Cyano-Substituted Polyester, Polyurethanes, and Epoxy Resin Derived from 2,6-Bis(4-hydroxybenzylidene)-1-dicyanomethylene–Cyclohexane

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SYNOPSIS

The condensation of cyclohexanone with 4-hydroxybenzaldehyde utilizing dry HCl as the catalyst afforded 2,6-bis(4-hydroxybenzylidene)cyclohexanone. The latter was condensed with malononitrile to yield 2,6-bis(4-hydroxybenzylidene)-1-dicyanomethylene–cyclohexane, which was used as the starting material for the preparation of a novel class of polyesters, polyurethanes, and epoxy resins. In addition, a model diester and diurethane were synthesized and their spectroscopic data were correlated with those of the corresponding polymers. It was shown that the introduction of the dicyanomethylene groups in the polymer backbone remarkably improved the polymer solubility as well as its thermal stability. The cross-linked polymers obtained upon curing the polyester and polyurethanes at 300°C for 40 h were stable up to 365–407°C in N_2 or air and afforded anaerobic char yields of 64–70% at 800°C. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Oligomers and polymers with pendant or terminal groups that undergo thermally induced cross-linking or chain-extension reactions without evolving volatile byproducts are good precursors for high-performance polymers and composite matrices.[1] In this way, we recently synthesized various cyano-substituted polymers. More particularly, certain polyamides containing enamino nitrile moieties[2,3] and *N*-cyano-substituted polyamides[4] and polyamides bearing pendant cyano groups derived from 1,4-bis(2-cyano-2-carboxyvinyl)benzene[5] and 1-carboxy-4-(2-cyano-2-carboxyvinyl)benzene[6] as well as some polyamides and polyimides obtained from 2,7-diamino-9-dicyanomethylene–fluorene[7] and 2,6-bis(3-aminobenzylidene)-1-dicyanomethylene–cyclohexane[8] were prepared and cross-linked.

The present investigation deals with the synthesis, characterization, and cross-linking of a new series of cyano-substituted polyesters, polyurethanes, and epoxy resins based on 2,6-bis(4-hydroxybenzylidene)-1-dicyanomethylene–cyclohexane. They are expected to possess an increased solubility in common organic solvents due to the presence of the bulky pendant dicyanomethylene groups. In addition, they yield thermally stable network structures upon heat curing without the evolution of volatile byproducts.

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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 FTIR 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. DTA and TGA were performed on a DuPont 990 thermal analyzer system. DTA measurements were made using a high-temperature (1200°C) cell at a heating rate of 20°C/min in N_2 atmosphere at a flow rate of 60 cm^3/min. 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 or in concentrated H_2SO_4 at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyzer. The wide X-ray diffractions were obtained for powder specimens on an X-ray PW-1840 Phillips diffractometer. The epoxy equivalent weight (EEW) was expressed in g/mol of epoxy groups and determined by the pyridinium chloride–pyridine method.[9]

Reagents and Solvents

4-Hydroxybenzaldehyde, 4,4′-diaminodiphenylsulfone (DDS), and terephthaloyl dichloride were recrystallized from water, methanol, and *n*-hexane, respectively. Cyclohexanone and acetonitrile were purified by distillation. Benzoyl chloride, phenyl isocyanate, and methylenebis(4-phenylisocyanate) were distilled under reduced pressure. Tolylene diisocyanate, a mixture of the 2,4- and 2,6-isomers of 65 and 35%, respectively, was also distilled under reduced pressure. *N,N*-Dimethylformamide (DMF) was dried by distillation under reduced pressure over calcium hydride. Malononitrile, epichlorohydrin, triethylamine, and ethanol 95% were used as supplied.

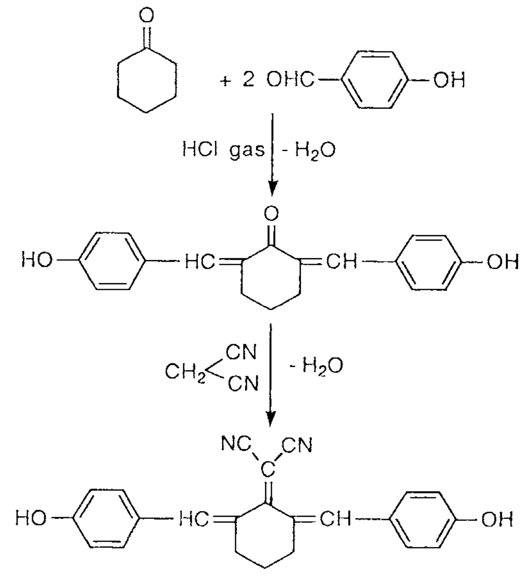
Preparation of Starting Materials (Scheme 1)

2,6-Bis(4-hydroxybenzylidene)cyclohexanone (1)

A flask equipped with a gas trap was charged with a mixture of cyclohexanone (4.0000 g, 40.74 mmol), 4-hydroxybenzaldehyde (9.9503 g, 81.48 mol), and ethanol 95% (50 mL). Dry HCl was bubbled as the catalyst through the stirred solution obtained by heating the mixture approximately at 50°C. The reaction was strongly exothermic and the temperature of the mixture was maintained at about 70°C. A green solid separated after 2 h of stirring, which was filtered off, washed with water, and dried to afford **1** in 86% yield (10.73 g). It was recrystallized from a mixture of DMF/water (vol ratio 1 : 2) and had an mp of 284–286°C (literature value[10,11] 282–288°C).

ANAL: Calcd for $C_{20}H_{18}O_3$: C, 78.39%; H, 5.92%. Found: C, 77.96%; H, 5.94%.

IR (KBr) cm^{-1}: 3256 (O—H stretching); 1654 (C═O); 1596 (C═C); 1513 (aromatic); 1382 (O—H deformation); 1245 (C—OH stretching). ^{1}H-NMR (DMSO-d_6) δ: 9.86 (b, 2H, OH); 7.53–7.43 (m, 2H, olefinic); 7.30–6.70 (m, 8H, aromatic); 2.76 and 1.6 (m, 6H, cyclohexanone).



Scheme 1

2,6-Bis(4-hydroxybenzylidene)-1-dicyanomethylene–Cyclohexane (2)

A mixture of compound **1** (9.0000 g, 29.37 mmol), malononitrile (3.8809 g, 58.74 mmol), acetonitrile (50 mL), glacial acetic acid (8 mL), and a catalytic amount of piperidine was refluxed for 3 h. It was concentrated under reduced pressure to remove about one-half of the solvent and the residue was poured into water. The yellow solid precipitated was filtered off, washed with water, and dried to afford **2** (9.47 g, 91%). A purified sample with an mp 136–140°C was obtained by recrystallization from a mixture of dioxane/water (vol ratio 1 : 4).

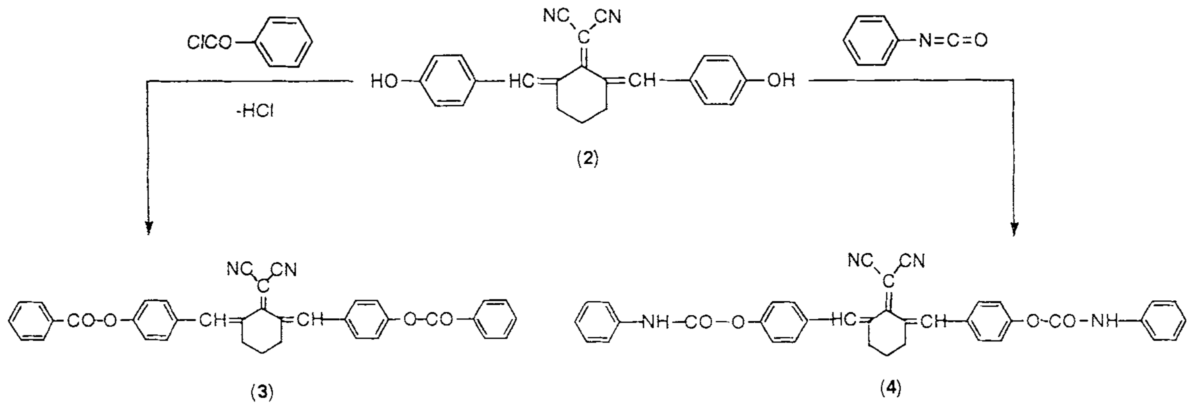
ANAL: Calcd for $C_{23}H_{18}N_2O_2$: C, 77.93%; H, 5.12%; N, 7.90%. Found: C, 77.54%; H, 5.13%, N, 7.74%.

IR (KBr) cm^{-1}: 3340 (O—H stretching); 2178 (C≡N); 1591 (C═C); 1513 (aromatic); 1366 (O—H deformation); 1235 (C—OH stretching). ^{1}H-NMR (DMSO-d_6) δ: 7.56–6.16 (m, 2H olefinic and 8H aromatic); 5.40 (b, 2H, OH); 2.86 and 1.50 (m, 6H, cyclohexane).

Preparation of Model Compounds (Scheme 2)

Model Diester 3

A flask was charged with a mixture of compound **2** (1.0000 g, 2.82 mmol), DMF (10 mL), and trieth-



Scheme 2

ylamine (0.5707 g, 5.64 mmol). Benzoyl chloride (0.7927 g, 5.64 mmol) diluted with DMF (5 mL) was added dropwise to the stirred mixture at 0°C under N_2. Stirring of the mixture was continued at ambient temperature in a stream of N_2 for 3 h. It was subsequently poured into water and the brown solid precipitated was filtered off, washed with water, and dried to afford **3** (1.44 g, 91%). It was recrystallized from a mixture of dioxane/water (vol ratio 1 : 3) and had an mp of 102–105°C.

ANAL: Calcd for $C_{37}H_{26}N_2O_4$: C, 78.98%; H, 4.66%; N, 4.98%. Found: C, 78.59%; H, 4.65%; N, 4.74%.

IR (KBr) cm^{-1}: 2178 (C≡N); 1738 (C=O); 1633–1607 (C=C); 1513 (aromatic); 1266, 1067 (C—O—C stretching). ^{1}H-NMR (DMSO-d_6) δ: 8.20–8.07 (m, 4H, aromatic ortho to COO); 7.73–6.76 (m, 2H olefinic and 14H aromatic); 3.33 and 1.50 (m, 6H, cyclohexane).

Model Diurethane 4

A mixture of compound **2** (1.0000 g, 2.82 mmol), acetone (15 mL), and phenyl isocyanate (0.6717 g, 5.64 mmol) was refluxed for 3 h under N_2. It was subsequently poured into water and the orange solid precipitated was collected by centrifugation, washed with water, and dried to afford **4** (1.50 g, 90%). A purified sample with an mp of 68–70°C was obtained by recrystallization from a mixture of dioxane/water (vol ratio 1 : 4).

ANAL: Calcd for $C_{37}H_{28}N_4O_4$: C, 74.97%; H, 4.76%; N, 9.45%. Found: C, 74.44%; H, 4.78%; N, 9.25%.

IR (KBr) cm^{-1}: 3319 (N—H stretching); 2178 (C≡N); 1654 (C=O); 1596 (C=C); 1560 (N—H deformation); 1497 (aromatic); 1235 (C—O stretching). ^{1}H-NMR (DMSO-d_6) δ: 8.63 (s, 2H, NHOCO); 7.88–6.73 (m, 2H olefinic and 18H aromatic); 2.73–2.63 and 1.46 (m, 6H, cyclohexane).

Preparation of Polymers (Scheme 3)

Polyester 5

Compound **2** (1.0000 g, 2.82 mmol) was dissolved in aqueous NaOH (20 mL) and a catalytic quantity of benzyltetramethylammonium bromide was added. Terephthaloyl dichloride (0.5725 g, 2.82 mmol) dissolved in chloroform (20 mL) was added at ambient temperature to the vigorously stirred solution. A red solid precipitated soon after the reagent mixing. Stirring of the mixture was continued for 1 h and the solid was filtered off, washed with water, and dried to afford polyester **5** (1.28 g, 94%, inherent viscosity 0.21 dL/g in DMF).

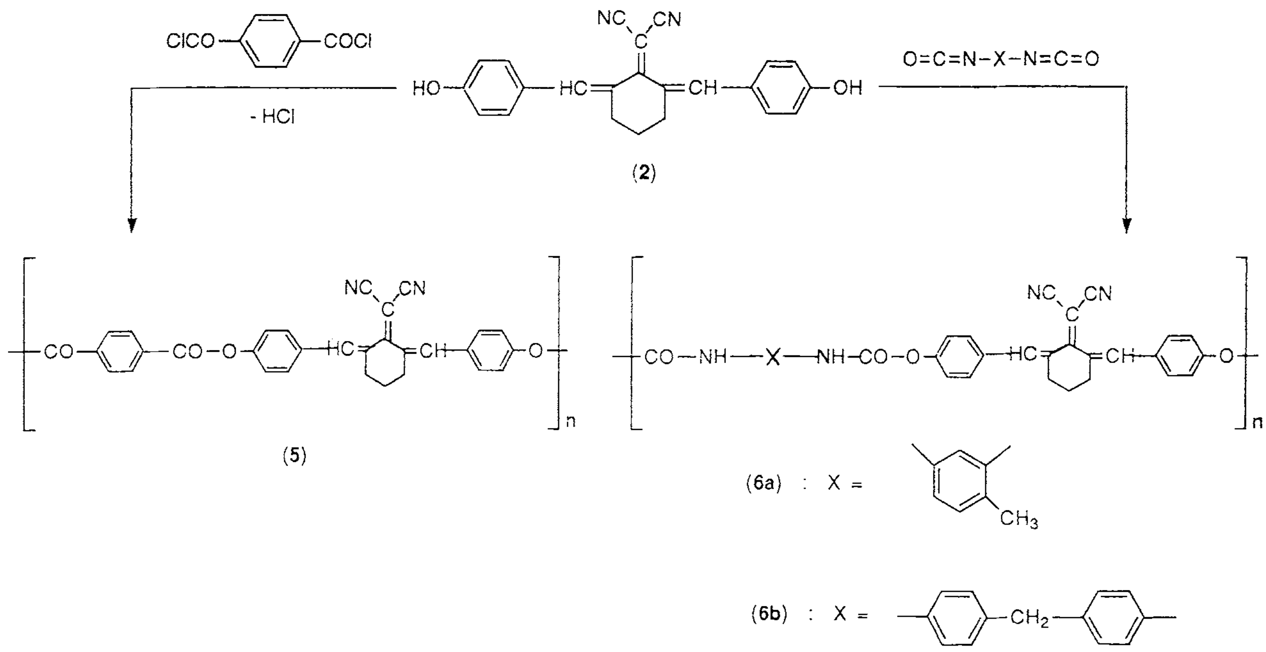
Polyurethanes 6a and 6b

A mixture of compound **2** (1.0000 g, 2.82 mmol), tolylene diisocyanate (0.4911 g, 2.82 mmol), and acetone (15 mL) was refluxed for 3 h under N_2. Polyurethane **6a** was obtained as an orange solid by pouring the mixture into water, centrifugating, washing with water, and drying (1.38 g, 93% inherent viscosity 0.20 dL/g in DMF).

Polyurethane **6b** was similarly prepared as an orange solid in 93% yield (1.58 g, inherent viscosity 0.19 dL/g in DMF) by reacting compound **2** (1.0000 g, 2.82 mmol) with methylenebis(4-phenylisocyanate) (0.7057 g, 2.82 mmol).

Curing of Polyester and Polyurethanes

The isolated polyester **5** as well as polyurethanes **6a** and **6b** were placed in an aluminum dish and curing was accomplished by heating in an oven at 300°C for 40 h.



Scheme 3

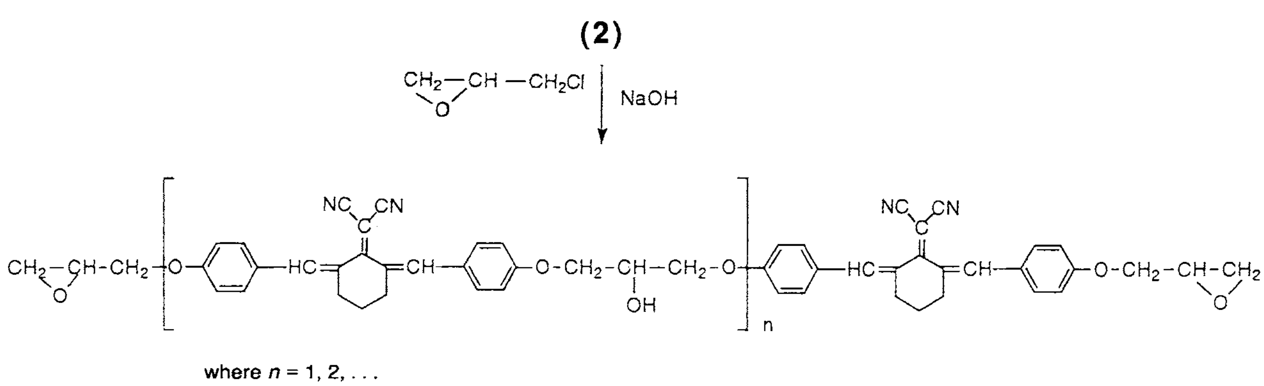
Preparation and Curing of Epoxy Compound (EC) (Scheme 4)

A mixture of compound **2** (0.7000 g, 1.97 mmol), excess epichlorohydrin (15 mL), and a catalytic amount of benzyltrimethylammonium bromide was refluxed for 1 h. The suspended solid was gradually dissolved during this period. The solution was subsequently stirred with dilute NaOH at 70°C for 2 h. The organic layer was separated and washed with water. Excess epichlorohydrin was removed by distillation under reduced pressure. The residue was dried to afford **EC** as a brown semisolid (0.83 g, 90%, mp 48–52°C).

EC (0.6000 g, 1.28 mmol) and DDS (0.1596 g, 0.64 mmol) were placed into an aluminum dish and heated on a heating plate. The reactants were melted and mixed thoroughly. The dish was subsequently placed into an oven and curing was accomplished by heating at 300°C for 40 h.

RESULTS AND DISCUSSION

A novel class of polyesters, polyurethanes, and epoxy resins was prepared from bisphenol **2**. The latter was prepared according to the reaction sequences of Scheme 1. More particularly, cyclohexanone was condensed[10,11] with 4-hydroxybenzaldehyde utilizing HCl gas as the catalyst to yield bisphenol **1**. The condensation of compound **1** with malononitrile in the presence of glacial acetic acid and a catalytic amount of piperidine afforded the dicyanomethy-



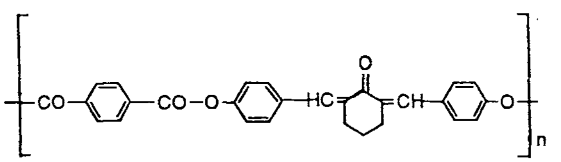
Scheme 4

lene-substituted bisphenol **2**. Excess malononitrile was used and the water produced was removed from the reaction mixture.

Scheme 2 presents the preparation of two model compounds. Particularly, bisphenol **2** reacted with a double molar amount of benzoyl chloride and phenyl isocyanate to yield model diester **3** and diurethane **4**, respectively.

Polyester **5** was synthesized by reacting bisphenol **2** with terephthaloyl dichloride using the phase-transfer catalyzed polycondensation (Scheme 3). Polyurethanes **6a** and **6b** were prepared from the reactions of **2** with tolylene diisocyanate and methylenebis(4-phenylisocyanate), respectively.

The reference polyester **7** with the following chemical structure:



(7)

was synthesized[12] for comparative purposes by reacting compound **1** with terephthaloyl dichloride according to the procedure described for the preparation of polyester **5** (inherent viscosity 0.21 dl/g in concentrated H_2SO_4).

The starting materials **1** and **2** as well as model compounds **3** and **4** were characterized by elemental analyses, FTIR, and ^{1}H-NMR spectroscopy (see Experimental). Figure 1 presents the FTIR spectra of bisphenols **1** and **2**. It is seen that bisphenol **2** lacked the adsorption band at 1654 cm^{-1} assigned to the carbonyl and displayed a new absorption at 2178 cm^{-1} associated with the cyano groups. Thus, the condensation of bisphenol **1** with malononitrile could be monitored by FTIR spectroscopy.

The FTIR spectra of model compounds were in agreement with those of the corresponding polymers (Figs. 2 and 3). Polyester **5** showed characteristic absorptions at 2178 (C≡N); 1738 (C=O); 1628–1596 (C=C); 1507 (aromatic) and 1266, 1078 cm^{-1} (C—O—C stretching). Polyurethane **6a** displayed absorptions at 3361 (N—H stretching); 2178 (C≡N); 1706 (C=O); 1596 (C=C); 1539 (N—H deformation); 1513 (aromatic) and 1225 cm^{-1} (C—O stretching). Polyurethane **6b** showed also absorption bands at these spectrum regions.

Figure 4 presents the ^{1}H-NMR spectrum of model diurethane **4**. It displayed peaks at 8.63 (NHOCO);

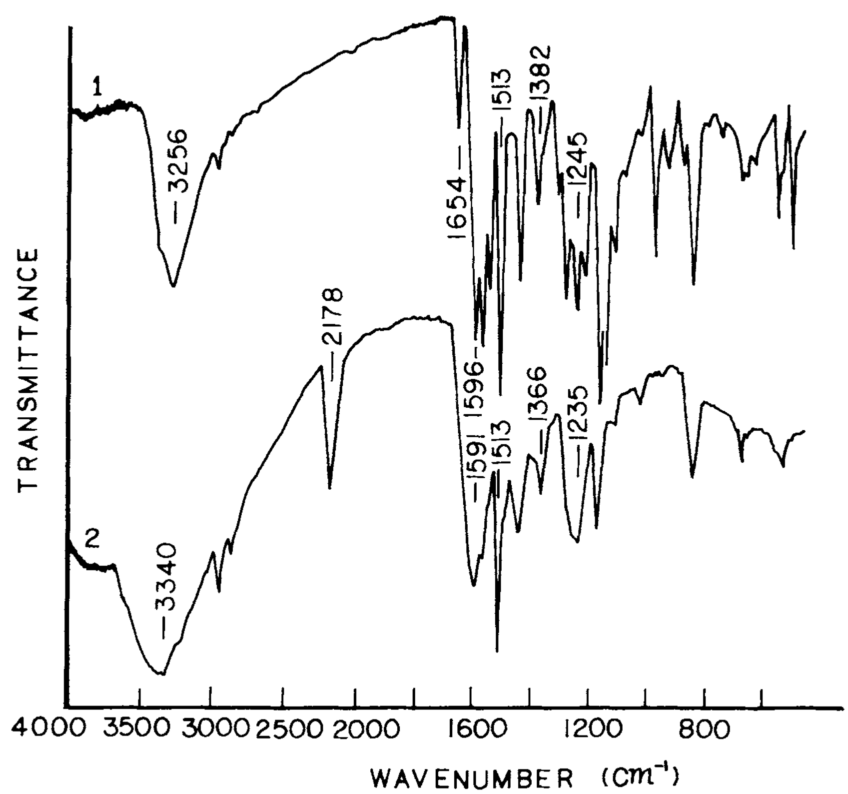


Figure 1 FTIR spectra of compounds **1** and **2**.

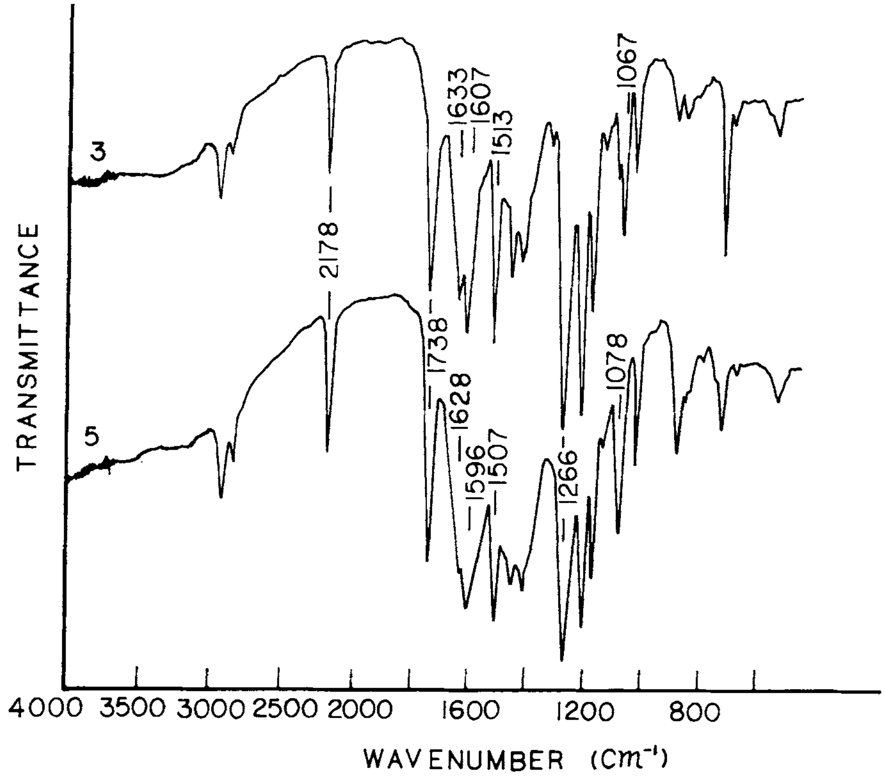


Figure 2 FTIR spectra of model diester **3** and polyester **5**.

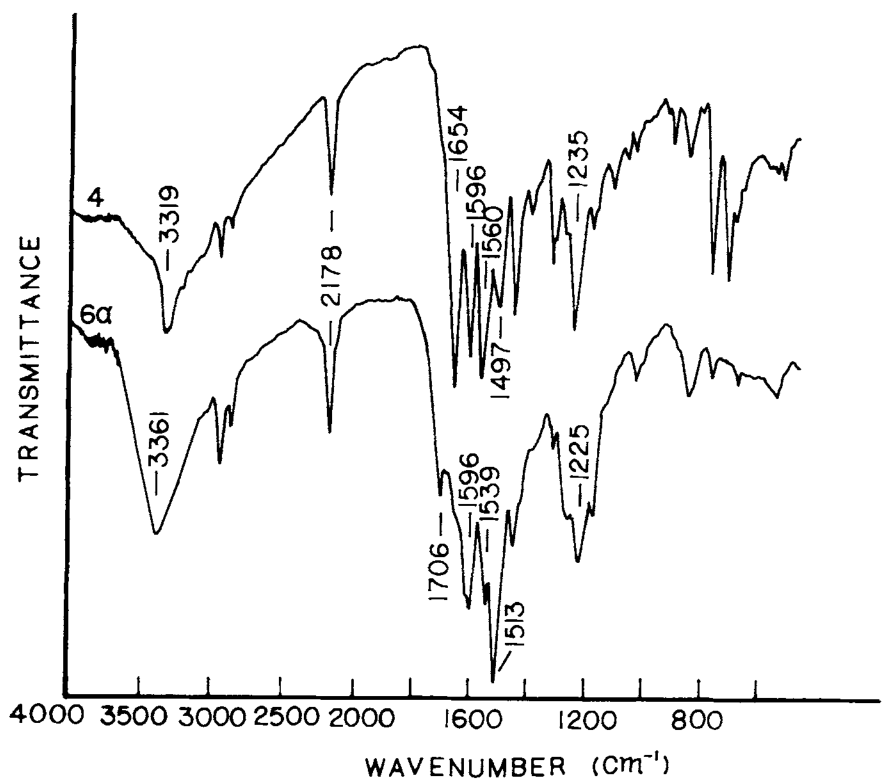


Figure 3 FTIR spectra of model diurethane **4** and polyurethane **6a**.

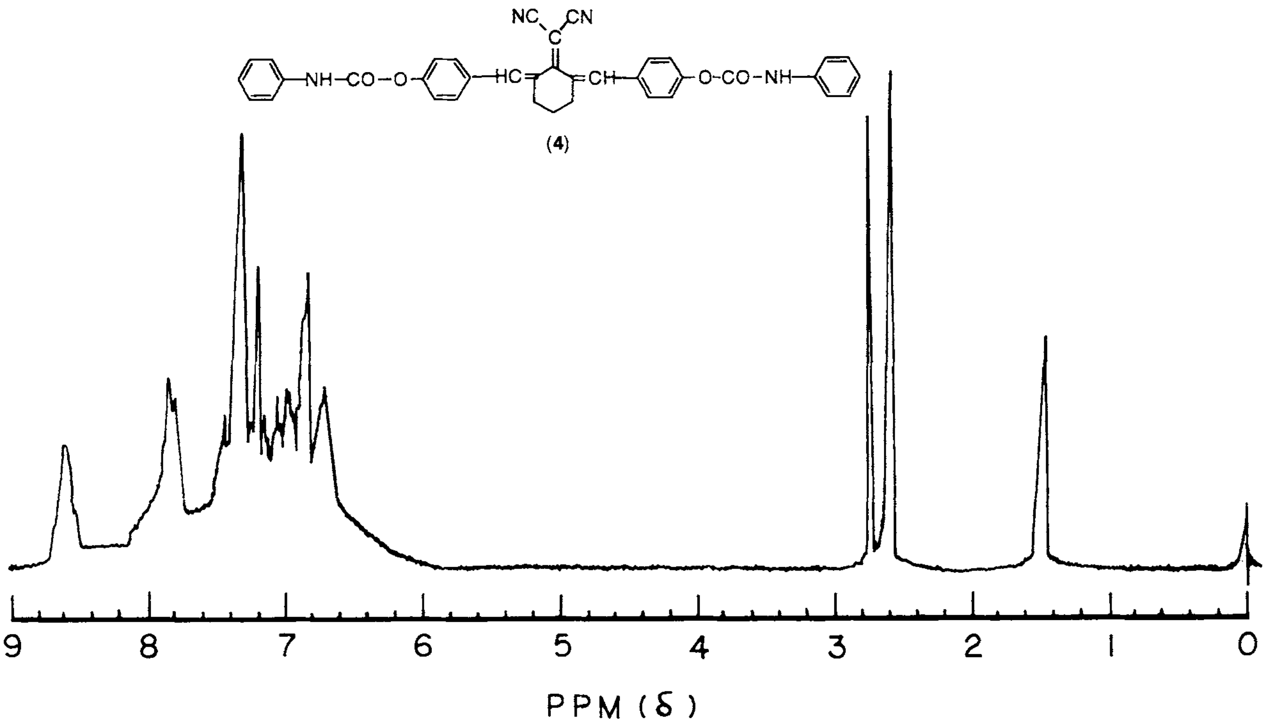


Figure 4 ^{1}H-NMR spectrum of model diurethane **4** in DMSO-d_6 solution.

7.88–6.73 (olefinic and aromatic); 2.73-2.63 and 1.46 δ (cyclohexane).

An objective of the present investigation was the improvement of the polymer solubility by introducing the bulky dicyanomethylene group. Table I presents the solubility behavior of the synthesized polymers as well as of reference polyester **7**. The cyano-substituted polyester **5** was readily soluble at ambient temperature in polar aprotic solvents, *m*-cresol, cyclohexanone, and certain strong inorganic and organic acids such as H_2SO_4 98% and CCl_3COOH. In contrast, the reference polyester **7** dissolved only in H_2SO_4 98% and CCl_3COOH. Polyurethanes **6a** and **6b** displayed almost the same solubility behavior as that of polyester **5.** The cyano-substituted polymers showed a relatively low degree of polymerization since their inherent viscosities ranged from 0.19–0.21 dL/g in DMF solution.

Figure 5 presents the X-ray diffraction patterns of two typical polymers **5** and **6a.** Polyester **5** displayed a few reflections of sharpness peaks in the 2θ = 28–50° region, indicating a degree of crystal-

Table I Solubilities of Polymers[a]

	Solvents									
Sample	DMF[b]	NMP[c]	DMSO[d]	$CHCl_3$	MEK[e]	1,4-Dioxane	*m*-Cresol	CH[f]	H_2SO_4 98%	CCl_3COOH
5	++	++	++	+−	+−	+	++	++	++	++
6a	++	++	++	−	+−	−	++	+	++	++
6b	++	++	++	−	+−	−	++	+	++	++
7	−	−	−	−	−	−	−	−	++	++

[a] Solubility: (++) soluble at room temperature; (+) soluble in hot; (+−) partially soluble or swollen; (−) insoluble.
[b] DMF = *N,N*-dimethylformamide.
[c] NMP = *N*-methylpyrrolidone.
[d] DMSO = dimethyl sulfoxide.
[e] MEK = metyl ethyl ketone.
[f] CH = cyclohexanone.

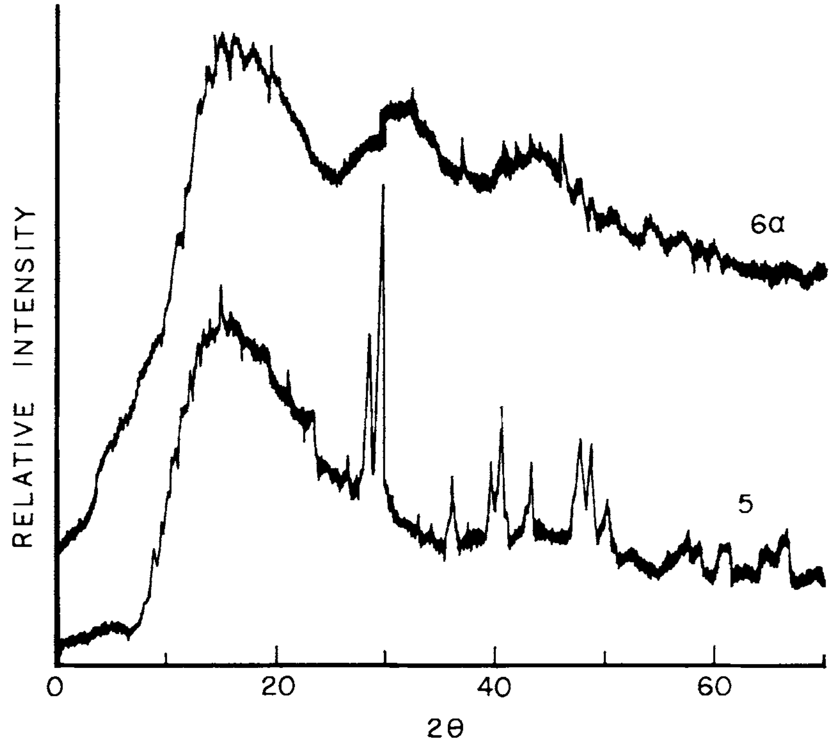


Figure 5 X-ray diffraction patterns of polyester **5** and polyurethane **6a**.

linity, whereas polyurethane **6a** showed an amorphous pattern.

The DTA trace in N_2 of polyurethane **6a** (Fig. 6) displayed a broad endotherm with an onset temperature of 223°C associated with its softening. Polyurethane **6a** softened also at this temperature region upon gradual heating into a capillary tube. The endotherm was followed by large exotherms attributable to their cross-linking reactions as well as to a partial thermal degradation. The DTA trace of the corresponding cured (at 300°C, for 40 h) sample **6a**′ showed only an exotherm beyond 380°C assigned to its thermal degradation. Polyurethane **6b** exhibited an analogous curing behavior with a softening temperature of 280–290°C. No softening endotherm was observed in the DTA trace of polyester **5**.

Cross-linked resins were obtained upon heat-curing the synthesized polymers at 300°C. It is believed that cross-linking occurred through the olefinic bonds as well as the cyano groups, and the FTIR spectral data supported this behavior. More particularly, the intensity of the absorption band of cyano groups around 2180 cm^{-1} of polyester **5** was significantly reduced during the curing process (Fig. 7). In addition, the cured samples became completely insoluble in solvents for the untreated samples.

To find the optimum curing time, polyester **5** and polyurethane **6b** were heated at 300°C for various periods and the initial decomposition temperature (IDT) and the char yield (Y_c) at 800°C in N_2 of the obtained network polymers were determined by TGA. The results are shown in Figure 8. The IDT and Y_c were increased up to 40 h and they were reduced beyond this time. The optimum time was therefore 40 h for curing at 300°C.

The cross-linked polymers obtained upon curing at 300°C for 40 h from polymers **5, 6a, 6b,** and **7** are referred to by the designations **5**′, **6a**′, **6b**′, and **7**′, respectively. Their thermal stabilities were ascertained by TGA (Fig. 9) 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 Y_c at 800°C in N_2 are listed in Table II. 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.

The cured polymers **5**′, **6a**′, and **6b**′ were stable up to 365–407°C in N_2 or air and afforded anaerobic char yields of 64–70% at 800°C. The reference poly-

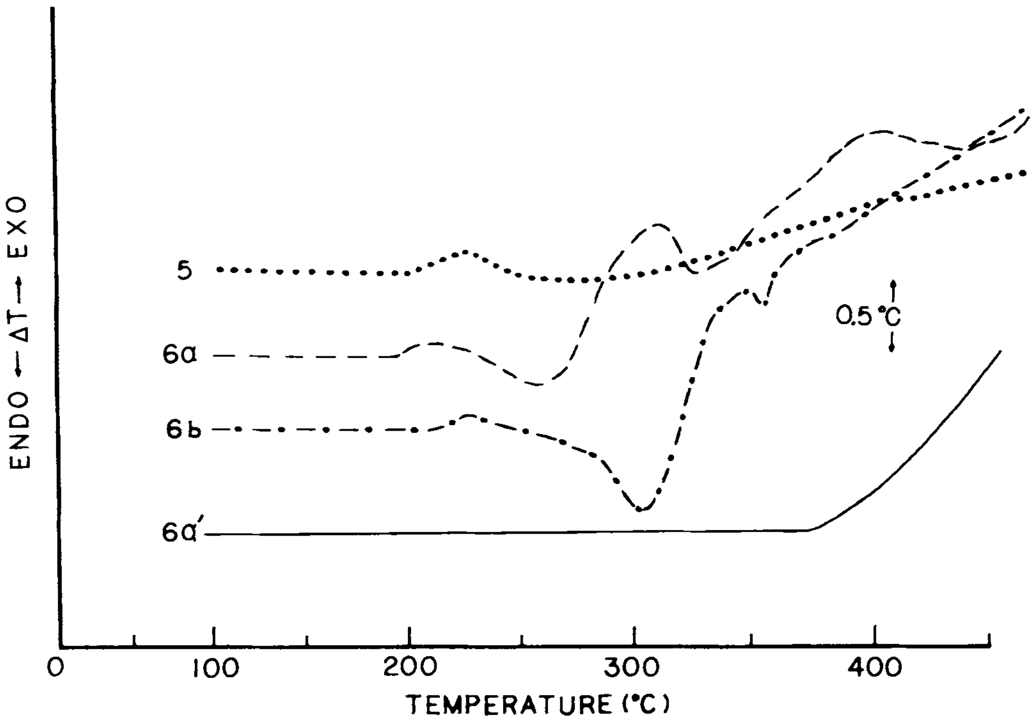


Figure 6 DTA traces of polyester **5** and polyurethanes **6a** and **6b** as well as of the cured (at 300°C, for 40 h) polyurethane **6a′**. Conditions: N_2 flow rate 60 cm^3/min; heating rate 20°C/min.

ester **7′** was remarkably less heat-resistant than was polyester **5′** since all its thermal characteristics were significantly inferior. This behavior was attributed to an additional cross-linking attained through the cyano groups of the latter. Furthermore, polyester **5′** displayed Y_c in air of 31% at 800°C.

Figure 10 presents the IGA traces in static air of cured polymers **5′**, **6b′**, and **7′**. Polyester **5′** showed weight losses of 21.6, 29.1, and 47.5% after 20 h isothermal aging at 320, 340, and 360°C, respectively. Polyurethane **6b′** and reference polyester **7′** showed weight losses of 52.9 and 61.6%, respectively, after 20 h isothermal aging at 320°C. The results revealed that the thermal stability of these cured polymers was of the order **5′** ≫ **6b′** > **7′**.

Diepoxide **EC** was prepared by reacting compound **2** with epichlorohydrin, utilizing benzyltrimethylammonium bromide as the catalyst (Scheme 4). The reaction took place at the boiling point of epichlorohydrin and the solution obtained was treated with aqueous NaOH.

The FTIR spectrum of **EC** (Fig. 11) showed absorption bands at 1251, 1183, and 952 cm^{-1} assigned to epoxy groups. In addition, the ^{1}H-NMR spectrum of **EC** in DMSO-d_6 solution displayed multiplet

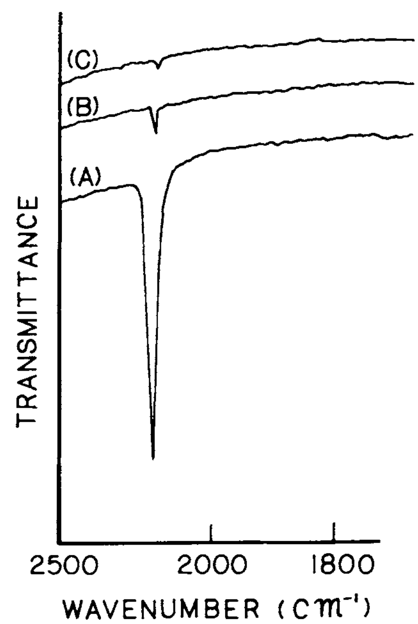


Figure 7 FTIR spectra of (A) polyester **5** uncured as well as of the corresponding cured samples at 300°C for (B) 20 h and (C) 40 h. All spectra were magnified by the same factor.

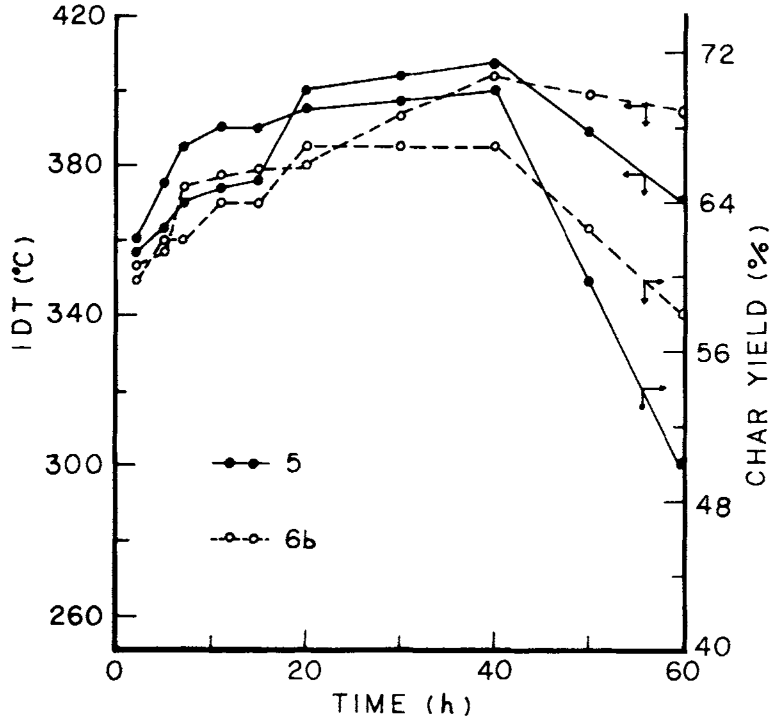


Figure 8 IDT and Y_c at 800°C in N_2 of polyester **5** and polyurethane **6b** as a function of the time for curing at 300°C.

peaks at 3.73–3.66, 3.10, and 2.86 δ associated with these groups. **EC** had an epoxy equivalent weight (EEW) of 241.10, whereas the calculated value of EEW was 233.22. **EC** was obtained as a semisolid and it was soluble in acetone, methyl ethyl ketone, ethanol, and acetonitrile.

EC was mixed with DDS in a molar ratio 2 : 1 (see Experimental) and the mixture was cured at

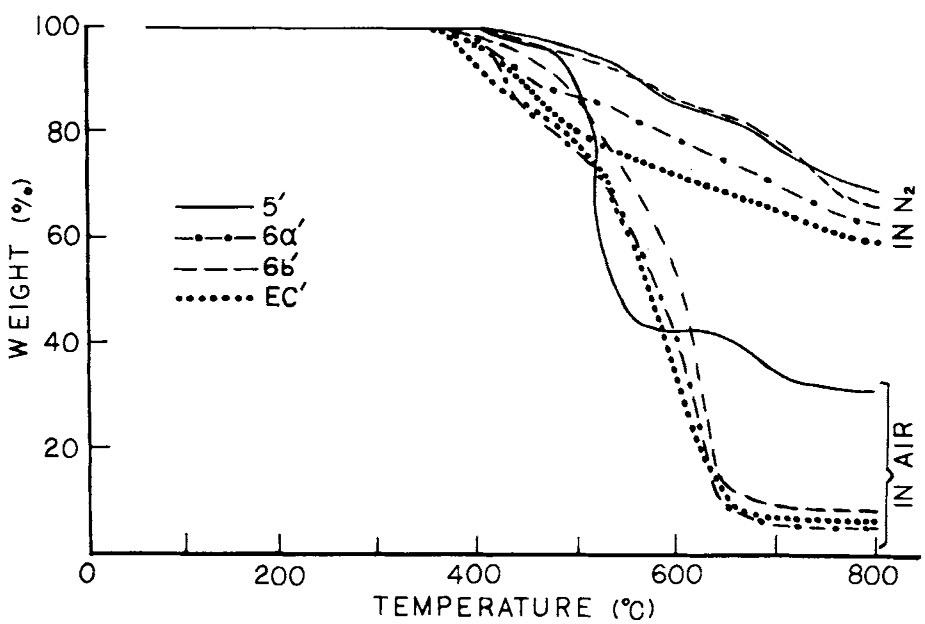


Figure 9 TGA thermograms of cured polyester **5′** and polyurethanes **6a′** and **6b′** as well as of **EC′** in N_2 and air. Conditions: gas flow 60 cm^3/min; heating rate 20°C/min.

Table II Thermal Stabilities of Cured Polymers

	N_2				Air		
Sample	IDT[a] (°C)	PDT[b] (°C)	PDT_{max}[c] (°C)	Y_c[d] (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)
5′	407	567	582	70	400	498	549
6a′	385	460	481	64	365	433	540
6b′	405	571	588	67	370	486	545
7′	374	493	537	30	360	444	501
EC′	352	434	455	61	347	420	542

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

300°C for 40 h to afford a cross-linked polymer **EC′**. The thermal stability of **EC′** was evaluated by TGA (Table II).

CONCLUSIONS

1. A novel series of polyesters, polyurethanes, and epoxy resins were prepared from 2,6-bis(4-hydroxybenzylidene)-1-dicyanomethylene–cyclohexane.
2. The synthesized polymers showed an enhanced solubility in common organic solvents in comparison to that of the corresponding reference polymers.
3. Cross-linked polymers were obtained upon curing at 300°C for 40 h and they were stable up to 365–407°C in N_2 or air and afforded anaerobic char yields of 64–70% at 800°C.
4. The cross-linked polymers were more heat-resistant than were the analogs obtained from the reference polymers.

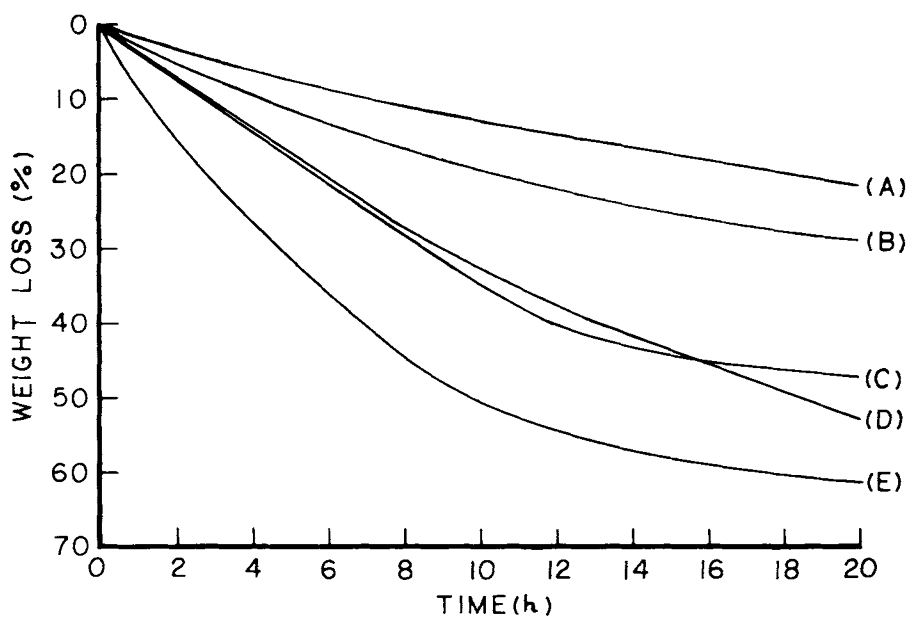


Figure 10 IGA traces in static air of cured polymers **5′** (A) at 320, (B) 340, and (C) 360°C; (D) **6b′** at 320°C; and (E) **7′** at 320°C.

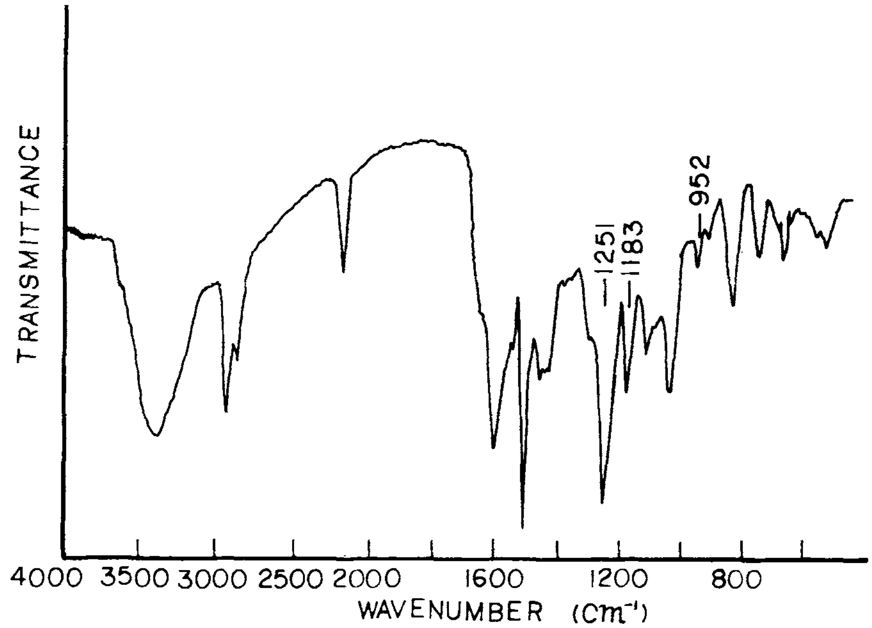


Figure 11 FTIR spectrum of **EC**.

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