

Processable precursors: 4. Synthesis and characterization of processable precursors to poly(phenylene bisbenzoxazoles)

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Processable precursor polymers to poly(phenylene bisbenzoxazole)s (PBOs) have been prepared and studied. The precursor polymers were synthesized by the polycondensation of 1,4-bicyclo[2.2.2]octyl-2,5-diethanoate dicarboxylic acid or 1,4-bicyclo[2.2.2]octyl-2,5-diol dicarboxylic acid with 3,3'-dihydroxy-4,4'-diaminobiphenyl or 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane in poly(phosphoric acid). The precursor polymers were characterized by solubility, viscosity, spectroscopy (infra-red, ^1H and ^{13}C nuclear magnetic resonance) and thermal analysis such as differential scanning calorimetry, thermogravimetric analysis and optical polarizing microscopy. Conversion of the more stable PBOs is achieved by pyrolysis in air or under argon atmosphere. © 1997 Elsevier Science Ltd.

(Keywords: poly(phenylene bisbenzoxazoles); precursor polymers; bicyclo[2.2.2]octane)

INTRODUCTION

High performance aromatic heterocyclic liquid crystalline polymers were initially synthesized at the Air Force Material Laboratory at Wright Patterson. Significant among these polymers are poly(*p*-phenylene-2,6-bisbenzoxazole)s (PBOs)^{1,2}. High molecular weight PBOs are usually prepared directly by the high temperature polycondensation of monomers such as 4,6-diaminoresorcinol dihydrochloride and terephthaloyl chloride in poly(phosphoric acid).

Poly(bisbenzoxazoles) belong to the class of rigid-rod aromatic heterocyclic polymers which exhibit a high degree of orientation, high resistance to solvents, high glass transition temperature, high modulus, high strength, high thermal and thermooxidative stability and low densities. *para*-Catenated poly(bisbenzoxazoles) are as tough as Kevlar[®], but with higher modulus and better thermal stability. On a specific basis, PBOs are stronger and higher in modulus than glass, steel and aluminium and are not as brittle as carbon fibres³.

Despite their highly desirable properties, PBOs, particularly the *para*-catenated polymers are essentially non-melting and exhibit poor solubility. The low solubilities of these polymers in organic and inorganic solvents and their high melting transitions are due essentially to the rigidity of the aromatic ring systems, which results in large van der Waals forces between individual polymer molecular chains. The polymers are soluble in strong acids, such as sulfuric acid and methanesulfonic acid (MSA), and insoluble in less corrosive organic solvents. Thus, suitable low cost fabrication techniques for PBOs are lacking^{4,5}. In order

to process these polymers into fibres and films, it is necessary that they be in solution or molten state.

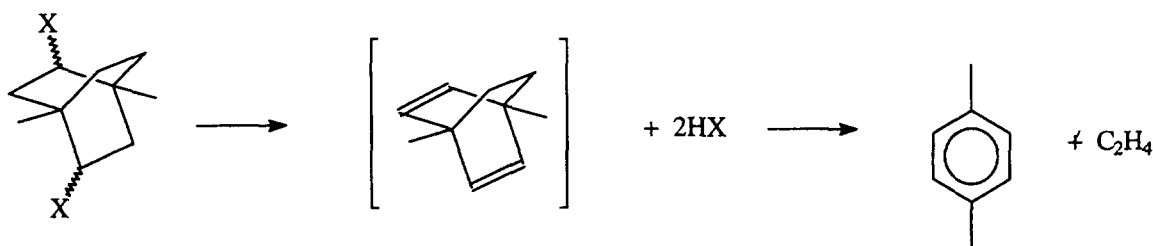
Intense synthetic efforts have been devoted to the development of more easily melt processed and more soluble liquid crystalline poly(bisbenzoxazoles) which would nevertheless retain the remarkable properties associated with these polymers⁶⁻⁸. This could be achieved through the following approaches often used in combination: random copolymerization, introduction of kinks or bends into the chain, asymmetric substitution and inclusion of randomly spaced flexible chain fragments. However, in these cases the new 'derivatized' polymer represents a compromise, which although can now be processable, has lower thermal and chemical stability.

These approaches, although meritorious, are also to some extent self-defeating, since two of the advantages of liquid crystalline polymers are the high heat performance and the solvent resistance. One approach that has been tried on a limited basis is to prepare liquid crystalline precursors which are more processable and which can be transformed to the desired high temperature liquid crystalline polymer after it has been processed into the desired shape⁹⁻¹¹. This concept, which has gained wide acceptability in the preparation of preceramic polymers, has not been widely explored for the preparation of intractable organic polymers. Preparation of prepolyphenylene polymers is one of the few examples in the literature¹².

The utilization of the benzene ring to form thermotropic and lyotropic liquid crystals is well established¹³⁻¹⁶. The linearity, similarity in geometry¹⁷ and polarizability¹⁸ of *para*-substituted benzene (width = 5.0 Å)* and disubstituted bicyclo[2.2.2]octane (width = 4.9 Å)* leads to

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* Molecular width measured with Courtauld atomic models



Scheme 1 Conversion of bicyclo[2.2.2]octyl system into aromatic moiety

the expectation of liquid crystalline properties for polymers which contain the 1,4-disubstituted bicyclo[2.2.2]-octane ring system^{19–21}.

We have prepared random copolyesters which form birefringent fluid states in the melt from *trans*-1,4-cyclohexanediol or hydroquinone with bicyclo[2.2.2]-octane-1,4-dicarbonyl chloride and sebacoyl chloride²². Furthermore, we have demonstrated the formation of thermotropic birefringent fluids in homopolyesters containing the bicyclo[2.2.2]octyl and bicyclo[2.2.2]oct-2-ene ring systems^{23,24}. In 1987, Dotrong *et al.* prepared soluble, colourless and lyotropic poly(phenylene benzobisthiazole)s based on the unsubstituted bicyclo[2.2.2]octyl ring system²⁵.

Herein, we report on the preparation of processable polymeric precursors to PBOs, which can subsequently be converted into the more stable PBOs. This can be accomplished by making polymers from a diacid which is a precursor to terephthalic acid, but which can be more readily processed (*Scheme 1*). We utilized the fact that replacement of the phenyl ring in a polymer system by a 2,5-substituted bicyclo[2.2.2]octyl moiety yields a more soluble and lower melting polymer without destroying the liquid crystalline properties. Furthermore, pyrolysis of the precursor polymer should result in aromatization of the 1,4-bicyclo[2.2.2]octyl ring system. For example, we demonstrated that 2,5-disubstituted-1,4-bicyclo[2.2.2]-octyl-containing polyamides exhibited lyotropic behaviour in *N*-methylpyrrolidone (NMP) and could be converted into the more stable aramids by pyrolysis in the presence of Lewis acids²⁶.

EXPERIMENTAL

Materials

The monomers 3,3'-dihydroxy-4,4'-aminobiphenyl and 2,2'-bis(3-aminohydroxyphenyl)hexafluoropropane were commercial products and were purified by recrystallization from methanol. 1,4-Bicyclo[2.2.2]octane-2,5-diol dicarboxylic acid and 1,4-bicyclo[2.2.2]octyl-2,5-diethanoate dicarboxylic acid were prepared as outlined below. Solvents were freshly distilled and stored over molecular sieves. All monomers were dried and their melting points, Fourier transform infra-red (*FT i.r.*), ¹H nuclear magnetic resonance (n.m.r.) and mass spectra were recorded.

Measurements

Infra-red spectra were obtained on KBr discs with the Nicolet Omnicon *FT i.r.* spectrometer, and ¹H and ¹³C n.m.r. spectra were obtained in deuterated dimethylformamide (DMF), acetone, dimethylsulfoxide (DMSO) or methanol with a Bruker WM-250 spectrometer and in the solid state with a Bruker L200 spectrometer equipped with an Aspect 3000 computer in the Fourier transform

mode. Proton and ¹³C n.m.r. spectra were referred to tetramethylsilane at 0.0 ppm internally and externally, respectively. Simulated ¹³C chemical shift assignments were obtained using the SoftShell[®] ¹³C module 1.1. Elemental analysis data were provided by Atlantic Microlab, Atlanta, GA, and Galbraith Laboratories, Knoxville, TN, USA.

Thermogravimetric analysis (t.g.a.) data were determined under nitrogen atmosphere and in air with the Seiko Scientific Instruments (SSI) TG/DTA220 thermogravimetric analyser. Opened platinum pans as reference and sample holders with heating rates of 10°C min⁻¹ were used. Differential scanning calorimetry (d.s.c.) curves were obtained on the SSI DSC 220 differential scanning calorimeter. Transitions were taken as peak minima (endotherm) and peak maxima (exotherm). D.s.c. curves were recorded using sealed aluminium sample pans and sealed aluminium reference pans with heating rates of 5°C min⁻¹. Visual observations of thermal transitions under cross-polarized light were made using the Laborlux Pol 12 polarizing optical microscope equipped with a heating stage. Melting points of the monomers and intermediates were determined using the Melt-temp capillary melting point apparatus.

Inherent viscosities were measured at 30°C with a calibrated Cannon–Fenske viscometer at concentrations of 0.5 g dl⁻¹ of precursor polymer in NMP or MSA. Solubilities were determined at room temperature.

Monomer syntheses

1,4-Bicyclo[2.2.2]octane-2,5-diol dicarboxylic acid (III). Compound **III** was prepared by the method reported by Humber *et al.* with minor modifications²⁷. Diethylcyclohexane-1,4-dione-2,5-dicarboxylate (110 g, 0.429 mol) and a 60% dispersion of sodium hydride in mineral oil (56 g, 2.33 mol) were added, alternately, in 10-g portions, to ethylene glycol dimethyl ether (400 ml) in a thoroughly dried 1-l three-necked round bottom flask equipped with a mechanical stirrer, thermometer and two reflux condensers over 20 min, with stirring continuously to yield the disodium salt as a pink suspension. After spontaneous reflux subsided, the mixture was heated under reflux with stirring for an additional 1 h. Ethylene glycol dimethyl ether (*ca* 200 ml) was removed from the mixture by vacuum distillation. 1,2-Dibromoethane (300 ml) was added to the mixture. The reaction mixture was refluxed with stirring until the pink suspension had disappeared and a cream suspension was observed (*ca* 24 h). The mixture was filtered while still hot and the salts washed three times with chloroform (3 × 25 ml). Dry hexane (500 ml) was added to the filtrate to produce ethyl-1,4-bicyclo[2.2.2]octane dione-2,5-dicarboxylate (**I**) (87 g, 81.5% yield), m.p.

107–109°C (lit.²⁸ 109–110°C). Infra-red spectrum (KBr) 1736 s (C=O, ester), 1722 cm⁻¹ s (C=O, ketone). Proton n.m.r. spectrum (methanol-*d*₄): δ 1.4 (CH₃), 2.2 (CH₂, bridge), 2.4 (CH₂, ring), 3.0 ppm (OCH₂). Mass spectrum (70 eV) *m/z* 282 [M]⁺; 236 (base peak), 209 (*m*-73, loss of O=COC₂H₅), 136 (*m*-146 loss of two O=COC₂H₅). Anal. calcd for C₁₄H₁₈O₆: C, 58.57; H, 6.38. Found: C, 58.33; H, 6.37.

To a stirred solution of **I** (12 g, 0.046 mol) and glacial acetic acid (50 ml) was added 48% hydrobromic acid (28 ml) and the mixture was refluxed for 24 h. The mixture was filtered to give 1,4-bicyclo[2.2.2]octane-2,5-dione dicarboxylic acid (**II**) (7.85 g, 81.6% yield). Infra-red spectrum (KBr) 1715 s (C=O, acid); 1702 cm⁻¹ s (C=O, ketone). Proton n.m.r. spectrum (methanol-*d*₄): δ 2.2 (CH₂, bridge), 2.4 ppm (CH₂, ring); the chemical shift of the acid proton is off scan. Carbon-13 n.m.r. ((CD₃)₂SO): δ 19.2 (CH₂, bridge), 29.0 (CH₂, ring), 62.1 (C, quart.), 210.5 (C=O, ketone), 175.5 ppm (C=O, acid). Anal. calcd for C₁₀H₁₀O₆: C, 53.10; H, 4.42. Found: C, 53.11; H, 4.51.

Compound **III** was formed by the reduction of **II**. A stirred mixture of **II** (10.0 g, 0.044 mol) and methanol (100 ml) was cooled in an ice-water bath. Sodium borohydride (6.0 g, 0.158 mol) was added in small portions to the mixture at 0°C and maintained at 0°C with stirring for 5 h. The mixture was acidified with cold dilute 1/1 hydrochloric acid, to a pH of 2–3. The mixture was filtered and the filtrate was concentrated *in vacuo* to dryness. Acetone (100 ml) was added to the solids, filtered and concentrated *in vacuo* to dryness to give **III** (6.70 g, 65.9% yield). Infra-red spectrum (KBr) 1703 s (C=O, acid), 3400 cm⁻¹ b (OH). Proton n.m.r. (methanol-*d*₄): δ 2.0 (CH₂, bridge), 2.4 (CH₂, ring), 3.8 ppm (OH, alcohol). Carbon-13 n.m.r. [(CD₃)₂SO]: δ 24.3 (CH₂, bridge), 31.3 (CH₂, ring), 37.6 (C, quart.), 73.3 (CH), 182.3 ppm (C=O acid). Anal. calcd for C₁₀H₁₄O₆: C, 52.20; H, 6.10. Found: C, 52.08; H, 6.51.

1,4-Bicyclo[2.2.2]octyl-2,5-diethanoate dicarboxylic acid (**IV**). Compound **IV** was prepared by esterification of **III**. Compound **III** (2.0 g, 0.0086 mol), acetic anhydride (5 ml) and a catalytic amount of sulfuric acid were placed into a thoroughly dried 100-ml single-necked round bottom flask, and the reaction mixture was warmed in a water bath with constant swirling for 15 min. The mixture was allowed to cool to room temperature, and anhydrous ether (10 ml) was added to the mixture. The mixture was allowed to stand for *ca* 24 h and filtered to produce **IV** (1.48 g, 54.2% yield). Infra-red spectrum (KBr) 1821 s (C=O, ester), 1749 s (C=O, acid), 2973 cm⁻¹ (CH). Proton n.m.r. (methanol-*d*₄): δ 1.8 (CH₃, ester), 2.1 (CH₂, bridge), 2.4 ppm (CH₂, ring). Carbon-13 n.m.r. [(CD₃)₂SO]: δ 24.8 (CH₃), 25.8 (CH₂, bridge), 31.3 (CH₂, ring), 41.5 (C, quart.), 75.4 (CH), 174.6 (C=O, ester), 180.1 ppm (C=O, acid). Mass spectrum (70 eV) *m/z* 314 [M]⁺; 181 (base peak), 156 (*m*-158, loss of two OCOCH₃), 224 (*m*-90, loss of two COOH), 280 (*m*-34, loss of two OH). Anal. calcd for C₁₄H₁₈O₈: C, 53.50; H, 5.73. Found: C, 53.48; H, 5.73.

Polymer syntheses

Poly[(biphenyl[3,4-d:3',4'-d']bisoxazole-2,6-diyl)]-2,5-dihydroxyl-1,4-bicyclo[2.2.2]octylene (**V**). A thoroughly dried 100-ml three-necked round bottom flask

equipped with a mechanical stirrer, a nitrogen inlet tube, a reflux condenser with calcium chloride drying tube and a thermometer was flame dried and simultaneously flushed with nitrogen. The flask was allowed to cool to room temperature and charged with 3,3'-dihydroxy-4,4'-diaminobiphenyl (0.50 g, 0.00428 mol) and poly(phosphoric acid) (50 g). The mixture was maintained at room temperature under a stream of nitrogen for 24 h and at 60–70°C for 34 h; a yellow-green solution formed. The mixture was stirred rapidly at 110°C for 15 min and charged with **III** (0.47 g, 0.00472 mol). The temperature was raised to 110–165°C for 5 h and finally to 180–200°C for 24 h. The mixture was precipitated in water and the solids collected by filtration. The solids were extracted several times with water using a Soxhlet extractor until the extract was pH neutral. The solid was dried in a vacuum oven at 120°C for 36 h, 0.810 g of polymer being obtained (conversion 99.6%). Infra-red spectrum (KBr) 3600–3400 br (OH), 1500–1471 w (C=N), 3100–3000 w (Ar-H), 2800–2900 w (CH₂, CH), 1610 s (Ar C=C), 1247 cm⁻¹ s (C-O-C). Anal. calcd for C₂₂H₁₈N₂O₄: C, 70.58; H, 4.85; N, 7.48. Found: C, 68.85; H, 4.62; N, 7.03.

Poly[(biphenyl[3,4-d:3',4'-d']bisoxazole-2,6-diyl)]-2,5-diethanoate-1,4-bicyclo[2.2.2]octylene (**VI**). 3,3'-Dihydroxy-4,4'-diaminobiphenyl (0.50 g, 0.00229 mol) and 1,4-bicyclo[2.2.2]octyl-2,5-diethanoate dicarboxylic acid, (0.720 g, 0.00229 mol) in poly(phosphoric acid) (50 g) were reacted according to the procedure for **V** above. The solid was dried in a vacuum oven at 120°C for 36 h, 1.03 g of the polymer being obtained (conversion 98.3%). Infra-red spectrum (KBr) 1654 m (C=O), 1500–1471 w (C=N), 3100–3000 w (Ar-H), 2800–2900 w (CH₂, CH), 1610 s (Ar C=C), 1247 cm⁻¹ s (C-O-C). Anal. calcd for C₂₄H₂₁N₂O₆: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.15; H, 4.30; N, 5.95.

Poly[(2,2'-dibenzohexafluoropropyl-[3,4-d:3',4'-d']bisoxazole-2,6-diyl)]-2,5-dihydroxyl-1,4-bicyclo[2.2.2]octylene (**VII**). 2,2'-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (0.79 g, 0.00217 mol) and **III** (0.50 g, 0.00217 mol) in poly(phosphoric acid) (50 g) were reacted according to the procedure for **V** above. The solid was dried in a vacuum oven at 120°C for 36 h, 1.07 g of the polymer being obtained (conversion 98.7%). Infra-red spectrum (KBr) 3500 s (OH), 1500–1471 s (C=N), 3100–3000 w (Ar-H), 2800–2900 w (CH₂, CH), 1610 s (Ar C=C), 1247 cm⁻¹ s (C-O-C). Anal. calcd for C₂₅H₁₈F₆N₂O₄: C, 57.26; H, 3.43; F, 21.74; N, 5.34. Found: C, 58.80; H, 3.38; F, 20.81; N, 5.03.

Poly[(2,2'-dibenzohexafluoropropyl-[3,4-d:3',4'-d']bisoxazole-2,6-diyl)]-2,5-diethanoate-1,4-bicyclo[2.2.2]octylene (**VIII**). 2,2'-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (0.50 g, 0.00198 mol) and **IV** (0.623 g, 0.00198 mol) in poly(phosphoric acid) (50 g) were reacted according to the procedure for **V** above. The solid was dried in a vacuum oven at 120°C for 36 h, 0.97 g of the polymer being obtained (conversion 99.1%). Infra-red spectrum (KBr) 1658 m (C=O), 1500–1471 s (C=N), 3100–3000 w (Ar-H), 2800–2900 w (CH₂, CH), 1610 s (Ar C=C), 1247 cm⁻¹ s (C-O-C). Anal. calcd for C₂₇H₂₁F₆N₂O₆: C, 57.24; H, 3.64; F, 18.73; N, 4.60. Found: C, 58.29; H, 3.68; F, 17.97; N, 3.95.

RESULTS AND DISCUSSION

Preparation of polymers

The isomers of **III** and **IV** were not separated because isomeric mixtures of the precursor polymers to be prepared would result in a decrease in the melting transitions. The synthetic route leading to the processable precursor polymers, **V**, **VII** and **VIII**, is presented in *Scheme 2*.

The syntheses of the precursor polymers were designed to liberate water as the by-product. The percentage conversions of the polymers were based on the total weight of the monomers used. The precursor polymers were prepared by the high temperature polycondensation of the monomers in poly(phosphoric acid). Poly(phosphoric acid) was used as a reaction medium and a condensing agent. The precursor polymers were heated stepwise: initially to form polymer linkages with loss of water and at higher temperatures (*ca* 185–200°C) to cause cyclization with the further elimination of water. Spectroscopic evidence did not show the hydrolysis of the hydroxyl functionalities on polymers **V** and **VII** to generate unsaturation while being prepared in poly(phosphoric acid).

Structural characterization

The ¹³C n.m.r. chemical shift assignments of the precursor polymers are summarized in *Tables 1* and *2*.

Thermal characterization

The d.s.c. and optical polarizing microscopy data for

the precursor polymers are summarized in *Table 3*. Glass transition temperatures (T_g) were not observed. The solid to liquid crystalline transition temperatures obtained by optical polarizing microscopy were induced by shearing the polymers between the glass plate and cover slide. The birefringent fluids observed under cross-polarized light exhibited schlieren texture typical of nematic liquid crystals.

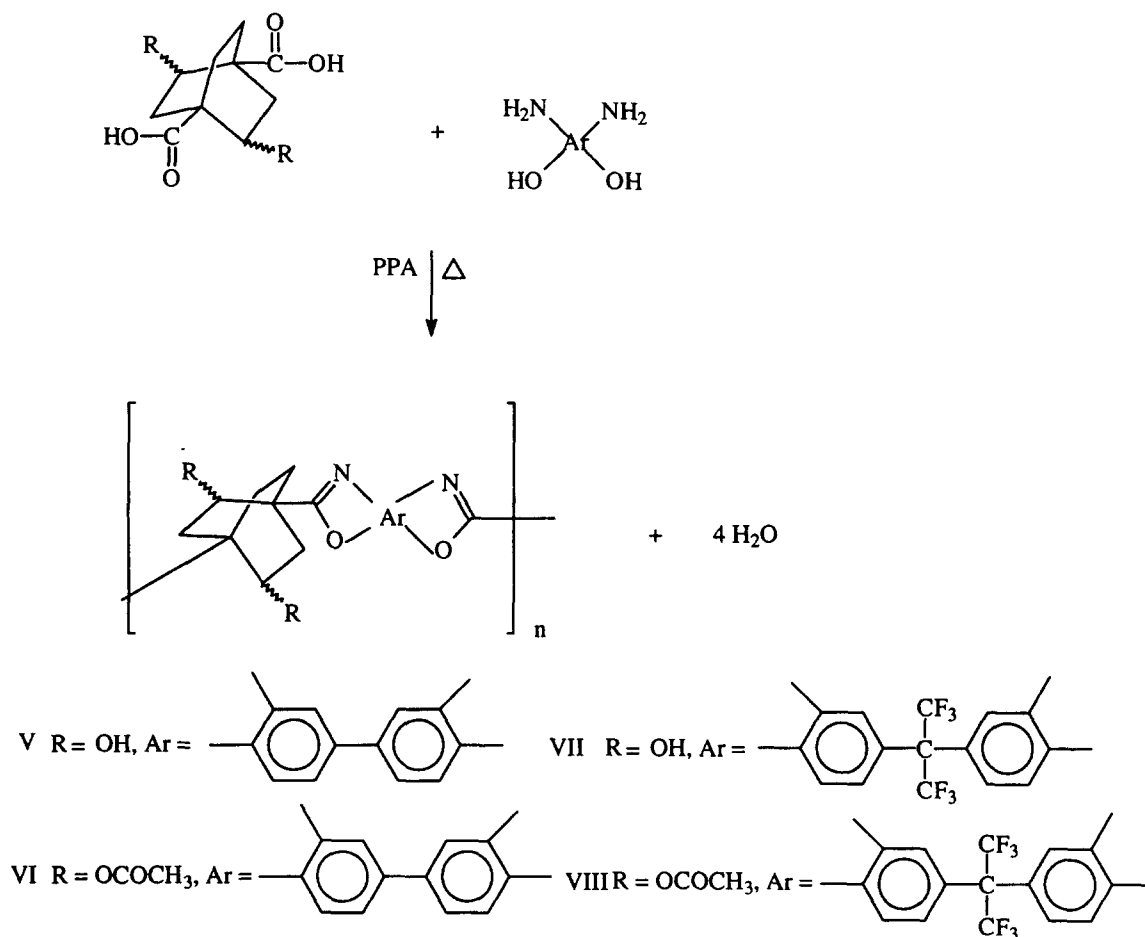
The t.g.a. curves of the precursor polymers under argon atmosphere and in air are presented in *Figures 1* and *2*, respectively. The precursor polymers containing the acetyl (OCOCH₃) groups tend to decompose at lower temperatures than the hydroxyl (OH) containing analogues. This is attributed to the good leaving ability of the acetyl groups. The decomposition temperatures are summarized in *Table 3*.

Solubility properties

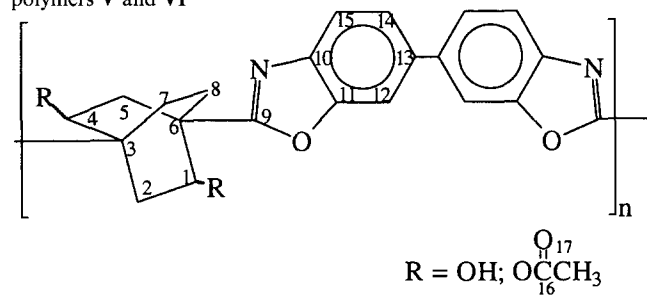
The solubility properties and inherent viscosity measurements of the precursor polymers and heat treated polymers are presented in *Table 4*. The solubility data obtained at room temperature show that precursor polymers containing hydroxyl substituents (**V** and **VII**) are generally soluble in NMP and dimethylacetamide (DMAc). Precursor polymers containing acetyl substituents (**VI** and **VIII**) are partially soluble in NMP, DMSO, tetramethylurea (TMU) and dimethylacetamide. The heat treated polymers and the precursor polymers are soluble in sulfuric acid and MSA.

Aromatization

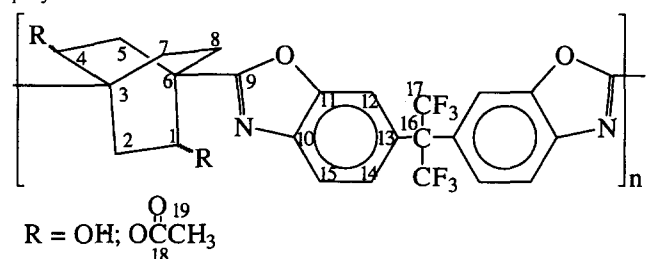
Table 5 shows the theoretical weight losses and the



Scheme 2 Synthetic route to precursor polymers

Table 1 ^{13}C n.m.r. chemical shift assignments (ppm) for precursor polymers V and VI

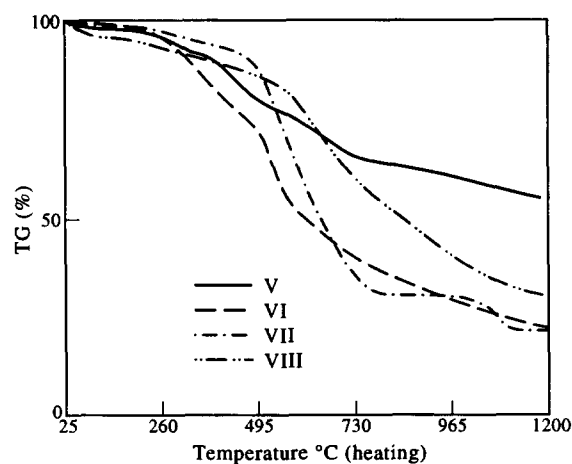
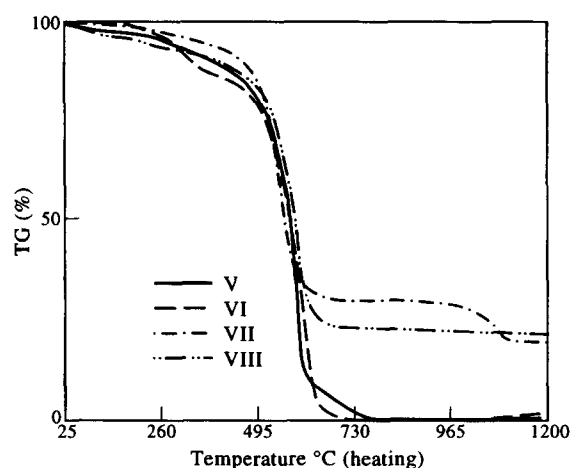
Carbon number	Simulated	Experimental	
		V	VI
1, 4	69.1	67.8	70.0
2, 5	31.0	30.2	34.5
3, 6	21.0	20.5	20.1
7, 8	23.6	25.1	25.5
9	152.6	150.9	150.3
10	138.6	140.3	139.4
11	149.9	148.1	146.1
12, 14, 15	126.1	128.2	125.6
13	132.6	130.0	132.9
16	171.0	—	170.9
17	17.6	—	19.6

Table 2 ^{13}C n.m.r. chemical shift assignments (ppm) for precursor polymers VII and VIII

Carbon number	Simulated	Experimental	
		VII	VIII
1, 4	69.6	68.0	65.1
2, 5	30.9	31.6	32.1
3, 6	19.9	18.2	19.9
7, 8	23.6	22.1	23.4
9	152.6	151.2	149.5
10	139.0	142.3	140.0
11	149.9	147.0	150.1
12, 14, 15	122.1	128.0	126.1
13	133.7	130.1	131.0
16	59.9	57.9	57.8
17	109.3	104.4	113.0
18	171.0	—	170.9
19	17.8	—	17.5

experimental weight losses due to aromatization. The theoretical weight losses were calculated based on the loss of 2 mol of HX ($\text{X} = \text{OH}$ or OOCCH_3) and 1 mol of ethylene ($\text{CH}_2=\text{CH}_2$). Experimental percentage weight losses were obtained from the t.g.a. curves. The t.g.a. curves show the formation of more stable compounds upon aromatization. Further heating results in the degradation of the aromatic PBOs.

The FT i.r. spectra show the disappearance of the O-H absorption peaks at 3436 and 3400 cm^{-1} for V and VII,

**Figure 1** T.g.a. curves of precursor polymers under Ar atmosphere**Figure 2** T.g.a. curves of precursor polymers in air

respectively, upon heating under Ar atmosphere for 60 min at 247 and 279°C , respectively. The FT i.r. spectra of the precursor polymers VI and VIII indicate the loss of the acetyl (OOCCH_3) absorption peaks at 1654 and 1659 cm^{-1} , respectively after heating under Ar atmosphere for 60 min at 199 and 220°C , respectively. The elemental analysis results for the heat treated polymers are summarized in Table 6.

CONCLUSIONS

A route to making processable precursor polymers to (PBOs) was achieved by making precursor polymers containing the bicyclo[2.2.2]octane moiety substituted at the 2,5-positions with hydroxyl or acetyl groups. Subsequent conversions to the desired aromatic PBOs were obtained by the bulk pyrolysis of the precursor polymers. Bulk pyrolysis results in the transformation of the 2,5-disubstituted bicyclo[2.2.2]octyl ring to the phenylene ring system with liberation of 2 mol of HX ($\text{X} = \text{OH}$ or OOCCH_3) and 1 mol of ethylene ($\text{CH}_2=\text{CH}_2$).

The precursor polymers containing the hydroxyl substituents exhibited greater thermal and thermooxidative stability than the acetyl substituted polymers. The precursor polymers containing the ester substituents

Table 3 Summary of thermal characteristics of precursor polymers

Precursor polymer	D.s.c. transition temperature (°C)				Optical polarizing microscopy transition temperature (°C)		T.g.a. transition temperature (°C)	
	Ar		Air		T_m	T_d	Ar (T_d)	Air (T_d)
	T_m	T_d	T_m	T_d				
V	214	240	214	235	215	230	247	236
VI	152	195	150	176	156	166	199	180
VII	203	271	204	251	203	249	279	255
VIII	185	219	187	209	189	208	220	204

Table 4 Solubility properties and inherent viscosity measurements of the polymers

Polymer	η_{inh} . (g dl ⁻¹)	NMP	DMF	DMSO	TMU	DMAc
V	0.67 ^a	Soluble	Insoluble	Soluble	Partially soluble	Soluble
VI	0.59 ^b	Partially soluble	Insoluble	Partially soluble	Partially soluble	Partially soluble
VII	0.74 ^a	Soluble	Soluble	Insoluble	Soluble	Soluble
VIII	0.61 ^b	Partially soluble	Partially soluble	Partially soluble	Partially soluble	Partially soluble
V*		Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
VI*		Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
VII*		Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
VIII*		Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

^a Viscosities measured in *N*-methylpyrrolidione

^b Viscosities measured in methanesulfonic acid; V*, VI*, VII* and VIII* are heat treated polymers of precursor polymers V, VI, VII and VIII, respectively. Polymers were heated isothermally for 60 min under Ar atmosphere at 247 (V), 199 (VI), 279 (VII) and 220°C (VIII)

Table 5 Percentage weight losses due to aromatization

Polymer	Theoretical wt loss (%)	Experimental wt loss (%)	
		Ar	Air
V	17	18 at 247°C	18 at 236°C
VI	32	29 at 199°C	28 at 180°C
VII	12	14 at 279°C	13 at 255°C
VIII	24	27 at 220°C	27 at 204°C

Experimental weight losses (%) were measured at the specified temperatures with an isothermal hold of 60 min

Table 6 Elemental analyses of polymers after aromatization

Polymer	Calculated (%)				Found (%)			
	C	H	F	N	C	H	F	N
V*	77.41	3.25	—	9.03	76.94	3.27	—	8.89
VI*	77.41	3.25	—	9.03	77.43	3.24	—	8.88
VII*	60.01	2.19	24.76	6.09	59.51	2.25	23.64	6.73
VIII*	60.01	2.19	24.76	6.09	60.12	2.18	23.77	6.15

(VI and VIII) exhibited sharper melting endotherms in the d.s.c.

The precursor polymers exhibited thermotropic behaviour. Up to precursor polymer concentrations of 20 (w/v)% in solvents, lyotropic fluid formation was not observed. The precursor polymers containing both the hexafluoropropyl group and hydroxyl substituents were generally more soluble in NMP.

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