

Synthesis of poly(enaryloxynitrile)s containing styrylpyridine segments

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New poly(enaryloxynitrile)s bearing styrylpyridine segments were synthesized by interfacial polycondensation of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene with various bisphenols such as 6-(4-hydroxystyryl)-3-hydroxypyridine (HSHP), 2,6-di(4-hydroxystyryl)pyridine and 2-(4-hydroxystyryl)-8-hydroxyquinoline. They were characterized by viscosity, elemental analysis, FT i.r., ¹H and ¹³C n.m.r., X-ray, d.t.a., t.m.a., t.g.a. and isothermal gravimetric analysis. The polymer prepared from HSHP was crystalline and had a *T*_g at 270°C. The other polymers were amorphous and showed *T*_gs at 200–210°C and softening at 235–247°C. All the polymers displayed an enhanced solubility in common organic solvents. Upon heat-curing, crosslinked polymers were obtained which were stable up to 370–397°C in N₂ and afforded anaerobic char yields of 76–80% at 800°C. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The production of new organic thermally stable polymers is of particular interest. Of the wide variety of these materials the development of new heat-resistant curable polymers constantly attracts much interest because of their application in the fields of aerospace and electronics. Functional groups such as biphenylene, acetylene, styryl, maleimide and nadimide have been used for the preparation of polymers that upon heat-curing produce network thermally stable resins without evolution of volatile byproducts¹.

Over the last decade, the synthesis of novel poly(enaminonitrile)s^{2–7} and poly(enaryloxynitrile)s^{8–11}, prepared by a vinyl nucleophilic substitution, has been reported. These polymers, containing the dicyanovinyl group in the main chain, showed enhanced solubility in common organic solvents, and upon heat-curing afforded resins with outstanding thermal stability comparable to that of polyimides. Previously, studies on the dielectric properties indicated that these polymers are candidates for polymeric dielectrics². It is known that some of the poly(enaminonitrile)s form miscible blends with some electron-rich polymers¹².

The present work deals with the synthesis and characterization of poly(enaryloxynitrile)s containing styrylpyridine units in the main chain. The preparation of these polymers is an attempt to combine two different functional groups suitable for preparing heat-resistant resins. Specifically, the synthesized polymers are expected to combine the attractive properties of poly(styrylpyridine)s, such as processability, fire-resistance, solubility and mechanical strength, with those of poly(enaryloxynitrile)s. Earlier studies showed that the incorporation of

dicyanovinyl group into polyesters^{13,14}, polyurethanes^{15,16} and polyazomethines¹⁷ enhanced the solubility in common organic solvents as well as the thermal stability.

In previous papers we have reported the synthesis and characterization of polyamides^{18–21}, polyesters, polyurethane and epoxy resins²² bearing dicyanovinyl or cyanovinyl groups.

EXPERIMENTAL

Characterization methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. Infra-red (i.r.) spectra were recorded on a Perkin-Elmer 16PC FT i.r. spectrometer as KBr pellets (1% w/w). The ¹H n.m.r. (400 MHz) and ¹³C n.m.r. (100 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as internal standard. Differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) were performed on a DuPont 990 thermal analyser. The d.t.a. measurements were made using a high temperature (1200°C) cell at a heating rate of 20°C min⁻¹ in a N₂ atmosphere at a flow rate of 60 cm³ min⁻¹ and with a ΔT sensitivity of 0.5°C in⁻¹. Dynamic t.g.a. measurements were made at a heating rate of 20°C min⁻¹ in atmospheres of N₂ or air at a flow rate of 60 cm³ min⁻¹. Thermomechanical analysis (t.m.a.) was recorded on a DuPont 943 thermomechanical analyzer using a loaded penetration probe at a scan rate of 20°C min⁻¹ in N₂ with a flow rate of 60 cm³ min⁻¹. The t.m.a. experiments were conducted in duplicate. The t.m.a. specimens were pellets of 8 mm diameter and 2 mm thickness prepared by pressing powdered polymer for 3 min under 5–7 kilopounds per square inch (kpsi)

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at ambient temperature. The inherent viscosities of polymers were determined using solutions of 0.5 g of polymer per 100 ml of *N,N*-dimethylacetamide (DMAc) at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyser. Wide-angle X-ray diffraction patterns were obtained for powder specimens on an X-ray PW-1840 Philips diffractometer.

Reagents and solvents

p-Bis(1-chloro-2,2-dicyanovinyl)benzene² (CDVB), 6-(4-hydroxystyryl)-3-hydroxypyridine²³ (HSHP) and 2,6-di(4-hydroxystyryl)pyridine^{24,25} (DHSP) were synthesized according to methods previously reported. 4-Hydroxybenzaldehyde and 8-hydroxyquinoline were recrystallized from distilled water and a mixture of methanol/water (3/1, v/v), respectively. Acetic anhydride and chloroform were used as received.

Preparation of 2-(4-hydroxystyryl)-8-hydroxyquinoline (HSHQ) (Scheme 1)

A mixture of 8-hydroxyquinoline (3.18 g, 20.0 mmol), 4-hydroxybenzaldehyde (2.44 g, 20.0 mmol) and acetic anhydride (20 ml) was stirred and heated at 135°C for 24 h under N₂. It was subsequently poured into water and stirred for about 2 h. The yellow-brown solid obtained was filtered off, washed with water, then with acetone and dried to afford 2-(4-acetoxystyryl)-8-acetoxyquinoline (4.39 g, 63%). This was recrystallized from ethanol (95%); m.p. 156–158°C.

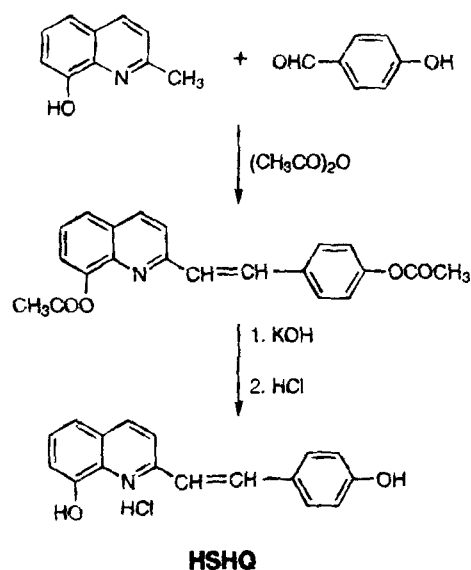
Elemental analysis (%): calculated for C₂₁H₁₇NO₄, C = 72.61, H = 4.93, N = 4.03%; found. C = 72.58, H = 4.90, N = 4.11. I.r. (KBr, cm⁻¹): 1762 (C=O); 1594 (olefinic bond and aromatic); 1562, 1508 (aromatic); 1368 (C-CH₃ stretching); 1206, 1170 (C-O-C) and 972 (*trans* olefinic bond). ¹H n.m.r. (DMSO-*d*₆), δ (ppm): 7.45–7.17 (*m*, 9H, aromatic and 2H olefinic); 2.40 (*s*, 6H, CH₃COO).

2-(4-Acetoxystyryl)-8-acetoxyquinoline (3.08 g, 8.9 mmol) was refluxed with 0.75 N alcoholic KOH (25 ml) for 1.5 h. The hydrochloride salt of HSHQ was obtained as a yellow solid by adding 35% aqueous HCl. It was filtered off, washed with water and then with ethanol and dried (2.45 g, 92%). A purified sample was obtained by recrystallization from a mixture DMSO/H₂O (1/3, v/v); m.p. >300°C.

Elemental analysis (%): calculated for C₁₇H₁₄NO₂Cl, C = 68.12, H = 4.71, N = 4.67; found. C = 67.94, H = 4.67, N = 4.58. I.r. (KBr, cm⁻¹): 3471–3349 (O-H stretching); 3110–2748 (NH⁺ stretching); 1624, 1592 (olefinic bond and aromatic); 1538, 1514 (aromatic); 1392, 1376 (O-H deformation); 1210, 1168 (O-H stretching) and 970 (*trans* olefinic bond). ¹H n.m.r. (DMSO-*d*₆), δ (ppm): 7.40 (*m*, 9H, aromatic); 6.87–6.72 (*m*, 2H, olefinic). The phenolic and NH⁺ protons were unobserved.

Preparation of polymers (Scheme 2)

A typical interfacial polymerization of CDVB with a bisphenol disodium salt was carried out as follows: HSHQ (0.68 g, 2.30 mmol) was dissolved in distilled water containing NaOH (0.28 g, 6.90 mmol) and the solution was stirred at room temperature for 1 h. This solution was mixed at once and stirred vigorously with a solution of CDVB (0.68 g, 2.30 mmol) in chloroform (10 ml). Stirring at room temperature was continued for 5 min. The yellow



Scheme 1

solid precipitate was filtered off, washed with water, then with methanol and dried to afford **1**.

The reaction yields, the inherent viscosities and the elemental analysis for all polymers thus prepared are listed in Table 1.

RESULTS AND DISCUSSION

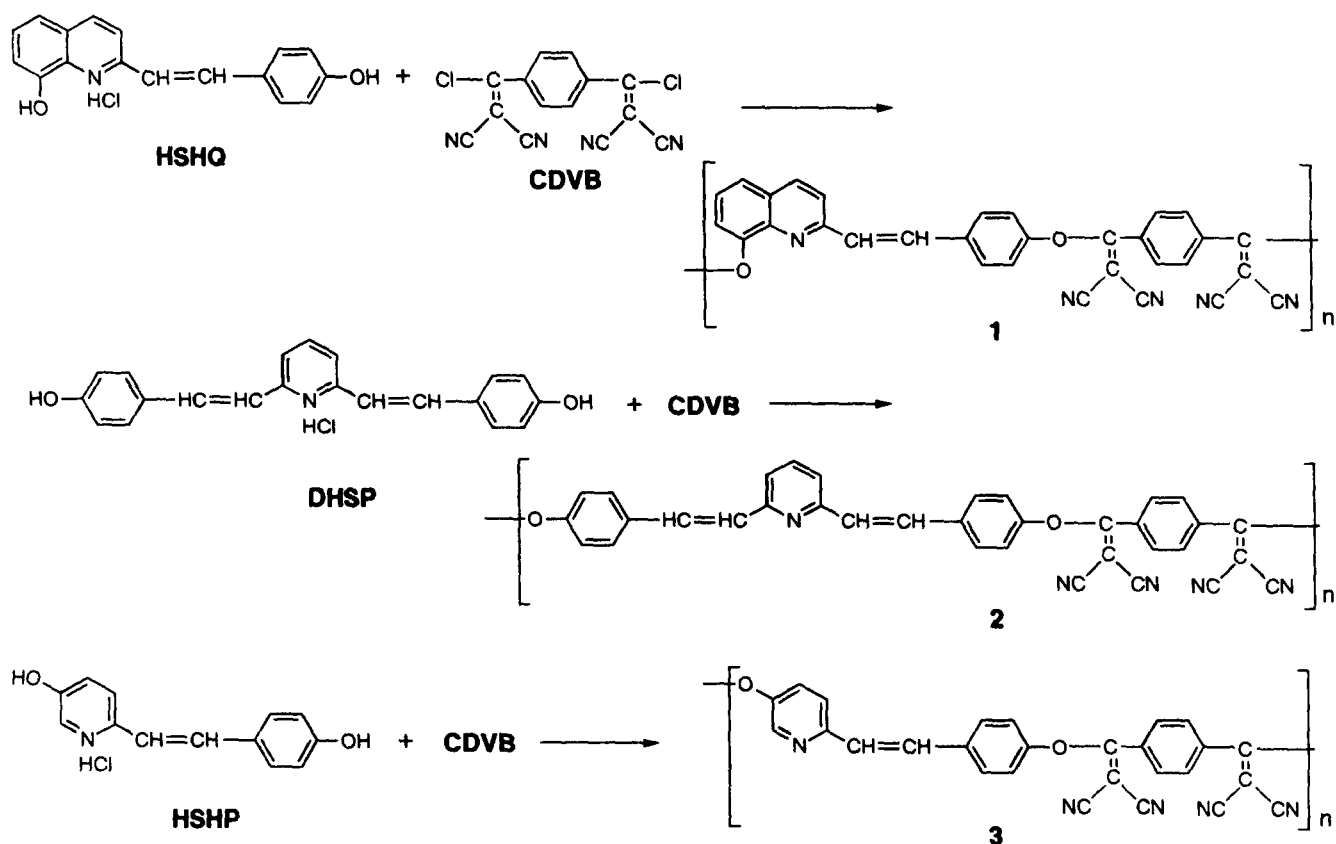
A new class of poly(enaryloxynitrile)s bearing styrylpyridine segments were prepared. Three bisphenols containing styrylpyridine units were used as starting materials. Scheme 1 presents the synthesis of HSHQ. The synthesis and characterization of the other two bisphenols DHSP and HSHP have been reported^{23,24}. The monomers were characterized by i.r. and ¹H n.m.r. spectroscopy and elemental analyses.

Scheme 2 outlines the polymerization reactions. They were carried out utilizing interfacial polymerization techniques. Poly(enaryloxynitrile)s **1**, **2** and **3** were synthesized from the polycondensation of CDVB with HSHQ, DHSP or HSHP, respectively. The polymers precipitated soon after the reagent mixing and were obtained in nearly quantitative yields. Their inherent viscosities ranged from 0.22 to 0.27 dl g⁻¹. It is well known that in most cases, poly(enaryloxynitrile)s obtained by interfacial polymerization display a relatively low degree of polymerization^{8,9}.

The FT i.r. spectrum of polymer **1** (Figure 1) showed characteristic absorptions at 2230 (C≡N); 1622 (olefinic bond and aromatic); 1576, 1502 (aromatic); 1232, 1170 (ether bond) and 970 (*trans* olefinic bond).

As the polymers were soluble in polar aprotic solvents, their n.m.r. spectra were recorded. The ¹H n.m.r. spectrum of polymer **2** in DMSO-*d*₆ solution showed multiplets in the range δ 7.87–6.79, assigned to aromatic, olefinic and pyridine protons. Figure 2 presents the ¹³C n.m.r. spectrum of the same polymer. Assignments of peaks are given in the figure. The ¹³C n.m.r. spectrum was less complex than that of ¹H n.m.r. and, therefore, all peaks were assigned.

The crystallinity of the polymers was estimated by the X-ray method (Figure 3). Polymers **1** and **2** were



Scheme 2

Table 1 Reaction yields, inherent viscosities and elemental analysis of polymers

Polymer	Yield (%)	η_{inh}^a (dl g ⁻¹)	Empirical formula	Elemental analyses (%)			
				C	H	N	
1	91	0.27	(C ₃₁ H ₁₅ N ₅ O ₂) _n	Calcd	76.07	3.09	14.31
				Found	75.34	2.92	14.15
2	97	0.26	(C ₃₅ H ₁₉ N ₅ O ₂) _n	Calcd	77.62	3.54	12.93
				Found	76.78	3.67	12.71
3	93	0.22	(C ₂₇ H ₁₃ N ₅ O ₂) _n	Calcd	71.46	3.25	17.36
				Found	70.53	3.03	16.98

^a Inherent viscosity in DMAc (0.5 g dl⁻¹) at 30°C

generally amorphous whereas polymer **3** was crystalline and showed peaks at 26.97, 31.22 and 44.70°. The higher crystallinity of polymer **3** was attributed to the *p*-substitution of all benzene and pyridine rings, which can lead to better packing of the chains.

Figure 4 presents the optimized geometry for one repeat unit of typical polymer **3** as calculated by means of CSC ChemDraw 3D Plus Σ Molecular Modeling System. It is seen that the segment of bisphenol HSHP and that of CDVB are each coplanar and the ether oxygen is a common atom of two planes forming a dihedral angle at 60°.

The solubility behaviour of polymers is shown in Table 2. All polymers were soluble in polar aprotic solvents (DMF, DMSO and NMP), certain inorganic and organic acids (H₂SO₄ and trichloroacetic acid) and cyclohexanone. They dissolved also at room temperature or by heating in *m*-cresol and pyridine. Upon comparing the solubilities of poly(enaryloxynitrile)s in less efficient solvents such as

o-dichlorobenzene and acetonitrile, the relative solubility of these polymers could be assessed. Specifically, polymer **3**, which displayed the most crystalline structure (see above), showed lower solubility than the other polymers in these solvents. Generally, the synthesized polymers exhibited an enhanced solubility in common organic solvents, which could be attributed to the presence of the pendent dicyanovinyl groups. It is notable that a polyester, prepared by the polycondensation of HSHQ with the terephthaloyl chloride showed poor solubility in organic solvents, but was soluble in hot, polar, aprotic solvents containing 5 wt% LiCl²⁶.

The glass transition (T_g) and the softening (T_s) temperatures were determined by the t.m.a. method utilizing a suitably loaded penetration probe (Figure 5). The T_g and T_s values were obtained from the onset temperatures of these transitions. Both polymers **1** and **2** showed both T_g and T_s transitions, whilst polymer **3** only displayed a T_g transition. Specifically, polymers **1** and **2**

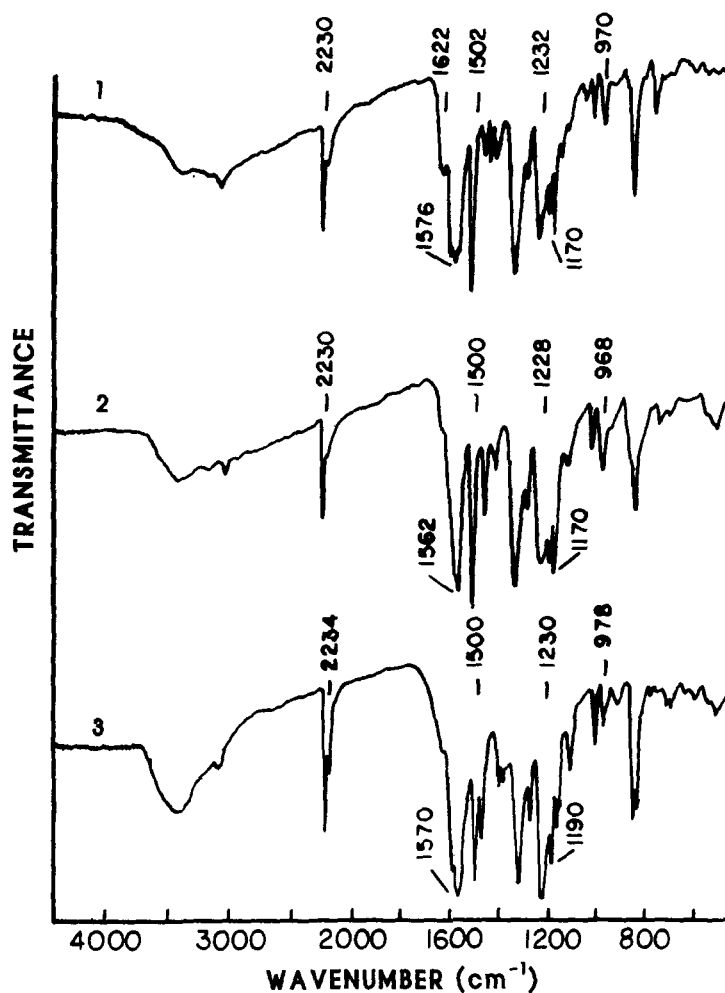


Figure 1 FT i.r. spectra of polymers 1-3

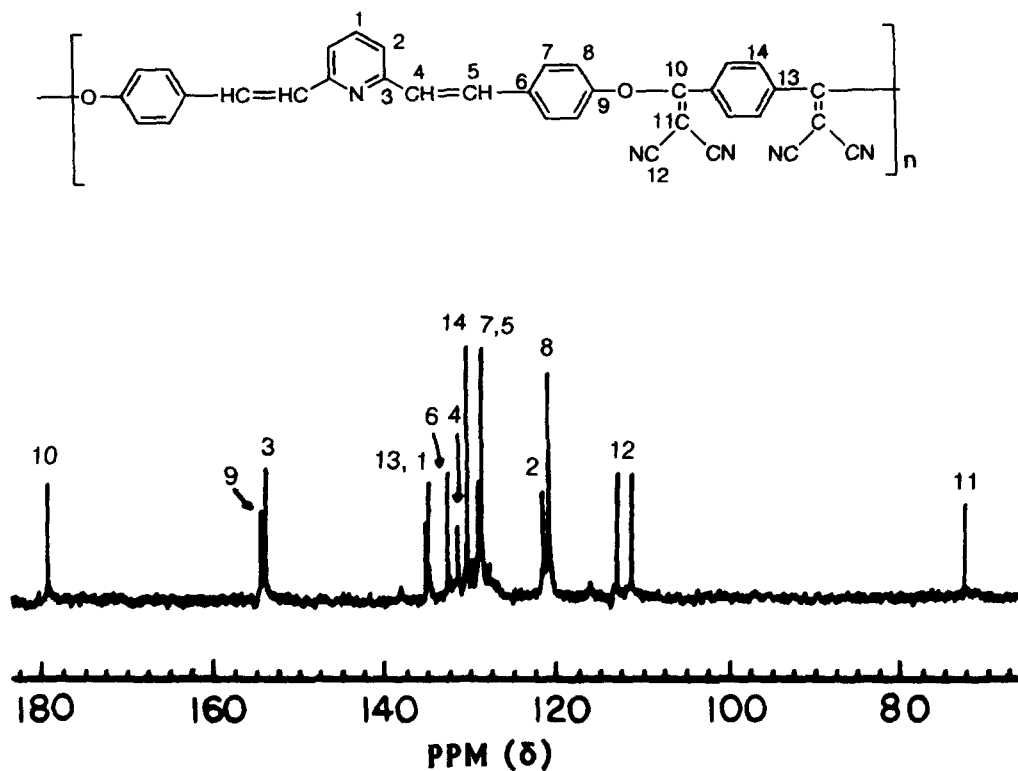


Figure 2 ^{13}C n.m.r. spectrum of polymer 2 in $\text{DMSO}-d_6$ solution at room temperature

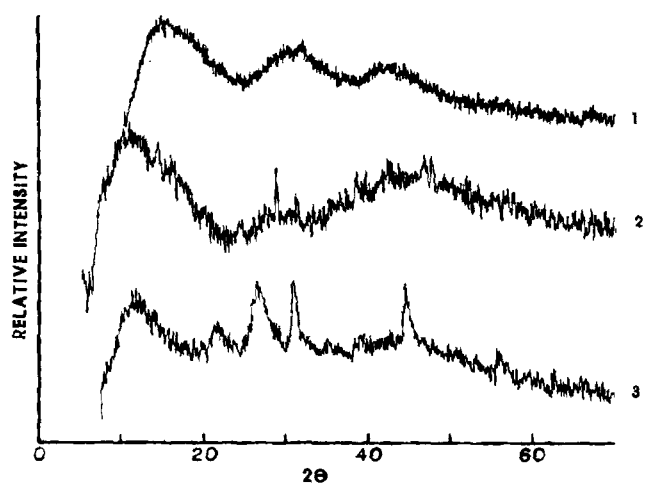


Figure 3 X-ray diffraction patterns of polymers 1-3

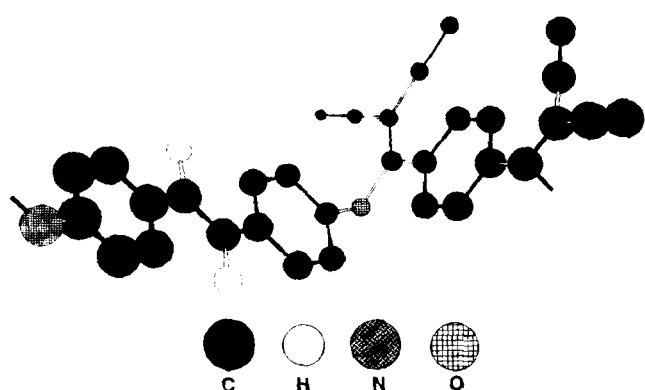


Figure 4 Optimized geometry for one repeat unit of polymer 3 (CSC ChemDraw 3D PlusΣ Molecular Modeling System, version 3.1.1, 1993; Cambridge Scientific Computing). (The hydrogens of aromatic and pyridine rings are omitted for clarity)

displayed T_g at 200 and 210°C as well as T_s at 235 and 247°C, respectively. Polymer 3 showed only T_g at 270°C. Thus, a higher value of T_g for the more crystalline polymer 3 was observed.

The d.t.a. traces in N_2 of polymers 1 and 2 displayed a broad exotherm with a maximum around 360°C assigned to the crosslinking reactions through the styrylpyridine olefinic bonds and the dicyanovinyl groups as well as to a partial thermal degradation. When these samples were quenched to room temperature and then resampled, the exotherm disappeared. In contrast, the d.t.a. trace for polymer 3 lacked a distinct exotherm in this temperature region. The absence of an exotherm could be attributed to the higher crystallinity of polymer 3, which therefore has less mobile chains and consequently

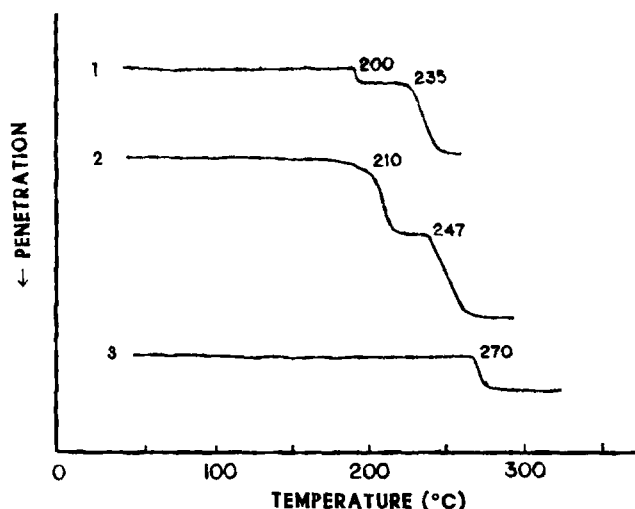


Figure 5 T.m.a. thermograms of polymers 1-3. Conditions: N_2 flow rate $60\text{ cm}^3\text{ min}^{-1}$; heating rate $20^\circ\text{C min}^{-1}$

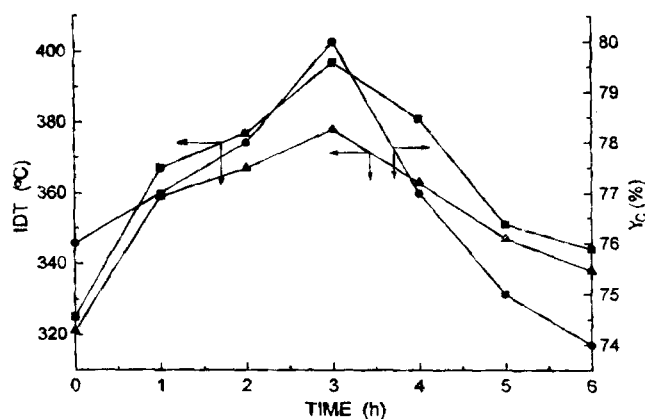


Figure 6 The IDT in N_2 (■) and air (▲) as well as the anaerobic Y_c (●) of cured polymer versus the time of curing at 320°C

it requires higher temperature to cause the crosslinking reactions⁵.

The polymers synthesized were thermally crosslinked through their olefinic bonds and the cyano groups. Figure 6 presents the initial decomposition temperature (IDT) both in N_2 and air as well as the anaerobic char yield (Y_c) at 800°C of the resins obtained from polymer 2 upon heating at 320°C as a function of the curing time. It is seen that these thermal features increased with increasing the curing time up to 3 h and they reduced beyond this value. Therefore, the optimum time for curing at 320°C was 3 h.

Table 2 Solubilities of polymers^a

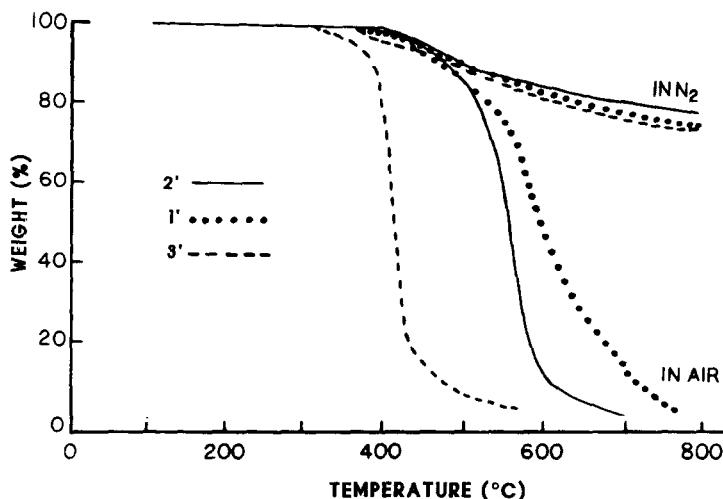
Polymer	Solvents ^b										
	DMF	NMP	DMSO	Trichloroacetic acid	H_2SO_4	<i>m</i> -Cresol	CH	$CHCl_3$	DCB	Acetonitrile	Py
1	++	++	++	++	++	++	++	-	+	+	++
2	+-	++	++	++	++	+	++	-	+	+	++
3	++	++	++	++	++	+	++	-	-	-	+

^a Solubility: ++, soluble at room temperature; +, soluble in hot solvent; -, insoluble

^b DMF, *N,N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethylsulfoxide; CH, cyclohexanone; DCB, *o*-dichlorobenzene; Py, pyridine

Table 3 Thermal stabilities of polymers

Polymer	% Extractable in DMF	In N ₂				In air		
		IDT ^a (°C)	PDT ^b (°C)	PDT _{max} ^c (°C)	Y _c ^d (%)	IDT (°C)	PDT (°C)	PDT _{max} (°C)
1'	5	374	512	460	76	367	474	584
2'	2	397	541	471	80	378	463	562
3'	13	370	530	460	76	329	397	411

^a Initial decomposition temperature^b Polymer decomposition temperature^c Maximum polymer decomposition temperature^d Char yield at 800°C**Figure 7** T.g.a. thermograms in N₂ and air of cured polymers 1'–3'. Conditions: gas flow rate 60 cm³ min⁻¹; heating rate 20°C min⁻¹

The crosslinked polymers obtained from poly(enaryloxynitrile)s **1**, **2** and **3** by curing at 320°C for 3 h are referred to by the designations 1', 2' and 3', respectively. They were dark brown solids insoluble in solvents for the untreated samples.

The extent of crosslinking of cured polymers 1'–3' was evaluated by extraction of them with DMF at 100°C for 30 min. The percentage soluble fraction was calculated as

$$\% \text{ soluble fraction} = \frac{100 \times (a - b)}{a}$$

where *a* is the initial weight of materials and *b* is the weight of insoluble material. The results of the % extractable quantity in DMF for the cured polymers are summarized in Table 3. It is seen that polymers 1' and 2' showed high degree of crosslinking whereas polymer 3' had appreciable amounts of low weight materials. This feature of 3' could be attributed to incomplete crosslinking of the base polymer **3**, since its d.t.a. trace did not display a distinct curing exotherm (see above).

The thermal stability of cured polymers 1'–3' was ascertained by t.g.a. in N₂ and air (Figure 7) as well as isothermal gravimetric analysis (i.g.a.). The IDT, the polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}) both in N₂ and air as well as the anaerobic Y_c at 800°C for all polymers are summarized in Table 3. The IDT and PDT were determined for the temperature at which 0.5 and 10% weight loss was observed, respectively. PDT_{max}

corresponds to the temperature at which the maximum rate of weight loss occurred.

The polymers showed an excellent thermal stability being stable up to the 370–397°C in N₂ and 329–378°C in air and affording anaerobic Y_c of 76–80% at 800°C. Polymer 3' was the less thermally stable, because it showed the lowest IDT and Y_c values. This behaviour conforms with the relatively low degree of crosslinking evaluated by extraction with DMF. The i.g.a. results were in agreement with the t.g.a. data. Specifically, after 20 h isothermal ageing at 300°C in static air, the cured polymers 1', 2' and 3' suffered weight losses of 23.3, 21.3 and 40.0%, respectively.

CONCLUSIONS

Three structurally different poly(enaryloxynitrile)s containing styrylpyridine segments were successfully synthesized from the reactions of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene with various bisphenols. The polymer **3** prepared from bisphenol HSHP was crystalline whereas the other polymers were generally amorphous. All polymers were readily soluble in polar aprotic solvents, certain inorganic and organic acids and cyclohexanone. The polymers **1** and **2** had *T_g* at 200 and 210°C as well as *T_s* at 235 and 247°C, respectively. Polymer **3** showed only *T_g* at 270°C. The d.t.a. thermograms of polymers **1** and **2** displayed crosslinking exotherms around 360°C whereas polymer **1** lacked a distinct exotherm. The crosslinked polymers obtained upon heating at 320°C

for 3 h were stable up to 370–397°C in N₂ and afforded anaerobic char yields of 76–80% at 800°C. The extent of crosslinking of cured polymers was estimated by extraction with DMF. Polymers 1' and 2' showed a higher degree of crosslinking than polymer 3'.

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