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Synthesis of imide-aryl ether benzoxazole block copolymers

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Summary

Imide-aryl ether benzoxazole multiblock copolymers were investigated. A key feature of these copolymers was the preparation of bis(amino) terminated aryl ether benzoxazole oligomers (PBO) via a novel nucleophilic aromatic displacement polymerization. Oligomers with number average molecular weights of 10,500 and 26,000 g/mol were prepared, which displayed T_g's of 210 and 227°C, respectively. The oligomers were co-reacted with 4,4′-oxydianaline (ODA) and pyromellitic dianhydride (PMDA) diethyl ester diacyl chloride in a NMP/ cyclohexanone solvent mixture in the presence of N-methylmorpholine. The resulting amic ester-aryl ether benzoxazole copolymers were isolated and washed to remove homopolymer contamination. Copolymer compositions were analyzed by ^{13}C NMR. Solutions of the copolymers were cast and cured to effect the imidization, affording tough films with high elongations. Multiphase morphologies were obtained for both of the PBO block lengths used in the copolymerization.

Introduction

Aromatic polyimides represent an important class of high temperature polymers. These materials may be processed as poly(amic-acids) and cured to give films with exceptional properties, including high thermal and dimensional stability and good mechanical properties. Although polyimides show these desirable properties, they have received little attention as components in the synthesis of block and segmented macromolecules. Most of these reports have limited their attention to polyimide copolymers with polydimethylsiloxane coblocks (2).

We believed it would be of interest to prepare and study block copolymers derived from polyimide and a variety of other structures, particularly, amorphous high T_g engineering thermoplastics. Incorporation of semi-flexible coblocks with ductile mechanical behavior could modify the semi-rigid polyimide to afford new materials with improved modulus, ductility *etc.* Moreover, through the judicious choice of block molecular weights and solubility parameter differences, either random or microphase separated morphologies should be possible, allowing an additional means of influencing the properties of these materials. One aspect of our research has focused on the preparation of imide-aryl ether benzoxazole copolymers since poly(aryl ether benzoxazoles) (PBO) are tough thermoplastics with high T_g's and excellent thermal stability. A novel synthetic route for the preparation of poly(aryl ether benzoxazoles) has been developed which affords soluble oligomers of controlled molecular weight and functionality which may be readily utilized in polyimide syntheses (3). In this communication, we will describe our preliminary investigations on the synthesis of these novel copolymers and also summarize their thermal and mechanical properties.

Experimental

Bis(amino) (aryl ether benzoxazole) oligomers were synthesized by the reaction of 4,4′-(hexafluoroisopropylidene)diphenol (Bis-AF), 2,2′-bis[2-(4-fluorophenyl)benzoxazol -6-ylhexafluoropropane (6F-BFPB) and 3-aminophenol in N-methyl-2-pyrrolidone (NMP) in the presence of K_2CO_3. A detailed procedure of this synthetic route has been developed in our laboratory and is given elsewhere (3). The number average molecular weights, $\langle M_n \rangle$, of the oligomers were determined by ^1H-NMR after derivatization the end groups with trimethylpropionyl chloride (4). Integration of the resonance assigned to the trimethylsilyl groups in the oligomers was compared to the trimethyl integration of the aromatic protons, and the ratio of the integrated areas per proton gave the degree if polymerization from which $\langle M_n \rangle$ was calculated.

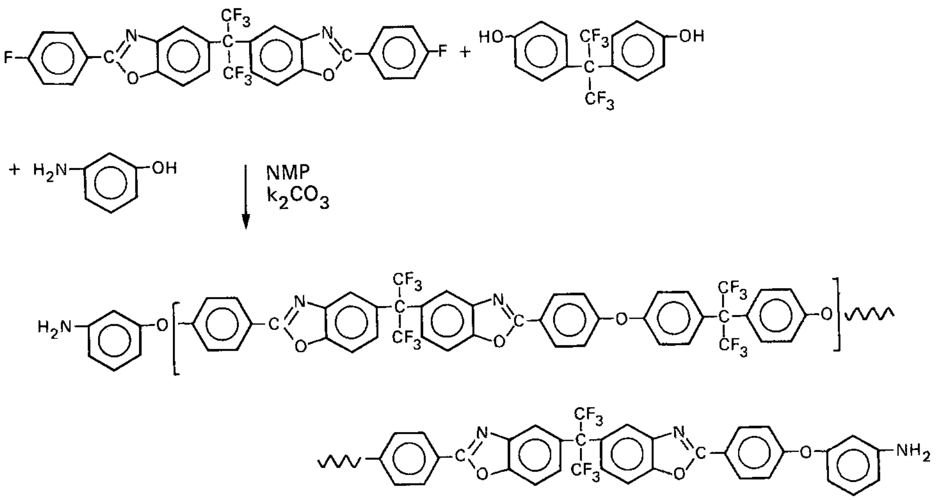
The amic ester-aryl ether benzoxazole copolymers were prepared by the co-reaction of the PBO oligomers with ODA and PMDA ethyl ester diacyl chloride in a NMP/cyclohexanone (70/30) solvent mixture in the presence of N-methylmorpholine according to literature procedures (5-9). The copolymers were isolated by precipitation in water and rinsed with chloroform to remove PBO homopolymer contamination.

Films for thermal and mechanical analysis were cast from a NMP/cyclohexanone (70/30) solvent mixture and heated to 350°C (5°C/min. heating rate) and held for 30 min. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a DuPont DSC 1090 instrument with a heating rate of 10°C/min. The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at 10 Hz and a heating rate of 10°C/min. in the tension mode. Isothermal and variable temperature (5°C heating rate) thermal gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer model TGA-7 in a nitrogen atmosphere. Mechanical property measurements were performed on a Instron tensile tester at a strain rate of 10 mm/min.

Results and Discussion

Generally, poly(aryl ethers) are synthesized by the nucleophilic displacement of an aryl halide with a phenoxide in aprotic dipolar solvents, where the aryl halide is activated by an electron withdrawing group, e.g., carbonyl or sulfone (10). We have recently demonstrated that an aryl fluoride para to a 2-benzoxazolyl group is readily displaced by phenoxides (3). In this case, the oxazole ring has the effect of an electron withdrawing group and can accept a negative charge through a Meisenheimer complex which stablizes the transition state during the transformation (3,10). High molecular weight poly(aryl ether benzoxazoles) were prepared by reacting various bisphenols with bis(fluorophenyl) substituted bibenzoxazoles in either NMP in the presence of K_2CO_3. This synthetic route was used to prepare oligomers from 6F-BFPB, Bis-AF and 3-aminophenol in NMP with K_2CO_3 as the base (Scheme 1). The Carother's equation was used to determine the quantity of aminophenol required to control both molecular weight and chain end functionality. This polymer structure was chosen since it is soluble in a number of solvents including NMP at room temperature and it should have a sufficient solubility parameter difference with polyimide to allow for microphase separated morphologies at modest block lengths.

Table 1 contains the the characteristics of the aryl ether benzoxazoles oligomers prepared. The number average molecular weights, determined by ^1H NMR, were 10,500 and 26,000 g/mol, somewhat higher than predicted. We attributed this to the loss of polymer from the low end of the molecular weight distribution during the methanol



precipitation affording a higher $\langle M_n \rangle$. Both the viscosity and and T_g of the oligomers increased with molecular weight (Table 1).

The imide-aryl ether benzoxazole copolymers were prepared via the poly(amic-ester) precurser route (Scheme 2). This intermediate route to polyimides allows for isolation and characterization of the prepolymer prior to imidization. Furthermore, the poly(amic-ester) route affords greater synthetic flexibility since it is soluble in a variety of solvents and more hydrolytically stable than the poly(amic-acid) analog. The synthesis involved the incremental addition of a methylene chloride solution of PMDA ethyl ester diacyl chloride to a solution (NMP/cyclohexanone 70/30) of the aryl ether benzoxazole oligomer and ODA in the presence of N-methylmorpholine. The solids content for the copolymerization was maintained at 12-13 solids content (w/v). The N-methylmorpholine was used as the acid acceptor and the N-methylmorpholinium hydrochloride salt precipitated from the reaction mixture. High molecular weight was readily achieved as judged by the dramatic increase in viscosity. The resulting poly(amic ester-aryl ether benzoxazoles) were isolated (water) and rinsed (chloroform) to remove PBO homopolymer contamination.

TABLE 1

Characteristics of Bis(amino) Aryl Ether Benzoxazole Oligomers

Sample Number	$\langle M_n \rangle$, g/mol Predicted	$\langle M_n \rangle$,g/mol Experimental	[n] 25°C NMP dl/g	T_g, °C
1	7,500	10,500	0.18	210
2	18,000	26,000	0.30	227

Table 2 contains the characteristics of the amic ester-aryl ether benzoxazole copolymers prepared. The PBO compositions were maintained in the 20 wt. % range so as to have a continuous polyimide matrix with a descrete PBO phase. The PBO compositions, determined by ^{1}H-NMR, in the resulting copolymers were comparable to that charged. The viscosity measurements were high and comparable to the high molecular weight poly(amic-ester) homopolymer (11).

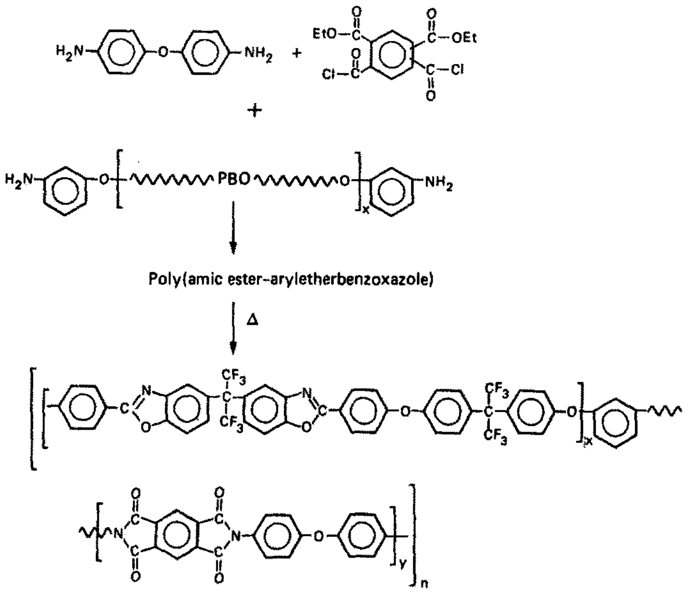


TABLE 2

Characteristics of Amic Ester - Aryl Ether Benzoxazole Copolymers

Sample Number	PBO Block Length, g/mol	PBO Incorporation		$[\eta]_{25}^{NMP^\circ C}$ dl/g
		Charged	Actual*	
3	10,500	25	21	0.50
4	26,000	18	13	0.32
5	Poly(amic ester) homopolymer	–	–	0.35'

*Determined by H-NMR

Solutions of the copolymers were cast and cured (350°C) to effect the imidization yielding clear, tough films. The thermal analysis for the imide-aryl ether benzoxazole copolymers (PI/PBO) prepared are shown in Table 3, together with a polyimide homopolymer control to facilitate comparison. No detectable T_g was observed for the polyimide homopolymer or for the block copolymers, irrespective of the block length used, giving no insight as to morphology achieved. The thermal stability, as determined by the polymer decomposition temperature (PDT) and isothermal weight loss upon aging at 400°C (N_2), for the copolymers and the parent polyimide are also shown in Table 3. The PDT for the copolymers is comparable to that of polyimide, however, the weight loss on isothemal aging is somewhat higher.

The dynamic mechanical behavior for the PI/PBO copolymers containing PBO-block lengths of 10,500 and 26,000 g/mol are shown in Figure 1. In each case, a two phase morphology is achieved as evidenced by the two transitions observed in the spectra. The copolymer containing the lower molecular weight PBO block length has a PBO transition significantly higher than the T_g of the PBO oligomer of molecular weight, 10,500 g/mol indicative of a phase mixed morphology. Conversely, the copolymer containing the 26,000 g/mol PBO block length has a PBO transition in the copolymer the same as that of the oligomer characteristic of a heterophase morphology with high phase purity. These effects are consistent with other glassy-glassy copolymers with similar multiblock microstructures (12,13).

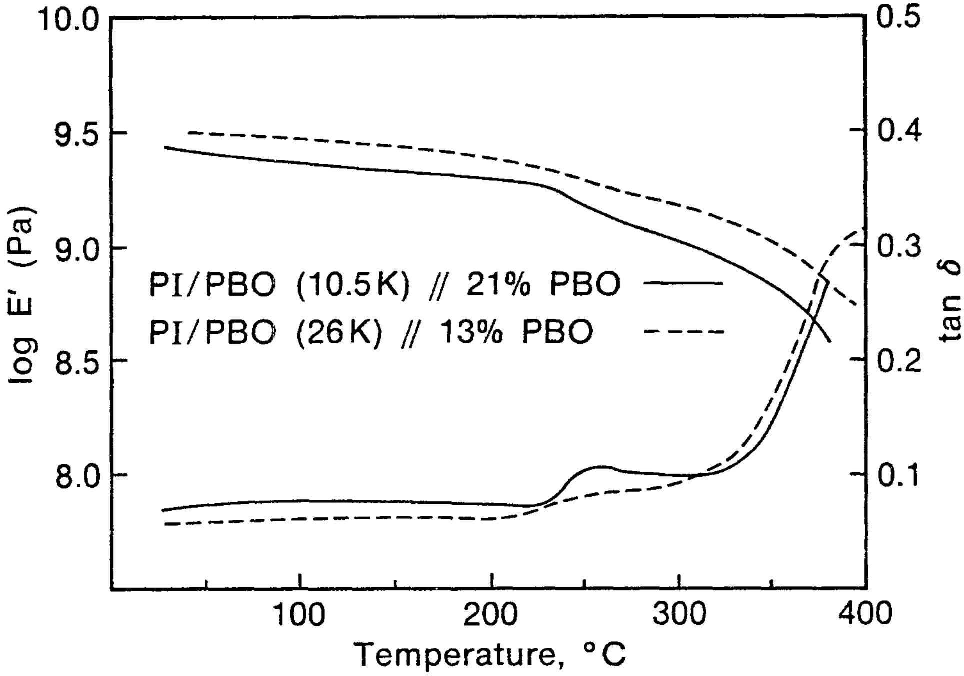


Figure 1. Dynamic mechanical behavior of PI/PBO block copolymers containing PBO block lengths of 10,500 and 26,000 g/mol.

TABLE 3

Characteristics of Imide - Aryl Ether Benzoxazole Copolymers

PBO Sample Number	PBO Block Length, g/mol	Composition wt.%	T_g, °C	Isothermal PDT, °C	wt. loss, 400°C
6	10,500	21	–	490	0.13
7	26,000	13	–	490	0.12
8	PMDA/ODA Polyimide homopolymer	–	–	480	0.04

The mechanical properties of the block copolymers together with the respective homopolymers are shown in Table 4. As expected, the incorporation of the glassy PBO coblock at these low compositions did not compromise the modulus of the polyimide. The tough, ductile mechanical properties associated with PBO were also reflected in the copolymers. The PI/PBO block copolymers showed elongations of 52 and 63 percent somewhat higher than the parent polyimide.

TABLE 4

Mechanical Properties of Imide-Aryl Ether Benzoxazole Block Copolymers

Sample Number	PBO Block Length, g/mol	PBO Composition, wt.%	Modulus, MPa	Tensile Strength, MPa	Elongation %
6	10,500	21	2100	110	63
7	26,000	13	2300	120	52
8	PMDA/ODA Polyimide	–	2000	110	40
9	PBO Homopolymer	–	1900	74	25

Conclusions

This preliminary communication describes our initial results in the synthesis of imide-aryl ether benzoxazole multiblock copolymers (14). These materials were prepared by the co-reaction of bis(amino) terminated PBO oligomers with ODA and PMDA ethyl ester diacyl chloride in a NMP/cyclohexanone solvent mixture in the presence of N-methylmorpholine. The resulting poly(amic esters) were isolated and rinsed to remove PBO homopolymer contamination. Films of the poly(amic-esters) were cast (NMP/cyclohexanone) and cured to effect the imidization affording clear, tough films. Multiphase morphologies and ductile mechanical properties were achieved irrespective of the PBO block lengths in the copolymer.

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