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SYNTHESIS and CHARACTERIZATION of THIANTHRENE CONTAINING POLY(BENZOXAZOLE)S

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ABSTRACT: New thioether and thianthrene containing poly(benzoxazole)s (PBOs) were synthesized from 4,4'-thiobis[3-chlorobenzoic acid] and thianthrene-2,7- and -2,8-dicarbonyl chlorides with commercially available bis-o-aminophenols. Polymers were prepared via solution polycondensation in poly(phosphoric acid) at 90-200 °C. Transparent PBO films were cast directly from polymerization mixtures or m-cresol. The films were flexible and tough. Nonfluorinated PBOs were soluble only in strong acids and $AlCl_3/NO_2R$ systems by forming complexes with the benzoxazole heterocycle. Glass transition temperatures ranged from 298-450 °C and thermogravimetric analysis showed good thermal stabilities in both air and nitrogen atmospheres.

Introduction

Aromatic poly(benzoxazole)s (PBOs) are a class of heterocyclic polymers that are known to have excellent thermal stability, high mechanical properties, and good environmental resistance.[1,2,3,4] These outstanding properties have been the driving force to investigate their use in fibers, films, coatings and composites. However, uses of PBOs has been limited since they generally have poor solubility in organic solvents, high glass transition temperatures, and decompose below their melting points.

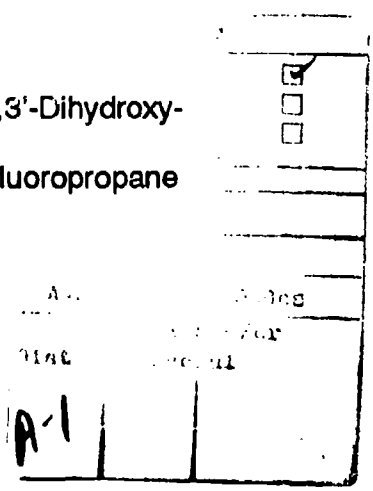
Processing of PBOs has been improved by the incorporation of the 2,2-

hexafluoroisopropylidene (6F) group into the polymer backbone.[4,5,6] These polymers have increased flexibility and solubility plus decreased color, dielectric constant, and crystallinity. However, high-performance polymers containing the 6F group have been shown to be less resistant to UV degradation.[7] Other bridging groups such as ethers and ketones have slightly increased the solubility of PBOs.[8] The thianthrene moiety has not been incorporated into the backbone of poly(benzoxazole)s, although it offers potential for improving solubility without sacrificing other properties.

Aromatic poly(benzoxazole)s are commonly prepared by one of two methods. The first is very similar to the low temperature, two-step synthesis of polyimides. Bis(o-aminophenol)s are reacted with aromatic diacid chlorides to form soluble poly(o-hydroxy amide)s which are processed. Thermal cyclodehydration then converts the backbone groups into benzoxazoles (Figure 1).[6] The second method is a direct polycondensation reaction of bis(o-aminophenol)s with aromatic dicarboxylic acids or diacid chlorides in polyphosphoric acid (PPA) (Figure 2).[9] Dicarboxylic acids have lower costs and are easier to handle than acid chlorides, but are less reactive. The PPA acts both as reaction medium and condensing agent. It has been shown that a high P_2O_5 content provides good monomer and polymer solubility. Specifically, at the end of the polymerization, the PPA should contain ~83.0 % P_2O_5 to ensure high molecular weight PBOs that are still soluble and not too viscous to process.

Experimental

All reagents were purchased from Aldrich Chemical Company. 3,3'-Dihydroxy-4,4'-diaminobiphenyl (HAB) and 2,2-bis(3-amino-4-hydroxy-phenyl)hexafluoropropane



(6F) were purchased from Chriskev Co. and used as received. The following compounds were prepared as previously described: thianthrene-2,7-dicarboxylic acid (mp > 350 °C), thianthrene-2,8-dicarboxylic acid (**1** and **2**)(mp > 350 °C) and 4,4'-thiobis[3-chlorobenzoic acid] (**3**) (mp 273-275 °C).[10] 2-Aminophenol, phosphoric acid (61.8% P_2O_5) and phosphorus pentoxide (P_2O_5) were used without further purification. All other solvents were used as obtained or purified via standard methods.

Monomer and polymer structures were confirmed by ^{13}C and ^{1}H solution NMR (Bruker ACE 300), and FTIR (Perkin-Elmer 1600A). NMR solvents included dimethyl sulfoxide-d_6 (DMSO-d_6) and chloroform-d_1 ($CDCl_3$). Differential scanning calorimetry (DSC) was conducted on a TA Instruments 2920 DSC module (2100 data station) at a heating rate of 10 °C/min. The glass transition temperature (T_g) was taken at the inflection point of the ΔT vs. temperature curve. Thermogravimetric analyses (TGA) were performed with a TA instruments 2960 TGA module (2100 data station) at a heating rate of 10 °C/min in nitrogen and air atmospheres. Dynamic mechanical analysis was conducted on a Polymer Lab Mark III DMTA at a heating rate of 4 °C/min. Intrinsic viscosities [*n*] were measured in m-cresol at 30 °C. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Thianthrene-2,7-dicarbonyl chloride (4).[11] A mixture composed of thianthrene-2,7-dicarboxylic acid (9.60 g, 31.5 mmol), 120 mL of thionyl chloride, and 3 drops of *N,N*-dimethylformamide (DMF) was stirred under reflux for 5 h. Excess thionyl chloride was removed by vacuum distillation. The crude product was recrystallized twice from benzene to give light tan crystals; yd 7.24 g (67.3 %); mp 206

°C; ^{1}H NMR (DMSO-d_6): δ 7.60 (d, 2 H, J = 8 Hz), 8.01 (d, 2 H, J = 8 Hz), 8.17 (s, 2 H); ^{13}C NMR (DMSO-d_6): δ 167.0, 143.3, 134.8, 133.2, 130.8, 128.9.

Anal. Calc. for $C_{14}H_6Cl_2O_2S_2$: C, 49.28 %; H, 1.77 %; Cl, 20.78 %; S, 18.79 %; Found: C, 49.19 %; H, 1.89 %; Cl, 20.91 %; S, 18.71 %.

Thianthrene-2,8-dicarbonyl chloride (5). This monomer was prepared using the same procedure as for 1 to give yellow crystals; yd 80.3 %; mp 201-203 °C; ^{1}H NMR (DMSO-d_6): δ 7.58 (d, 2 H, J = 8 Hz), 8.00 (dd, 2 H, J = 2 Hz and 8 Hz), 8.17 (d, 2 H, J = 2 Hz); ^{13}C NMR (DMSO-d_6): δ 167.0, 142.8, 135.1, 133.2, 130.9, 130.6, 128.8.

Anal. Calc. for $C_{14}H_6Cl_2O_2S_2$: C, 49.28 %; H, 1.77 %; Cl, 20.78 %; S, 18.79 %; Found: C, 49.05 %; H, 1.70 %; Cl, 20.93 %; S, 18.61 %.

2,7-Bis(benzoxazol-2-yl)thianthrene (6). A mixture of 24.5 g of phosphoric acid and 36.0 g of P_2O_5 was prepared in a flask equipped with a nitrogen inlet. It was mixed at 90 °C until homogeneous. To another reaction vessel was added thianthrene-2,7-dicarboxylic acid (1, 0.7522, 2.472 mmol), 2-aminophenol (0.6113 g, 5.602 mmol) and 35 g of the freshly prepared PPA. The mixture was heated under nitrogen at 150 °C for 6 h, 175 °C for 4 h and 190 °C for 2 h. The product was isolated by precipitating into water followed by washing with hot CH_3OH, and vacuum drying; yd 0.88 g (79 %); ^{13}C NMR ($CDCl_3$): δ 161.7, 150.8, 141.9, 138.8. 135.7, 129.1, 127.4, 126.9, 125.6, 124.9, 120.1, 110.7.

2,8-Bis(benzoxazol-2-yl)thianthrene (7). A mixture of 21.9 g of phosphoric acid and 14.9 g of P_2O_5 was prepared in a reaction vessel equipped with a nitrogen

inlet, and mixed at 90 °C until homogeneous. After cooling to ambient temperature, 2-aminophenol (0.8075 g, 7.326 mmol) was added and the vessel was heated again to 90 °C for 2 h and then cooled. Thianthrene-2,8-dicarbonyl chloride (**5**, 1.009 g, 2.957 mmol) was added to the dark, homogeneous mixture at ambient temperature. After heating at 90 °C for 6 h, the mixture was cooled to 40 °C and 12.88 g of P_2O_5 was added. The reaction vessel was then heated at 120 °C for 6 h, 165 °C for 4 h, 175 °C for 4 h and 190 °C for 2 h. The product was isolated by precipitating into water followed by washing with hot CH_3OH and vacuum drying; yd 1.30 g (98.5 %); mp 338-348 °C; ^{13}C NMR ($CDCl_3$): δ 161.7, 141.9, 138.6, 135.8, 129.0, 127.5, 127.1, 126.8, 125.5, 124.8, 120.2, 110.7.

Polymer Synthesis. A typical procedure was as follows. Phosphoric acid (17.99 g) and P_2O_5 (12.29 g) were charged to a 125 mL three-neck flask equipped with a mechanical stirrer and N_2 inlet and outlet. The solution was stirred at 100 °C for 6 h to give an initial PPA mixture of 77.3% P_2O_5. HAB (1.086 g, 5.022 mmol) was added to the clear solution at 60 °C which was then stirred for 1 h. Monomer **4** (1.714 g, 5.022 mmol) was added to the heterogenous mixture, the temperature increased to 90 °C and stirring continued for 4 h. The temperature was reduced to 50 °C and 10.04 g of P_2O_5 added. The following temperature profile was used during polymerization: 12 h @ 90 °C; 6 h @ 140 °C; 12 h @ 160 °C; 12 h @ 175 °C; 24 h @ 195 °C. Over this time the solution evolved from a heterogeneous yellow mixture to a homogeneous, extremely viscous amber solution. The polymerization was stopped at this point due to the extremely high viscosity stopping the mechanical stirrer.

The work-up consisted of splitting the polymerization mixture into two parts. Half the sample was stretched into a thin film and thoroughly washed with water and methanol. The yellow film was transparent and slightly flawed from leaching out the PPA. The other half was precipitated into water and ground in a blender to a fine fibrous form. The precipitated polymer was washed repeatedly with water and then with dilute ammonium hydroxide, water, and methanol. The copper colored polymer was vacuum dried at 120 °C for 24 h. Yields were quantitative.

Transparent PBO films were cast directly from polymerization mixtures or m-cresol solutions. The latter was only applicable to those polymers containing the 6F group and gave more uniform films. Films derived from both techniques were flexible and tough.

Results and discussion

Thianthrene-2,7- and -2,8-dicarbonyl chlorides (**4** and **5**) were prepared from the dicarboxylic acids with thionyl chloride in approximately 65-80% yield after purification.

Poly(phosphoric acid) was used as the polycondensation medium for these polymers. The initial 77.3% P_2O_5 content kept the viscosity low enough to thoroughly disperse the monomers and was adjusted after dehydrochlorination to give a value of 83.0 % at the end of polymerization. This value has been shown to solubilize monomers and polymers, drive the condensation reaction to completion, and keep the viscosity low enough to process directly from the polymerization mixture.[9]

Initial model compound syntheses and polymerizations were done directly with

the thianthrene dicarboxylic acids. These monomers had poor solubility in PPA even after P_2O_5 adjustment and with temperatures above 175 °C. Particle size was reduced as much as possible to help solubilization, but apparently the carboxylic acid-to-monomer molecular weight ratio limits solubility of rigid, high melting dicarboxylic acids in the acidic medium. High molecular weight PBOs were obtained from dicarboxylic acid **3** which had good solubility in PPA.

Diacid chlorides **4** and **5** were more reactive and dissolved readily in the acidic medium at lower temperatures. Figure 3 shows the poly(benzoxazole) polymerization scheme for the prepared diacid derivatives (**3**, **4**, **5**) and bis(o-aminophenol)s HAB and 6F. Polymerizations were usually completed within 24 h at 195 °C due to the viscous reaction mixtures stopping the mechanical stirrer. Monomer solubility and polymer viscosity restricted polymer concentration to < 5%. The 5% polymerization mixtures did not exhibit spontaneous birefringence, the signature of lyotropic liquid crystallinity.

Figure 4 shows the solution and solid-state ^{13}C NMR of model compound **6** and PBO (**4** and HAB), respectively. The solid-state NMR peaks of the polymer correlate well to those of the purified model compound. FTIR spectra for both the model compound and polymer did not show the O-H and N-H (3000-3500 cm-1) or C=O (1690 cm-1) stretching bands of the monomers as shown in Figure 5.

The PBOs derived from HAB were insoluble in common organic solvents. This required processing of the PBOs directly from the polymerization mixture into films. The films were transparent and tough, but flawed after leaching out the PPA. Solubility could be achieved in strong acids and $AlCl_3/NO_2R$ systems, which form

complexes with the benzoxazole heterocycle to enhance solubility. The 6F containing polymers had good solubility in m-cresol and films were obtained by casting from 5% m-cresol solutions. Table 1 qualitatively shows the solubility of the PBOs in several solvents. Intrinsic viscosities of the 6F containing polymers were measured in m-cresol at 30 °C and were between 0.88-1.51 dL/g (Table 2).

Glass transition temperatures ranged from 298-450 °C (Table 2). No melt transitions were observed for the polymers. The bent thianthrene structure limited crystallinity and chain packing as determined by wide angle X-ray (no crystalline peaks seen above strong broad amorphous bases). Thermogravimetric analysis showed good thermal stabilities in both air and nitrogen atmospheres. PBOs derived from 4,4'-thiobis[3-chlorobenzoic acid] (**3**) showed an initial weight loss corresponding to elimination of both chlorine substituents followed by catastrophic degradation of the polymer.

Conclusions

New thianthrene containing PBOs were synthesized by the polycondensation reaction of thianthrene dicarbonyl chlorides with bis-o-aminophenols in PPA. The PBOs exhibit high glass transition temperatures and excellent thermal stabilities. No solubility improvements were observed for nonfluorinated PBOs. The films obtained were transparent and tough.

Acknowledgement

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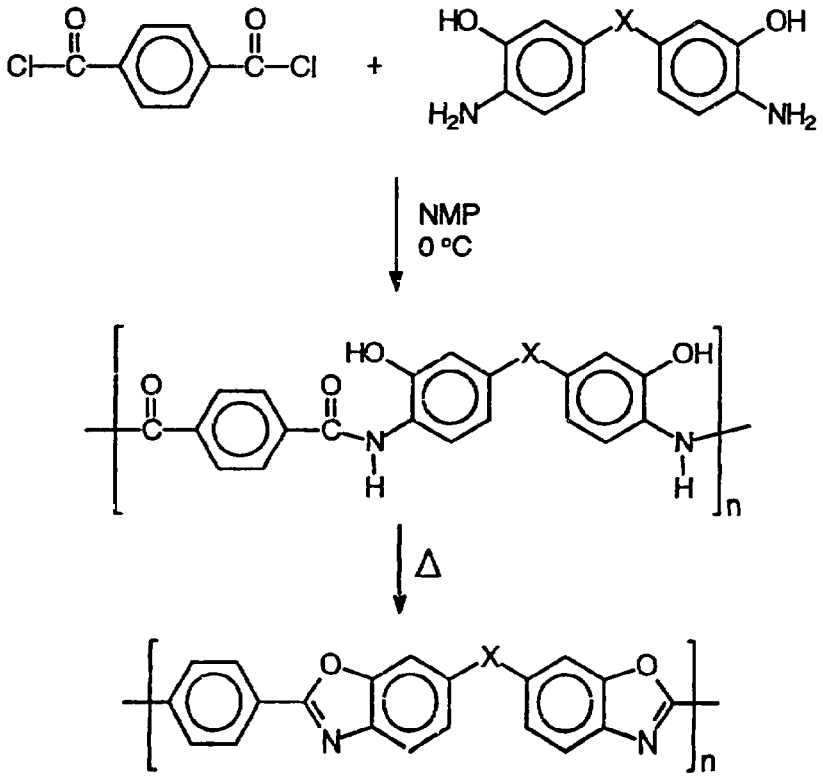
References

1. C. Arnold, *J. Polym. Sci., Macromol. Rev.*, **14**, 265 (1979).
2. P. E. Cassidy, *Thermally Stable Polymers: Syntheses and Properties*; Marcel Dekker: New York, 1980; pp 154-156.
3. M. Ueda, H. Sugita, M. Sato, *J. Polym. Sci.: Part A: Polym. Chem.*, **24**, 1019 (1986).
4. Y. Maruyama, Y. Oishi, M. Kakimoto, Y. Imai, *Macromolecules*, **21(8)**, 2305 (1988).
5. M. Dotrong, M. H. Dotrong, R. C. Evers, G. J. Moore, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **31(2)**, 675 (1990).
6. W. S. Joseph, J. C. Abed, R. Mercier, J. E. McGrath, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **34(1)**, 397 (1993).
7. C. E. Hoyle, D. Creed, P. Subramanian, R. Nagarajan, C. Pandey, E. T. Anzures, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **34(1)**, 369 (1993).
8. J. G. Hilborn, J. W. Labadie, J. L. Hedrick, *Macromolecules*, **23**, 2854 (1990).
9. J. F. Wolfe, *Encyclopedia of Polymer Science and Engineering* 1988; Vol. 11, pp 601-635.
10. R. A. Johnson, L. J. Mathias, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **34(1)**, 493 (1993).
11. Ciba Ltd. Swiss Patent 243 008,1946; *Chem. Abstr.*, **43**, 5966 (1949).

List of Figures



FIGURE

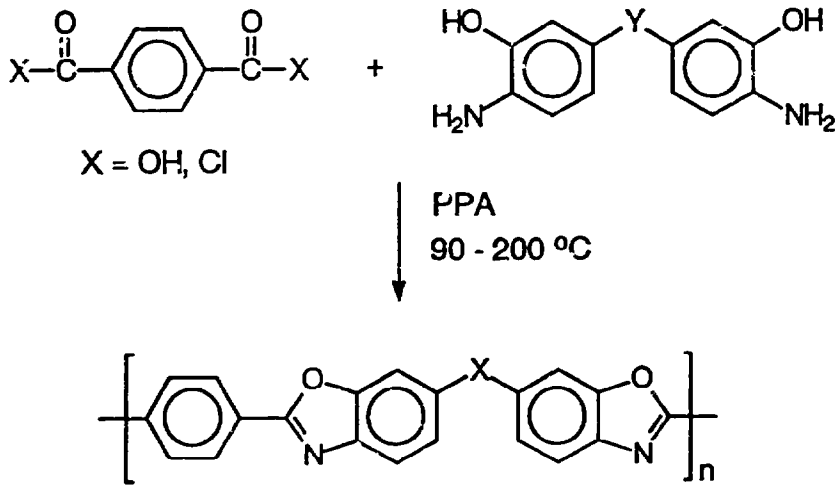
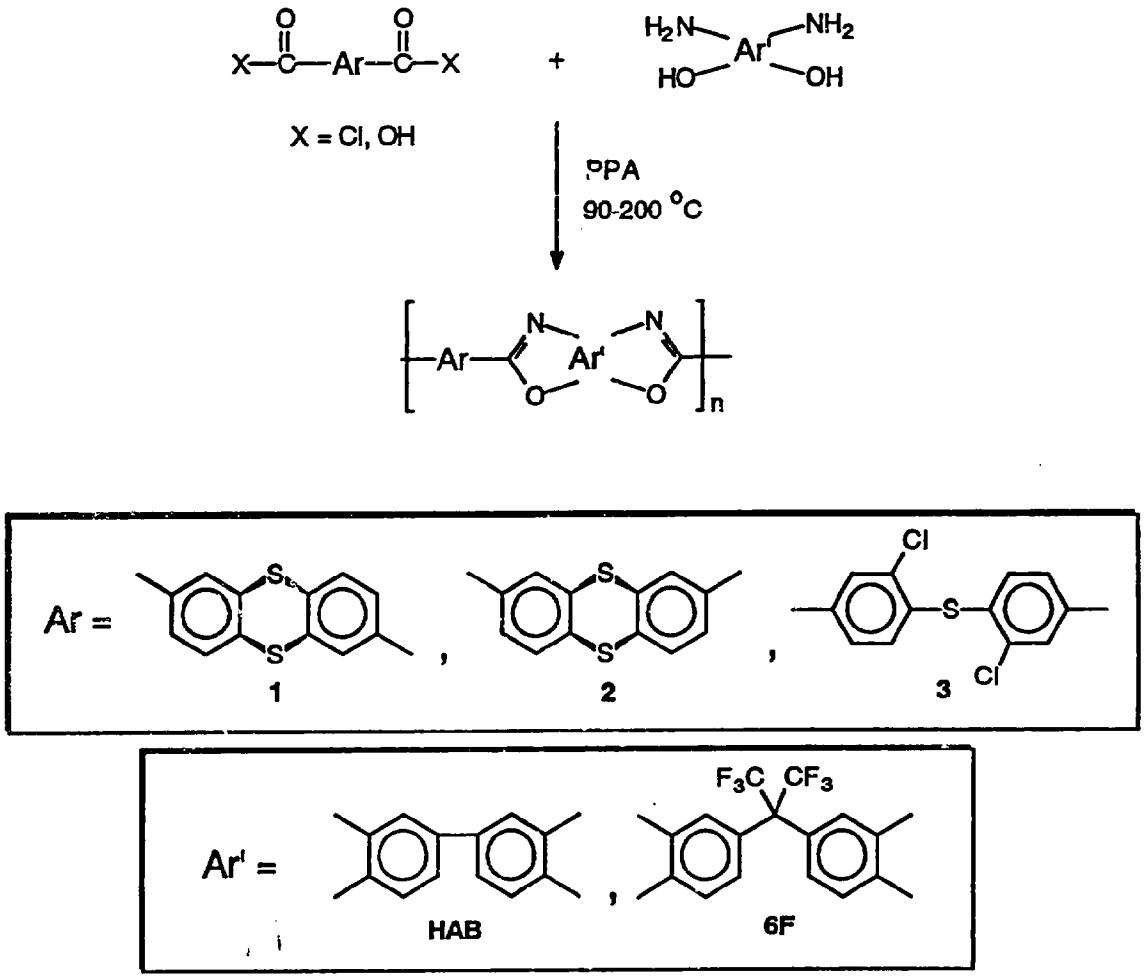


FIGURE 2



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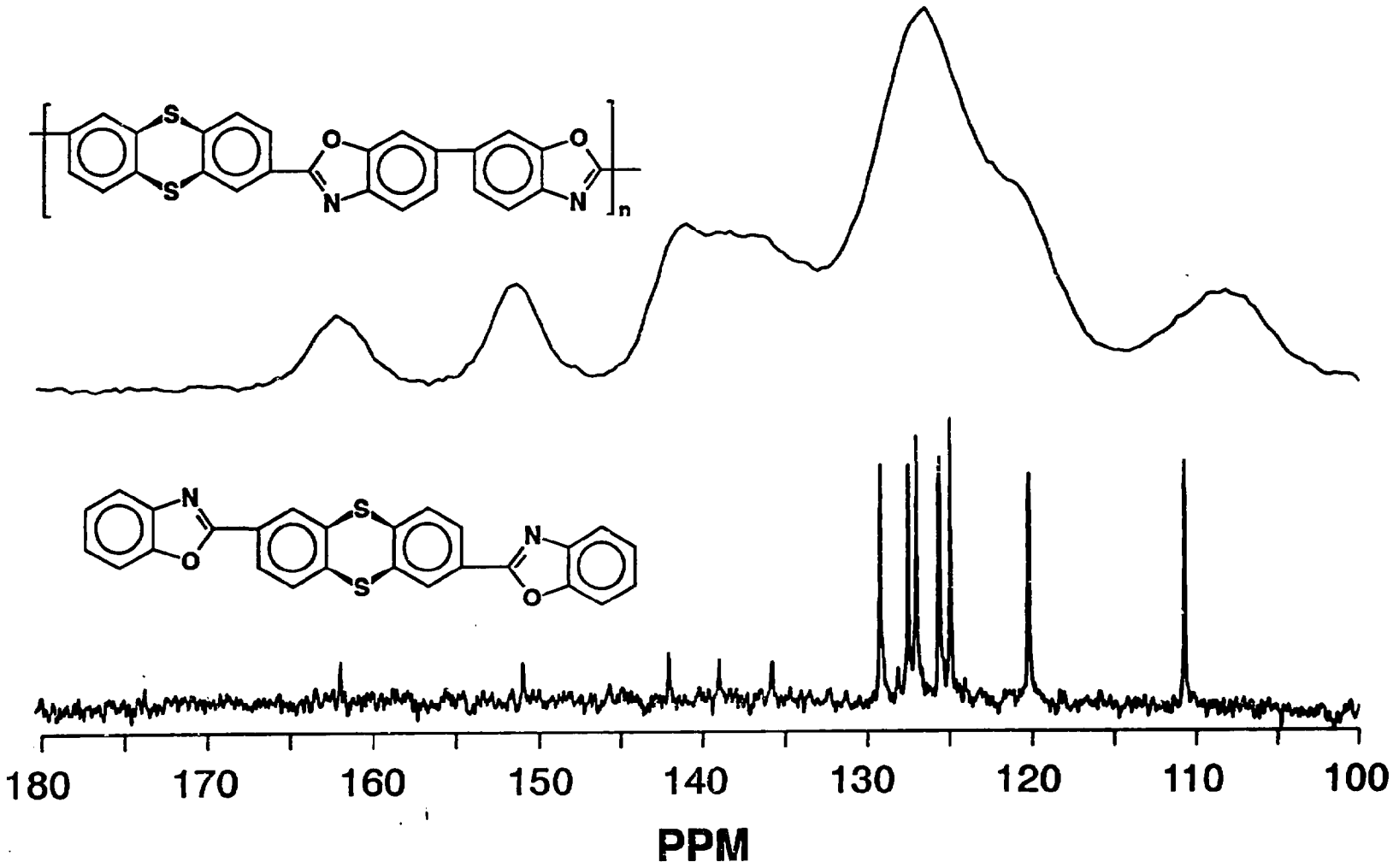

Figure 4

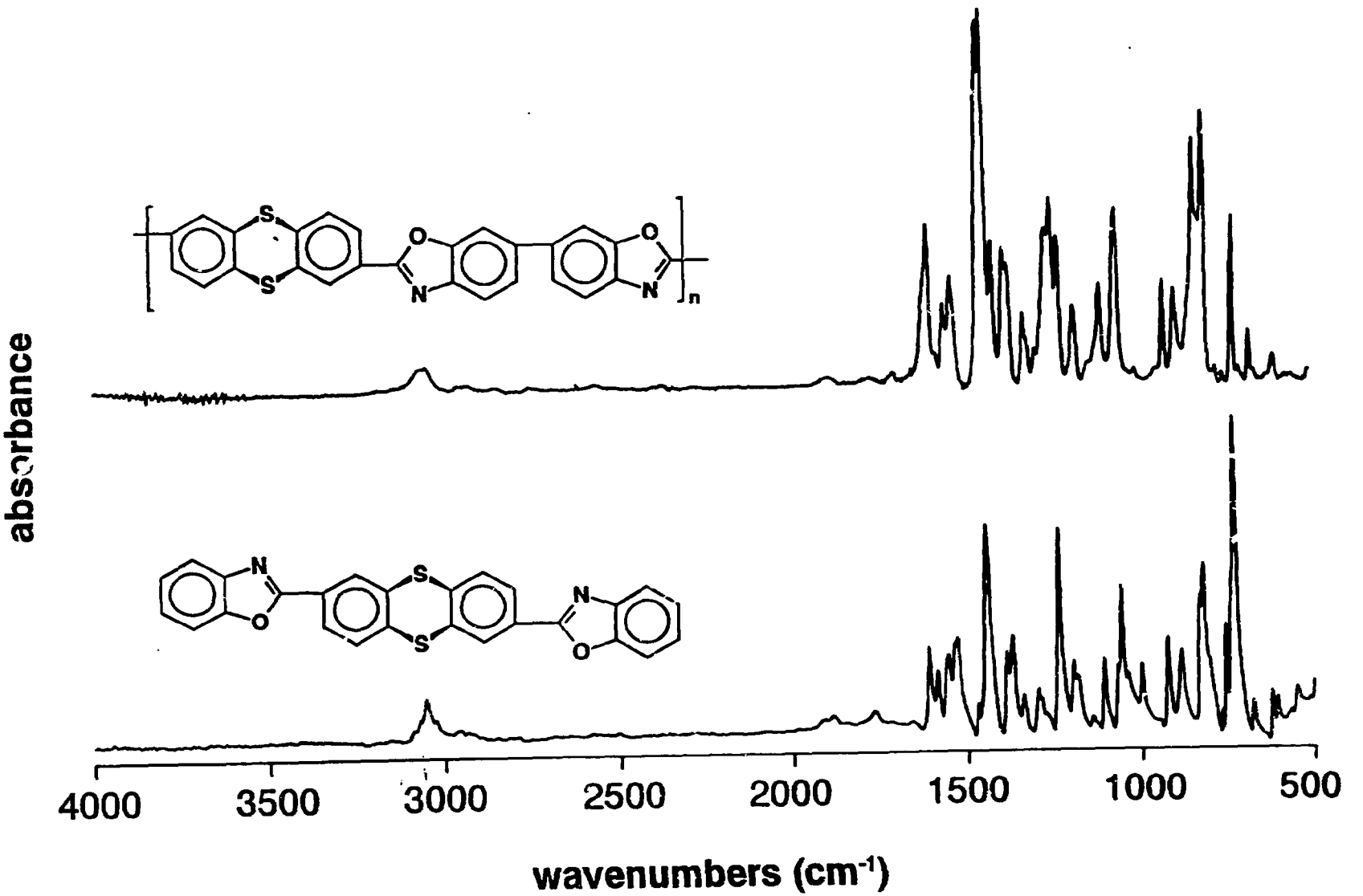
absorbance
4000
3500
3000
2500
2000
1500
1000
500
wavenumbers (cm-1)

Figure 5

Table 1: Poly(benzoxazole) solubility.

POLYMERS	H_2SO_4	$MeSO_3H$	m-cresol	$CHCl_3$	THF	diCl benzene	$MeNO_2$[a] $AlCl_3$
4 - HAB	b	b	--	--	--	--	-+
4 - 6F	++	++	++	--	--	--	++
5 - HAB	b	++	--	--	--	--	++
5 - 6F	++	++	++	--	--	-+	++
3 - HAB	++	++	--	--	--	--	++
3 - 6F	++	++	++	-+	--	++	++

[a] 18 wt% $AlCl_3$.

[b] Partially soluble.

++ Soluble at ambient temperature.

-+ Soluble hot.

-- Insoluble.

Table 2: Polymer Characterization.

POLYMERS	$[\eta]$	T_g (°C)	TGA[a] (°C)	
			onset temp. (N_2 / air atm.)	10% wt. loss (N_2 / air atm.)
4 - HAB	--	450[c]	451 / 450	643 / 551
4 - 6F	0.92[b]	372[d]	478 / 455	533 / 528
5 - HAB	--	--	462 / 391	655 / 590
5 - 6F	1.51[b]	357[d]	435 / 442	545 / 526
3 - HAB	--	--	473 / 459	533 / 511
3 - 6F	0.88[b]	298[d]	453 / 449	500 / 488

[a] Measured at heating rate of 10 °C/min.

[b] Measured in m-cresol at 30 °C.

[c] DMA, measured at a heating rate of 4 °C/min.

[d] DSC, measured at a heating rate of 10 °C/min.