Imide–aryl ether oxadiazole copolymers

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Imide–aryl ether oxadiazole copolymers were prepared and their morphology and mechanical properties investigated. A general method for the preparation of aryl ether oxadiazole-containing diamines has been developed in which the generation of the aryl ether linkage was the monomer-forming reaction. The electron-deficient oxazole ring activated a fluoro-substituent towards nucleophilic aromatic substitution. Facile displacement occurred at the *para* position of a 2-phenyl substituted oxadiazole heterocyclic since the oxadiazole can stabilize the negative charge developed in the transition state through a Meisenheimer complex, analogous to conventional activating groups (i.e. sulphone, ketone, etc.). The synthesis involved the reaction of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole with either 3- or 4-aminophenol in an *N*-methyl-2-pyrrolidone/*N*-cyclohexyl-2-pyrrolidone solvent mixture in the presence of potassium carbonate. These novel diamines were purified by recrystallization, polymerized with various compositions of 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) and thermally cured, producing two series of novel imide–aryl ether oxadiazole random copolymers. The resulting copolymers showed mechanical properties comparable to PMDA/ODA polyimide with elongations in the 40% range and moduli in the 2500 MPa range. The copolymers showed T_gs in excess of 300°C. However, the thermal stability was somewhat compromised by the incorporation of the oxadiazole-containing diamine relative to PMDA/ODA polyimide.

(Keywords: copolymers; imide; aryl ether oxadiazole; synthesis; morphology; mechanical properties)

INTRODUCTION

The material requirements for many microelectronics applications are becoming more demanding and as a consequence thermal stability, thermal expansion coefficient (*TEC*), mechanical properties and residual thermal stress are becoming more important design criteria. Rigid and semi-rigid polyimides, such as those derived from biphenyl dianhydride (BPDA) with 1,4-phenylenediamine (PDA) and pyromellitic dianhydride (PMDA) with 4,4′-oxydianiline (ODA), are finding applications in the microelectronics industry owing to their exceptional properties, including high thermal and dimensional stability, good mechanical properties and processing (i.e. poly(amic acid) precursor). Furthermore, polyimide films derived from BPDA/PDA show low residual stress upon thermal cycling owing to the low *TEC*, which minimizes the mismatch with a rigid substrate. These desirable properties reflect the high degree of molecular packing[1,2]. This ordering, once formed, coupled with the absence of a T_g results in poor self- or auto-adhesion (i.e. the adhesion of polyimide to itself) in the fabrication of multilayer polyimide components especially when the first layer has been imidized to high temperatures[3]. There is insufficient mobility in the polymer, which is required for interdiffusion and adhesion. Our synthetic efforts have focused on the preparation of new polyimides that show a better balance of properties (i.e. low *TEC*, low stress and sufficient mobility at high temperatures for adhesion). The synthetic strategy employed has been the design of new diamines amenable towards polyimide syntheses[4–6]. Diamines containing preformed oxazole, thiazole and phenylquinoxaline heterocycles have been prepared by novel heterocyclic-activated halo-displacements, and in many cases the resulting polyimides showed lower *TEC* values and significantly improved auto-adhesion.

There have been numerous other reports by Preston and coworkers on the preparation of polyimides with preformed heterocyclic linkages, including oxadiazole, triazole, thiazole, benzimidazole, benzoxazole, benzothiazole, phenylquinoxaline and others[7,8]. Diamines containing these preformed heterocyclic moieties were polymerized with various dianhydrides via the soluble poly(amic acid) form and subsequently thermally cured to the polyimide form. The resulting polymers showed good mechanical properties and thermal stability, and, in many cases, a highly ordered morphology.

A series of imide–aryl ether oxadiazole random copolymers were prepared from their soluble poly(amic acid) precursor and thermally cured to the imide. The oxadiazole-based poly(aryl ethers) can be prepared via an oxadiazole-activated fluoro-displacement polymerization[9]. This heterocyclic-activated halo-displacement has been extended to the preparation of oxadiazole-containing diamines, analogous to the sulphone[10], ketone[11], phenylquinoxaline[6], thiazole[4] and oxazole[5] based diamines previously reported as polyimide comonomers. Since poly(oxadiazoles) are known to be highly ordered materials, the incorporation of such rigid components into polyimide should enhance or refine the molecular packing to produce a low *TEC* material. Concurrently, the incorporation of the aryl ether linkage should enhance the mobility at high temperatures to allow for interdiffusion and self-adhesion.

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EXPERIMENTAL

Materials

4,4′-Oxydianiline (ODA; Davos Chemical Corp.), pyromellitic dianhydride (PMDA; Chriskev Co.) and hydrazine (Aldrich) were used as received without further purification. *N*-Methyl-2-pyrrolidone (NMP) and *N*-cyclohexyl-2-pyrrolidone (CHP) were vacuum distilled from P_2O_5. 4-Fluorobenzoyl chloride was prepared by the reaction of 4-fluorobenzoic acid (32.6 g, 232.7 mmol) with oxalyl chloride (44 g, 349.0 mmol) in ethyl acetate under nitrogen for 24 h (room temperature). The reaction mixture was concentrated and the product was distilled at 173°C (N_2 atmosphere) to give 32.3 g (88% yield) of 4-fluorobenzoyl chloride as a colourless liquid.

1,4-Bis(4-fluorophenyl)hydrazide (1). A round-bottomed flask equipped with a condenser was charged with 4-fluorobenzoyl chloride (14.0000 g, 0.0886 mol) and washed in with 80 ml of NMP. The reaction mixture was then cooled to −10°C and hydrazine (1.100 g, 0.0443 mol) dissolved in NMP (10 ml) was added incrementally. The reaction mixture turned red, then to a light yellow. Upon completion (6 h) the reaction mixture was isolated in excess water, filtered and subjected to both isopropanol and ethyl acetate rinses. The crude product was recrystallized (methanol/chloroform) to afford **1** as a white crystalline solid; m.p. = 244–246°C. I.r. (KBr) 3160, 3053, 1493, 1471 cm^{-1}. Analysis calculated for $C_{14}H_{10}N_2O_2F_2$: C, 60.88; H, 3.65; N, 10.14. Found: C, 60.98; H, 3.63; N, 10.22.

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (2). A 50 ml round-bottomed flask equipped with a Dean–Stark trap and condenser was charged with 20 g of **1** and ~25 ml of CHP. The reaction mixture was incrementally heated to 260°C over a 3 h period. At temperatures above 80°C CHP is no longer miscible with water and serves as an effective dehydrating agent. The reaction was held at 260°C (24 h) and t.l.c. analysis showed quantitative conversion of **1** with the formation of a single product peak in most experiments. In several cases, another unidentified peak was observed, which could be selectively removed with a subsequent isopropanol rinse. Upon cooling, the resulting monomer crystallized from the CHP, and the crystalline product was isolated in excess water to remove the CHP. The product was filtered, rinsed with isopropanol, and recrystallized (ethyl acetate/hexane) to afford **2** as a white crystalline solid; m.p. = 199–201°C. I.r. (KBr) 1471, 1413, 1304, 1272, 1095 cm^{-1}. Analysis calculated for $C_{14}H_8F_2N_2O_1$: C, 65.12; H, 3.12; N, 10.85. Found: C, 65.00; H, 3.08; N, 10.97.

2,5-Bis[4-(3-aminophenoxy)]-1,3,4-oxadiazole (3). A 25 ml three-necked flask, equipped with an overhead stirrer and Dean–Stark trap with a condenser, was charged with 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (2.8900 g, 0.01119 mol), 3-aminophenol (2.6460 g, 0.02406 mol) and K_2CO_3 (4.9804 g, 0.0369 mol). The monomers were carefully rinsed in the flask with 8 ml of NMP and 8 ml of CHP. The reaction mixture was heated to 145–155°C for 6–8 h, and the water generated on phenoxide formation was removed through the Dean–Stark trap. The reaction mixture was then heated to 185°C (20 h) to effect the displacement reaction. The crude product was isolated in deoxygenated water (~90% yield) and rinsed with methanol to remove excess 3-aminophenol. The isolated product was recrystallized (chloroform/hexane) to afford a light brown crystalline powder, **3**: m.p. = 187–191°C. I.r. (KBr) 1509, 1489, 1250, 1245, 1230 cm^{-1}. Analysis calculated for $C_{26}H_{20}O_3N_4$: C, 17.55; H, 4.62; N, 12.84. Found C, 71.48; H, 4.81; N, 12.80.

2,5-Bis[4-(4-aminophenoxy)]-1,3,4-oxadiazole (4). A 50 ml three-necked flask, equipped with an overhead stirrer and Dean–Stark trap with a condenser, was charged with 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (3.775 g, 0.0146 mol), 4-aminophenol (3.4500 g, 0.0314 mol) and K_2CO_3. The monomers were rinsed into the flask with 15 ml of NMP and 15 ml of CHP. The reaction mixture was heated to 145–155°C for 6–8 h, and the water generated upon phenoxide formation was collected in the Dean–Stark trap. The reaction mixture was then heated to 180°C (20 h) to effect the displacement reaction. The crude product was isolated in deoxygenated water (~90% yield) and rinsed with methanol to remove unreacted 4-aminophenol. The product was recrystallized (THF/isopropanol) to afford a crystalline brown powder, **4**: m.p. = 224–227°C. I.r. (KBr) 1489, 1481, 1250, 1233, 1229 cm^{-1}. Analysis calculated for $C_{26}H_{20}O_3N_4$: C, 71.55; H, 4.62; N, 12.84. Found: C, 71.52; H, 5.09; N, 12.51.

Polymerizations

The copolymers were prepared according to a literature procedure in a three-necked flask equipped with an overhead stirrer and nitrogen inlet and exit[12]. The diamines (ODA and **3** or **4**) were charged and rinsed in with NMP. The diamine mixture had to be heated in order to solvate either **3** or **4**. The temperature varied from 80 to 190°C, with the higher benzoxazole compositions requiring the higher temperatures. Once the diamines were in solution, they remained in solution even after cooling to −10°C. Solid PMDA was added to this solution 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.

Measurements

Films for thermal and mechanical analyses 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 midpoint of the change in slope of the baseline, were measured on a DuPont DSC 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 (d.m.t.a.) at 10 Hz and a heating rate of 10°C min^{-1} in the tension mode. Iosthermal and variable-temperature (5°C min^{-1} heating rate) thermal gravimetric analyses (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}. Wide-angle diffraction measurements were performed in both reflection and transmission geometries using a sealed-tube X-ray source where the incident radiation was monochromatized using pyrolytic graphite. The wavelength of 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)oxadiazoles was based on an oxadiazole-activated fluoro-displacement by amino-substituted phenoxides, analogous to the synthetic procedure of poly(aryl ether oxadiazoles)[9]. The synthesis of poly(aryl ethers) is based on the nucleophilic aromatic displacement of an aryl halide with a phenoxide, where the aryl halide is activated by an electron-withdrawing group like carbonyl or sulphone[13–15]. In addition, these activating groups can accept a negative charge, lowering the activation energy for the displacement through a Meisenheimer complex. The rationale for the facile nucleophilic aromatic substitution from the oxadiazole-substituted benzene ring was that the electron-poor oxadiazole ring would have the effect of an activating group. The effectiveness of the oxadiazole heterocyclic as an activating group may be evaluated by ^{1}H n.m.r., as the de-shielding of the protons *ortho* to a substituent is indicative of an electron-withdrawing group (*Figure 1*)[16,17]. The ^{1}H n.m.r. spectra assignments for **2** show that the protons *ortho* to the oxadiazole are shifted downfield, indicative of an electron-withdrawing group. Comparison of the assignments of **2** with a conventional activated dihalide, 4,4′-difluorobenzophenone, shows that the protons *ortho* to the oxadiazole gave a chemical shift of $\delta = 8.0$ ppm, as compared to $\delta = 7.9$ ppm for the protons *ortho* to the ketone group. This demonstrates that the electron-withdrawing effect of the oxadiazole on the benzene ring in the ground state is comparable to that of a ketone. In addition, an oxadiazole heterocyclic can accept the negative charge developed in the transformation through the formation of a Meisenheimer complex, analogous to a ketone group (*Scheme 1*). These features indicate the likelihood of facile nucleophilic aromatic substitution at the *para* position of an oxadiazole-substituted benzene ring.

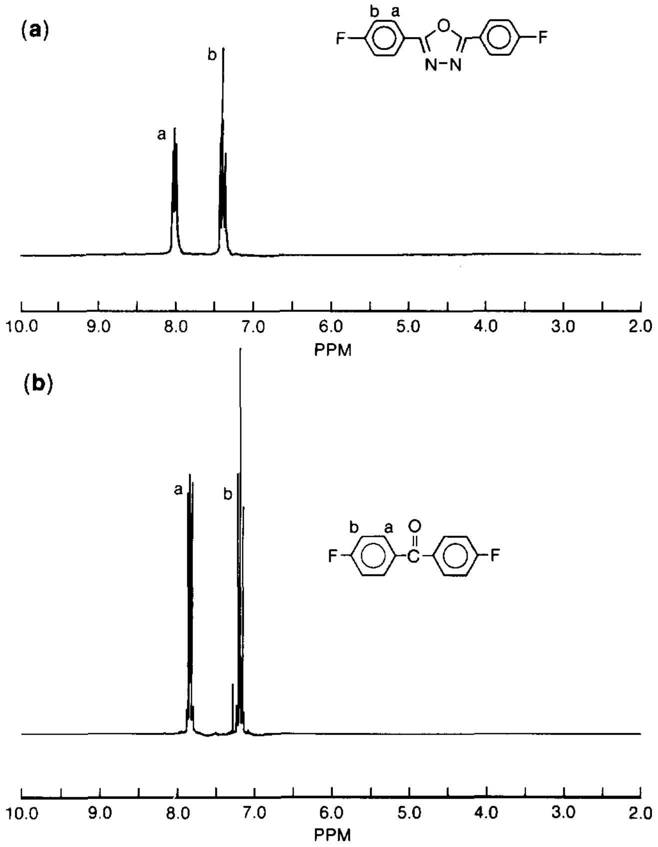
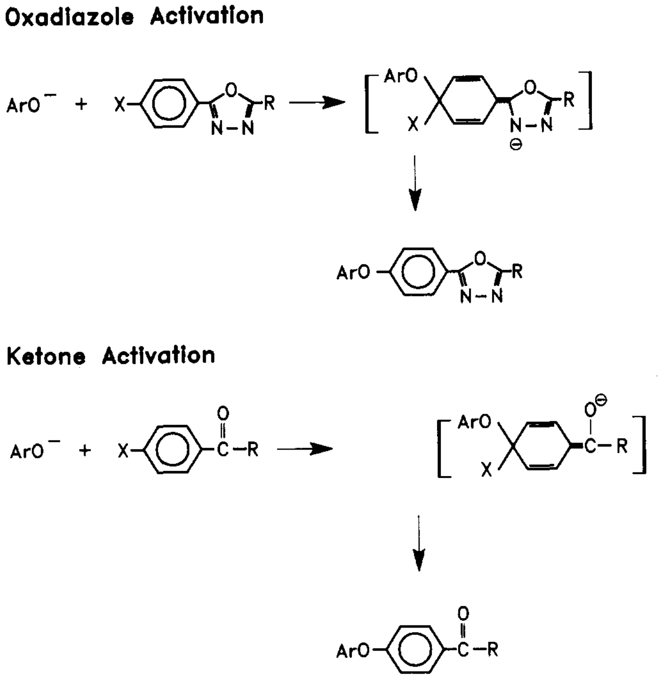
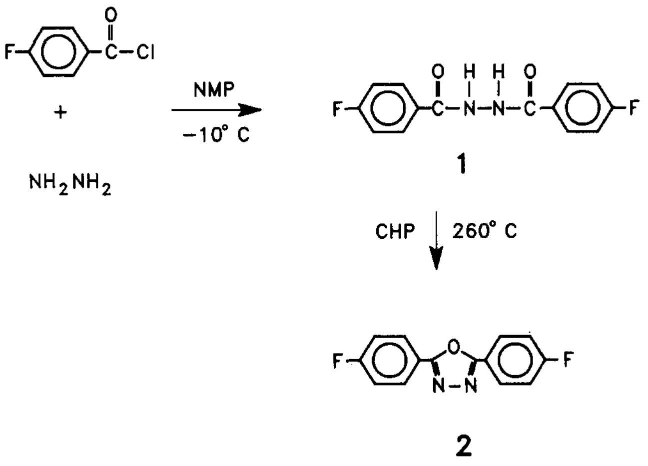


Figure 1 (a) ^{1}H n.m.r. spectrum of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (**2**) and (b) ^{1}H n.m.r. spectrum of 4,4′-difluorobenzophenone



Scheme 1



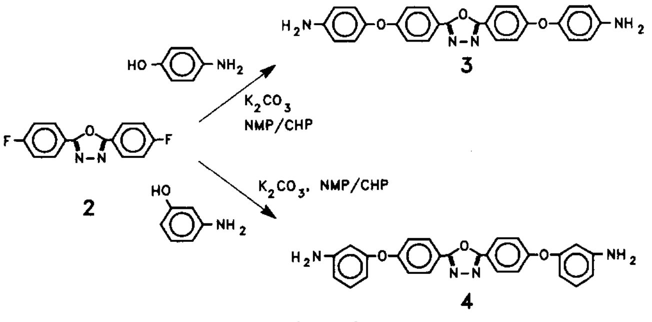
Scheme 2

The preparation of the oxadiazole-based diamines required the synthesis of a bis(fluorophenyl)oxadiazole to react with aminophenol. The synthesis of 1,4-bis(4-fluorophenyl)hydrazide (**1**) involved the reaction of 4-fluorobenzoyl chloride with hydrazine in NMP at −10°C (*Scheme 2*). Quantitative conversion of the hydrazine was observed (t.l.c.) with the formation of a single product peak with no evidence of side reactions. The crude product was isolated in water and recrystallized (methanol/chloroform) to afford **1** as a white crystalline powder. The oxadiazole-containing monomer, 2,5-bis(fluorophenyl)-1,3,4-oxadiazole (**2**), was prepared by the thermal cyclodehydration of **1** in CHP at 260°C. Since CHP is not miscible with water at temperatures above 80°C, the water generated from ring closure was effectively removed and collected in the Dean–Stark trap (8–10 h). In most cases, quantitative conversion of **1** was observed with the formation of a single product peak (t.l.c.). However, in several experiments an unidentified side product was observed. After isolation (water), a selective isopropanol rinse could quantitatively remove the side product when formed. Recrystallization (ethyl acetate/hexane) of the crude product afforded **2** as a white crystalline solid. Alternatively, the thermal cyclodehydration could be mediated in polyphosphoric acid (150°C) in high yields (>95%) with no evidence of side reactions.

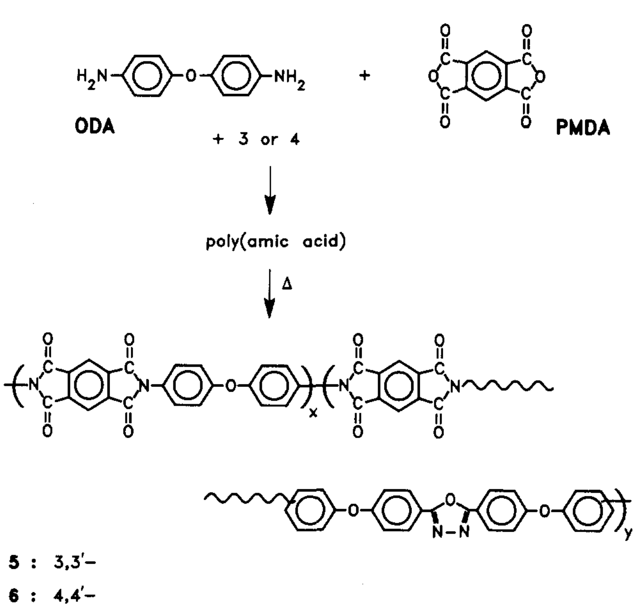
Two new oxadiazole-based diamines were prepared by the nucleophilic aromatic substitution reaction of the bis(fluorophenyl)oxadiazole with either 3- or 4-aminophenol (*Scheme 3*). The first example involved the preparation of 2,5-bis[4-(3-aminophenoxy)]-1,3,4-oxadiazole (**3**), which was synthesized by the reaction of **2** with 3-aminophenol in a NMP/CHP solvent mixture in the presence of potassium carbonate. CHP was used as a cosolvent since it is not miscible with water at temperatures above ~100°C, and interestingly, this effect is observed even if CHP is used as a cosolvent, precluding the need for a lower-boiling cosolvent to azeotrope the water generated. The reaction mixture was heated to 150°C, where the water generated by phenoxide formation was effectively removed and collected in a Dean–Stark trap. Upon dehydration, the reaction temperature was increased to 185°C to effect the displacement reaction (20 h). Quantitative conversion of **2** was observed with the formation of a single product peak by t.l.c. (ethyl acetate/hexane). The resulting **3** was isolated in 90% yield and recrystallized to afford a polymer-grade monomer. The spectral characteristics and C, H and N values were consistent with the assigned structure.

The second example involves the synthesis of 2,5-bis[4-(4-aminophenoxy)]-1,3,4-oxadiazole (**4**), which was prepared in an analogous fashion to **3** except that **2** was reacted with 4-aminophenol. Once again the reaction was mediated in a NMP/CHP solvent mixture in the presence of potassium carbonate. Quantitative conversion of **2** was observed with the formation of a single product peak (t.l.c.), which showed the spectral characteristics and C, H and N values of the expected **4**.

The imide–aryl ether oxadiazole copolymers were prepared via the standard polyimide synthetic route through the poly(amic acid) precursor (*Scheme 4*). For our experiments we used PMDA as the dianhydride owing to its availability, and, since polyimides derived from PMDA/ODA have been widely studied, this polymer was used to facilitate comparison with the imide–aryl ether oxadiazole copolymers. ODA and **3** or **4** were charged into the flask and carefully washed in with NMP. The flask was then cooled and the PMDA was added in increments as a solid to the solution of the respective diamines. PMDA was only marginally soluble in NMP at this temperature and the polymerization occurred at the solid/solution interface, analogous to an interfacial synthesis. This effect generated very high molecular weight early in the polymerization; however, upon stirring (24 h) the viscosities dropped somewhat owing to the molecular-weight equilibration which precluded a blocky structure and afforded the most probable molecular-weight distribution[12]. The high-molecular-weight poly(amic acid) solutions were then cast into films and cured to 350°C to effect imidization.



Scheme 3



Scheme 4

Two series of copolymers were prepared where either **3** or **4** were polymerized with various compositions of PMDA and ODA, affording copolymer series **5** and **6**, respectively. Copolymer compositions were prepared so as to vary the composition or weight per cent of the oxadiazole component, **3** or **4**, relative to the weight per cent of PMDA and ODA or the polyimide component. The oxadiazole compositions ranged from 25 to 66 wt% denoted as copolymers series **5a–c** and **6a–c**, with the latter copolymers **5c** and **6c** being either **3** or **4** chain-extended with PMDA, respectively.

The thermal analyses for copolymer series **5** and **6** are shown in *Table 1* together with PMDA/ODA polyimide to facilitate comparison. The thermal stability was assessed by isothermal ageing at 400°C and the polymer decomposition temperature (*PDT*). The thermal stability was severely affected by the incorporation of the aryl ether oxadiazole segment. The decomposition temperature dropped from 480°C for PMDA/ODA polyimide to ~445 to 465°C for the copolymers. Furthermore, the copolymers showed substantially higher weight loss upon isothermal ageing at 400°C than the PMDA/ODA polyimide analogue. As a consequence of the loss in high-temperature thermal stability, the cure temperature for the copolymers was limited to 350°C.

Table 1 Characteristics of imide–aryl ether oxadiazole copolymers

Sample no.	Oxadiazole composition (wt%)	T_g (°C)	*PDT* (°C)[b]	Isothermal wt loss, 400°C (N_2)	*TEC* (ppm)	Solvent uptake (wt%)[c]
5a	25	–[a]	460	0.55	40	29
5b	50	306	455	0.75	42	0
5c	66	274	445	0.75	45	5
6a	25	–[a]	470	0.45	45	30
6b	50	–[a]	460	0.90	40	4.5
6c	66	–[a]	460	0.60	40	4.0
PMDA/ODA polyimide		–[a]	480	0.04	40	35

[a] T_g not detectable by d.s.c.
[b] Polymer decomposition temperature
[c] NMP uptake after 72 h (25°C)

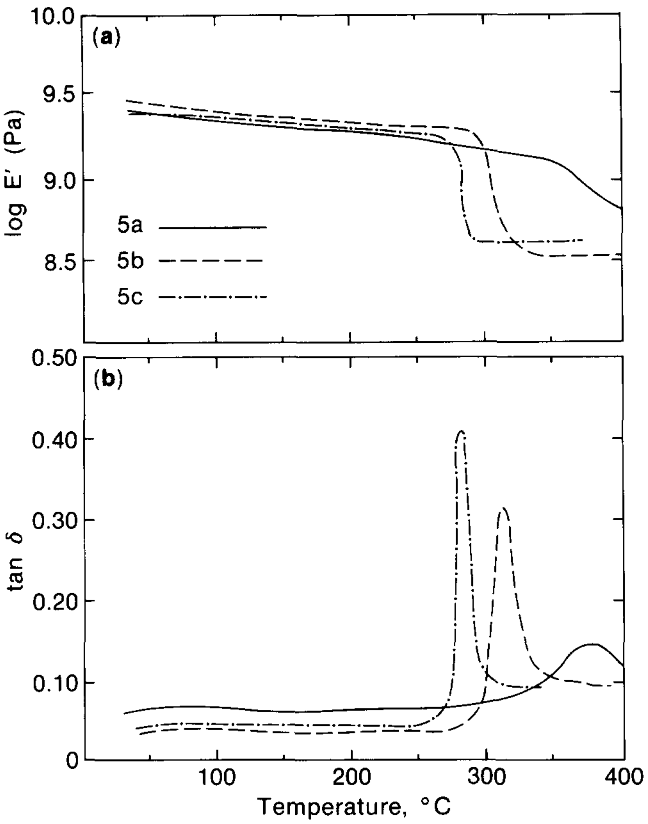


Figure 2 (a) Storage modulus *versus* temperature and (b) tan δ *versus* temperature for copolymer series **5**

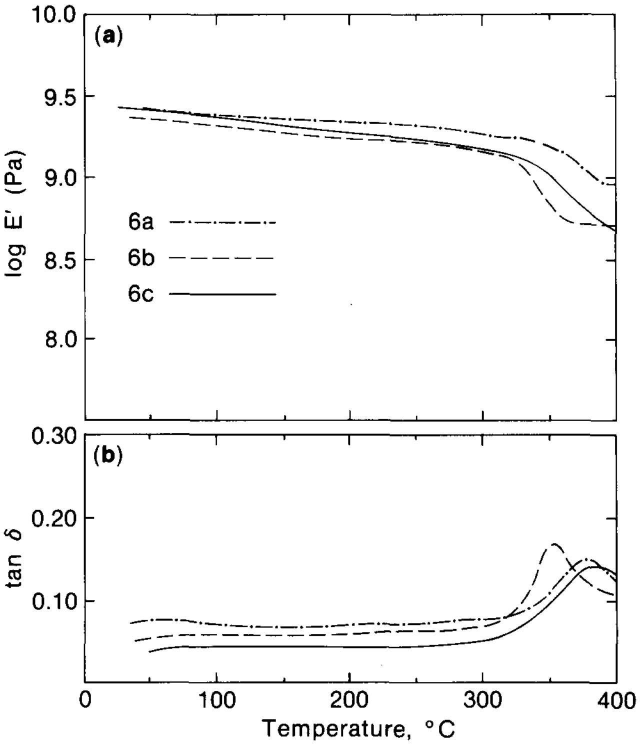


Figure 3 (a) Storage modulus *versus* temperature and (b) tan δ *versus* temperature for copolymer series **6**

The calorimetry measurements for **5a–c** and **6a–c** are also shown in *Table 1*. PMDA/ODA polyimide does not show a T_g by this technique, and likewise the copolymers containing the high imide compositions in copolymer series **5** (**5a**) and copolymers **6a–c** do not show detectable T_g values. However, copolymers **5b** and **5c** showed T_g values in the 300°C range, consistent with the introduction of both *meta* and aryl ether linkages. The dynamic mechanical spectrum for copolymers **5a–c** and **6a–c** are shown in *Figures 1* and *3*, respectively. The modulus–temperature profile for PMDA/ODA is essentially invariant except for a small drop at ~365°C, which shifts to high temperature and diminishes with repetitive thermal cycling[18,19]. This behaviour reflects the liquid-crystalline-type morphology manifested by this material[1,2]. Copolymer **5a** shows a similar modulus–temperature profile to that of PMDA/ODA polyimide with a modulus invariance up to ~370°C with only a small drop (~half decade) at this temperature. The modulus then levels out analogously to PMDA/ODA polyimide, suggesting that the ordered morphology is retained in this copolymer. At higher oxadiazole compositions (**5b** and **5c**), a large drop in modulus was observed, indicative of a T_g, consistent with the calorimetry measurements. However, at temperatures above this transition, the samples did not flow into an amorphous melt as evidenced by the retention in the modulus to high temperatures. Instead, the copolymers appear somewhat ordered (semicrystalline), with a melting point above the decomposition temperature. Copolymer series **6** showed markedly different behaviour. Irrespective of the oxadiazole composition, the modulus–temperature profile was essentially invariant except for a small drop at elevated temperatures and no T_g was observed, analogous to the behaviour of PMDA/ODA polyimide.

The morphologies of PMDA/ODA polyimide and related structures have been investigated by a number of techniques including swelling, WAXS and mechanical property measurements[18,19]. PMDA/ODA polyimide shows a local ordering of the molecules as well as an orientation of the molecules with respect to the film surface. Both factors can markedly alter both the swelling characteristics and mechanical properties of the polymer. Wide-angle X-ray diffraction studies (WAXS) on PMDA/ODA polyimide shows reflections at $2\theta = \sim 5.5\text{–}6°$ and a broad halo centred at $2\theta = \sim 17.5°C$. The first reflection, corresponding to a Bragg spacing of ~15.5 Å, characterizes the intramolecular repeat of the PMDA/ODA molecule projected onto the chain axis or the ordered regions. The second reflection, with a Bragg spacing of ~5 Å, characterizes the separation distance of the adjacent chains. Furthermore, it has been shown that the surface induces an in-plane orientation of the molecules parallel to the surface. This molecular orientation results in anisotropic swelling behaviour in NMP, a non-solvent for the polyimide, and approximately 30–35% solvent uptake is observed in the direction normal to the surface. The ordered regions act as effective crosslink junctions to limit the swelling to ~35% (*Table 1*).

The WAXD profiles for copolymer series **5** and **6** are shown in *Figure 4*. Copolymers **5a** and **6a** have somewhat similar profiles to that of PMDA/ODA polyimide, except that the intramolecular reflection was considerably weaker, indicating that the ordering was diminished in each case. *Table 1* also contains the results of the swelling measurements for the copolymers and polyimide for comparison. Copolymers **5a** and **6a** showed comparable solvent uptake to that of PMDA/ODA polyimide, indicating that both the ordering and the surface-induced in-plane molecular orientation of the polymer molecules are retained to some extent. Conversely, copolymer **4b** shows considerably different behaviour, with the disappearance of the intramolecular reflection and the development of higher-order reflections, indicative of a semicrystalline morphology. Consistent with these data, the copolymer showed no solvent uptake (*Table 2*), and the modulus above the T_g dropped several decades and levelled out. The remaining copolymers (**4c**, **5b** and **5c**) were essentially armorphous by WAXD, and showed minimal solvent uptake as expected for isotropic polyimides[18].

Table 2 contains the results of the mechanical property measurements for selected imide–aryl ether oxadiazole copolymers together with PMDA/ODA polyimide for comparison. The moduli of **5** and **6** were substantially higher than that of PMDA/ODA, while the elongations and tensile strengths were comparable to the parent polyimide and in the 40% range. The mechanical behaviour of PMDA/ODA polyimide is considerably different from that of other glassy polymers, with a stress–strain curve similar to a work-hardened metal with no distinguishable yield point[19]. This is characteristic of local or small-scale plastic deformation. Conversely, the copolymers **5** and **6** show mechanical behaviour intermediate to that of a rigid polyimide and an engineering thermoplastic that yields, necks and draws to high elongations. The imide–aryl ether oxadiazole

Table 2 Mechanical properties of imide–aryl ether oxadiazole copolymers

Sample No.	Modulus (MPa)	Yield stress (MPa)	Tensile stress (MPa)	Elongation (%)
5b	2900	121	119	40
5c	2900	134	140	41
6b	2700	121	120	20
PMDA/ODA polyimide	2000	–	120	40

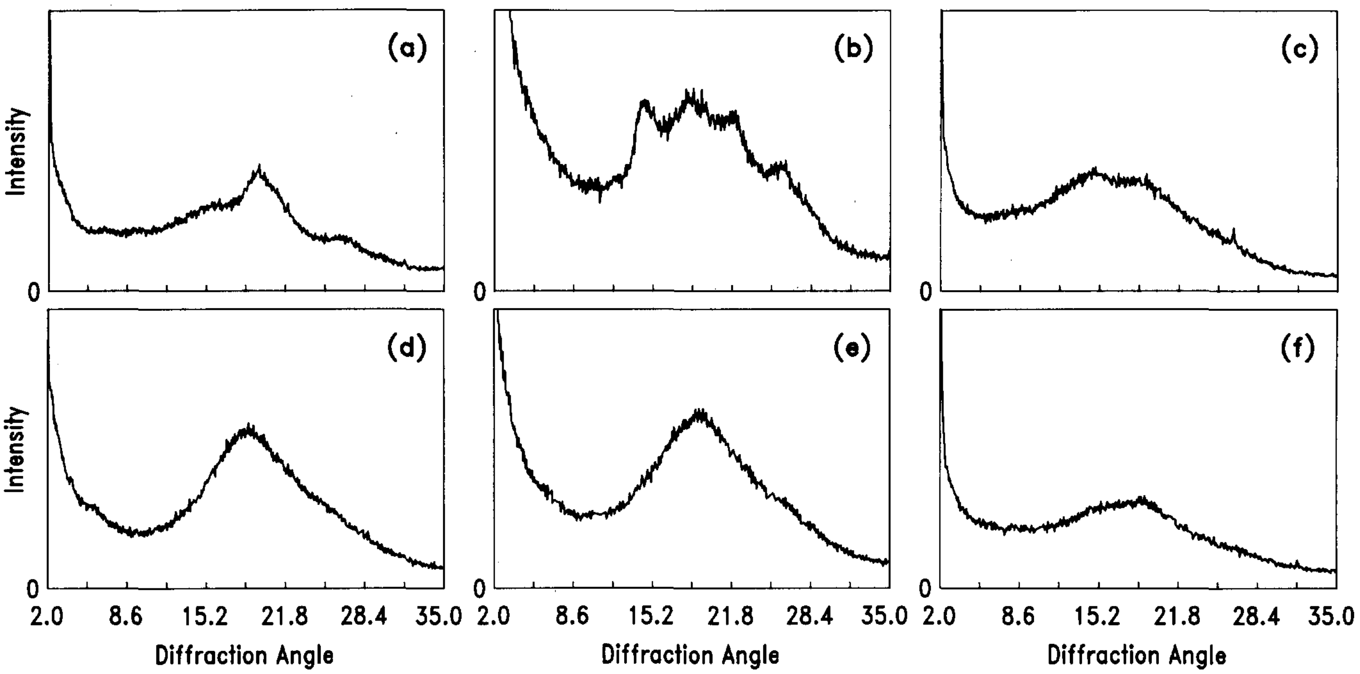


Figure 4 Transmission diffraction profiles for copolymers (a) **5a**, (b) **5b**, (c) **5c**, (d) **6a**, (e) **6b** and (f) **6c**

copolymers show a small, yet detectable, yield point that necks and elongates to high elongations. These data are consistent with other reports of heterocyclic-containing polyimides.

SUMMARY

Imide–aryl ether oxadiazole random copolymers were prepared and their thermal and mechanical properties investigated. Oxadiazole-containing diamines were prepared via a novel nucleophilic aromatic substitution reaction, where the oxadiazole heterocyclic activated an aryl fluoride towards displacement with amine-substituted phenoxides. The diamines were co-reacted with various compositions of PMDA and ODA, producing poly(amic acid) solutions, which were subsequently cast and cured to the imide form. The resulting copolymers showed mechanical properties comparable to PMDA/ODA polyimide with high elongations and moduli in the 2500 MPa range. However, the incorporation of the oxadiazole-containing diamine resulted in a compromise to the thermal stability. In several cases a T_g was observed in the 350°C range, and the ordered morphology characteristic of the parent polyimide was retained in the copolymers with the high imide compositions. This represents another example of an aryl-ether-containing diamine based on nucleophilic aromatic substitution of aryl fluorides activated by a heterocyclic ring. Furthermore, heterocyclic-activated nucleophilic displacement should prove effective with monomers derived from other ring systems.

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