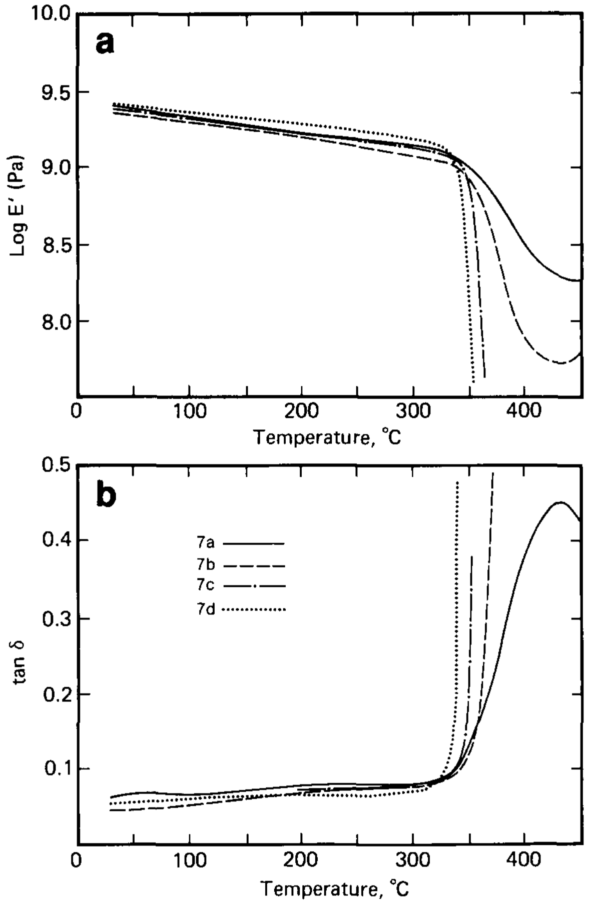


Figure 4 (a) Storage modulus *versus* temperature and (b) tan δ *versus* temperature for series **7** copolymers

polymer. Shown in *Figure 5* is the fractional weight uptake of PMDA/ODA polyimide and phenylquinoxaline upon immersion in NMP as a function of time. The swelling response of the two polymers is dramatically different. PMDA/ODA swells by 20–25% with NMP after 72 h and, in fact will take up c. 35% NMP at longer times. PPQ on the other hand does not swell with NMP. Copolymers in series **6** show a swelling in NMP that is markedly reduced over that of PMDA/ODA. In *Figure 6*, the uptake of NMP is shown for the PMDA/ODA and copolymers **6a** and **b**. Addition of 10% of the phenylquinoxaline causes a significant drop in the swelling, much more than would have been expected from the fraction of phenylquinoxaline in the copolymer. Based strictly on the volume fraction of PPQ a swelling of 18% could be expected after 72 h. However, as shown, only 5% swelling is observed. Continued increase of the phenylquinoxaline content continues to reduce the amount of swelling further and at 25% phenylquinoxaline the amount of swelling is only marginal after 72 h. Changing only the isomerization of the phenylquinoxaline containing diamine from **4** to **5** produces dramatically different results. In *Figure 7* are shown the swelling data for copolymers **7a**–**d** where the fraction of phenylquinoxaline in the copolymer is varied from 0 to 65%. The swelling after 72 h is similar to the parent polyimide with approximately 20% swelling in NMP. Consequently, the explanation of the swelling behaviour of series **6** and **7** copolymers must lie in the effect of the PPQ on the morphology of the films. Composition arguments cannot explain the observed behaviour.

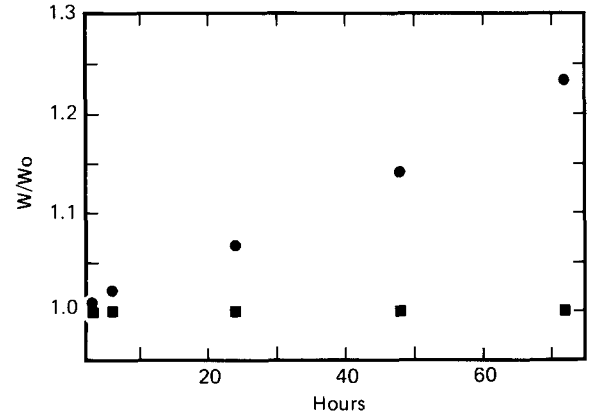


Figure 5 Fractional weight uptake upon solvent (NMP) swelling *versus* time for PMDA/ODA polyamide (●) and PPQ (■)

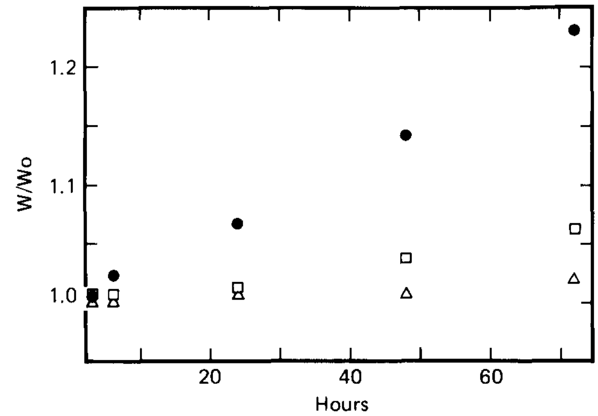


Figure 6 Fractional weight uptake upon solvent (NMP) swelling *versus* time for PMDA/ODA polyimide (●) and **6a** (□) and **6b** (△)

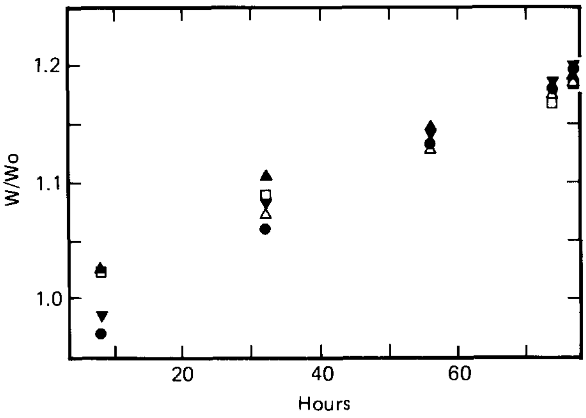


Figure 7 Fractional weight uptake upon solvent (NMP) swelling *versus* time for series 7 copolymers. ●, PMDA–ODA polyimide; ▲, **7a**; ▼, **7b**; ▽, **7c**; □, **7d**

To obtain a better understanding of this response and the effect of the addition of phenylquinoxaline on both the ordering and orientation of the molecules, X-ray diffraction studies were performed on the films in both transmission and reflection geometries. In the transmission geometry the diffraction vector is oriented parallel to the surface of the film whereas in the reflection geometry the diffraction vector is normal to the film surface. Combining these two geometries affords the opportunity of probing electron density correlations parallel and perpendicular to the film surface and hence, investigating the molecular orientation.

Diffraction profiles for the copolymers are shown in *Figure 8a–f* where *Figure 8a–c* are for copolymers **6a**–**c** and *Figure 8d–f* are for copolymers **7a**–**c**. All the copolymers have been annealed at 350°C for 1 h prior to these studies. The difference between the two series is striking. It is very clear that the copolymers derived from **4** have retained the order seen in the parent PMDA/ODA homopolymer. In fact, the ordering appears to be somewhat enhanced. The reflection occurring at a Bragg spacing of c. 16 Å ($2\theta \simeq 6°$) is quite sharp in the transmission profile and is sharper than results on PMDA/ODA homopolymer published previously[2,3]. Diffraction reflections at higher angles which are characteristic of crystalline ordering are clearly evident in all the profiles of copolymer series **6**. The strong differences between the transmission and reflection profiles unequivocally demonstrate the retention of molecular orientation. Because the intra chain reflection at 16 Å is very strong in the transmission diffraction profile where the diffraction vector is in the plane of the film, it is evident that the molecules preferentially are oriented parallel to the film surface[16]. The data in *Figure 8a–c* also show that the fraction of the specimen giving rise to diffraction decreases with increasing phenylquinoxaline concentration as would be expected, because it is unlikely that the PPQ would be incorporated in the ordered regions of PMDA/ODA.

In *Figure 8d–f*, the transmission and reflection diffraction profiles for series **7** copolymers are shown. Unlike the copolymer series **6** the addition of the **5** into PMDA/ODA polyimide does not enhance the ordering but diminishes the amount of ordering as a function of phenylquinoxaline content. It is also evident from these

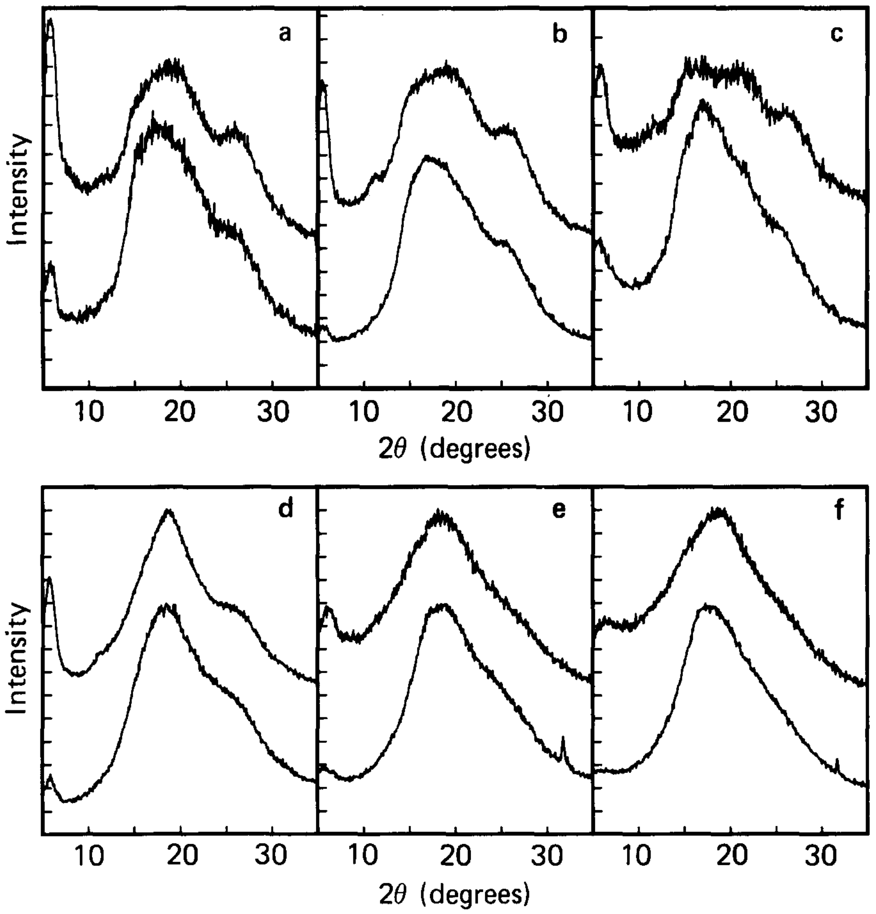


Figure 8 Wide angle X-ray diffraction profiles in transmission (T) and reflection (R) for the series **6** copolymer containing (a) 10%, (b) 25% and (c) 45% PPQ and for the series **7** copolymer containing (d) 10%, (e) 25% and (f) 45% PPQ

data that the orientation of the molecules parallel to the film surface is retained at least as evidenced by the 16 Å intramolecular reflection of PMDA/ODA.

Thus, the addition of **4** enhances the amount and degree of ordering of PMDA/ODA to the extent that apparent crystalline ordering is evident whereas the addition of **5** does not noticeably alter the PMDA/ODA ordering. In both cases, the molecular orientation parallel to the film surface is retained. These results can easily explain the observed swelling behaviour since the formation of more highly ordered regions of the PMDA/ODA and, possibly three-dimensionally ordered regions similar to that seen for the parent PMDA/ODA imidized at temperatures in excess of 375°C, will dramatically reduce the swelling. In fact, for PMDA/ODA homopolymer imidized at 400°C no swelling with NMP is found, similar to that observed here. In the case of the copolymer series **7**, the ordering of the PMDA/ODA is not affected and the overall orientation of molecules parallel to the film surface is retained. As with PMDA/ODA homopolymers only swelling normal to the film surface is seen. The enhanced ordering of the series **6** copolymers over that seen in the series **7** can be due to the enhanced mobility of series **6** copolymers. This is reflected by the lower T_g values of series **6** copolymers. It should also be noted that the enhanced ordering observed in copolymers series **6** is reflected in the higher modulus of these copolymers as shown in *Table 4* and will be discussed later in the text. In fact the modulus of these copolymers is close to that of Kapton which is a PMDA/ODA type polyimide exposed to relatively high imidization temperatures and where the ordering in the polymers is effectively a crystalline ordering. Therefore, it is the variation in the ordering of the PMDA/ODA sequences with the presence of the **4** or **5** co-monomer that ultimately defines the properties and overall characteristics of the copolymer.

The auto- or self-adhesion of polyimide, i.e. the adhesion of polyimide to itself, is important in the fabrication of multilayer components. It has been demonstrated that the interfacial strength of polyimide depends on the interdiffusion between layers which, in turn, depends on the initial cure temperature (T_1) and the temperature (T_2) where interdiffusion is performed[17]. Good auto-adhesion was found when $T_1 < T_2$ and adhesion was improved with lower T_1 values. However, if $T_1 \geqslant 400$°C the strength between the bonds was weak[17]. The peel strength results reported here were performed under cure conditions where the auto-adhesion of the parent polyimide films is good, i.e. $T_1 = 200$°C and $T_2 = 400$°C, as well as under conditions where the peel strength of parent polyimide films is poor, i.e. $T_1 = T_2 = 400$°C (ref. 17).

Tables 2 and *3* contain the auto-adhesion characteristics of copolymer series **6** and **7**, respectively, together with PMDA/ODA polyimide for comparison. As expected, under cure conditions where $T_1 = 200$°C and $T_2 = 400$°C the auto-adhesion of polyimide is marginal ($\approx 10\ \mathrm{g\ mm^{-1}}$). In contrast, copolymer series **6** showed markedly different behaviour. Improvements in the

Table 2 Adhesion characteristics of the imide–aryl ether phenylquinoxaline series 6 copolymers

Polymer number	T_1 °C	T_2 °C	Peel strength, g mm^{-1}
PMDA–ODA	200	400	10
polyimide	400	400	<1
6a	200	400	laminate
	400	400	6
6b	200	400	laminate
	400	400	laminate
6c	200	400	laminate
	400	400	laminate
6d	200	400	laminate
	400	400	laminate
6e	200	400	laminate
	400	400	laminate

Table 3 Adhesion characteristics of the imide–aryl ether phenylquinoxaline series 7 copolymers

Polymer number	T_1 °C	T_2 °C	Peel strength, g mm^{-1}
7a	200	400	103
	400	400	3
7b	400	400	laminate
	400	400	21
7c	200	400	laminate
	400	400	29
7d	200	400	laminate
	400	400	laminate

Table 4 Mechanical properties of imide–aryl ether phenylquinoxaline copolymers based on PMDA/ODA polyimide

Sample no.	Modulus MPa	Tensile stress MPa	Elongation %
6a	3000	160	95
6b	3000	160	95
6c	2950	150	60
6d	3000	150	70
6e	2870	160	110
7a	2200	130	35
7b	2250	120	35
7c	2150	110	30
7d	2200	100	25
PMDA/ODA polyimide	2000	120	40
Kapton	3000	–	–

auto-adhesion characteristics were observed with the addition of only 10 wt% PPQ, **6a**, particularly under milder cure conditions (*Table 2*). In fact, with $T_1 = 200°\mathrm{C}$ and $T_2 = 400°\mathrm{C}$, sequentially cast and cured layers were indistinguishable after the T_2 cure cycle, and no peel measurements could be made. Thus, the adhesion was characterized as a 'laminate'. Surprisingly, under the more stringent cure conditions $T_1 = T_2 = 400°\mathrm{C}$ significant improvement in the adhesion was observed, and in most cases the adhesion was characterized as a 'laminate'. Copolymers **6d** and **e** with phenylquinoxaline compositions of 65 and 75 wt% showed exceptional adhesion, regardless of the composition or cure cycle. The improvement in adhesion in these copolymers was not unexpected because these materials have T_g values ranging from 50 to 70°C below T_2 providing sufficient mobility for interdiffusion and auto-adhesion. However, copolymer **6b** does not have a T_g, yet still demonstrates excellent auto-adhesion. This presumably results from the enhanced mobility of this copolymer series as reflected in the damping in the tan δ spectrum.

The peel test results for copolymer series **7** are shown in *Table 4*. Significant improvement in the peel strength was observed for the copolymers cured under conditions where $T_1 = 200°\mathrm{C}$ and $T_2 = 400°\mathrm{C}$, and in most cases the adhesion was characterized as a 'laminate'. However, if $T_1 = T_2 = 400°\mathrm{C}$, then only marginal improvement in auto-adhesion was observed for copolymers **7a**–**c** containing up to 45 wt% phenylquinoxaline content. This is not entirely unexpected because these copolymers retain, to some extent, the ordered morphology of PMDA/ODA polyimide as well as the high T_g, and the enhanced mobility of copolymer series **6** at high temperatures was not realized. It should be noted that this is consistent with the scattering, swelling and dynamic mechanical measurements previously discussed. Conversely, copolymer **7d** showed exceptional auto-adhesion at both cure schedules. Since this material has a $T_g \approx 40°\mathrm{C}$ below the final cure temperature, sufficient mobility for interdiffusion and self-adhesion was realized.

Table 4 contains the mechanical properties of the copolymer series **6** and **7** together with PMDA/ODA polyimide and a commercially available Kapton film for comparison. Interestingly, copolymer series **6** showed moduli in the 3000 MPa range which is significantly higher than that of PMDA/ODA polyimide (2000 MPa) and comparable to that of the biaxially oriented Kapton film (3000 MPa). The apparent elongations ranged from 60 to 110% which is higher than that of the parent polyimide. In fact, those samples containing the higher phenylquinoxaline compositions (**6d** and **e**) showed ductile mechanical behaviour as characterized by necking and drawing similar to other engineering thermoplastics (i.e. polysulphone, poly(ether-imide), etc.). In each case the tensile strengths were in excess of 150 MPa. Conversely, copolymer series **7** showed moduli and tensile strengths in the same range as PMDA/ODA polyimide. The elongations were also comparable to that of parent polyimide in the 20 to 35% range. Furthermore, the shape of the stress–strain curve for copolymer series **7** was very similar to that of the PMDA/ODA polyimide as well as other rigid aromatic polyimides. Instead of a defined yield point with necking and drawing, the stress–strain curve appeared more as a cold drawn metal.

CONCLUSIONS

We have successfully synthesized imide–aryl ether phenylquinoxaline statistical copolymers in high molecular weight by reacting various diamines containing preformed phenylquinoxaline moieties with PMDA/ODA based polyimides. Copolymers of various phenylquinoxaline compositions were prepared and those containing the high phenylquinoxaline compositions displayed T_g values in the 300°C range while retaining the desired thermal stability. Ordering characteristics of the polyimides were found to be retained and even refined in copolymer series **6**. At high compositions of PPQ, however, the interchain packing was sufficiently hampered to disrupt this ordering. The variation in the ordering of the PMDA/ODA sequences ultimately defined the properties of the copolymers. The moduli were high (2000–3000 MPa) and the elongations ranged from 25 to 110%. The auto-adhesion characteristics of the polyimides were significantly improved by the incorporation of the PPQ.

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