PREPARATION, PROPERTIES AND CROSSLINKING OF CYANO-SUBSTITUTED POLYESTER, POLYURETHANES AND EPOXY RESIN DERIVED FROM 1-(2,2-DICYANOVINYL)-3,4-DIHYDROXYBENZENE

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Abstract—1-(2,2-Dicyanovinyl)-3,4-dihydroxybenzene was synthesized from the condensation of 3,4-dihydroxybenzaldehyde with malononitrile and used as a starting material for the preparation of a novel class of cyano-substituted polyesters, polyurethanes and epoxy resins. In addition, model compounds were synthesized and their spectroscopic data were correlated with those of the corresponding polymers. The polyester showed an enhanced solubility in common organic solvents and higher thermal stability after heat-curing compared with the reference polyester synthesized from 1,2-dihydroxybenzene. The cross-linked polymers obtained from polyester and polyurethanes upon curing at 300°C for 20 hr were stable up to 385–400°C in N_2 or air and afforded anaerobic char yields of 64–68% at 800°C. The synthesized epoxide was polymerized in the presence of 4,4'-diaminodiphenylsulfone.

INTRODUCTION

It is generally admitted that cyano-substituted monomers and polymers can be crosslinked yielding heat-resistant structures. However, the products obtained are insoluble in common organic solvents and therefore the investigation of their structure is difficult.

Recently, certain unsaturated polyesters, polyurethanes and epoxy resins containing styrylpyridine segments derived from 2,6-di(4-hydroxystyryl)pyridine [1], 2,2'-(1,4-phenylenedivinylene)bis-5-hydroxypyridine [2], 2,2'-(1,4-phenylenedivinylene)bis-8-hydroxyquinaldine [3], and 6-(4-hydroxystyryl)-3-hydroxypyridine [3] have been prepared and crosslinked in our laboratory. Unsaturated cyano-substituted polyester, polyurethanes and epoxy resins obtained from 2,6-bis(4-hydroxybenzylidene)-1-dicyanomethylene-cyclohexane have been also synthesized [4]. Kawatsuki *et al.* [5] have reported the synthesis and characterization of aromatic polyesters derived from 1-(2,2-dicyanovinyl)-3,4-dihydroxybenzene (DDB) and 1-(2,2-dicyanovinyl)-3,4-dihydroxy-5-methoxybenzene. However, crosslinking of these polyesters has not been performed. In addition, polyurethanes and epoxy resins obtained from DDB have not been prepared.

The present investigation deals with the synthesis and characterization of a new series of polyesters, polyurethanes and epoxy resins bearing pendant 2,2-dicyanovinyl groups. They were derived from DDB which was synthesized from a very simple reaction utilizing inexpensive starting materials. The synthesized polymers are expected to present an enhanced solubility in common organic solvents due to the presence of the bulky pendant groups. In addition, they are crosslinked through their cyano groups as well as the olefinic bonds upon heat-curing without the evolution of volatile by-products to afford heat-resistant resins which could be used as matrix resins for composites.

EXPERIMENTAL

Characterization methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. FTIR spectra were recorded on a Perkin–Elmer 16PC FT-IR spectrometer with KBr pellets. ^{1}H-NMR spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. TGA measurements were performed on a DuPont 990 thermal analyser system and dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 ml in *N,N*-dimethylformamide (DMF) at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett–Packard model 185 analyser. The wide X-ray diffractions were obtained for powder specimens on a X-ray PW-1840 Philips diffractometer. The epoxy equivalent weight (EEW) of epoxide was determined by the pyridinium chloride-pyridine method [6] and was expressed in g/mol of epoxy groups.

Reagents and solvents

3,4-Dihydroxybenzaldehyde was recrystallized from toluene. Terephthaloyl dichloride and 4,4'-diaminodiphenylsulfone (DDS) were recrystallized from *n*-hexane and methanol

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respectively. Tolylene diisocyanate, a mixture of the 2,4 and 2,6 isomers of 65 and 35%, respectively, methylenebis(4-phenylisocyanate), benzoyl chloride and phenyl isocyanate were distilled under reduced pressure. Acetonitrile was purified by distillation. Malononitrile, triethylamine and epichlorohydrin were used as supplied.

Preparation of starting material

1-(2,2-Dicyanovinyl)-3,4-dihydroxybenzene (DDB) (Scheme 1). A mixture of 3,4-dihydroxybenzaldehyde (9.0000 g, 65.16 mmol), malononitrile (8.6089 g, 130.32 mmol), acetonitrile (50 ml), glacial acetic acid (8 ml) and a catalytic amount of piperidine was refluxed for 20 hr. It was subsequently concentrated under reduced pressure to remove about 30 ml of the solvent and volatile components and the residue was poured into water. The yellow solid precipitated was filtered off, washed with water and dried to afford DDB (8.89 g, yield 74%). A purified sample with m.p. 220–222°C (lit [7] 221°C) was obtained by recrystallization from water.

Anal: Calculated for $C_{10}H_6N_2O_2$: C, 64.50%;
    H, 3.25%; N, 15.04%.
Found: C, 63.92%; H, 3.24%; N, 14.86%.

Infra-red (KBr) cm^{-1}: 3455, 3288 (O—H stretching); 2230 (C≡N stretching); 1617 (olefinic bond); 1602, 1570, 1528 (aromatic); 1408 (O—H deformation); 1314 (C—OH stretching).
    ^{1}H-NMR (DMSO-d$_6$) δ:8.06 (s, 2H, OH); 7.46–6.77 (m, 3H, aromatic and 1H, olefinic).

Preparation of model compounds (Scheme 1)

Model diester (DE). Triethylamine (1.3034 g, 12.88 mmol) was added to a solution of DDB (1.2000 g, 6.44 mmol) in acetonitrile (10 ml). Benzoyl chloride (1.8110 g, 12.88 mmol) diluted with acetonitrile (5 ml) was added dropwise to the stirred solution at 0°C under N$_2$. Stirring of the mixture was continued at ambient temperature in a stream of N$_2$ for 3 hr. It was subsequently poured into water and the brown solid precipitated was filtered off washed with water and dried to afford DE (2.38 g, yield 93%). It was recrystallized from a

mixture of acetone/water (vol. ratio 1:2) and had m.p. 60–62°C.

Anal: Calculated for $C_{24}H_{14}N_2O_4$: C, 73.08%;
    H, 3.58%; N, 7.11%.
Found: C, 72.54%; H, 3.57%; N, 6.89%.

Infra-red (KBr) cm^{-1}: 2230 (C≡N); 1748 (C=O); 1602 (olefinic bond); 1565, 1507 (aromatic); 1251, 1065 (C—O—C stretching).
    ^{1}H-NMR (DMSO-d$_6$) δ:8.00–7.86 (m, 4H, aromatic ortho to C=O); 7.56–6.93 (m, 9H, other aromatic and 1H olefinic).

Model diurethane (DU). A mixture of DDB (1.0000 g, 5.36 mmol), phenyl isocyanate (1.2792 g, 10.72 mmol) and acetonitrile (15 ml) was refluxed for 3 hr under N$_2$. It was subsequently concentrated under reduced pressure to remove about 10 ml of the solvent and the residue was poured into water. The yellow solid precipitated was filtered off, washed with water and dried to afford DU (2.04 g, yield 90%). A purified sample obtained by recrystallization from a mixture of acetone/water (vol. ratio 1:1) had m.p. 91–94°C.

Anal: Calculated for $C_{24}H_{16}N_4O_4$: C, 67.91%;
   H, 3.80%; N, 13.21%.
Found: C, 67.39%; H, 3.81%; N, 13.01%.

Infra-red (KBr) cm^{-1}: 3319 (N—H stretching); 2230 (C≡N); 1727 (C=O); 1654 (olefinic bond); 1602, 1507 (aromatic); 1554 (N—H deformation); 1240 (C—O stretching).
    ^{1}H-NMR (DMSO-d$_6$) δ:8.60 (b, 2H, OCONH); 8.10 (b, 4H, aromatic ortho to NH); 7.53–6.96 (m, 9H, other aromatic and 1H olefinic).

Preparation of polymers (Scheme 2)

Polyester 1. DDB (1.6000 g, 8.59 mmol) was dissolved in acetonitrile (15 ml) and triethylamine (1.7364 g, 17.18 mmol) was added to the solution. Terephthaloyl dichloride (1.7448 g, 8.60 mmol) dissolved in acetonitrile (5 ml) was added to the stirred solution at 0°C under N$_2$. Stirring of the mixture at ambient temperature was continued for 3 hr in a stream of N$_2$. It was subsequently poured into water and the brown solid obtained was filtered off,
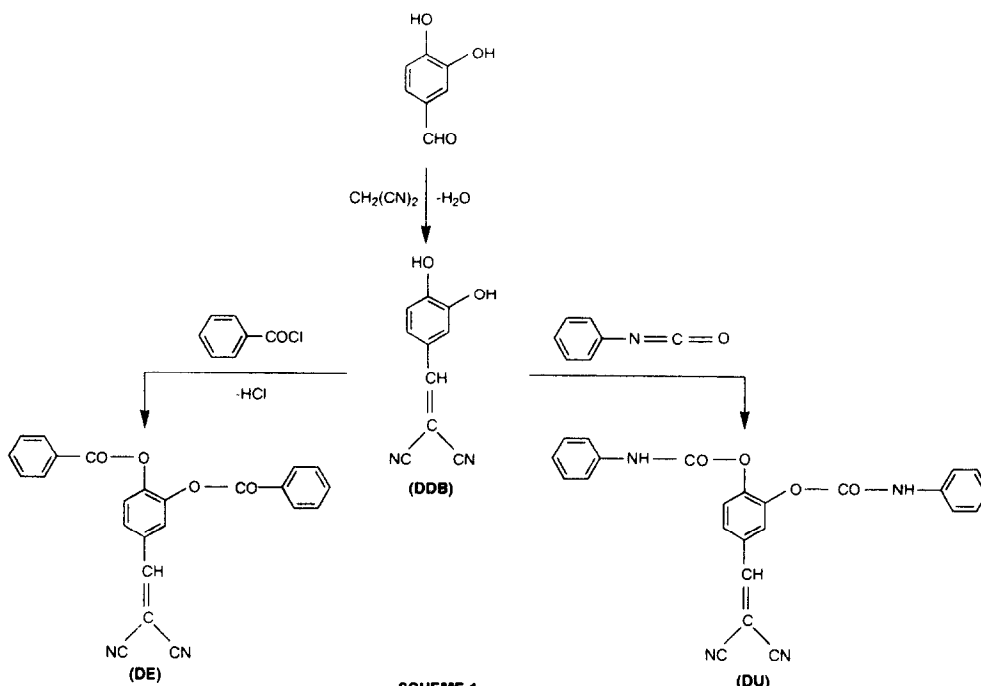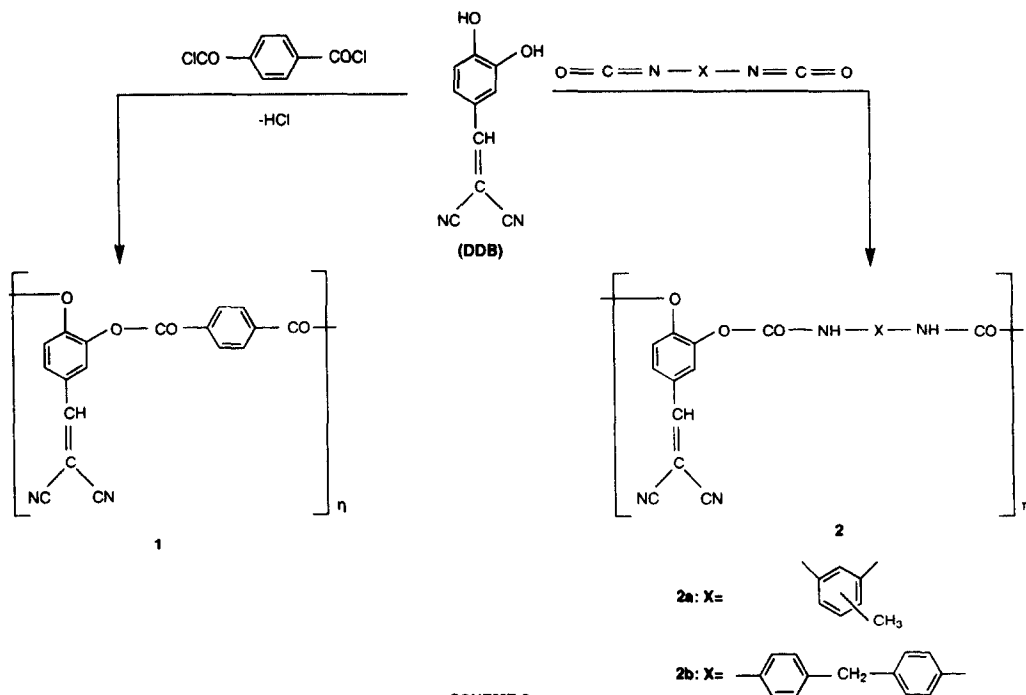
SCHEME 1

SCHEME 2

washed with water and dried to afford polyester 1 (2.52 g, yield 93%).

Polyurethane 2a and 2b. A mixture of tolylene diisocyanate (0.9334 g, 5.36 mmol), DDB (1.0000 g, 5.36 mmol) and acetonitrile (10 ml) was refluxed for 3 hr under N_2. It was subsequently concentrated under reduced pressure to remove about the half amount of the solvent and polyurethane 2a was isolated as a yellow solid by pouring the residue into water, filtering, washing with water and drying (1.76 g, yield 91%).

Polyurethane 2b was similarly prepared as a yellow solid in 91% yield (2.12 g) by reacting DDB (1.0000 g, 5.36 mmol) with methylenebis(4-phenylisocyanate) (1.3414 g, 5.36 mmol).

Curing of polyester and polyurethanes

The isolated polyester 1 as well as polyurethanes 2a and 2b were placed separately in an aluminium dish and curing was accomplished by heating in an oven at 300°C for 20 hr.

Preparation and curing of epoxy compound EC (Scheme 3)

A mixture of DDB (1.0000 g, 5.37 mmol), excess epichlorohydrin (10 ml) and a catalytic amount of benzyltrimethylammonium bromide was refluxed for 1 hr. The suspended solid was gradually dissolved during this period. The solution was subsequently stirred with dilute NaOH at 70°C for 2 hr. The organic layer was separated and washed with water. Excess epichlorohydrin and volatile components were subsequently removed by distillation under reduced pressure. The residue was dried to yield epoxy compound EC as a brown solid (1.53 g, yield 96%, m.p. 105–110°C).

EC (1.2000 g, 4.02 mmol) together with 4,4′-diaminodiphenylsulfone (DDS) (0.4992 g, 2.01 mmol) were placed in an aluminium dish and heated on a heating plate. The reactants were melted and mixed thoroughly to obtain a homogeneous mixture. The dish was subsequently placed into an oven and curing was accomplished by heating at 300°C for 20 hr.

RESULTS AND DISCUSSION

1-(2,2-Dicyanovinyl)-3,4-dihydroxybenzene (DDB) was used as starting material for the preparation of a novel class of polyesters, polyurethanes and epoxy resins. Scheme 1 presents the synthesis of DDB. More particularly, the condensation of 3,4-dihydroxybenzaldehyde with excess malononitrile in the presence of glacial acetic acid and a catalytic amount of piperidine afforded DDB. Acetonitrile was used as solvent and the water produced was removed by distillation from the reaction mixture.

Scheme 1 also presents the preparation of two model compounds which were synthesized to obtain fundamental information about the structure of polymers. Specifically, DDB reacted with a double molar amount of benzoyl chloride and phenyl isocyanate to yield model diester DE and diurethane DU, respectively.

The preparation of polyester and polyurethanes is outlined in Scheme 2. More particularly, DDB reacted with terephthaloyl dichloride in acetonitrile utilizing triethylamine as acid acceptor to afford polyester 1. Polyurethanes 2a and 2b were prepared from the reactions of DDB with tolylene diisocyanate and methylenebis(4-phenylisocyanate), respectively.

A reference polyester 3 with the following chemical structure
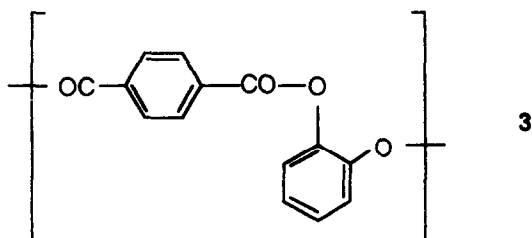
was synthesized for comparative purposes by reacting 1,2-dihydroxybenzene with terephthaloyl dichloride in the presence of triethylamine according to the procedure described for the preparation of polyester **1** (inherent viscosity 0.22 dl/g in DMF).

The starting material as well as the model compounds DE and DU have not been previously synthesized and they were characterized by elemental analyses, FTIR and ^{1}H-NMR spectroscopy (see Experimental). Figure 1 presents the FTIR and ^{1}H-NMR spectra of DDB. It is seen that DDB lacked the
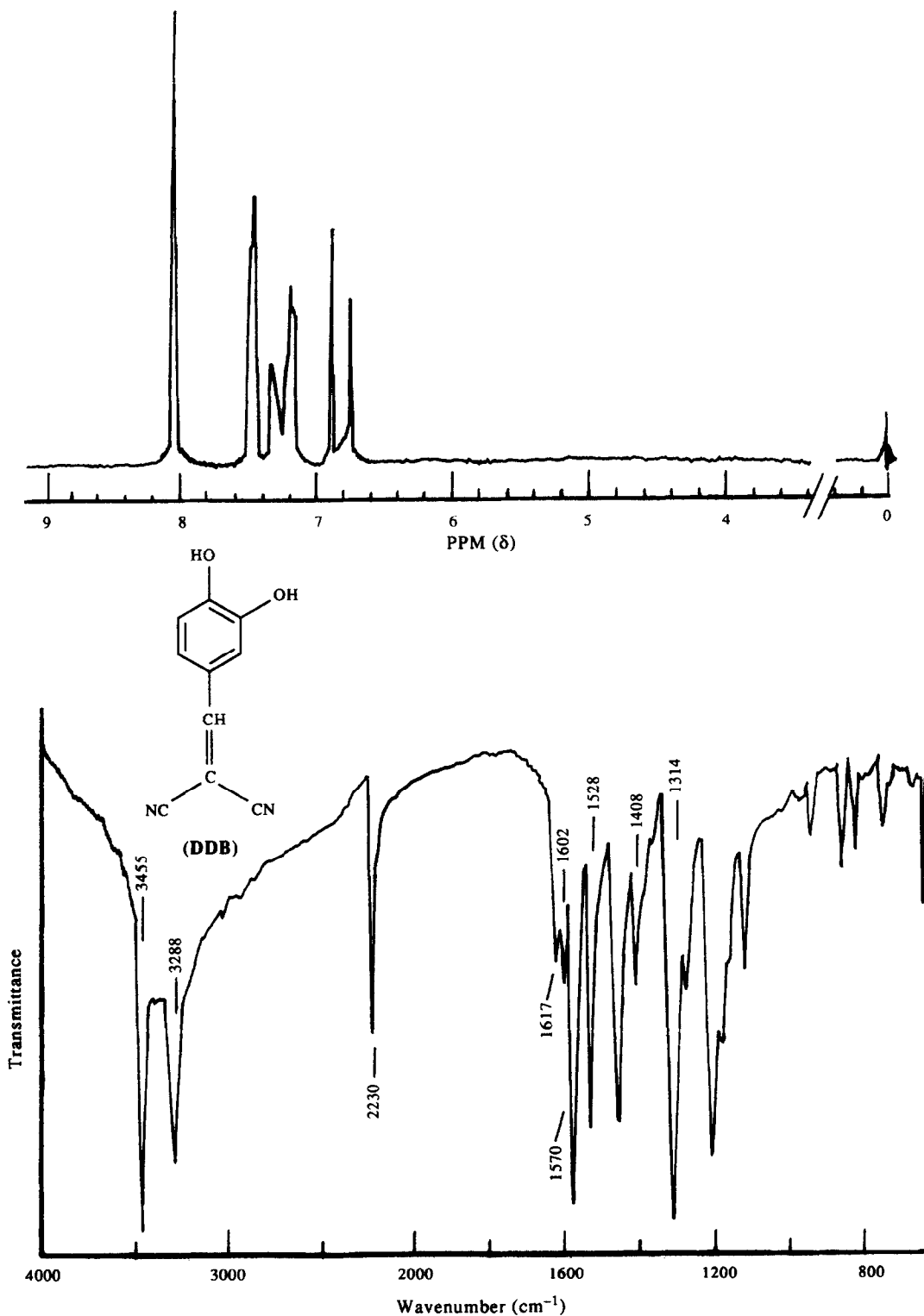
Fig. 1. FTIR and ^{1}H-NMR spectra of DDB.

absorption at 1654 cm^{-1} assigned to the carbonyl of 3,4-dihydroxybenzaldehyde and in addition displayed new absorptions at 2230 and 1617 cm^{-1} associated with the cyano groups and the olefinic bond, respectively. On the other hand, the ^{1}H-NMR spectrum of DDB lacked the singlet at 10.06 δ of the aldehyde proton of the starting material thus supporting that the condensation reaction of 3,4-dihydroxybenzalde-

hyde with malononitrile could be monitored by FTIR and ^{1}H-NMR spectroscopy.

The FTIR spectra of model compounds were in agreement with those of the corresponding polymers (Figs 2 and 3). More particularly, polyester 1 showed characteristic absorptions at 2230 (C≡N), 1743 (C=O), 1612 (olefinic bond), 1570, 1513 (aromatic) and 1251, 1073 cm^{-1} (C—O—C stretching).
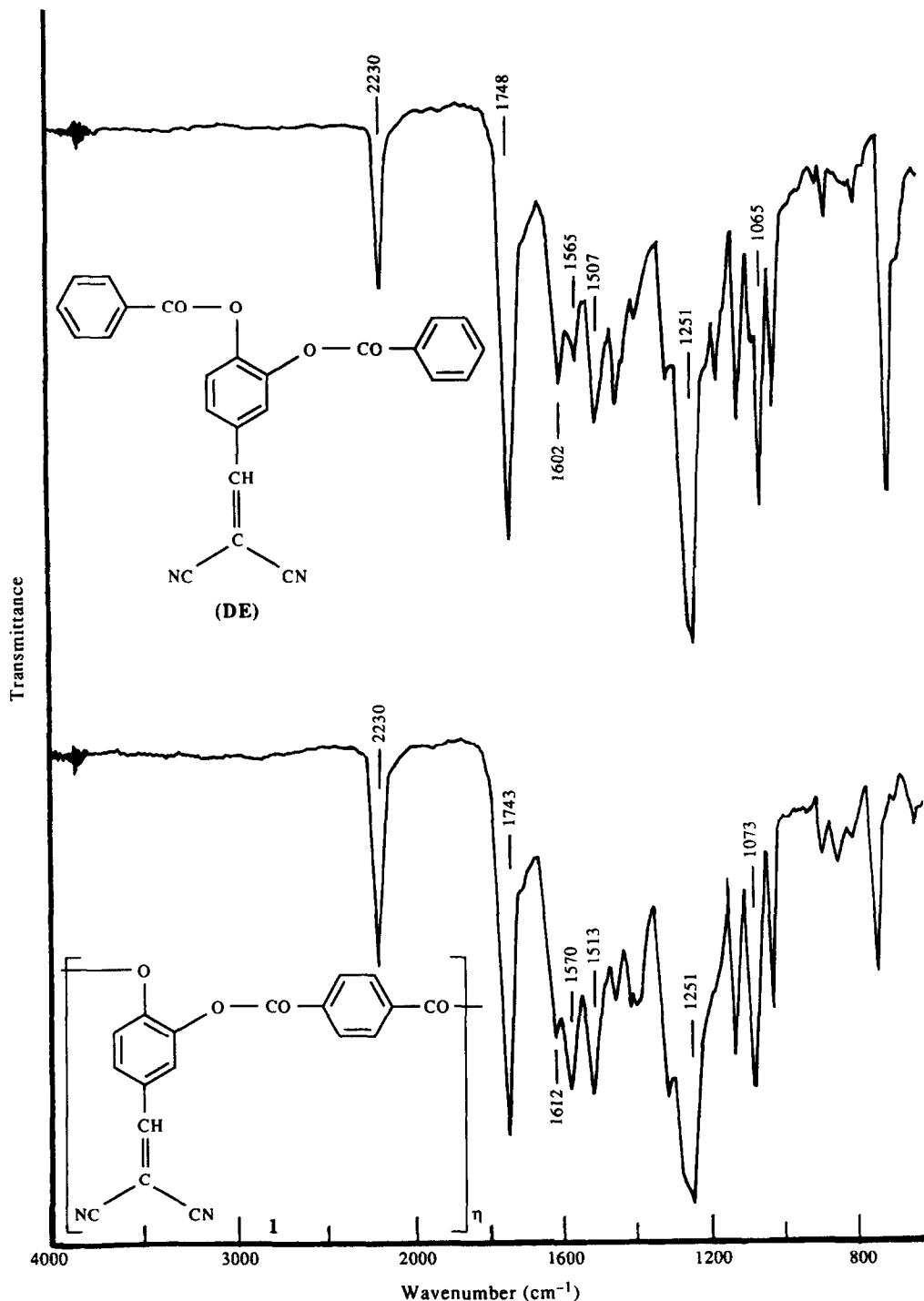

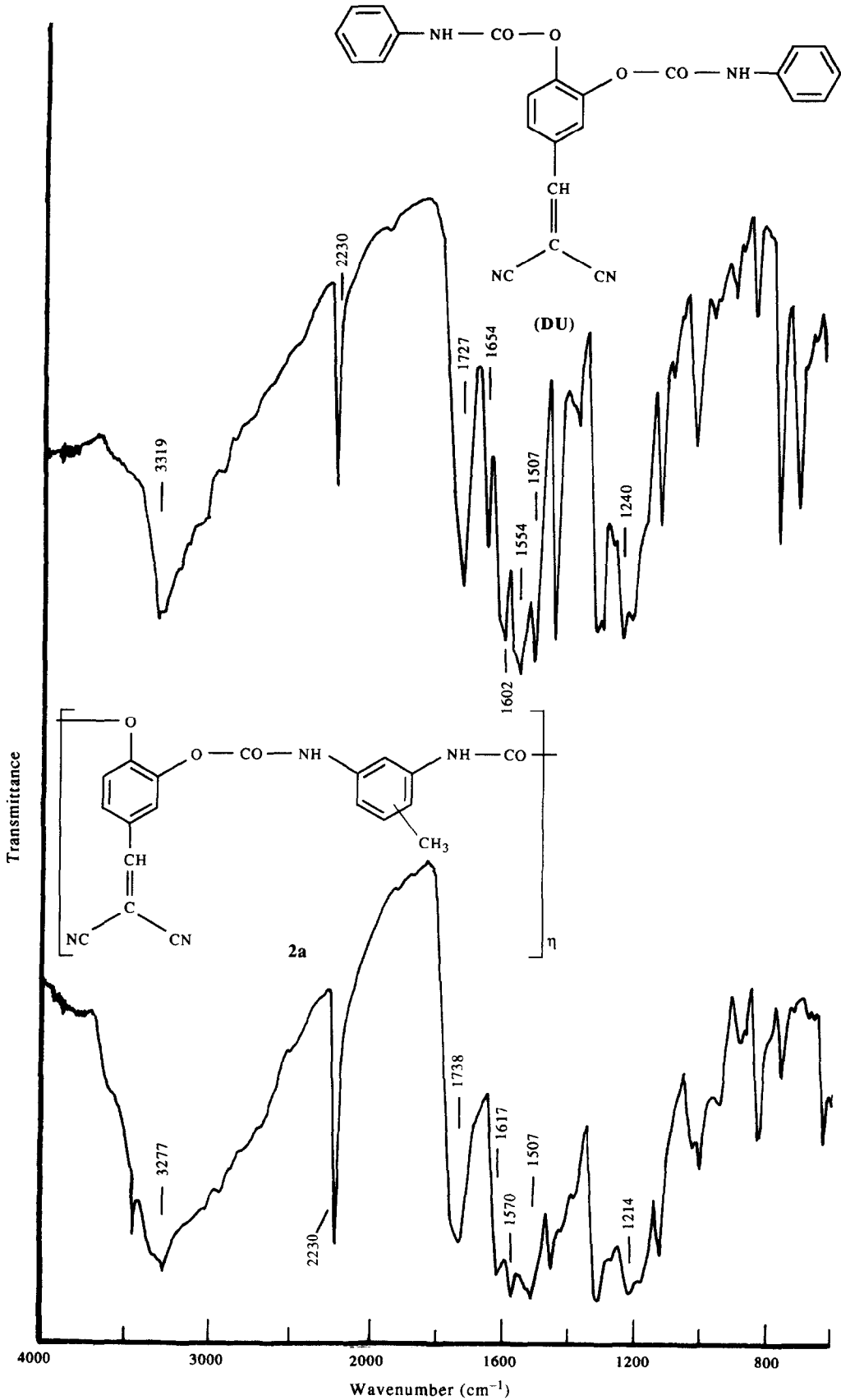Fig. 2. FTIR spectra of model diester DE and polyester 1.

Fig. 3. FTIR spectra of model diurethane DU and polyurethane **2a**.

Polyurethane **2a** displayed absorptions at 3277 (N—H stretching), 2230 (C≡N), 1738 (C=O), 1617 (olefinic bond) 1570 (N—H deformation), 1507 (aromatic) and 1214 cm^{-1} (C—O stretching). Polyurethane **2b** showed also absorption bands in these spectrum regions.

The ^{1}H-NMR spectra of model compounds in DMSO-d$_6$ solution are shown in Fig. 4. Model diester DE displayed peaks at 8.00–7.86 (aromatic ortho to C=O) and 7.56–6.93 δ (other aromatic and olefinic). Model diurethane DU showed peaks at 8.60 (OCONH), 8.10 (aromatic ortho to NH) and 7.53–6.96 δ (other aromatic and olefinic).

Wide X-ray measurements for powder specimens were obtained for the synthesized polymers (Fig. 5). Typical X-ray diffractogram of modified polyester **1** showed some reflections at $2\Theta = 31.6$ and 45.4. Certain sharp peaks were also observed in the diffractogram of reference polyester **3** in the region $2\Theta = 20$–43. These data indicated some degree of crystallinity for the polyesters **1** and **3** whereas polyurethane **2b** showed an amorphous pattern.

Polyester **1** showed an enhanced solubility in common organic solvents compared with reference polyester **3** due to the pendant dicyanovinyl groups which disrupted the chain packing (Table 1).
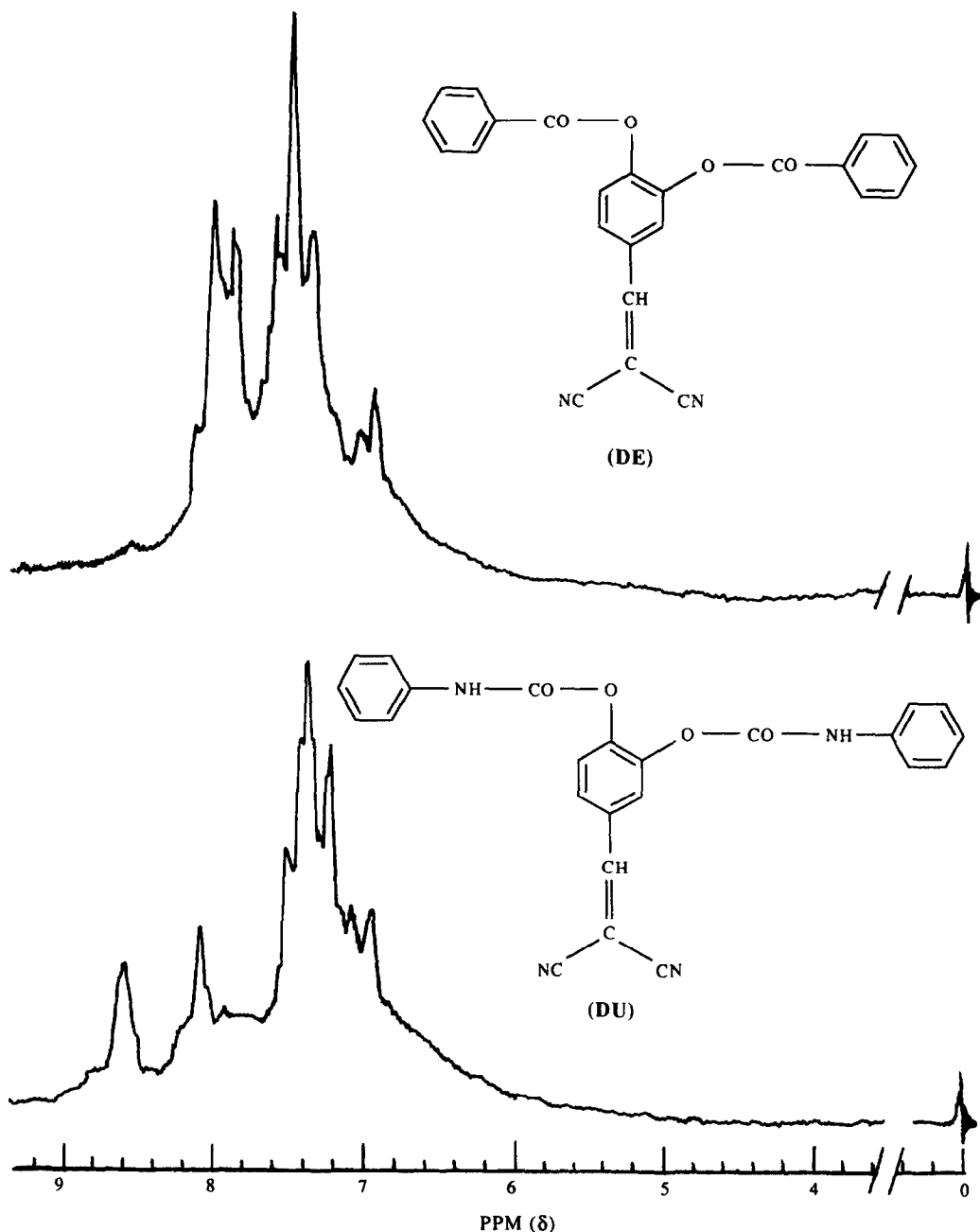

Fig. 4. ^{1}H-NMR spectra in DMSO-d$_6$ solution of model diester DE and model diurethane DU.
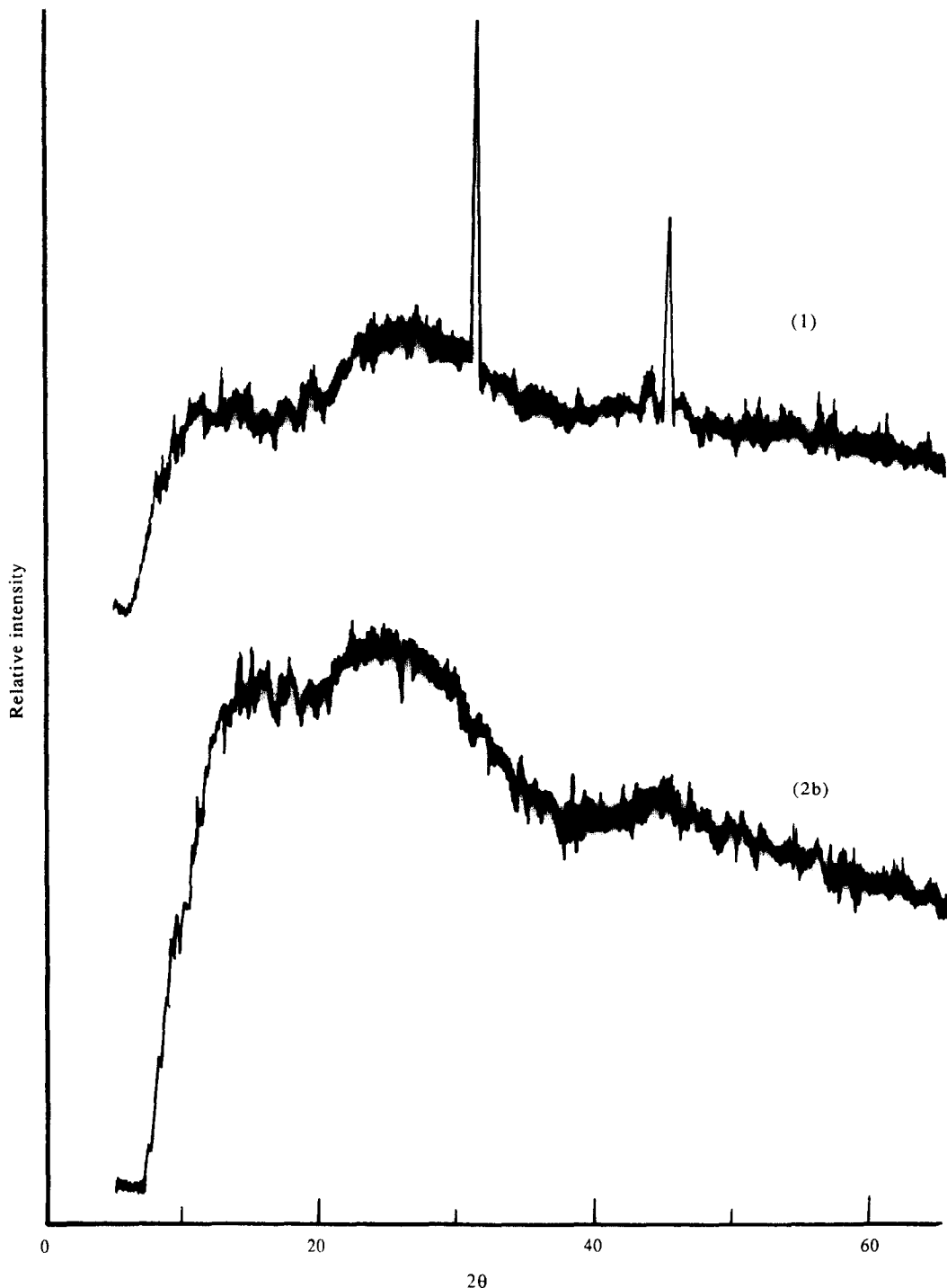
Fig. 5. X-ray diffraction patterns of polyester **1** and polyurethane **2b**.

Specifically, polyester **1** was readily soluble at ambient temperature in N,N-dimethylformamide, N-methylpyrrolidone, dimethylsulfoxide, 1,4-dioxane, m-cresol as well as in certain acids such as H_2SO_4 98% and trichloroacetic acid. In contrast, reference polyester **3** dissolved in these solvents upon heating. In addition, modified polyester **1** was soluble in warm acetonitrile whereas reference polyester **3** was completely insoluble. Polyurethanes

2a and **2b** displayed a slightly lower solubility than polyester **1**.

The modified polymers showed a relatively low degree of polymerization since their inherent viscosities (n_{inh}) ranged from 0.21 to 0.25 dl/g in DMF solution (Table 1).

The synthesized polymers are expected to afford crosslinked resins through their cyano groups as well as the olefinic bonds upon heat-curing at relatively

Table 1. Solubilities of polymers[a]

Sample	η_{inh}[b] (dl/g)	DMF[c]	NMP[d]	DMSO[e]	CH_3CN	1,4-Dioxane	m-Cresol	H_2SO_4 98%	CCl_3COOH
1	0.25	+ +	+ +	+ +	+	+ +	+ +	+ +	+ +
2a	0.21	+	+	+	+ −	+ −	−	+	+ −
2b	0.24	+	+	+	+ −	+ −	−	+	+ −
3	0.22	+	+	+	−	+	+	+	+

[a]Solubility: (+ +) soluble at room temperature; (+) soluble in hot; (+ −) partially soluble or swollen; (−) insoluble.
[b]Inherent viscosity in N,N-dimethylformamide (0.5 g/100 ml) at 30°C.
[c]DMF = N,N-dimethylformamide.
[d]NMP = N-methylpyrrolidone.
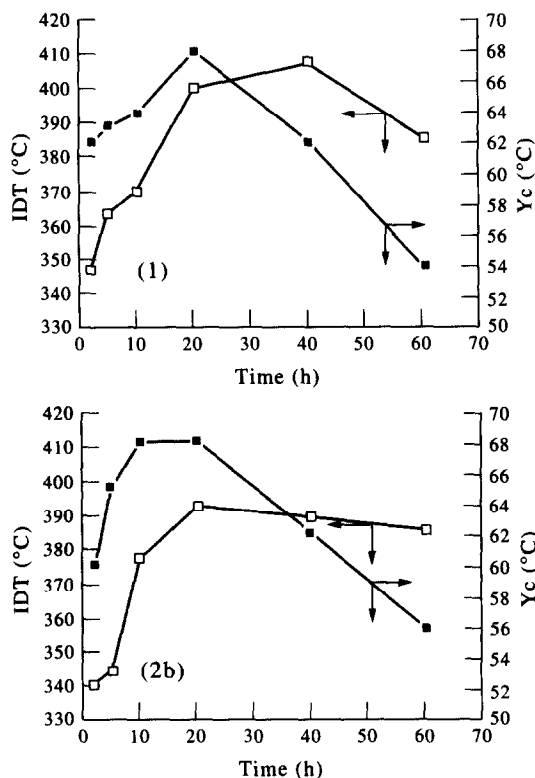[e]DMSO = dimethylsulfoxide.

Fig. 6. IDT and Y_c at 800°C in N_2 of polyester 1 (top) and polyurethane 2b (bottom) as a function of the curing time at 300°C.

high temperatures ($\geqslant 300°C$). To optimize the curing conditions with respect the thermal stability of the resulting resin, polyester 1 and polyurethane 2b were heated at 300°C for various periods and the initial

decomposition temperature (IDT) and the char yield (Y_c) of the obtained resins were determined and correlated with the curing time (Fig. 6). It is seen that both IDT and Y_c were increased with increasing the curing time up to 20 hr and they were decreased beyond this time. The optimum curing time was therefore 20 hr for heat-curing at 300°C.

Evidence for the network structure of the cured resins were obtained from their FTIR spectra which showed a remarkable reduction of the absorption band at 2230 cm^{-1} associated with the cyano groups. In addition, they became completely insoluble in solvents for the untreated samples.

The resins obtained from polymers 1, 2a, 2b, and 3 by curing at 300°C for 20 hr are referred to by the designations 1', 2a', 2b' and 3', respectively. Their thermal stabilities were evaluated by TGA and isothermal gravimetric analysis (IGA). The IDT, the polymer decomposition temperature (PDT) and the maximum polymer decomposition temperature (PDT_{max}) both in N_2 and air as well as the anaerobic Y_c at 800°C for all cured resins are listed in Table 2. The IDT and PDT were determined for a 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. Figure 7 presents the TGA traces in N_2 and air for all modified resins 1', 2a' and 2b' as well as for reference resin 3'.

The relative thermal stability of cured resins could be assessed from their IDT and Y_c values. Modified polyester 1' was remarkably more thermally stable than reference polyester 3' due to the network structure of the former. Thus polyester 1' had IDT and Y_c, 400°C and 68%, respectively, whereas the corresponding values for polyester 3' were 325°C and 48%. In addition, the thermal stabilities of polyurethanes 2a' and 2b' were comparable or slightly lower than

Table 2. Thermal stabilities of cured resins

Sample	N_2				Air		
	IDT[a] (°C)	PDT[b] (°C)	PDT_{max}[c] (°C)	Y_c[d] (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)
1'	400	549	627	68	397	493	589
2a'	392	549	571	68	385	489	571
2b'	400	560	627	64	392	493	560
3'	325	460	498	48	321	444	556
EC'	367	512	516	68	363	482	600

[a]Initial decomposition temperature.
[b]Polymer decomposition temperature.
[c]Maximum polymer decomposition temperature.
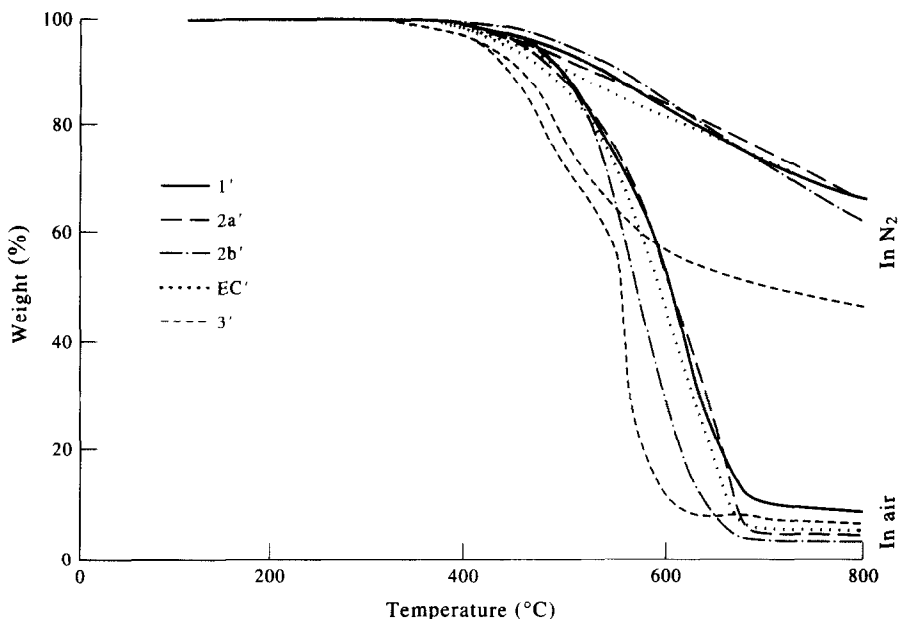[d]Char yield at 800°C.

Fig. 7. TGA thermograms of cured polyesters 1', 3' and polyurethanes 2a', 2b' as well as of EC' in N_2 and air. Conditions: gas flow 60 cm³/min; heating rate 20°C/min.

that of polyester 1'. Generally, the modified resins were stable up to 385–400°C in N_2 or air and afforded anaerobic Y_c of 64–68% at 800°C.

The thermal stabilities of cured resins were furthermore ascertained by IGA. Figure 8 presents the IGA traces in static air of polyester 1' at 320, 340 and 360°C. After 20 hr isothermal aging at these temperatures, 1' showed weight losses of 56.5, 64.6 and 72.5%, respectively. Figure 8 presents also the IGA trace in static air of polyurethane 2a' at 340°C which displayed a weight loss of 75% after 20 hr isothermal aging.

The present investigation included moreover the preparation, characterization and polymerization of diepoxide EC (Scheme 3). It was prepared by reacting DDB with excess epichlorohydrin in the presence of benzyltrimethylammonium bromide as catalyst and subsequent treatment with aqueous NaOH. The product thus obtained consisted of a mixture of monomer and oligomer due to the high reactivity of the epoxy ring.

The FTIR spectrum of EC showed characteristic absorption bands at 1266, 1172 and 965 cm^{-1}
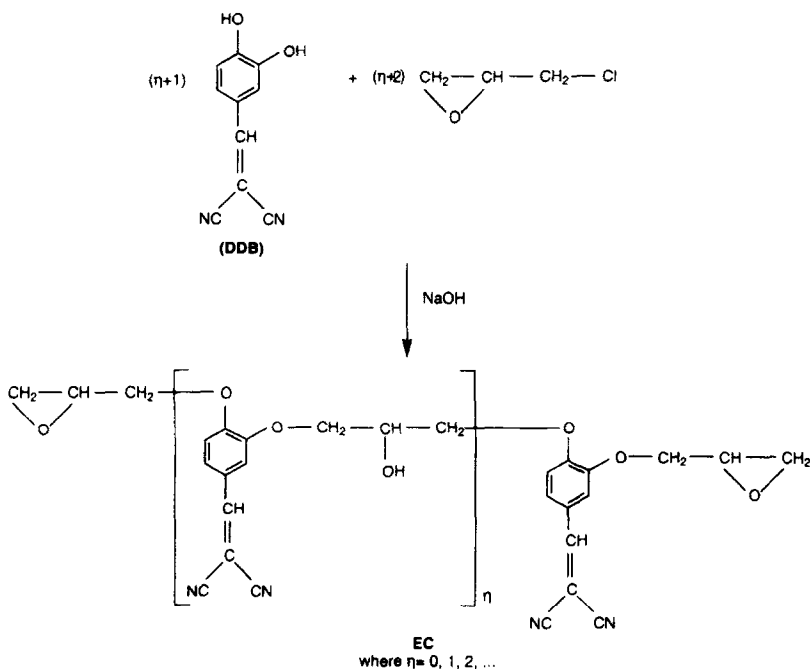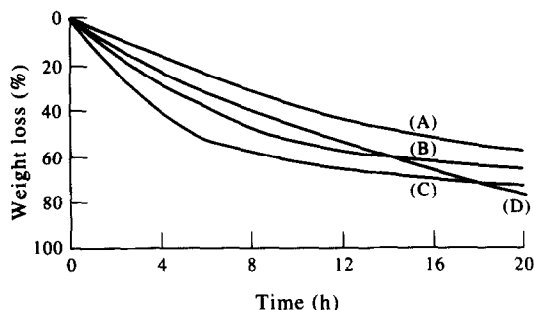

SCHEME 3

Fig. 8. IGA traces in static air of cured polymers, **1′** at 320 (A), 340 (B), and 360°C (C) as well as of **2a′** at 340°C (D).

assigned to epoxy groups. The presence of these groups was furthermore confirmed from the ¹H-NMR spectrum of EC in DMSO-d_6 solution which displayed multiple peaks at 3.81–3.58, 3.32 and 3.02 δ. The epoxy equivalent weight (EEW) was 156.2 whereas the calculated value for EC was 149.1 thus supporting the presence of oligomer in the product. EC was obtained as a brown solid and it dissolved readily in acetone, chloroform, acetonitrile and 1,4-dioxane at room temperature as well as in methanol and ethanol upon heating.

4,4′-Diaminodiphenylsulfone (DDS) was used as curing agent for the polymerization of EC. The molar ratio of EC and DDS was 2:1. They were melted and mixed thoroughly and the homogenous mixture was heated at 300°C for 20 hr to afford resin EC′. Certain TGA data for EC′ are summarized in Table 2. It was stable up to 363–367°C in N_2 or air and afforded anaerobic Y_c of 68% at 800°C.

CONCLUSIONS

(1) 1-(2,2-Dicyanovinyl)-3,4-dihydroxybenzene (DDB) was used as starting material for the preparation of a novel class of cyano-substituted polyesters, polyurethanes and epoxy resins.
(2) The cyano-substituted polymers showed an enhanced solubility in common organic solvents compared with corresponding reference polymers.
(3) The crosslinked polymers obtained upon curing at 300°C for 20 hr were stable up to 385–400°C in N_2 or air and afforded anaerobic char yields of 64–68% at 800°C.
(4) The crosslinked polymers derived from DDB were more heat-resistant than those derived from the reference polymers.

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