

# Crosslinkable Polyesters Containing Styrylpyridine Segments

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**ABSTRACT:** Polyesters containing styrylpyridine segments were synthesized with the bisphenols 2,6-di[2-(2-hydroxy-1-naphthyl)vinyl]pyridine, 2-[2-(2-hydroxy-1-naphthyl)vinyl]-8-hydroxyquinoline, and 2-(4-hydroxystyryl)-8-hydroxyquinoline as starting materials. The polyesters were characterized by inherent viscosity measurements, Fourier transform infra-red,  $^1\text{H}$  nuclear magnetic resonance, X-ray, differential thermal analysis, thermomechanical analysis, thermogravimetric analysis, and isothermal gravimetric analysis. The polymers were amorphous or microcrystalline and were soluble in hot, polar, aprotic solvents containing 5 wt % LiCl. They showed  $T_g$  at 112–175°C and  $T_m$  at 165–295°C. After heat curing, the polyesters yielded resins which were stable up to 367–335°C in  $\text{N}_2$  and 347–329°C in air and afforded anaerobic char yields of 72–64% at 800°C. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1135–1141, 1997

**Key words:** polyesters; styrylpyridine; synthesis; crosslinking; thermal stability

## INTRODUCTION

The class of heat-resistant curable polymers constantly attracts much interest because of their applications in the fields of aerospace and electronics. To this class belongs the poly(styrylpyridine)s (PSP), which were prepared from the polycondensation of methyl-substituted pyridine with terephthaldehyde.<sup>1–4</sup> These materials exhibit attractive properties such as thermal stability, fire resistance, high char yield, processability, and good mechanical properties. They have been used as matrix resins for high-temperature composites. The curing behavior of PSP has been extensively investigated. The formation of fused aromatic rings by a Diels-Alder reaction,<sup>5</sup> as well as the addition of a methyl group of methylpyridine to the C=C bond of the styrylpyridine derivative,<sup>6</sup> has been reported.

Because of the attractive properties of PSP,

polymers such as epoxy<sup>7</sup> or photonegative resins<sup>8</sup> based on a styrylpyridinium unit have been synthesized. A number of polymers containing styrylpyridine units have been prepared in our laboratory. Particularly, polyesters and polyurethanes derived from 2,6-di(4-hydroxystyryl)pyridine<sup>9</sup> and 2,2'-(1,4-phenylenedivinylene)bis-5-hydroxypyridine<sup>10</sup> were synthesized and characterized. In addition, polyamides, polyimides, and bismaleimides were prepared from 2,6-di(3-aminostyryl)pyridine<sup>11</sup> and 2,2'-(1,4-phenylenedivinylene)bis-aminoquinoline.<sup>12</sup> Recently, we have reported the synthesis and characterization of poly(enaryloxynitrile)s containing styrylpyridine units.<sup>13</sup>

This investigation deals with the synthesis and characterization of polyesters containing styrylpyridine units in the main chain. After curing, they afforded thermally stable crosslinked polymers which could be used as matrix resins for heat-resistant composites.

## EXPERIMENTAL

### Characterization Methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304

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and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets.  $^1\text{H}$  nuclear magnetic resonance (NMR), spectra were obtained with a Varian T-60A spectrometer at 60 MHz. Chemical shifts ( $\delta$  values) are given in parts per million with tetramethylsilane as an internal standard. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a DuPont 990 thermal analyzer. DTA measurements were made with a high-temperature (1,200°C) cell at a heating rate of 20°C/min in  $\text{N}_2$  atmosphere at a flow rate of 60  $\text{cm}^3/\text{min}$  and with a  $\Delta T$  sensitivity of 0.5°C/in. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA with a loaded penetration probe at a scan rate of 20°C/min in  $\text{N}_2$  with a flow rate of 60  $\text{cm}^3/\text{min}$ . The TMA experiments were conducted in duplicate. The TMA specimens were pellets of 8 mm in diameter and 2 mm thickness, prepared by pressing powder of polymer for 3 min under 5-7 kpsi at ambient temperature. Dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of  $\text{N}_2$  or air at a flow rate of 60  $\text{cm}^3/\text{min}$ . The inherent viscosities of polymers were determined for solutions of 0.5 g/100 mL in *N,N*-dimethylacetamide (DMAc) containing 5% LiCl at 30°C with an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyzer. The wide-angle X-ray diffraction patterns were obtained for powder specimens on a X-ray PW-1840 Philips diffractometer.

### Reagent and Solvents

2-Hydroxy-1-naphthaldehyde and 8-hydroxyquinoline were recrystallized from 95% ethanol. Terephthaloyl chloride was recrystallized from *n*-hexane. 2,6-Lutidine was purified by distillation. DMAc and triethylamine were dried by distillation over  $\text{CaH}_2$  and KOH, respectively. The preparation of 2-(4-hydroxystyryl)-8-hydroxyquinoline [see Scheme 2 (2c)] has been described elsewhere.<sup>13</sup>

### Preparation of Starting Materials

#### 2,6-Di[2-(2-hydroxy-1-naphthyl)vinyl]pyridine (2a)

A mixture of 2-hydroxy-1-naphthaldehyde (4.99 g, 29.0 mmol), 2,6-lutidine (1.55 g, 14.5 mmol), and acetic anhydride (10 mL) was stirred and

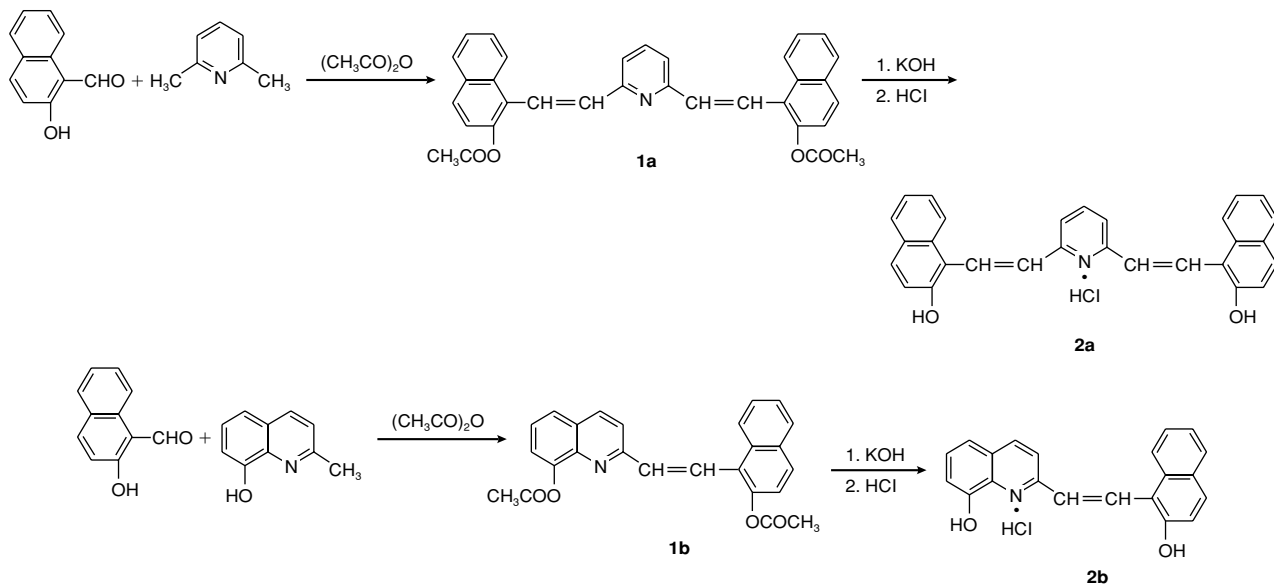
heated at 130°C for 35 h. It was subsequently poured into water and stirred for about 8 h. The brown solid obtained was filtered off, washed with water and then with cold methanol, and dried to afford 1a (5.07 g, 70%) (melting point [MP], 118–120°C). IR (KBr,  $\text{cm}^{-1}$ ) measurements were: 1,768 (C=O); 1,628, 1,610, 1,586, 1,512 (olefinic bond and aromatic rings); 1,370 (C—CH<sub>3</sub> stretching); 1,242, 1,206, 1,090, 1,016 (C—O—C); 974 (trans olefinic bond).  $^1\text{H}$  NMR measurements (DMSO- $d_6$ )  $\delta$  were: 8.60–8.40 (multiplets, 2H, ortho to CH<sub>3</sub>COO); 7.80–6.90 (multiplets, 13H, other aromatic and 4H olefinic); 2.80 (single, 6H, CH<sub>3</sub>COO).

Compound 1a (3.00 g, 6.0 mmol) was refluxed with 0.75*N* alcoholic KOH (15 mL) for 1.5 h. The 2a hydrochloride was obtained as a yellow solid by adding 35% aqueous HCl (1.70 g, 63%). It was recrystallized from a mixture of *N,N*-dimethylformamide/water (1 : 1 v/v) (MP, 173–176°C). Anal. Calcd. for C<sub>29</sub>H<sub>22</sub>NO<sub>2</sub>Cl were: C, 77.07%; H, 4.91%; N, 3.10%; Found were C, 76.96%; H, 4.96%; N, 3.07%. IR (KBr,  $\text{cm}^{-1}$ ) measurements were: 3,381–3,198 (O—H stretching); 1,622, 1,608, 1,570, 1,510 (olefinic bond and aromatic rings); 1,339 (O—H deformation); 1,260, 1,184 (C—OH stretching); 968 (trans olefinic bond).  $^1\text{H}$  NMR measurements: (dimethylsulfoxide- $d_6$ )  $\delta$  were: 8.70 (broad, 2H, OH); 8.40–7.80 (multiplets, 2H, aromatic ortho to OH); 7.70–6.90 (multiplets, 13H, other aromatic and 4H olefinic).

#### 2-[2-(2-hydroxy-1-naphthyl)vinyl]-8-hydroxyquinoline (2b)

A mixture of 2-hydroxy-1-naphthaldehyde (2.58 g, 15 mmol), 8-hydroxyquinoline (1.83 g, 15 mmol), and acetic anhydride (20 mL) was stirred and heated at 130°C overnight. It was poured into water, and the whitish solid precipitate was filtered off, washed with water and then with methanol, and dried to afford 1b (4.55 g, 76%). It was recrystallized from 30% ethanol (MP, 111–113°C). IR (KBr,  $\text{cm}^{-1}$ ) measurements were: 1,760 (C=O); 1,618, 1,592, 1,562, 1,502 (olefinic bond and aromatic rings); 1,368 (C—CH<sub>3</sub> stretching); 1,207, 1,190 (C—O—C); 972 (trans olefinic bond).  $^1\text{H}$  NMR measurements (DMSO- $d_6$ )  $\delta$  were: 8.50–8.30 (m, 2H, aromatic ortho to CH<sub>3</sub>COO); 7.80–6.90 (m, 9H, other aromatic and 2H olefinic); 2.45 (s, 6H, CH<sub>3</sub>COO).

Compound 1b (4.00 g, 10.1 mmol) was refluxed with 0.75*N* alcoholic KOH (15 mL) for 1.5 h. 2b hydrochloride was obtained as a red solid by add-

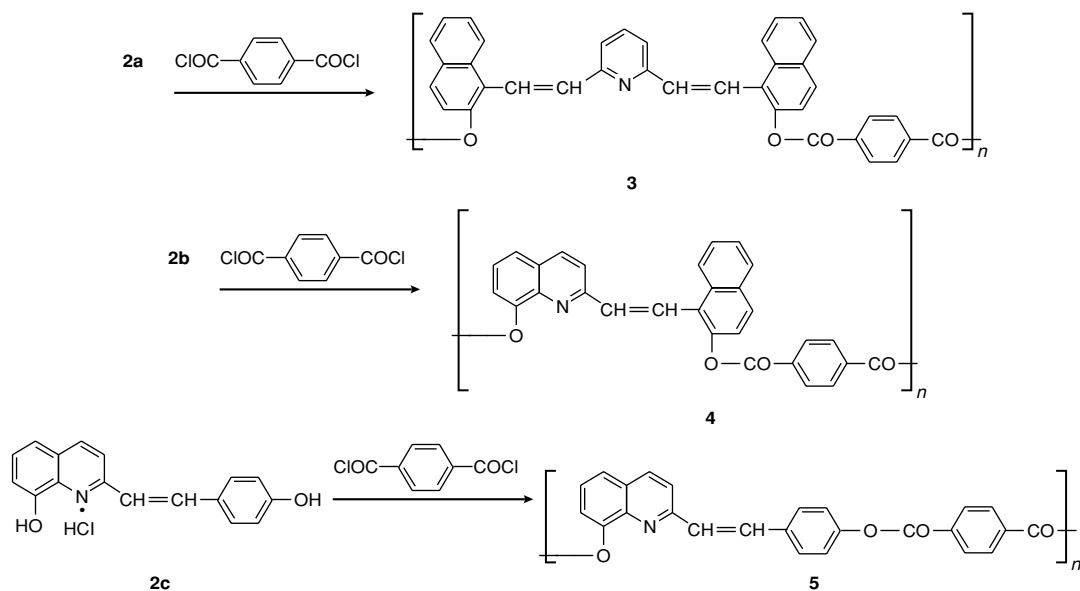


ing 35% aqueous HCl (3.2 g, 91%). It was recrystallized from a mixture of DMSO/water (1 : 1 v/v) (MP, > 300°C). Anal. Calcd. for  $C_{21}H_{16}NO_2Cl$  were C, 72.10%; H, 4.61%; N, 4.00%; Found were C, 71.01%; H, 4.57%; N, 3.98%. IR (KBr,  $cm^{-1}$ ) measurements were: 3,349–3,106 (O—H stretching); 1,638, 1,598, 1,566, 1,514 (olefinic bond and aromatic rings); 1,362 (O—H stretching); 1,238, 1,158 (C—OH stretching); 962 (trans olefinic bond).  $^1H$ -NMR measurements (DMSO- $d_6$ )  $\delta$

were: 9.06 (br, 2H, OH); 8.67–8.42 (m, 2H, aromatic ortho to OH and 1H aromatic at position 5 of quinaldine); 7.80–7.00 (m, 8H other aromatic and 2H olefinic).

#### Preparation of Polyesters

As a typical example, the preparation of polyester 3 is given (Scheme 2). A flask equipped with a magnetic stirrer was charged with a mixture of

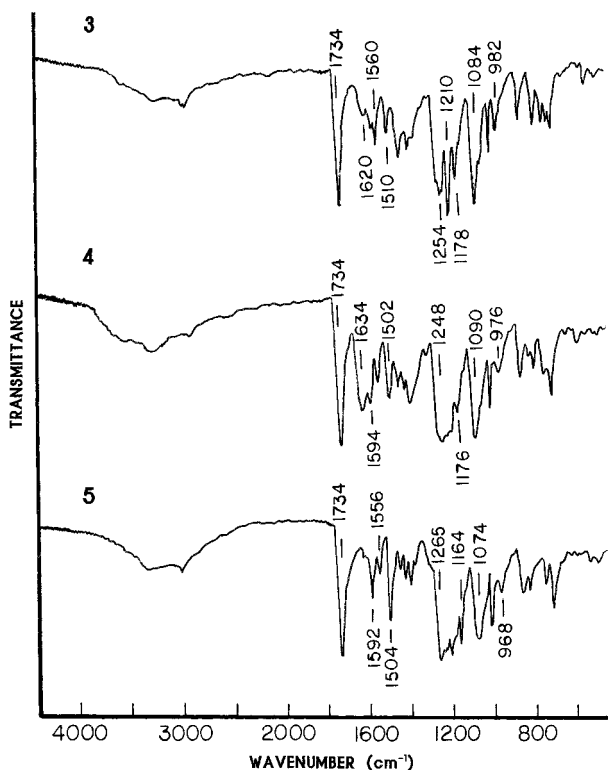
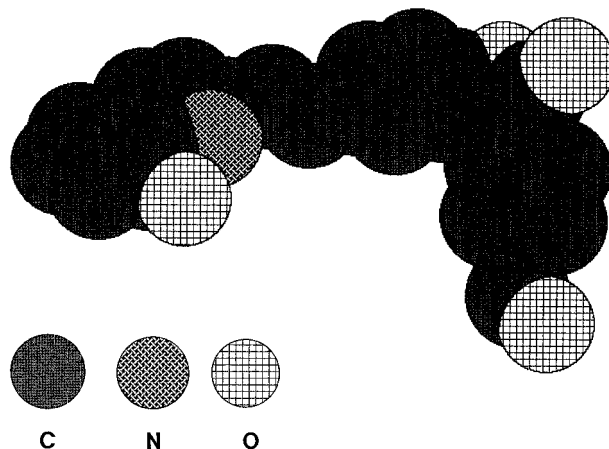


**Table I** Reaction Yields and Inherent Viscosities of Polyesters

Polyester	Yield (%)	$n_{inh}^a$
3	96	0.42
4	97	0.41
5	93	0.46

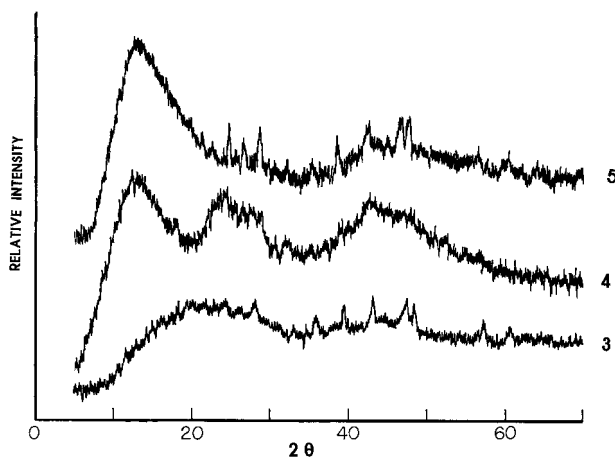
<sup>a</sup> Inherent viscosities in DMAc containing 5 wt % LiCl (0.5 g/dL at 30°C).

2a (0.40 g, 0.89 mmol), and DMAc (10 mmol) containing 5 wt % LiCl. Triethylamine (0.27 g, 2.67 mmol) was added to the mixture, and compound 2a was dissolved. Terephthaloyl chloride (0.18 g, 0.89 mmol) dissolved in DMAc (2 ml) was added dropwise to the mixture at 0°C under N<sub>2</sub>. Stirring of the mixture was continued at room temperature overnight in a stream of N<sub>2</sub>. The polymer precipitated during polymerization. The mixture was poured into water, and the brownish solid was filtered off, washed with water and then with acetone, and dried to afford 3 (0.48 g, 93%). The reaction yields and the inherent viscosities for all polyesters are listed in Table I.

**Figure 1** FTIR spectra of polyesters 3-5.**Figure 2** Optimized geometry for one repeat unit of polyester 5 (CSC ChemDraw 3D Plus  $\Sigma$  Molecular Modeling System, Version 3.1.1, 1993, Cambridge Scientific Computing, Inc.).

## RESULTS AND DISCUSSION

Scheme 1 outlines the synthesis of bisphenols 2a and 2b. More particularly, 2-hydroxy-1-naphthaldehyde was condensed with 2,6-lutidine in the presence of acetic anhydride to afford 1a. The acetoxy groups of the latter were hydrolyzed in alcoholic KOH, and 2a hydrochloride was obtained by means of hydrochloric acid. 2b hydrochloride was similarly prepared from the condensation of 2-hydroxy-1-naphthaldehyde with 8-hydroxyquinoline. These two bisphenols as well as 2c<sup>13</sup> were used as starting materials for the preparation of polyesters containing styrylpyridine segments (Scheme 2). The solution polycondensation method in DMAc in the presence of triethylamine was used. A triple molar amount of triethylamine

**Figure 3** X-ray diffraction patterns of polyesters 3-5.

**Table II Solubilities of Polyesters<sup>a</sup>**

Polyesters	Solvents <sup>b</sup>							
	DMF <sup>c</sup>	NMP <sup>c</sup>	DMSO <sup>c</sup>	CCl <sub>3</sub> COOH	H <sub>2</sub> SO <sub>4</sub>	<i>m</i> -Cresol	CH	Py
3	+	+	+	+	+–	+	+	+
4	+	+	+	+	+–	+	–	+–
5	+	+	+	+	+–	–	–	–

<sup>a</sup> Solubility: +, soluble in hot solvent; +–, partially soluble; –, insoluble.

<sup>b</sup> DMF, *N,N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethylsulfoxide; CH, cyclohexanone; Py, pyridine.

<sup>c</sup> Solvents containing 5 wt % LiCl.

was added to form bisphenols free of hydrochloric acid from the corresponding hydrochloride salts.

The polyesters were obtained in 97–93% yield, and their inherent viscosities ranged from 0.41 to 0.46 dL/g (Table I). The relative low degree of polymerization is owed to the precipitation of polymers during the polymerization.

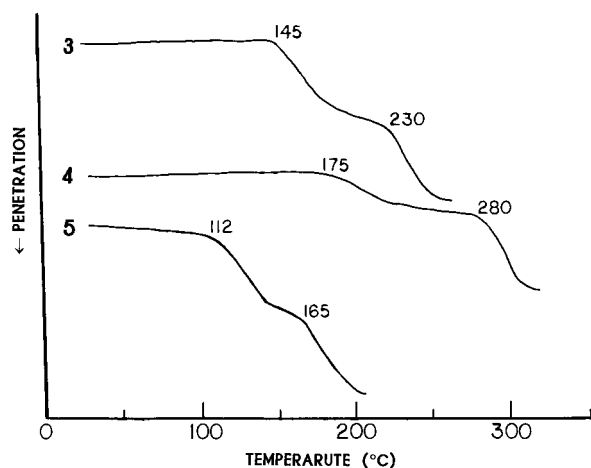
The characterization of polyesters was accomplished by FTIR, <sup>1</sup>H NMR, X-ray, DTA, TMA, TGA, and isothermal gravimetric analysis (IGA). Figure 1 presents the FTIR spectra of polyesters. They showed characteristic absorptions around 1,734 (C=O); 1,634–1,500 (olefinic bond, aromatic and pyridine rings); 1,265–1,070 (C–O–C), and 980–970 cm<sup>-1</sup> (trans olefinic bond).

Because the polymers were soluble in polar aprotic solvents, their <sup>1</sup>H NMR spectra were recorded. The <sup>1</sup>H NMR spectrum of a typical polyester 3 showed a singlet at 8.07 (aromatic of terephthalic acid moieties), 7.81–7.32 (aromatic of positions 3, 4, 5, and 8 of naphthyl rings as well as

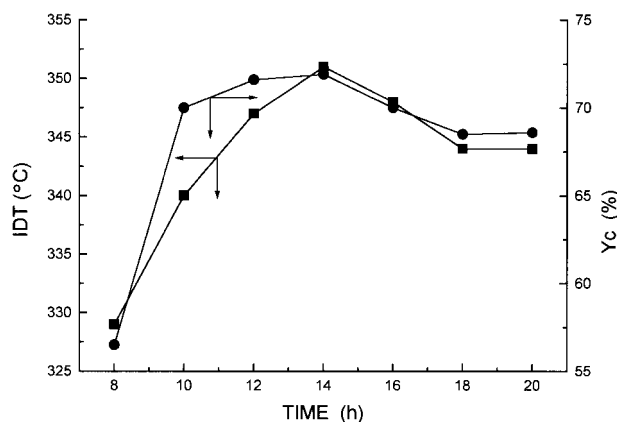
of position 4 of pyridine rings), and 7.15–6.80 (aromatic of positions 3 and 5 of pyridine rings as well as olefinic protons).

Table II summarizes the solubility behavior of polyesters. All polyesters dissolved in hot, polar, aprotic solvents (*N,N*-dimethylformamide, dimethylsulfoxide, *N*-methylpyrrolidone) containing 5 wt % LiCl as well as in trichloroacetic acid. When LiCl was not added to the polar aprotic solvents, polyester 3 dissolved at high temperature, but polyesters 4 and 5 were partially soluble or dissolved and precipitated from them after cooling. When comparing the solubility behavior of polyesters in *m*-cresol, cyclohexanone, and pyridine, the following order of relative solubility could be assessed: 3 > 4 > 5.

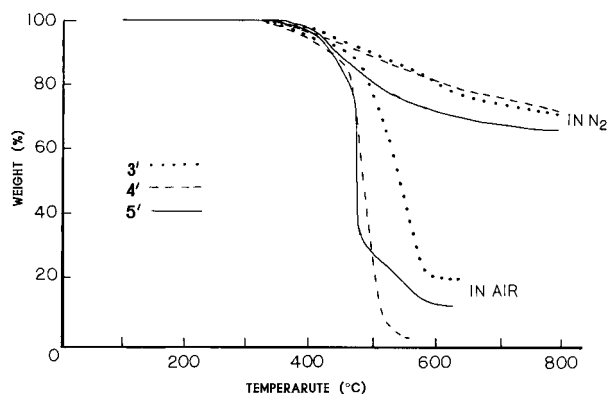
Estimations of certain structural characteristics of polyesters were attempted by utilizing a modeling system. Figure 2 presents typical optimized geometry for one repeat unit of a macromolecule of 5 as calculated by means of the CSC ChemDraw 3D PlusΣ Molecular Modeling System. It is seen that each segment of bisphenols and terephthalic acid is almost a plane, and the



**Figure 4** TMA thermograms of polyesters 3-5. Conditions: N<sub>2</sub> flow, 60 cm<sup>3</sup>/min; heating rate, 20°C/min.



**Figure 5** IDT (■) and  $Y_c$  (●) in N<sub>2</sub> of polyester 4 versus the time of curing at 280°C.



**Figure 6** TGA thermograms in  $N_2$  and air of cured polyesters 3'-5'. Conditions: Gas flow,  $60 \text{ cm}^3/\text{min}$ ; heating rate,  $20^\circ\text{C}/\text{min}$ .

two planes form a dihedral angle of approximately  $90^\circ$ . Such a configuration does not allow a dense chain packing.

Figure 3 shows the X-ray diffractograms of polyesters for as-prepared powders. Polyester 4 was amorphous, while 3 and 5 were microcrystalline. The higher crystallinity of 3 than that of 4 could be attributed to the longer structure length of the plane bisphenol segment, which can better accommodate a parallelization of the main chain. The crystallinity of 5 was ascribable to the more regular structure of the repeat unit having mostly p-substitution of aromatic rings, which lead to a better chain packing.

Thermomechanical characterization of polyesters was accomplished to determine their glass transition ( $T_g$ ) and melting ( $T_m$ ) temperatures. Figure 4 presents the TMA curves for polyesters, which were recorded with a loaded penetration probe. The  $T_g$  and  $T_m$  values were obtained from

the onset temperatures of these transitions. Unexpectedly, the microcrystalline polyesters 3 and 5 showed lower  $T_g$  values ( $145$  and  $112^\circ\text{C}$ , respectively) than the amorphous 4 ( $175^\circ\text{C}$ ). On the other hand, the polyesters displayed  $T_m$  transitions at  $165$ – $295^\circ\text{C}$ .

The DTA traces of polyesters showed broad exotherms above  $280^\circ\text{C}$ , ascribable to crosslinking reactions through the olefinic bonds. The polyesters were cured by heating at  $280^\circ\text{C}$  in static air. The initial decomposition temperature (IDT) and the char yield ( $Y_c$ ) at  $800^\circ\text{C}$  in  $N_2$  of the resins thus obtained were correlated with the curing time (Fig. 5). Both IDT and  $Y_c$  increased with increasing the time up to 14 h, and they were reduced beyond this value. Therefore, the time of 14 h was accepted as optimal under these curing conditions. After heating at  $280^\circ\text{C}$  for 14 h, polyesters 3-5 afforded resins named 3'-5', respectively. The resins were obtained as dark-brown solids insoluble in all solvents, and their TMA traces did not show any transition up to  $300^\circ\text{C}$ .

The thermal stability of the resins was evaluated by TGA in  $N_2$  and air (Fig. 6), as well as by IGA. The IDT, the polymer decomposition temperature (PDT), and the maximum polymer decomposition temperature ( $PDT_{\text{max}}$ ) in both  $N_2$  and air, as well as the anaerobic char yield ( $Y_c$ ) at  $800^\circ\text{C}$  for all polymers, are summarized in Table III. The IDT and PDT were determined for the temperature at which 0.5 and 10% weight losses were observed, respectively.  $PDT_{\text{max}}$  corresponds to the temperature at which the maximum rate of weight loss occurred. The resins were stable up to  $367$ – $335^\circ\text{C}$  in  $N_2$  and  $347$ – $329^\circ\text{C}$  in air and afforded an anaerobic  $Y_c$  of 72–64% at  $800^\circ\text{C}$ . The ratio  $(IDT)_{\text{air}}/(IDT)_{N_2}$  ranged from 0.94 to 0.98,

**Table III** Thermal Stabilities of Polyesters

Polyester	In $N_2$				In Air			$(IDT)_{\text{air}}/(IDT)_{N_2}$	Wt Loss <sup>e</sup> (%)
	IDT <sup>a</sup> ( $^\circ\text{C}$ )	PDT <sup>b</sup> ( $^\circ\text{C}$ )	$PDT_{\text{max}}$ <sup>c</sup> ( $^\circ\text{C}$ )	$Y_c$ <sup>d</sup> (%)	IDT ( $^\circ\text{C}$ )	PDT ( $^\circ\text{C}$ )	$PDT_{\text{max}}$ ( $^\circ\text{C}$ )		
3'	335	421	582	70	329	456	545	0.98	8.3
4'	351	489	517	72	329	437	470	0.94	10.5
5'	367	442	448	64	347	437	498	0.95	12.4

<sup>a</sup> Initial decomposition temperature.

<sup>b</sup> Polymer decomposition temperature.

<sup>c</sup> Maximum polymer decomposition temperature.

<sup>d</sup> Char yield at  $800^\circ\text{C}$ .

<sup>e</sup> Weight loss after 20 h of isothermal aging at  $300^\circ\text{C}$ .

which suggests that thermal degradation was affected significantly by the presence of oxygen in the cases of 4' and 5' (Table III). Resin 5' displayed the highest IDT both in N<sub>2</sub> and in air but afforded the lowest anaerobic Y<sub>c</sub> at 800°C. The IGA thermograms of resins 3', 4', and 5' at 300°C in static air showed weight losses of 8.3, 10.5, and 12.4%, respectively, after 20 h of isothermal aging.

## CONCLUSIONS

A new series of crosslinkable polyesters containing styrylpyridine segments were synthesized. They were amorphous or microcrystalline and dissolved in polar aprotic solvents containing LiCl as well as in trichloroacetic acid. The T<sub>g</sub> and T<sub>m</sub> values were determined by TMA, and they were in the range of 112–175°C and 165–295°C, respectively. The resins obtained by curing at 280°C for 14 h were stable up to 367–335°C in N<sub>2</sub> and 347–329°C in air and afforded anaerobic char yields of 64–72% at 800°C.

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