Synthesis of 4,4′-isopropylidene diphenol (bisphenol A) based polybenzoxazoles via an acid-catalysed solution cyclization process*

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Polybenzoxazoles were successfully prepared from bisaminophenols based upon 4,4′-isopropylidene diphenol (bisphenol A) and terephthaloyl chloride and optionally isophthaloyl chloride monomers. The successful 'one-pot' process involves a low-temperature polycondensation followed by an acid-catalysed solution cyclization reaction. The fully cyclized copolymers were isotropic in nature, displayed glass transition temperatures as high as 300°C, and formed tough films when prepared from *m*-cresol. Semicrystallinity could be developed in the 100% terephthaloyl chloride polybenzoxazole (PBO) system when annealed 40°C above its T_g. Characterization of the fully cyclized materials was demonstrated via the aid of spectroscopic and solution characterization techniques. The process is also amenable to higher-performance PBO systems.

(Keywords: polybenzoxazole; bisphenol A; synthesis; acid catalysis; solution process; semicrystalline polymer)

INTRODUCTION

Research in the area of high-performance polymeric matrix resins or adhesives has been an ongoing challenge and will continue to be until some ideal material is discovered that allows cost-effective synthesis, feasible processability and thermo-oxidative stability in hostile environments. Polyimides and poly(arylene ethers) are currently dominating the research effort and with good reason; their synthetic simplicity, chemical resistance, excellent thermomechanical properties and acceptable processability are all desirable traits. Although much less investigated, polybenzoxazoles (PBOs) are another polymeric system that should be considered as a high-performance matrix resin or adhesive. Over the past 20 years much research has been conducted with the aim of generating wholly aromatic polybenzoxazoles that could be spun into ultra-high-strength fibres, capable of being used in the area of conventional or molecular composites[1–4]. While these materials possess thermal and mechanical properties far superior to partially aromatic systems, they require further improvements in the area of processability and transverse strength. Recently, several research groups have increased the overall efforts in the search for processable polybenzoxazoles by incorporating flexible linkages that can withstand hostile environments and by refining the synthetic methods[5–11]. These efforts include fluorinated monomers, alternative catalyst systems and copolymers via preformed benzoxazole linkages.

Our research efforts are also along these lines, but emphasize the generation of soluble, fully cyclized PBOs that could be solution or preferably melt processed. Based on the fact that many of the engineering thermoplastics commercially available (polycarbonates, polysulphones, poly(arylene ethers), etc.) are based on the bisphenol A building block, we found it advantageous to begin our research efforts with this starting material. It was expected that many of the desirable characteristics attributed to the bis-A linkage (e.g. good solubility, toughness, thermo-oxidative stability and melt processability) could be extended to polybenzoxazole systems. In addition, the chemistry is equally applicable to higher-performance fluorinated or phosphine oxide monomers. Our preliminary results demonstrated that the PBO generated from the bis-*o*-aminophenol derivative of bis-A and terephthaloyl chloride exhibits a crystalline melting point around 380°C after thermal cyclization and annealing[12]. The resulting polymer is insoluble in all organic solvents. Although this is attractive in terms of achieving solvent resistance, it was also of interest to develop more soluble systems. It was hypothesized that the incorporation of some percentage of isophthaloyl linkages would decrease the crystallinity content, but generate soluble polybenzoxazoles. This paper will detail just such an effort and describe a new acid-catalysed solution cyclization reaction capable of generating polybenzoxazoles. Thermal, solution and crystalline properties of the resulting bis-A based copolymers will also be discussed.

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EXPERIMENTAL

Materials

Isophthaloyl chloride (IC) and terephthaloyl chloride (TC) were obtained from Aldrich and distilled prior to use. The solvents *N*-methylpyrrolidinone (NMP) and *o*-dichlorobenzene (DCB) were distilled from P_2O_5, tetrahydrofuran (THF) was distilled from Na/benzophenone, and pyridine was distilled from 5 Å molecular sieves. All of the solvents were stored under N_2 in sealed flasks.

2,2′-Bis(3-amino-4-hydroxyphenyl)propane. To 300 ml of cold, deoxygenated 0.70 M NaOH, 31.829 g (0.10 mol) of 2,2′-bis(3-nitro-4-hydroxyphenyl)propane[13] was added with stirring. Once the orange-red solution became homogeneous, it was transferred to a pressure reactor, treated with 0.15 g of 10% Pd/C, purged with H_2 and pressurized to 50 psi (~345 kPa). After 6 h at 35°C, the contents were filtered through Celite under N_2 and neutralized in cold, deoxygenated 0.22 M acetic acid. The off-white solid was collected via vacuum filtration, washed with water and dried under vacuum at 90°C for 20 h. Recrystallization from 50/50 THF/$CHCl_3$ resulted in a 50% yield of an off-white powder. M.p. = 248°C with decomposition (lit.[13] 251°C).

Polymerizations

The poly(hydroxy amide) (PHA) preparations were performed in a three-necked flask equipped with an overhead stirrer, N_2 inlet and a liquid addition funnel. 2,2′-Bis(3-amino-4-hydroxyphenyl)propane (bA-bAP) (0.01 mol, 2.5832 g) was washed into the flask with 10 ml of NMP and 1.345 g of pyridine. The solution was allowed to become homogeneous, cooled to 5–10°C and then treated dropwise with 2.0302 g (0.01 mol) of acid chlorides in 4.5 ml of THF. After addition, the funnel was washed with NMP until the solids concentration (w/v) was 15–18%. After 30 min, the temperature was raised to 25°C and maintained for 12 h. Conversion to the polybenzoxazole was achieved by adding 6.3 ml of *o*-dichlorobenzene (25% v/v) to the reaction mixture, replacing the addition funnel with a reverse Dean–Stark trap, condenser and drying tube, and ramping the temperature to 165–175°C. The cyclodehydration reaction was complete after 3 h as judged by *FT*i.r. Upon cooling, some of the polymers precipitated from the reaction mixture at approximately 90°C. The solutions were precipitated in methanol, filtered, washed with water and methanol, and finally dried in a vacuum oven at 180°C for 24 h and 220°C for 2 h. Yield: 95–99%. The resulting polymers were blonde in colour. Films cast from *m*-cresol were tough and transparent but brown in colour.

Measurements

Intrinsic viscosity measurements yielded relative molecular weights and were performed with Cannon–Ubbelohde viscometers in *m*-cresol and a bath temperature of 25°C. Solution ^{13}C and ^{1}H n.m.r. analysis was performed in deuterated dimethylsulphoxide (DMSO) or chloroform on a Varian 400 MHz spectrometer, while solid-state ^{13}C n.m.r. analysis was performed on a Bruker 300 MHz spectrometer. *FT*i.r. data were obtained on a Nicolet MX-1 *FT*i.r. spectrometer using thin films. A DuPont 912 (dual-head) differential scanning calorimeter (d.s.c.) was used to determine the glass transition temperatures (T_g), taken as the midpoint of the change in slope of the baseline. Reported values were obtained from the second scan after heating and annealing at 20–50°C above the T_g for 2 h and at a heating rate of 10°C min^{-1}. Five per cent weight losses were determined on a DuPont 951 thermogravimetric analyser at a heating rate of 10°C min^{-1} in air. T.g.a.-m.s. data were obtained on a Perkin–Elmer TGS-2 thermogravimetric analyser equipped with a Hewlett–Packard 5971A mass selective detector. The carrier gas was helium, the heating rate was 40°C min^{-1} and the mass selective detector was configured to scan the 15–300 *m/z* region, completing 0.7 scans per second.

RESULTS AND DISCUSSION

Initial studies carried out in our laboratories and work by others[14] indicated that acid-catalysed solution cyclodehydration of bA-bAP-TC poly(hydroxy amide) was of little value owing to the premature precipitation of the partially cyclized polybenzoxazoles. It is believed that premature precipitation of the polymer is related to the formation of crystallinity during cyclization. Efforts to maintain solubility by controlling the molecular weight of the polymer to $\langle M_n \rangle = 10\,000\ g\ mol^{-1}$ also resulted in premature precipitation, indicating that high molecular weight was not the cause of premature precipitation. Alternatively, cyclodehydration by thermal methods resulted in PBOs that exhibited a sharp exotherm at 380°C after annealing for 2 h at 350°C (*Figure 1*). Therefore, examination of the effect that positional isomers would have on the crystallinity and solubility of bA-bAP based polybenzoxazoles was conducted using acid-catalysed solution cyclization techniques.

The reaction pathway used to generate the precursor poly(hydroxy amides) and polybenzoxazoles is outlined in *Scheme 1*. The reaction takes advantage of the 'one-pot' synthesis concept by utilizing the pyridine hydrochloride generated in the first step as a reagent for the second step. Degradation of pyridine hydrochloride liberates HCl, which acts as a catalyst for the cyclization reaction. Azeotropic distillation is employed during the second step to minimize hydrolysis and aid in the removal of pyridine and HCl from the system. All the polybenzoxazoles, except bA-bAP-TC, stayed in solution during the cyclization reaction, giving credence to

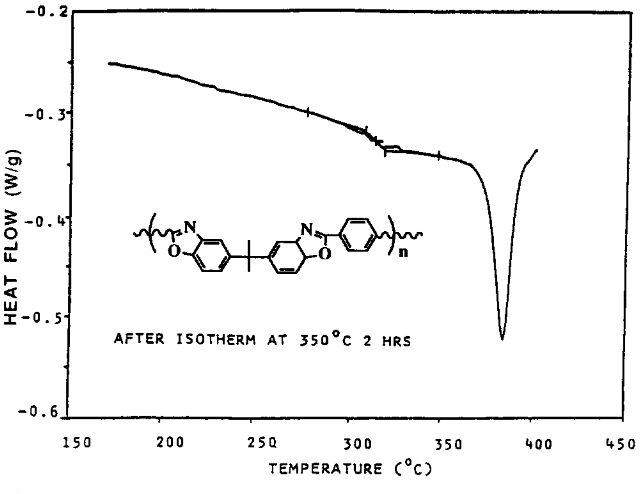
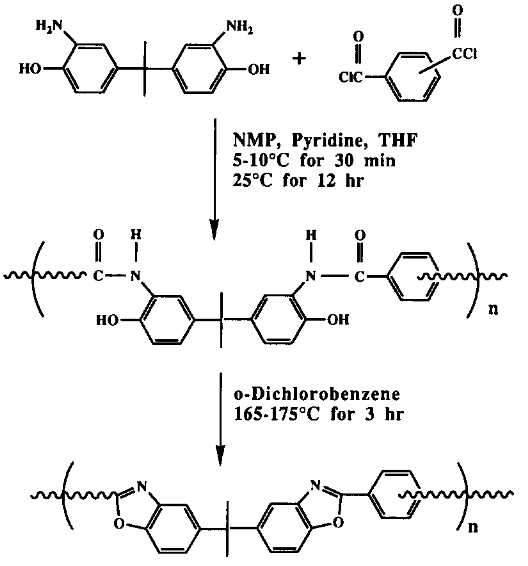


Figure 1 D.s.c. thermogram of a semicrystalline bA-bAP-TC PBO



Scheme 1 Polybenzoxazole reaction scheme

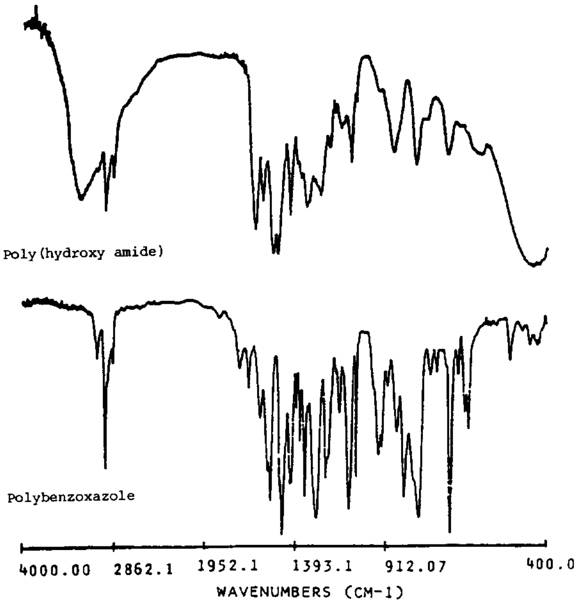


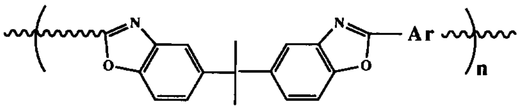
Figure 2 Infra-red spectra of poly(hydroxy amide) (upper) and polybenzoxazole (lower)

the concept that premature precipitation was due to the development of a semicrystalline morphology. Verification of ring closure was investigated by *FT*i.r., ^{1}H n.m.r. and ^{13}C n.m.r. spectroscopy, as well as t.g.a.-m.s. Infra-red spectroscopy showed a complete disappearance of the amide and hydroxy stretches (3000–3300 cm^{-1}) and the carbonyl stretch (1650 cm^{-1}) (upper spectrum), along with the appearance of a characteristic oxazole stretch and vibration at 1620 and 1060 cm^{-1} (lower spectrum) (*Figure 2*). Investigation of ring closure by t.g.a.-m.s. showed no detectable water loss for any of the polymers until decomposition occurred around 420°C. Decarboxylation was noticed, however, around 350°C. Solid-state ^{13}C n.m.r. spectroscopic analysis gave inconclusive results owing to the broad character of the ^{13}C resonances, and solution ^{1}H n.m.r. studies were impossible owing to the insolubility of the polybenzoxazoles in common deuterated solvents.

Solution and thermal properties of the PHAs and PBOs were monitored by intrinsic-viscosity measurements and differential scanning calorimetry (d.s.c.). Results of these experiments (*Table 1*) indicate that positional isomers have a much larger effect on the PBO solution properties relative to those of the PHAs. Intrinsic viscosities of the PHAs remained relatively constant with the incorporation of isophthaloyl linkages, while the PBOs showed a marked decrease in intrinsic viscosity in going from 100% *para*-linked to 60/40 *para*/*meta* catenation. These decreases would be expected as the number of conformational constraints is removed from the 100% *para*-linked system. One would also expect a steady decrease in glass transition temperature as the content of *meta* links is increased; as *Table 1* indicates, this trend is observed. Thermal stabilities, as measured by dynamic t.g.a. in air, were as expected and resulted in 5% weight losses around 490°C. No obvious trends in thermal stability were observed relative to positional isomer content.

Crystallinity and solubility were the major concerns of this work, and we noted a total loss of crystallinity in going from 100% terephthaloyl chloride to an 80/20 TC/IC mixture. Crystallinity was detected by d.s.c. only after an annealing period of 2 h. Optical microscopy showed no anomalies in any of the copolymer systems investigated, even after annealing above their respective T_g for 2 h. Solubility of the resulting mixed monomer systems was changed significantly relative to the 100% TC system (*Table 2*). While the highly *para*-linked

Table 1 Solution, thermal and crystalline properties of isomeric poly(hydroxy amides) and polybenzoxazoles



Ar composition		$[\eta]_{PHA}$[a]	$[\eta]_{PBO}$[b]	T_g	5% weight loss	
TC	IC	(dl g^{-1})	(dl g^{-1})	(°C)	T(°C)	Cryst.[c]
100	0	0.67	–	313	492	Yes
80	20	0.63	1.16	307	489	No
60	40	0.61	0.81	296	489	No
50	50	0.49[d]	0.73	287	477	No
40	60	0.67	0.72	283	493	No
20	80	0.71	0.73	278	498	No
0	100	0.34[e]	0.57	267	486	No

[a] *IV* of PHA measured in NMP at 25°C
[b] *IV* of PBO measured in *m*-cresol at 25°C
[c] Crystallinity as determined by d.s.c.
[d] *MW* controlled to 20 000
[e] Precipitated PHA at 150°C

Table 2 Solubility[a] of isomeric polybenzoxazoles in various solvents

Ar composition		Solvent					
TC	IC	DMAc	DCB	NMP	THF	*m*-Cresol	$CHCl_3$
100	0	I	I	I	I	S	I
80	20	I	I	I	I	S	I
60	40	I	SS	I	I	S	I
40	60	I	Sc	Sc	I	S	SS
20	80	I	SS	Sc	I	S	SS
0	100	I	SS	Sc	I	S	I

[a] I, insoluble; S, soluble; SS, slightly soluble; c, clouded on cooling

systems displayed absolutely no solubility in any of the solvents tested, the highly *meta*-catenated systems showed various degrees of solubility in *N*-methylpyrrolidinone (NMP), *o*-dichlorobenzene (DCB) and even chloroform. This increase in solubility can be attributed to the above-mentioned increase in the number of positional conformations available to the copolymers with an increase in *meta* catenations along the polymer backbone. It must be pointed out, however, that solubility (3–5% solids) was only achieved in boiling solvents and precipitation occurred upon cooling in every case except for *m*-cresol. All the solution-cyclized PBO systems were soluble in warm *m*-cresol, while the thermally cyclized bA-bAP-TC PBO was insoluble in hot *m*-cresol. It is interesting to note that all the solution-cyclized copolymers remained soluble in a 20/80 DCB/NMP solution (15% solids) during the reaction, but once precipitated and dried, their solubility is greatly decreased. The ability of the solvent mixture to solubilize the polybenzoxazoles during cyclization is attributed to the acidic nature of the reaction medium. It is believed that the HCl liberated during the degradation of pyridine hydrochloride protonates some of the oxazole rings and enhances the solubility. Upon precipitation and isolation, the protonated species are eliminated and therefore their solubility is decreased.

CONCLUSION

Synthesis of fully cyclized, high-molecular-weight polybenzoxazoles via an acid-catalysed azeotropic solution cyclization has resulted in a series of polymers containing the bis-A linkage. Crystallinity was not observed in any of the systems in question except for the 100% *para*-linked system. Nevertheless, excellent solvent resistance was observed for all solvents tested with the exception of *m*-cresol. Solubility was enhanced for the polymers with moderate to high isophthaloyl chloride incorporation, but this was only achieved at high temperatures, and precipitation occurred immediately upon cooling. Thermal properties were in the range expected and glass transition temperatures followed the anticipated trends. The techniques reported herein are also being applied to higher-performance PBO systems, and these results will be reported later.

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