

Imide-aryl ether benzoxazole random copolymers

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Novel imide-aryl ether benzoxazole copolymers were prepared and their morphology and mechanical properties investigated. A key feature of these copolymers is the incorporation of a benzoxazole moiety by the use of 2,2'-bis[4-(3-aminophenoxy)phenyl]-6,6'-bibenzoxazole or 2,2'-bis[4-(4-aminophenoxy)phenyl]-6,6'-bibenzoxazole as co-diamines in polyimide syntheses. The preparation of these diamines involved the nucleophilic aromatic substitution of 2,2'-bis(4-fluorophenyl)-6,6'-bibenzoxazole with either 3- or 4-aminophenol in the presence of K_2CO_3 . The diamines were co-reacted with various compositions of pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) to synthesize the desired poly(amic acids). Films were cast and cured (350°C) to effect the imide formation, affording films with elongations between 40 and 110% and moduli in the 2000–2750 MPa range. The copolymers exhibited good dimensional (T_g in excess of 300°C) and thermal stability. Wide-angle X-ray diffraction measurements on the copolymers showed that the ordered morphology characteristic of PMDA/ODA polyimide was retained. Improvements in the auto-adhesion were observed, particularly in those copolymers which displayed a T_g .

(Keywords: imide copolymers; benzoxazole diamine; thermal stability; ordered morphology; adhesion)

INTRODUCTION

Material requirements for many microelectronic applications are becoming increasingly more stringent due to processing conditions that require numerous high-temperature exposures. As a consequence, it is desirable to have a material with excellent thermal stability, good mechanical properties and low thermal expansion coefficient (*TEC*). Semi-rigid aromatic polyimides are finding many applications in the microelectronics industry due to their exceptional properties, including high thermal and dimensional stability ($T_g > 400^\circ\text{C}$), good mechanical properties and moderate *TEC* (~ 40 ppm)¹. The desirable properties associated with the aromatic polyimides result in part from the molecular packing^{2,3}. This ordering, once formed, coupled with the absence of a T_g results in poor self- or auto-adhesion in the multilayered polyimide components⁴. It has been shown that pyromellitic dianhydride/4,4'-oxydianiline (PMDA/ODA) polyimide has poor self-adhesion when the first layer has been imidized at high temperatures. Insufficient mobility of the polymer, even at high temperatures, prevents the interdiffusion necessary for adhesion. In contrast, poly(aryl ether phenylquinoxalines)⁵, poly(aryl ether benzoxazoles)⁶, poly(ether imides)⁷ and other^{8,9} thermally stable high- T_g amorphous engineering thermoplastics show good self-adhesion 50–70°C above their T_g . It has been demonstrated that PMDA/ODA polyimide can be modified with a semi-flexible aryl ether phenylquinoxaline comonomer to yield copolymers with T_g values in the 320–350°C range with amorphous morphologies at high phenylquinoxaline compositions¹⁰. Although these imide-aryl ether phenylquinoxaline co-

polymers showed improved ductility and auto-adhesion, the *TEC* values were somewhat higher than that of the parent PMDA/ODA polyimide. Our current synthetic approach, aimed at modifying the adhesion characteristics of polyimide without sacrificing the *TEC*, uses a semi-rigid aryl ether benzoxazole comonomer¹¹.

A number of reports have appeared in the literature dealing with the preparation and characterization of imide-benzoxazole random^{12,13} and block¹⁴ copolymers. Preston and coworkers^{12,13} have reported the synthesis of such random copolymers by preparing diamines containing preformed benzoxazole and similar heterocyclic moieties, which may be reacted with dianhydrides. These imide-benzoxazole copolymers were prepared in the form of their soluble poly(amic acid) precursor, which could be fabricated and thermally cured to obtain the desired material. Films of the copolymers demonstrated both good mechanical properties and thermal stability.

We have used a similar synthetic approach in the preparation of a series of imide-aryl ether benzoxazole random copolymers, which may be prepared via the amic acid precursor from *N*-methylpyrrolidone (NMP)¹¹. It has been demonstrated that benzoxazole-based poly(aryl ethers) can be synthesized by a fluoro displacement, where the pendent heterocyclic ring activates the displacement reaction⁶. This synthetic approach was used here for the preparation of bis(amino)bibenzoxazole-based diamines that are amenable to polyimide synthesis. This synthetic procedure is analogous to the sulphone¹⁵, ketone¹⁶ and phenylquinoxaline¹⁰ based diamines previously reported as polyimide comonomers. Moreover, the incorporation of the benzoxazole into the polyimide should maintain the good thermal stability and mechanical properties as well as favourably modify the *TEC* and self-adhesion characteristics.

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EXPERIMENTAL

Materials

4,4'-Oxydianiline (ODA; Davos Chemical Corp.) and pyromellitic dianhydride (PMDA; Chriskev Co.) were used without further purification. *N*-Methyl-2-pyrrolidone (NMP) and *N*-cyclohexyl-2-pyrrolidone (CHP) were vacuum distilled from P₂O₅ prior to use. 3,3'-Dihydroxy-4,4'-diaminobiphenyl (Chriskev Co.) and 4-fluorobenzoic acid (Aldrich) were used without further purification. 4-Fluorobenzoyl acid 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 (N₂ atmosphere) to give 32.3 g (88% yield) of 4-fluorobenzoyl chloride as a colourless liquid.

2-(4-Fluorophenyl)benzoxazole (1). 2-Aminophenol (5.800 g, 53.315 mmol) was stirred with *N,N*-dimethyltrimethylsilylamine (8.321 g, 70.956 mmol) for 2 h at 50°C. The excess silylamine was removed by vacuum distillation and the product was purified by distillation (86°C) to give 13.230 g (98% yield). The silylated aminophenol (9.517 g, 37.572 mmol) was charged into a round-bottomed flask, rinsed with 25 ml of dry tetrahydrofuran (THF) and cooled to -50°C. A 20 ml THF solution 4-fluorobenzoyl acid chloride (5.92 g, 37.57 mmol) was added dropwise and stirred for 6 h. The product was isolated into 800 ml of 5% K₂CO₃ solution, and the resulting white solid was filtered and dried. The product and 4 g of 4 Å molecular sieves were charged into a sublimator and heated to 200°C under vacuum to effect the ring closure. A light yellow crystalline powder of **1** was isolated (4.568 g, 40.2% yield). M.p. = 101–103°C. Analysis: calculated for C₁₃H₈O₁N₁F₁, C 73.23, H 3.78, N 6.57; found, C 73.34, H 3.64, N 6.58.

4-(3-Aminophenoxy)phenylbenzoxazole (2). A 25 ml three-necked flask, equipped with a stirrer, Dean–Stark trap with condenser and nitrogen inlet and exit, was charged with 3-aminophenol (0.9028 g, 8.2727 mmol), **1** (1.6652 g, 7.8044 mmol) and K₂CO₃ (1.71 g, 12.0 mmol). The contents were carefully washed into the flask with 8 ml of NMP and 5 ml of toluene. The reaction was heated to reflux temperatures (~140–150°C) where the refluxing toluene removed the water as an azeotrope (6–8 h). Toluene was periodically removed through the Dean–Stark trap and replaced with dry deoxygenated toluene to ensure dehydration. Toluene was then removed from the reaction through the Dean–Stark trap and the temperature was raised to 180°C (16 h) to effect the displacement reaction. Quantitative conversion of **1** was observed, via h.p.l.c., with the formation of a single product peak. The resulting solid was isolated and purified by chromatography (5% ethyl acetate/hexane/silica gel) to afford **2**. Yield 95%. M.p. = 96–98°C. Analysis: calculated for C₁₉H₁₄N₂O₂, C 75.47, H 4.66, N 9.26; found, C 75.19, H 4.65, N 9.13.

2,2'-Bis(4-fluorophenyl)-6,6'-bibenzoxazole (3). A 100 ml three-necked flask, equipped with a Dean–Stark trap and condenser, was charged with 4,4'-amino-3,3'-hydroxybiphenyl (17 g, 77 mmol), 4-fluorobenzoic acid (23 g, 164 mmol) and 50 ml of CHP. The reaction mixture was heated to 130°C for 24 h and then 260°C for 24 h. Initially,

nitrogen flow was passed through the reaction mixture for 2 h at 260°C to remove the water generated, then switched to a positive pressure. 4-Fluorobenzoic acid (5 g) was added to the reaction and maintained at 250°C for another 24 h. The product crystallized upon cooling and was isolated by filtration and rinsed with methanol (500 ml) to give 32 g (98% yield) of the crude product, **3**. Recrystallization from cyclohexanone gave pale yellow crystalline powder. M.p. = 279–281°C. Analysis: calculated for C₂₆H₁₄N₂O₂F₂, C 73.58, H 3.32, N 6.60; found, C 73.16, H 3.35, N 6.51.

2,2'-Bis[4-(3-aminophenoxy)phenyl]-6,6'-bibenzoxazole (4). A three-necked flask equipped with a nitrogen inlet, overhead stirrer and Dean–Stark trap was charged with **3** (6.3215 g, 0.0124 mol) and 3-aminophenol (3.5000 g, 0.0321 mol). The monomers were carefully rinsed in the flask with 40 ml of NMP and 25 ml of toluene. Finally, K₂CO₃ (6.5000 g, 0.0470 mol) was added to the flask. It is important to note that K₂CO₃ was used in excess. The reaction was heated at the reflux temperature (140–150°C) for 6–8 h, and the water generated by phenoxide formation was removed as an azeotrope with the toluene. Toluene was then removed from the system through the Dean–Stark trap, and the reaction temperature was increased to 180°C (20 h) to effect the displacement reaction. The product, **4**, was isolated in deoxygenated water (90% yield) and rinsed with methanol to remove excess 3-aminophenol. The isolated product was recrystallized (THF/methanol) to yield polymer-grade monomer. M.p. = 224–229°C. I.r. (KBr): 3428, 3405, 3229, 3043, 1554, 1314, 1282, 1108 cm⁻¹. Analysis: calculated for C₃₈H₂₆N₄O₄, C 75.73, H 4.34, N 9.29; found, C 74.4, H 4.54, N 8.99.

2,2'-Bis[4-(4-aminophenoxy)phenyl]-6,6'-bibenzoxazole (5). A three-necked flask equipped with nitrogen inlet, overhead stirrer and Dean–Stark trap was charged with **3** (5.3215 g, 0.0124 mol) and 4-aminophenol (3.5000 g, 0.0321 mol), which were carefully rinsed into the flask with 40 ml of CHP. An excess of K₂CO₃ (6.500 g, 0.0470 mol) was also added to the flask. The reaction mixture was heated to 120°C (6 h) to form the more reactive phenoxide. The reaction turned yellow-brown and the evolution of water was observed in the Dean–Stark trap. The temperature was gradually increased (1.5 h) to 220°C to effect the displacement reaction. Quantitative conversion of **3** was observed (h.p.l.c.) with the formation of a single product peak (4–5 h). The product was isolated in deoxygenated water (90% yield) and rinsed several times with deoxygenated water. The monomer was used without further purification. M.p. = 331–336°C. I.r. (KBr): 3430, 3400, 3230, 1550, 1312, 1280, 1108 cm⁻¹. Analysis: calculated for C₃₈H₂₆N₄O₄, C 75.73, H 4.34, N 9.29; found, C 74.53, H 4.64, N 9.01.

Polymerizations

The copolymers were prepared according to the literature procedure¹⁷ in a three-necked flask equipped with an overhead stirrer and nitrogen inlet and exit. The diamines (ODA and **4** or **5**) were charged and rinsed in NMP. The diamine mixture had to be heated in order to solvate either **4** or **5**. 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 . 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 ($0.5\ \mu\text{m}$) and stored cold until used.

Measurements

Films for thermal and mechanical analysis were cast from NMP and heated to 350°C ($5^{\circ}\text{C}\text{min}^{-1}$ 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 $10^{\circ}\text{C}\text{min}^{-1}$. 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 $10^{\circ}\text{C}\text{min}^{-1}$ in the tension mode. Isothermal and variable-temperature ($5^{\circ}\text{C}\text{min}^{-1}$ 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 $10\ \text{mm}\ \text{min}^{-1}$.

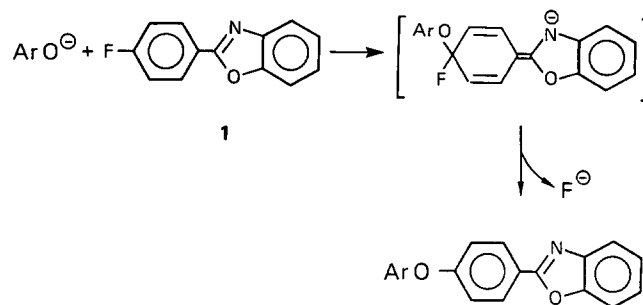
Samples for adhesion testing were prepared by doctor blading the poly(amic acid) solutions onto a glass slide and curing them to 80°C (1 h) and 400°C (1 h). An adhesion inhibitor was added to the ends of the films to generate the initial peel strips for testing. The second layer of polymer solution was 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 90° apart. Tests were performed using an Instron model 1120 Material Tester with a crosshead speed of $0.1\ \text{mm}\ \text{min}^{-1}$. 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 monochromatized using pyrolytic graphite. The wavelength of the incident radiation was $1.542\ \text{\AA}$. 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)bioxazole was based on an oxazole-activated fluoro displacement by amino-substituted phenoxides. It has been demonstrated that 2-(4-fluorophenyl)-bioxazoles undergo facile fluoro displacement with phenoxides, and high-molecular-weight poly(aryl ether benzoxazoles) were synthesized using this reaction⁶. The rationale for facile nucleophilic aromatic substitution from a benzoxazole-substituted benzene ring was twofold: (1) The electron-poor oxazole ring would have the effect of an electron-withdrawing group. (2) A Meisenheimer complex would form as a stabilized intermediate (and/or transition state) during the transformation due to resonance of the negative charge into the oxazole ring (Scheme 1).

The electronic effect of oxazole ring on both the benzo aromatic ring and the 2-phenyl group can be evaluated



Scheme 1

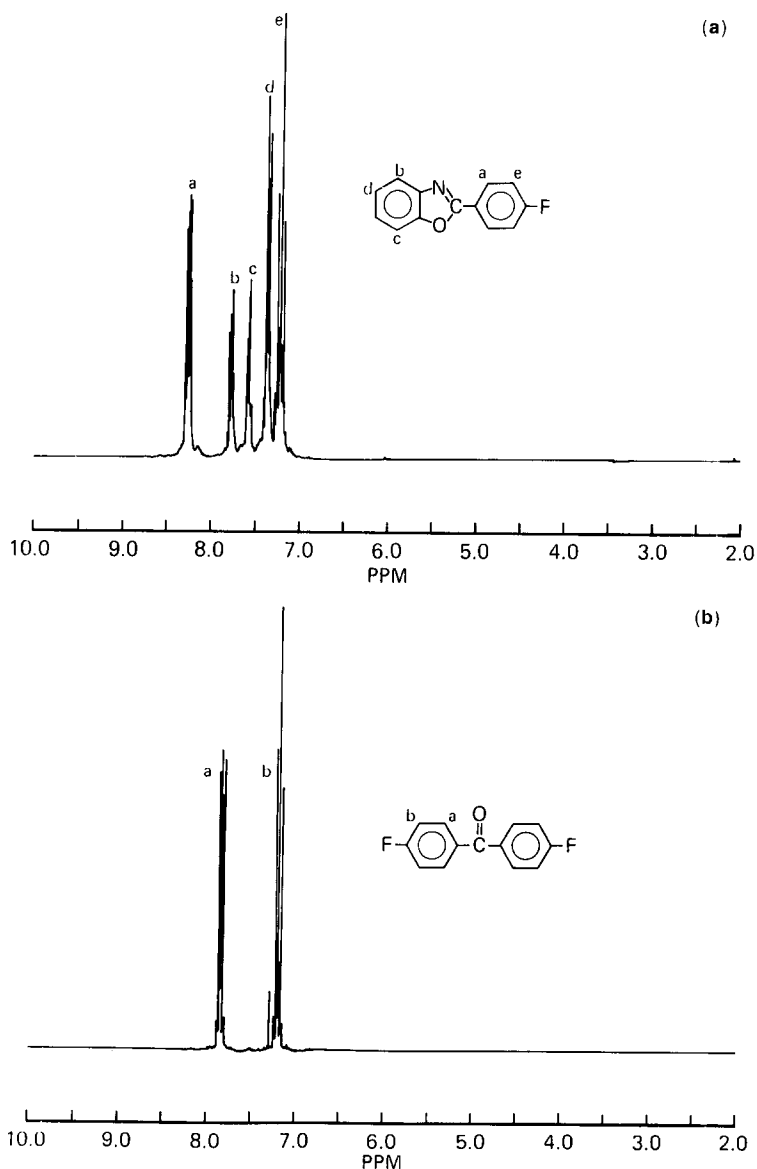
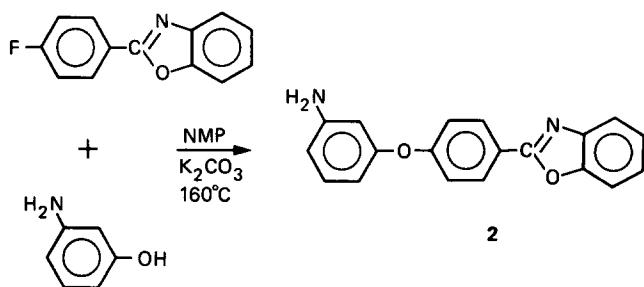


Figure 1 ^1H n.m.r. spectra of (a) 2-(4-fluorophenyl)benzoxazole (1) and (b) 4,4'-difluorobenzophenone

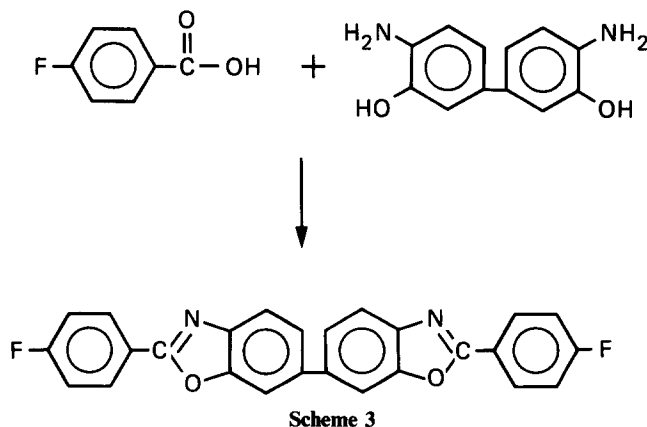
by ^1H n.m.r., as the de-shielding of the protons *ortho* to a substituent is indicative of an electron-withdrawing group (Figure 1). The ^1H n.m.r. spectral assignments for **1** show that the *ortho* protons of the 2-phenyl ring (H_a) are at $\delta=8.3\ \text{ppm}$, further downfield than the *ortho* protons of the benzo ring, H_b and H_c , at $\delta=7.8$ and $7.6\ \text{ppm}$, respectively. This indicates that oxazole has a greater electron-withdrawing effect on the 2-phenyl group than the benzo ring of the benzoxazole. Com-

parison of the assignments of **1** with 4,4'-difluorobenzophenone, a conventional activated dihalide, shows that the protons *ortho* to the benzoxazole (H_a) gave a chemical shift of $\delta = 8.3$ ppm, as compared to $\delta = 7.9$ ppm for the protons *ortho* to the ketone in 4,4'-difluorobenzophenone (Figure 1). This demonstrates that the electron-withdrawing effect of the 2-benzoxazolyl group on a benzene ring in the ground state is comparable to that of a ketone, and indicates the likelihood of facile nucleophilic aromatic substitution at the *para* position of the 2-phenyl ring.

To demonstrate the feasibility of the benzoxazole-activated aryl ether synthetic approach for the preparation of bis(amino)benzoxazole-based monomers, a model reaction between **1** and 3-aminophenol in the presence of K_2CO_3 was investigated (Scheme 2). Quantitative conversion of **1** was observed (h.p.l.c.) and the desired product, **2**, was obtained in high yield, clearly demonstrating the feasibility of the synthetic route for the preparation of benzoxazole-containing diamines.

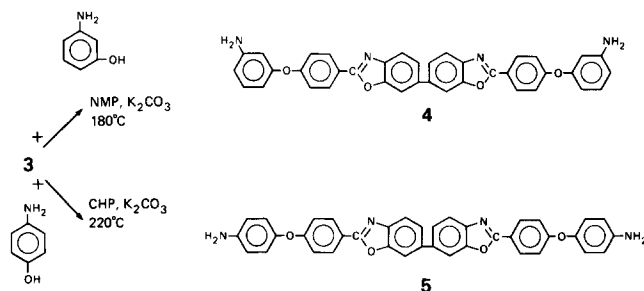


The preparation of the bibenzoxazole-based diamines required the synthesis of a bis(fluorophenyl)benzoxazole to react with aminophenol. For our experiments we used 2,2'-bis[2-(4-fluorophenyl)]-6,6'-bibenzoxazole, **3**, which was synthesized by the reaction of 4-fluorobenzoic acid with 4,4'-amino-3,3'-hydroxybiphenyl in CHP (Scheme 3). The reaction was performed in CHP, since water is not



miscible with CHP at elevated temperatures ($\geq 100^\circ C$), effectively dehydrating the reaction mixture, and high temperatures ($260^\circ C$) may be employed to effect the ring closure. Quantitative conversion of 4,4'-amino-3,3'-hydroxybiphenyl was observed (h.p.l.c.) with the formation of a single product peak and no evidence of side-reactions. Upon completion, the reaction mixture was cooled to room temperature, where the product precipitated. The crude product was isolated and recrystallized to afford **3** as polymer-grade monomer.

The synthesis of a number of benzoxazole-based diamines should be possible by the reaction of various fluorophenylbibenzoxazoles with two moles of either 3- or 4-aminophenol. Our first example involved the preparation of the monomer 2,2'-bis[4-(3-aminophenoxy)phenyl]-6,6'-bibenzoxazole, **4**, which was synthesized by the reaction of **3** with 3-aminophenol in an NMP/toluene solvent mixture in the presence of potassium carbonate (Scheme 4)¹⁸. The reaction was heated to the reflux



temperature ($\sim 145^\circ C$) where the water generated by phenoxide formation was removed as an azeotrope with toluene. Upon dehydration, the toluene was removed through the Dean-Stark trap and the reaction was heated to $180^\circ C$ to effect the displacement reaction. Quantitative conversion of **3** was observed (h.p.l.c.) with the formation of a single product peak. The resulting **4** was isolated in 90% yield and recrystallized (methanol/THF) to afford a polymer-grade monomer. The FT-i.r. spectrum of **4** is shown in Figure 2 and the characteristic bands are pointed out, including the aryl ether linkage, which is the monomer-forming reaction.

A second example involved the synthesis of 2,2'-bis[4-(4-aminophenoxy)phenyl]-6,6'-bibenzoxazole, **5**, which was prepared in an analogous fashion to **4** except that **3** was reacted with 4-aminophenol (Scheme 4). In this case the NMP/ K_2CO_3 synthetic route was not entirely suitable as a reaction solvent, since the resulting **5** was only marginally soluble in NMP at the specific reaction temperature ($180^\circ C$) and concentration (20% wt/vol). Furthermore, the use of toluene as a dehydrating agent also interfered with the solvation of **5**. CHP was found to be a more useful reaction solvent since higher temperatures could be employed (up to $260^\circ C$) to maintain solubility, and since CHP is not miscible with water at elevated temperatures ($> 100^\circ C$), a dehydrating agent was not required. Initially, the reaction mixture

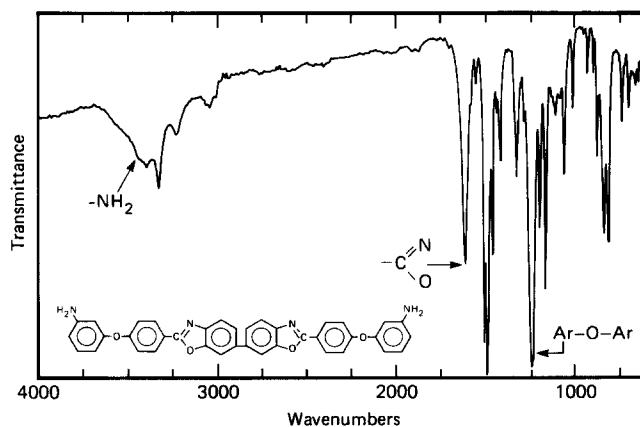


Figure 2 I.r. spectrum of **4**

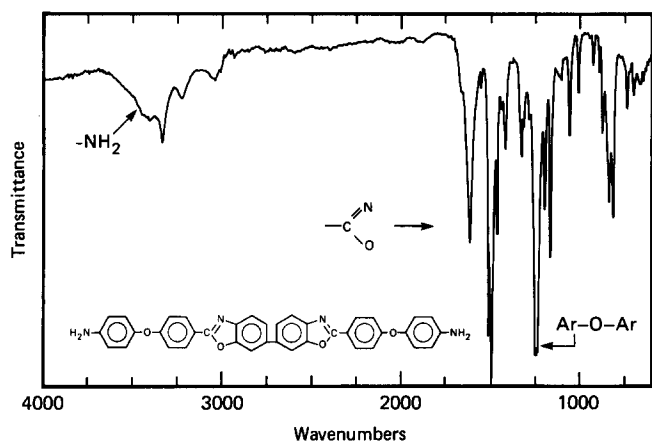
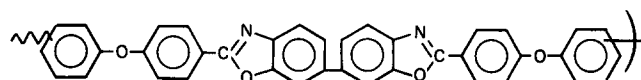
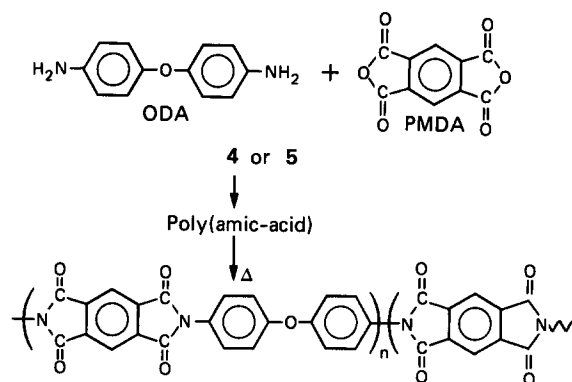


Figure 3 I.r. spectrum of 5

was heated to 120°C to form the more reactive phenoxide and to prevent sublimation of 4-aminophenol (6 h). The reaction was then heated to 220°C to effect the displacement reaction. As in the previous case, quantitative conversion of 3 was observed (h.p.l.c.) with the formation of a single product peak. The resulting 5 was isolated in 90% yield and used without further purification. The i.r. spectrum is shown in Figure 3 and the characteristic bands are illustrated, including the aryl ether moiety, which is the monomer-forming reaction.

The imide-aryl ether benzoxazole copolymers were prepared via standard polyimide synthesis (i.e. poly(amic acid) route) in NMP (Scheme 5). ODA and 4 or 5 were charged into the flask and carefully washed in with NMP. These mixtures had to be heated in order to dissolve the bis(amino)benzoxazoles. The temperature ranged from 80 to 190°C depending on the concentration of 4 or 5 in the copolymer. High compositions required higher temperatures. Upon cooling (−10°C) the diamines remained in solution so as to allow the poly(amic acid) formation without premature imidization. The copolymer synthesis involved the incremental addition of solid PMDA to the solution of diamines at −10°C¹⁷. PMDA was only marginally soluble in NMP at this temperature and polymerization occurred at the solution–solid interface, analogous to an interfacial synthesis¹⁷. High-molecular-weight poly(amic acid) solutions were obtained as judged by the dramatic increase in viscosity.



6 : 3,3'-

7 : 4,4'-

Scheme 5

Two series of copolymers were prepared that utilized 4 or 5 with PMDA and ODA, affording copolymer series 6 and 7, respectively (Scheme 5). Copolymer compositions were prepared so as to vary the weight percentage of 4 or 5, the benzoxazole component, relative to the total weight of PMDA and ODA, the polyimide component. The benzoxazole compositions ranged from 10 to 74 wt%, copolymer series 6a–d and 7a–d, with the latter copolymers 6d and 7d being either 4 or 5 chain extended with PMDA, respectively (Table 1). High-molecular-weight poly(amic acid) solutions were obtained in each case except 7d, which prematurely precipitated from solution. Since high molecular weight is achieved in the early stages of the polymerization, the resulting 7d was no longer soluble in NMP at these temperatures. Alternatively, the PMDA diethyl ester diacyl chloride was reacted with 5 in the presence of *N*-methylmorpholine (acid acceptor) in an attempt to obtain an NMP-soluble polymer¹⁹. However, the resulting poly(amic ester–benzoxazole) prematurely precipitated from NMP prior to the formation of high molecular weight.

Table 1 Characteristics of imide-aryl ether benzoxazole copolymers

Code	Benzoxazole composition (wt%)	T_g^a (°C)	Decomposition temperature (°C)	Isothermal weight loss, N ₂ , 400°C (wt% h ⁻¹)	TEC, 200°C (ppm)
6a	10	– ^b	500	0.04	44
6b	25	– ^b	500	0.04	42
6c	50	310	475	0.08	20
6d	74	290	465	0.15	20
7a	10	– ^b	480	0.06	42
7b	25	– ^b	470	0.06	40
7c	50	–	465	0.06	42
7d	74	– ^c	–	–	–
PMDA/ODA polyimide (control)		– ^b	480	0.04	35

^a D.s.c., 10°C min⁻¹ heating rate

^b No detectable T_g by d.s.c.

^c Polymer precipitated from solution

The thermal analyses for the copolymer series **6a-d** and **7a-c** are shown in Table 1 together with PMDA/ODA polyimide for comparison. The thermal stability was assessed by the polymer decomposition temperature (*PDT*) and isothermal weight loss upon ageing at 400°C (N₂ atmosphere). At high polyimide compositions, the thermal stability of the copolymers is comparable to that of PMDA/ODA polyimide with isothermal weight loss of 0.04 wt% h⁻¹ at 400°C and a *PDT* in the 480°C range. However, the copolymers containing the higher benzoxazole compositions were somewhat less thermally stable as judged by the lower *PDT* values and somewhat higher weight loss after isothermal ageing at 400°C (~0.15 wt% h⁻¹).

Table 1 also contains the thermal expansion coefficient (*TEC*) results for **6a-d**, **7a-c** and PMDA/ODA polyimide. Interestingly, significant changes were observed in the *TEC* for copolymers **6c** and **6d** with high benzoxazole compositions. The *TEC* was reduced from 40 ppm for polyimide to ~20 ppm. However, no change in the *TEC* was observed at the low benzoxazole compositions. In addition, no change in the *TEC* was observed in copolymer series **7** by the incorporation of the rigid **5** into polyimide.

The calorimetry for **6a-d** and **7a-c** are also shown in Table 1. As expected, no detectable *T_g* was observed for the polyimide homopolymer or for copolymers **6a**, **6b** and **7a-c**. However, **6c** and **6d** showed *T_g* values in the 300°C range, consistent with the introduction of both *meta* and ether linkages. The dynamic mechanical spectra for the **6** and **7** copolymers are shown in Figures 4 and

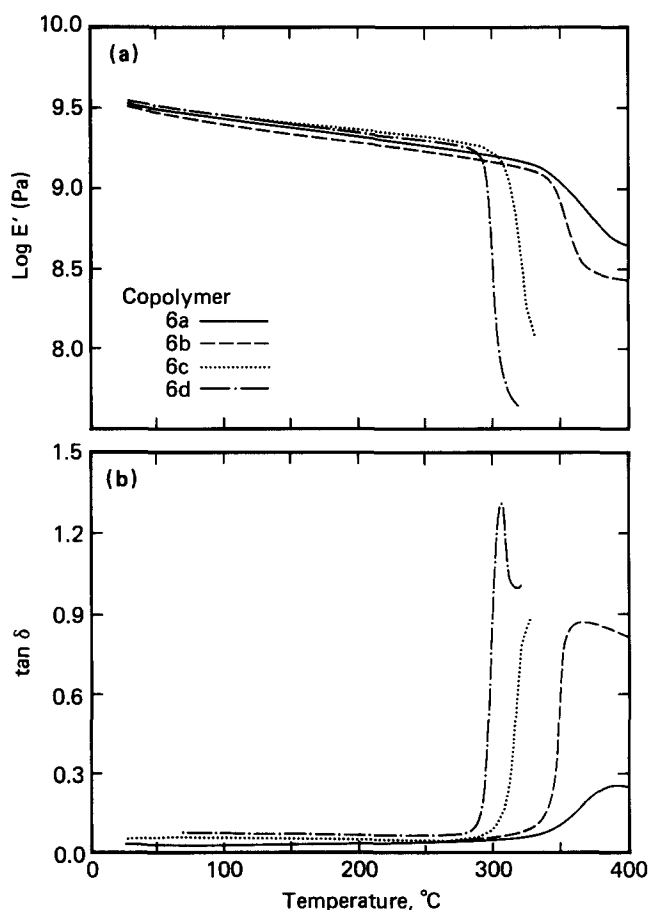


Figure 4 Dynamic mechanical behaviour for copolymers **6a-d**: (a) modulus versus temperature and (b) tan δ versus temperature

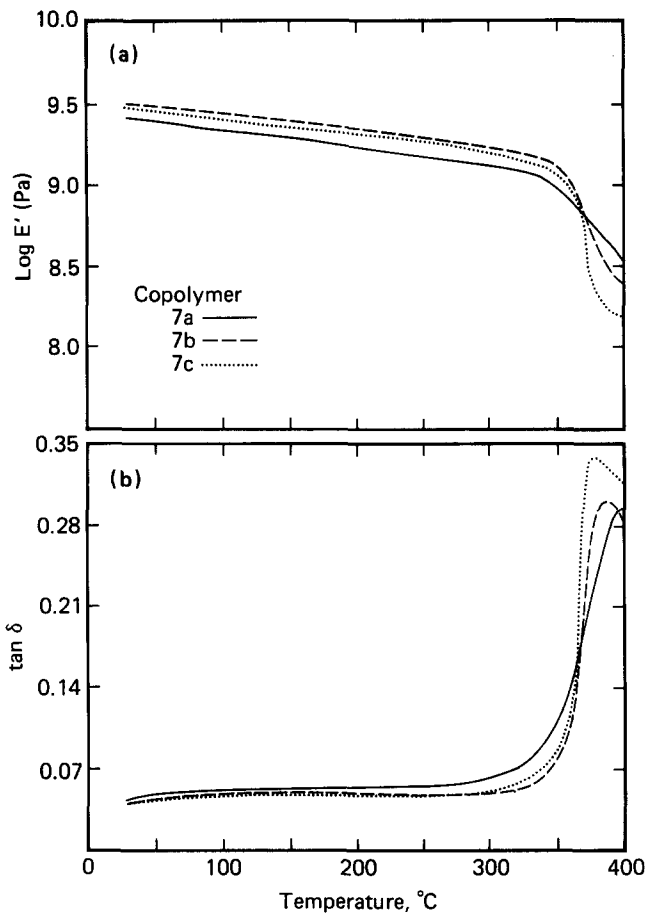


Figure 5 Dynamic mechanical behaviour for copolymers **7a-c**: (a) modulus versus temperature and (b) tan δ versus temperature

5, respectively. The modulus-temperature profile is essentially invariant except for a small drop in modulus at ~365°C. Copolymers **6a** and **6b** showed behaviour similar to that of the parent polyimide, indicating that the ordered morphology of polyimide is retained. At the higher benzoxazole compositions (**6c** and **6d**), a large drop in modulus was observed at high temperatures characteristic of the polymer undergoing a true glass transition into an amorphous melt. Incorporation of the rigid **5** into polyimide resulted in significantly different behaviour. Irrespective of the benzoxazole composition, no *T_g* was observed for copolymer series **7** and only a small drop in modulus was observed in the 370°C range. Furthermore, this transition shifts to higher temperatures with increasing benzoxazole compositions.

The auto-adhesion of polyimide, i.e. the adhesion of polyimide to itself, is important in the fabrication of multilayer circuitry. It has been demonstrated that the interfacial strength of polyimide depends on the interdiffusion between layers, which, in turn, depends on the initial curing temperature (*T*₁) and the temperature (*T*₂) where interdiffusion is performed⁴. Most importantly, it was observed that unusually high diffusion distances, of the order of 200 nm, were required to attain the native strength of the polymer at the interface. Good auto-adhesion was found when *T*₁ < *T*₂ and adhesion improved with lower *T*₁. However, if *T*₁ ≥ 400°C the strength of the bond between two polyimide layers was weak. The peel test results reported here were performed at *T*₁ = *T*₂ = 400°C, i.e. under conditions where the auto-adhesion of the parent polyimide films is poor.

Table 2 Adhesion characteristics of imide-aryl ether benzoxazole random copolymers, $T_1 = T_2 = 400^\circ\text{C}$

Sample no.	Peel strength (g mm^{-1})
6a	4.65
6b	Laminate
6c	Laminate
6d	Laminate
7a	—
7b	5.6
7c	2

Table 2 contains the adhesion characteristics of copolymer series 6 and 7 together with PMDA/ODA polyimide for comparison. The peel strength for polyimide under these conditions is minimal ($< 1 \text{ g mm}^{-1}$), and in many cases unmeasurable. In contrast, copolymer series 6 showed markedly different behaviour. Improvements in the peel strength were observed with the addition of only 10 wt% benzoxazole (6a) (Table 2). Copolymers 6b–d with benzoxazole compositions of 25–75 wt% showed exceptional auto-adhesion. Sequentially cast and cured layers were indistinguishable after the T_2 cure cycle, and no peel measurements could be made. Thus, in these cases, the adhesion was characterized as a 'laminate'. The improvement in adhesion for copolymers 6c and 6d is not unexpected since these materials have T_g values 50–70°C below T_2 . This provides sufficient mobility for interdiffusion and auto-adhesion. However, copolymer 6b does not have a T_g , yet still demonstrates excellent auto-adhesion.

For the series 7 copolymers, minimally improved adhesion was observed. The adhesion was found to decrease with increasing benzoxazole composition. Any effect of solvent on the interdiffusion process in either the 6 or 7 series copolymers must be minimal. For both series after 24 h of soaking in NMP only trace weight gains in the films were evident regardless of the content of the benzoxazole, whereas the parent polyimide swells approximately 20% under similar conditions. After much longer swelling times, the series 7 copolymers were found to swell in NMP by as much as 30%. This swelling decreased with increasing benzoxazole content. On the other hand, the series 6 copolymers swelled by at most 5% even after extended exposure to NMP.

The key to the swelling results and the interdiffusion studies lies in the local ordering of the polymers and orientation of the polymer molecules with respect to the film surface. Both factors can markedly alter the swelling and adhesion characteristics of the polymers. Wide-angle X-ray diffraction studies were performed on the series 6 and 7 copolymers over the entire polybenzoxazole (PBO) composition range. Transmission and reflection diffraction results for the series 6 copolymers are shown in Figures 6a and 6b, respectively, and for the series 7 copolymers in Figures 7a and 7b, respectively. In all cases the diffraction profiles are dominated by a broad halo centred near a scattering angle of $2\theta = 17.5^\circ$. This corresponds to a Bragg distance of $\sim 5 \text{ \AA}$, which characterizes the separation distance of adjacent chains. As expected, where there is a preferred orientation of molecules parallel to the film surface, this maximum is most pronounced in the reflection profile. It is important to note that, despite the drop in T_g for the series 6 copolymers, the extent of ordering has not changed

substantially from the original polyimide. This is in contrast to our previous studies on copolymers prepared from diamines containing polyphenylquinoxaline moieties¹⁰. In that case the reduction in the T_g of the polymer caused an enhanced ordering of the polymer molecules. It is important, however, to examine the reflection occurring near $2\theta = 5.5\text{--}6^\circ$ corresponding to a Bragg spacing of $\sim 15.5 \text{ \AA}$. This reflection characterizes the intramolecular repeat of the PMDA-ODA molecule projected onto the chain axis. For the series 7 copolymer this reflection is present in the transmission spectrum and only a slight vestige is seen in the reflection profile. This result demonstrates the retention of the orientation of the molecules parallel to the film surface even with the copolymerization with the PBO. This is also consistent with the retention of the high glass transition temperature of the copolymers. The molecular orientation would also give rise to the slight amount of swelling observed (i.e. without this orientation no swelling would be found)²⁰.

For the series 6 copolymers the situation is quite different. Here, the glass transition temperature allows the molecules in the film to relax during the imidization at 350°C . While the films are not fully isotropic it is clear from Figures 6a and 6b that the intramolecular reflection is quite pronounced in both the reflection and transmission

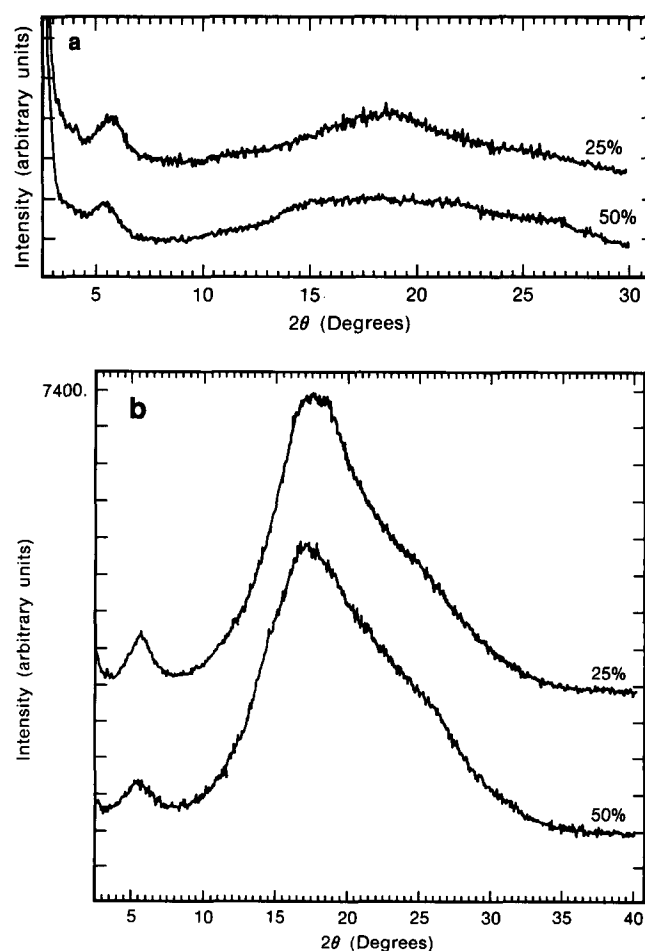


Figure 6 (a) Transmission wide-angle X-ray diffraction profiles for series 6 copolymers where the weight percentage of PBO in the copolymer is 25% (upper) and 50% (lower). Here the diffraction vector is in the plane of the film. (b) Reflection diffraction profiles for series 6 copolymers where the weight percentage of PBO in the copolymer is 25% (upper) and 50% (lower). The diffraction vector is normal to the film surface in these experiments

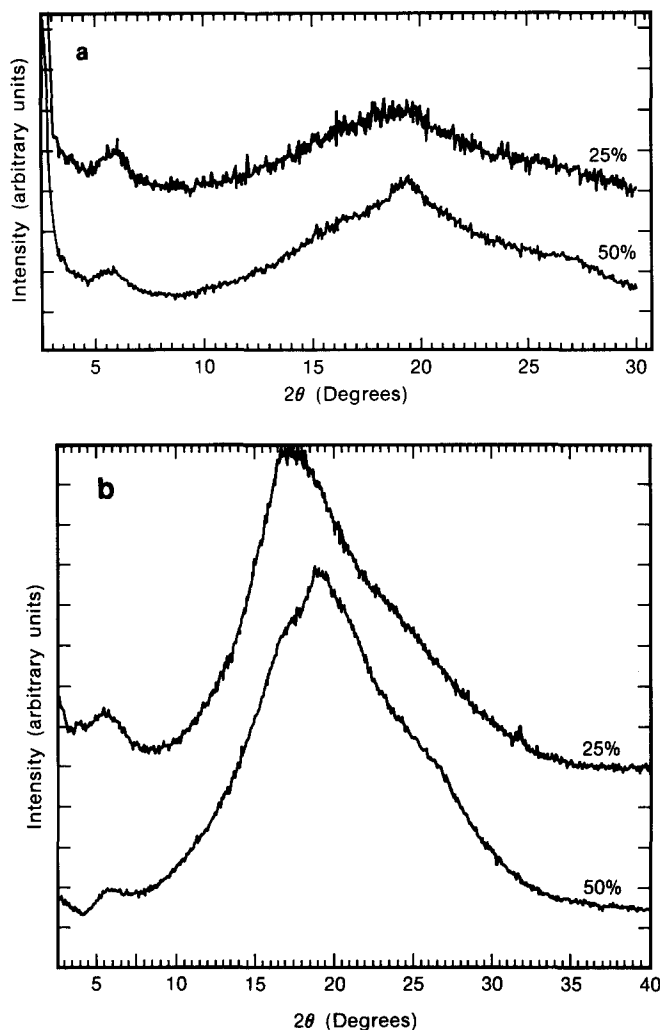


Figure 7 (a) Transmission diffraction profiles for series 7 (1,4-based) copolymers where the weight percentage of PBO in the copolymers is 25% (upper) and 50% (lower). (b) Reflection diffraction profiles for the series 7 copolymers where the weight percentage of PBO is 25% (upper) and 50% (lower)

Table 3 Mechanical properties of imide-aryl ether benzoxazole copolymers

Code	Modulus (MPa)	Stress at break (MPa)	Elongation (%)
6a	2330	145	80
6b	2450	190	110
6c	2600	170	90
6d	2650	150	80
7a	2100	165	60
7b	2330	130	40
7c	2750	182	63
PMDA/ODA polyimide (control)	1900	120	50

profiles, indicating that the chain axis is not confined to the plane of the film. This results from marked degree of molecular mobility, which would give rise to the enhanced adhesion. However, the ordering of the copolymers has not been enhanced by the larger degree of mobility.

Table 3 contains the mechanical properties of the random imide-aryl ether benzoxazoles together with PMDA/ODA polyimide as a control. The incorporation

of the benzoxazole-containing comonomer into polyimide (copolymer series 6 and 7) resulted in a modulus 10–45% higher than that of the parent polyimide. The moduli for the copolymers ranged from 2100 to 2750 MPa and increased with higher benzoxazole compositions. Copolymers 6c and 6d show both higher moduli and lower TECs than the parent polyimide. Also, the elongations and tensile strengths increased significantly. In the case of copolymer series 6, the elongations ranged from 80 to 110%, which is considerably higher than that of the parent polyimide (40–50%). The copolymers containing the low benzoxazole compositions (6a and 6b) showed mechanical behaviour very similar to that of polyimide, characterized as a localized or small-scale plastic deformation with a stress-strain curve similar to those of a 'work hardened' metal. Conversely, the copolymers containing the higher benzoxazole compositions showed ductile mechanical behaviour characterized by necking and drawing (large-scale plastic deformation) analogous to engineering thermoplastics such as polysulphone, polycarbonate and poly(ether imide). The imide-aryl ether benzoxazole copolymer series 7 showed mechanical behaviour similar to that of polyimide. The moduli were high (2100–2700 MPa), and the elongations were in the 50–60% range with stress-strain curves similar to that of the parent polyimide, indicative of local plastic deformation processes. In most cases, the tensile strengths were high and in excess of 150 MPa.

CONCLUSIONS

Imide-aryl ether benzoxazole random copolymers were prepared and their auto-adhesion characteristics, mechanical properties and morphology investigated. Benzoxazole-containing diamines, 2,2'-bis[4-(3-aminophenoxy)phenyl]-6,6'-bibenzoxazole and 2,2'-bis[4-(4-aminophenoxy)phenyl]-6,6'-bibenzoxazole, were prepared via a novel nucleophilic aromatic substitution reaction and co-reacted with various compositions of ODA and PMDA. The resulting poly(amic acids) were cast and cured at 350°C to effect imidization, affording films with elongations between 40 and 110% and moduli in the 2100–2750 MPa range. These good mechanical properties resulted in part from the retention of the liquid-crystalline morphology characteristic of PMDA-ODA polyimide. Finally, the auto-adhesion characteristics were investigated, and significant improvements in adhesion were observed for those copolymers which displayed a T_g .

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