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Synthesis and Properties of Poly(enaryloxynitriles) Containing Flexible Polyester Units

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ABSTRACT: New poly(enaryloxynitriles) with flexible alkyl units in the main chain were prepared by interfacial polymerization of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) with disodium salts of α,ω-bis-[(4-hydroxybenzoyl)oxy]alkanes. These polymers possess inherent viscosities of 0.12−0.27 dL/g and M_w in the range 10 000−12 000. They are easily soluble in polar aprotic solvents and even in common organic solvents such as THF and acetone. Flexible, tough films can be cast from DMF solutions. These polymers show a large exotherm in differential scanning calorimetry and undergo a curing reaction around 350 °C to form insoluble materials. Thermogravimetry displayed 60−80% residual weight at 500 °C and revealed a good thermal stability for polymers containing aliphatic segments.

Introduction

Polymers containing aromatic and/or heterocyclic moieties are known to have excellent thermal stability. Aromatic polyimides are some of the most attractive polymers because of their unusual chemical, thermal, and oxidative stability. Condensation type polyimides, however, usually suffer from processing problems due to insolubility, infusibility, and volatiles evolved during ring formation.[1] Among the thermally curable functions, acetylene, biphenylene, maleimide, styryl, nadimide, and *N*-cyanourea have been frequently employed to overcome these processing problems.[2,3] The dicyanovinyl group is one of the thermally curable functions, although its curing mechanism has not been completely elucidated. Thermally stable polymers containing dicyanovinyl units in the main chain can be prepared by the reaction of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (2) with diamines[4−8] and disodium salts of bis(phenol) derivatives.[9−13]

The introduction of the dicyanovinyl group as an enaminonitrile unit enhanced the thermal stability and solubility in solvent in the case of polyurethanes[13,14] and polyesters.[15] Recently, a similar approach has been taken to modify the solubility of aramide by incorporating an enaminonitrile unit.[16] The variety of structural modification allows the construction of chains with stiffnesses ranging from a relatively flexible polymer with a low glass transition temperature to a rodlike molecule with a high T_g. The incorporation of the flexible ester unit in the chain enhances the solubility in common organic solvents as well as should decrease the melting temperature of poly(enaryloxynitriles).

In this study, we report the synthesis and characterization of new poly(enaryloxynitriles) with flexible alkyl ester units in the main chain and their thermal properties including DSC and TGA data.

Experimental Section

Monochloride 1-chloro-1-phenyl-2,2-dicyanoethene (1) and dichloride *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (2) were prepared by the method previously reported.[4] α,ω-Bis[(4-hydroxybenzoyl)oxy]alkane derivatives were synthesized from [(ethoxycarbonyl)oxy]benzoyl chloride and corresponding diols as described in the literature.[14] Diol derivatives were purified by the conventional purification method. *p*-Hydroxybenzoic acid was used without further purification. 1,2-Dichloroethane was purified by distillation after drying over calcium hydride.

All melting points were determined on a Aldrich Mel-Temp II melting point apparatus using capillary tubes and are uncorrected. FT-IR spectra were obtained with a Midac spectrophotometer, and ^{1}H NMR spectra were recorded on a Varian 60A spectrometer. Elemental analyses were obtained with a Yanaco MT-3, CHN-Analyzer. GPC data were obtained with a Waters HPLC using three columns (μ-Styragel 10^2, 10^3, and 10^4 Å) in tetrahydrofuran and calibrated with polystyrene standards. Inherent viscosities of polymer solutions were measured in a Cannon-Ubbelohd viscometer at 25 °C. The polymer solutions for the viscosity measurements were filtered through a sintered glass filter. Thermal analyses of polymers were carried out on a DuPont 2100 and a Mettler thermal analyzer with a heating rate of 10 °C/min under nitrogen.

Synthesis of 1-[4-(Ethoxycarbonyl)phenoxy]-1-phenyl-2,2-dicyanoethene (3). Ethyl 4-hydroxybenzoate (0.88 g, 5.3 mmol) was dissolved in a solution of sodium hydroxide (0.22 g, 5.5 mmol) in 20 mL of distilled water, and the resulting solution was transferred to a blender. The solution of **1** (1 g, 5.3 mmol) in 20 mL of 1,2-dichloroethane was added quickly to the blender. After the mixture was stirred at full speed for 5 min, the organic layer was separated and the solvent was evaporated. The white solid product was filtered out, washed with distilled water several times, and recrystallized from carbon tetrachloride.

A similar procedure was applied to the synthesis of other model compounds *p*-bis[1-[4-(ethoxycarbonyl)phenoxy]-2,2-dicyanovinyl]benzene (**4**) and 1,2-bis[[4-[(1-phenyl-2,2-dicyanovinyl)oxy]benzoyl]oxy]ethane (**5**) by reacting dichloride **2** with 2 equiv of ethyl 4-hydroxybenzoate or 2 equiv of monochloride **1** with the disodium salts of 1,2-bis[(4-hydroxybenzoyl)oxy]-ethane. Model compounds **4** and **5** were recrystallized in methylene chloride/ethanol (50/50) and ethanol, respectively.

3: yield 95.5%; mp 148 °C (uncorrected); IR (KBr) 3065 (C−H), 2249 (C≡N), 1733 (C═O), 1570 (C═C), 1264, 1096 (C−O), 802, 657 cm^{-1}; ^{1}H NMR (DMSO-d_6 + $CDCl_3$) δ 7.7 (m, 5 H, phenyl), 7.1−7.9 (2 d, 4 H, aromatic protons in hydroxybenzoate), 4.27 (q, 2 H, −O−CH_2−), 1.4 (t, 3 H, −C*H*$_3$). Anal. Calcd for $C_{19}H_{14}N_{20}O_3$: C, 71.70; H, 4.40; N, 8.81. Found: C, 71.54; H, 4.38; N, 8.70.

4: yield 87.4%; mp 187 °C (uncorrected); IR (KBr) 3072 (C−H), 2258 (C≡N), 1727 (C═O), 1572 (C═C), 1372, 1241, 1122 (C−O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.7−6.9 (2 d, 8 H, 2 −O−*Ph*−CO−), 7.6 (s, 4 H, aromatic protons in fragment of **2**) 4.2 (q, 4 H, 2 −O−CH_2−), 1.5 (t, 6 H, 2 −C*H*$_3$). Anal. Calcd for $C_{32}H_{18}N_4O_4$: C, 73.56; H, 3.45; N, 10.73. Found: C, 73.47; H, 3.42; N, 10.69.

5: yield 63.4%; mp 267 (dec); IR (KBr) 3074 (C−H), 2265 (C≡N), 1574 (C═C), 1241, 1147, 1122 (C−O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9−7.0 (2 d, 8 H, 2 −O−*Ph*−CO−), 7.6 (m, 10 H, aromatic protons in fragment of **1**), 4.4 (s, 4 H, −OC*H*$_2$C*H*$_2$O−).

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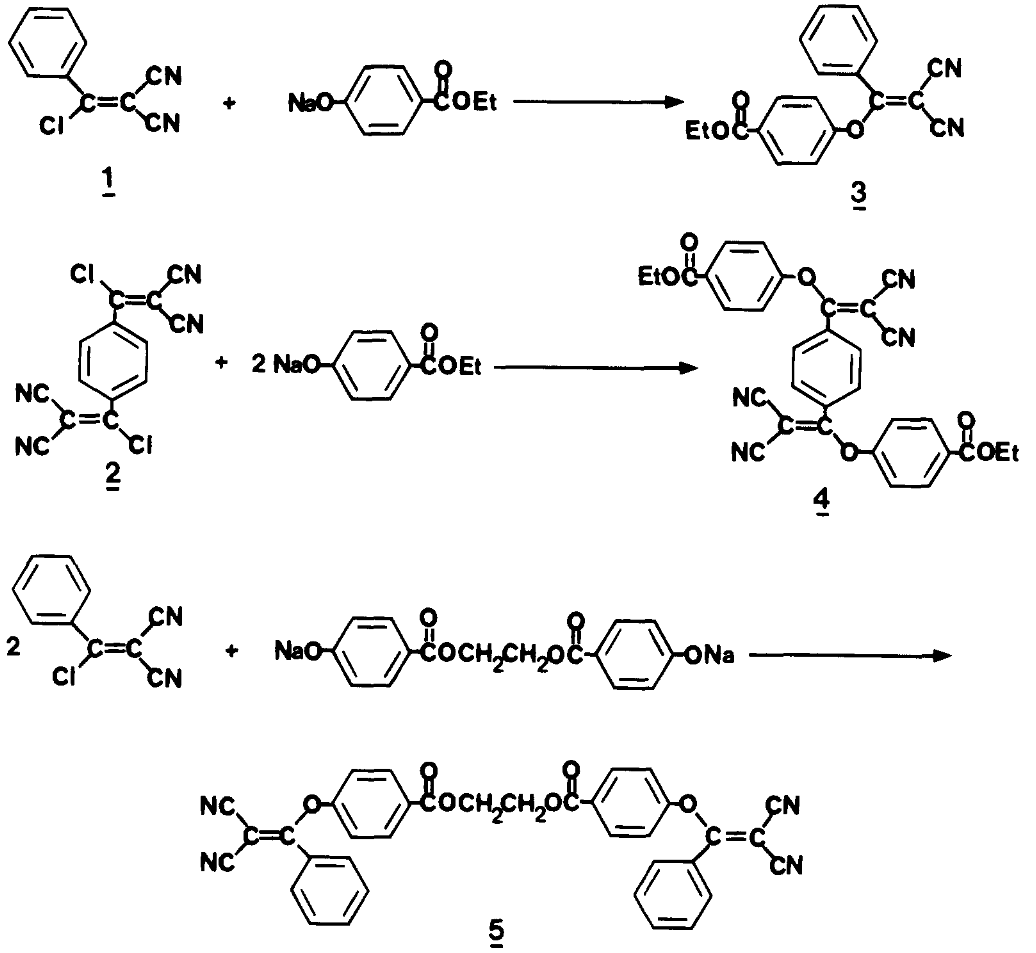
Scheme 1



Anal. Calcd for $C_{36}H_{22}N_4O_6$: C, 71.29; H, 3.63; N, 9.24. Found: C, 71.24; H, 3.59; N, 9.17.

Representative Polymerization of Dichloride 2 with Disodium Salts of α,ω-Bis[(4-hydroxybenzoyl)oxy]alkanes. A solution of dichloride **2** (1 g, 3.3 mmol) and 5 mol % of tetra-*n*-butylammonium chloride in 20 mL of 1,2-dichloroethane was transferred to the blender. The disodium salt of 1,4-bis[(4-hydroxybenzoyl)oxy]butane (1.23 g, 3.3 mmol) in 20 mL of water was added, in one portion, to the blender at full speed for 5 min. The polymer was collected by filtration and washed with distilled water several times. The polymer precipitated was purified by reprecipitation from THF solution into hexane. The poly(enaryloxynitriles) containing an ester linkage were dried at 60 °C under vacuum (0.1 Torr) for 8 h.

Similar synthetic procedures were applied to prepare other polymers derived from α,ω-bis[(4-hydroxybenzoyl)oxy]propane, −butane, −hexane, −octane, −cyclohexane, and −benzene, and bis[(4-hydroxybenzoyl)oxy]ethyl ether, respectively.

6: yield 91.2%; IR (KBr) 3106 (C−H), 2230 (C≡N), 1569 (C=C), 1383, 1122 (C−O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.8−7.2 (m, 8 H, aromatic protons in benzoate), 7.6 (m, 4 H, aromatic protons in fragment of **2**), 4.6 (s, 4 H, $-OCH_2CH_2O-$). Anal. Calcd for $(C_{30}H_{16}N_4O_6)n$: C, 68.18; H, 3.03; N, 10.69. Found: C, 68.31; H, 2.99; N, 10.89.

8: yield 92.5%; IR (KBr) 3078 (C−H), 2231 (C≡N), 1727 (C=O), 1572 (C=C), 1257, 1176, 1122 (C=O) cm^{-1}; ^1H NMR (CMSO-d_6) δ 7.8−7.0 (m, 8 H, aromatic protons in benzoate), 7.6 (s, 4 H, aromatic protons in fragment of **2**), Anal. Calcd for $(C_{32}H_{20}N_4O_6)n$: C, 69.09; H, 3.60; N, 10.07. Found: C, 68.95; H, 3.54; N, 10.11.

11: yield 90.9%; IR (KBr) 3083 (C−H), 2242 (C≡N), 1737 (C=O), 1572 (C=C), 1380, 1241, 1120, 1092 (C−O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.8 (s, 4 H, aromatic protons in fragment of **2**), 7.7−7.2 (2 d, 8 H, aromatic protons in benzoate). Anal. Calcd for $(C_{34}H_{20}N_4O_6)_n$: C, 70.34; H, 3.45; N, 9.66. Found: C, 69.89; H, 3.28; N, 9.54.

12: yield 92.2%; IR (KBr) 3079 (C−H), 2239 (C≡N), 1742 (C=O), 1559 (C−C), 1308, 1246, 1141, 1092 (C−O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8 (s, 4 H, aromatic protons in fragment of **2**), 7.7−7.1 (2 d, 8 H, aromatic protons in benzoate), 4.3 (m, 4 H, $-OC\underline{H}_2CH_2OCH_2C\underline{H}_2O-$), 3.8 (m, 4 H, $-OCH_2C\underline{H}_2OC\underline{H}_2CH_2O-$). Anal. Calcd for $(C_{32}H_{20}N_4O_7)n$: C, 67.13; H, 3.50; N, 9.79. Found: C, 67.24; H, 3.48; N, 9.96.

13: yield 93.6%; IR (KBr) 3110 (C−H), 2237 (C≡N), 1726 (C=O), 1387, 1242, 1127, 1092 (C−O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.8 (s, 4 H, aromatic protons in fragment of **2**), 7.7−7.1 (2 d, 8 H, aromatic protons in benzoate), 7.4−6.8 (m, 8 H, aromatic protons in Bisphenol A), 1.5 (s, 6 H, $-(CH_3)_2$). Anal. Calcd for $(C_{34}H_{16}N_4O_6)n$: C, 70.83; H, 2.78; N, 9.72. Found: C, 70.41; H, 2.68; N, 9.48.

Results and Discussion

Bis(phenol) derivatives with flexible alkyl or rigid aromatic units were synthesized by Ober and coworkers.[17] 1,2-Ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,4-cyclohexanediol, diethylene glycol, and hydroquinone were chosen for the preparation of bis(phenols) containing ester linkages.

The reactivity for dicyanovinyl chloride toward the phenoxide anion was tested by the preparation of appropriate model compounds. Although the reaction of phenoxide anions with dicyanovinyl chlorides has already been described,[10,11] these molecules were prepared to explore more fully the reactivity of sodium 4-(ethoxycarbonyl)phenoxide and to obtain the model enaryloxynitriles for the identification of the structure of polymers.

Three different model compounds, 1-[4-(ethoxycarbonyl)phenoxy]-1-phenyl-2,2-dicyanoethene (**3**), *p*-bis[1-[4-

Scheme 2

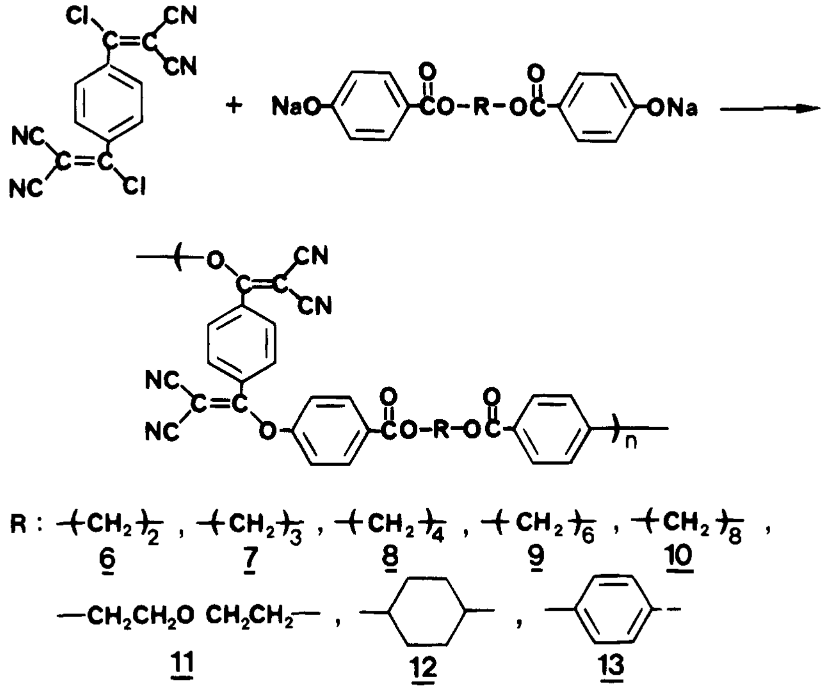


Table 1. Conditions and Results of Polymerization of Various Bis(phenol) Derivatives Containing Ester Units with Dichloride 2

polymer	diols[a]	time (min)	temp (°C)	yield (%)	η_{inh}[b]	M_w
6	EG	5	25	91.2	0.12	10 500
7	1,3-PD			86.6	0.14	11 000
8	1,4-BD			92.5	0.16	12 000
9	1,6-HD			92.8	0.20	12 500
10	1,8-OD			79.7	0.27	12 500
11	1,4-CHD			90.9	0.21	12 800
12	DEG			92.2	0.17	10 500
13	HQ[c]			93.6		

[a] EG: ethylene glycol. 1,3-PD: 1,3-propanediol. 1,4-BD: 1,4-butanediol. 1,6-HD: 1,6-hexanediol. 1,8-OD: 1,8-octanediol. 1,4-CHD: 1,4-cyclohexanediol. DEG: diethylene glycol. HQ: hydroquinone. [b] Measured in *N,N*-dimethylformamide in 1 g/dL at 25 °C. [c] Insoluble portion was formed in DMF solution.

(ethoxycarbonyl)phenoxy]-2,2-dicyanovinyl]benzene (**4**), and 1,2-bis[[4-[(1-phenyl-2,2-dicyanovinyl)oxy]benzoyl]oxy]ethane (**5**) were synthesized by reacting the corresponding phenoxide anion with dicyanovinyl compounds **1** or **2** by the interfacial technique,[18] Scheme 1.

In previous papers, interfacial polymerization techniques were found to be a convenient method for the preparation of poly(enaryloxynitriles).[10,11] Bis(phenol) derivatives containing flexible alkyl, cycloalkanoic, and aromatic ester units were selected, and their disodium salts were readily polymerized with **2**, Scheme 2.

The polymerization took place within 5 min at room temperature to form poly(enaryloxynitriles). The results and conditions of polymerization are summarized in Table 1.

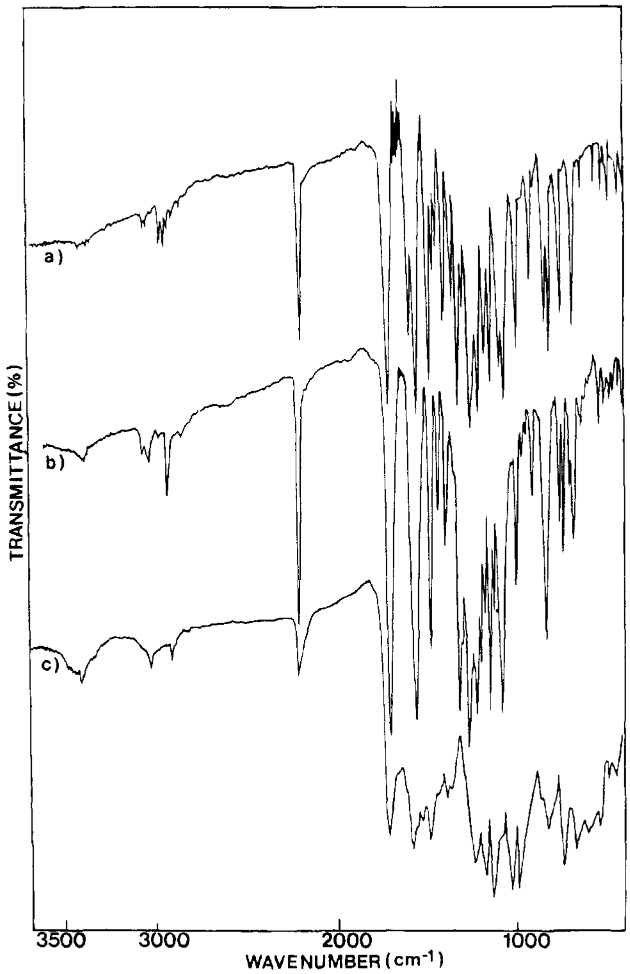


Figure 1. IR spectra of (a) model compound **5**, (b) poly(enaryloxynitriles) **8**, and (c) poly(enaryloxynitriles) cured at 320 °C for 1 h.

The formation of polymers was confirmed by IR, NMR spectroscopy, and elemental analyses. In the IR spectra shown in Figure 1b and Figure 1a, the poly(enaryloxynitrile) **8** prepared from dichloride **2** and 1,4-bis[(4-hydroxybenzoyl)oxy]butane is analogous to the model compound **4** obtained from **2** and ethyl 4-hydroxybenzoate. The characteristic bands in the IR spectrum appeared at 2230, 1739, 1580, and 1300–1100 cm^{-1} attributable to C≡N, C=O, and C–O, respectively. In the NMR spectra in Figure 2, polymer **8** showed peaks at 7.8 ppm corresponding to aromatic protons in **2**. On the other hand, peaks of aromatic protons of the bis-

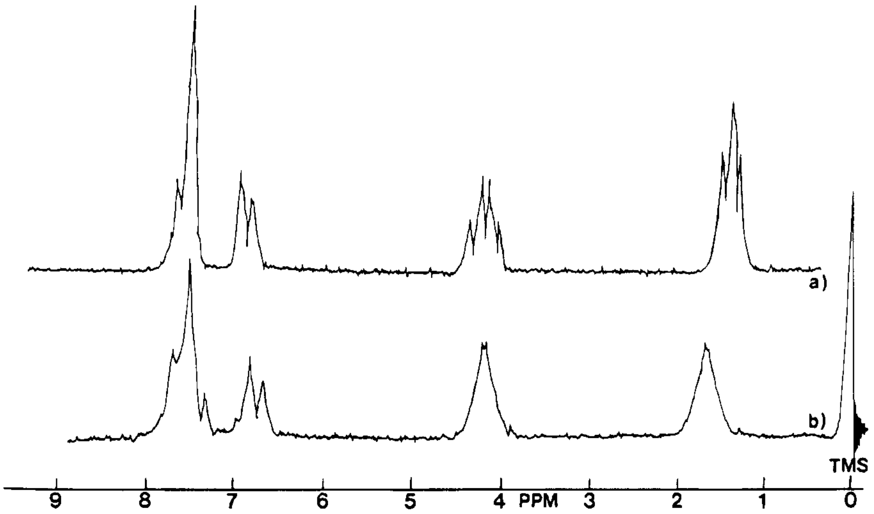


Figure 2. Comparison of ^{1}H NMR spectra of (a) model compound **5** with (b) poly(enaryloxynitriles) obtained from disodium salts of 1,4-bis[(4-hydroxybenzoyl)oxy]butane and dichloride **2**.

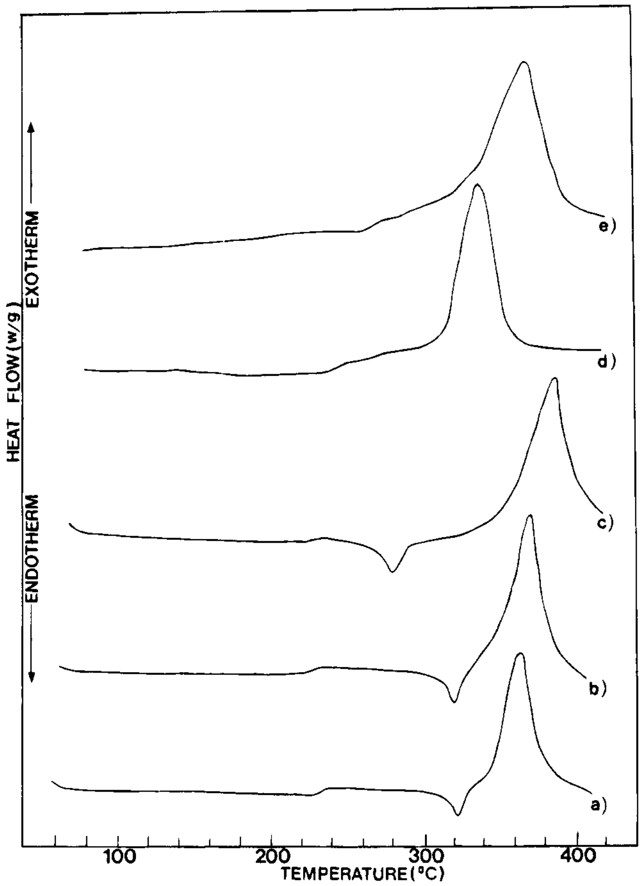


Figure 3. DSC thermograms of poly(enaryloxynitriles) (a) **6**, (b) **7**, (c) **8**, (d) **11**, and (e) **13** at a heating rate of 10 °C/min in nitrogen.

(phenol) units appeared at 7.7–6.8 ppm as two doublets. The peaks of protons of methylene units in the polymers were seen at 4.1 and 1.8 ppm as multiplets.

The elemental analyses of polymers were in fairly good agreement with the calculated values of the proposed structures. Other polymers with different alkyl chains showed similar NMR spectra increased at 1.8 ppm.

The poly(enaryloxynitriles) were very soluble in polar aprotic solvents such as DMF, DMAc, DMSO, and NMP, while they were insoluble in polar protic solvents such as methanol, ethanol, and 2-propanol. But the polymers are even soluble in THF, acetone, and ethyl acetate. The increased solubility in common organic solvents is mainly due to the incorporation of the flexible alkyl ester units into the main chain of the poly(enaryloxynitriles). Polymer **12** prepared from hydroquinone shows poor solubility in such solvents because of its rigid aromatic moiety. The polymers from ethylene glycol and 1,3-propanediol were somewhat less soluble in chloroform than those derived from longer chain diols.

The molecular weight did not tend to increase to some extent by changing the monomer concentration during interfacial polymerization. The reactivity of the phenoxide anion with dicyanovinyl compounds was determined according to the pK_a values of the phenol derivatives. Because ethyl 4-hydroxybenzoate has a pK_a value of 9.30,[19] the reaction with **1** or **2** proceeds at a slower rate than phenol itself (pK_a value 10.0). However, an examination of the products when the polymerization was carried out for 5 min in the presence of tetra-*n*-butylammonium chloride as a phase transfer agent indicated that the disodium salts of bis(phenols) containing an alkyl ester unit showed a good reactivity with **2** to form poly(enaryloxynitriles) by interfacial techniques. The poly(enaryloxynitriles) having inherent viscosities of 0.12–0.27 dL/g were obtained in good yield. The M_n of the polymers were in the range 3000–5000, and M_w, in the range 10 000–12 000. Although these are not high values of molecular weight, transparent yellow films cast from a DMF solution had some degree of toughness and flexibility.

Differential scanning calorimetry (DSC) of these polymers revealed T_g values between 110 and 260 °C, demonstrating the markedly increased flexibility of poly(enaryloxynitriles) prepared in this work over those containing only aromatic units.[10,11] The T_g is seen to increase as rigid and short aliphatic chains are introduced into the polymer backbone. In the DSC traces, Figure 3, higher glass transition temperatures were observed for polymers incorporating shorter chain aliphatic diols such as ethylene glycol and 1,3-propanediol.

Apparently, a exotherm indicating crystallization of the polymer was not observed in all the polymers **6**–**13**. The DSC experiments indicated the existence of an endothermic peak between 270 and 330 °C in the case of polymers **6**, **7**, **8**, and **12**, but they were not strong. This result implies that a high proportion of amorphous domains existed in the polymer textures. Moreover,

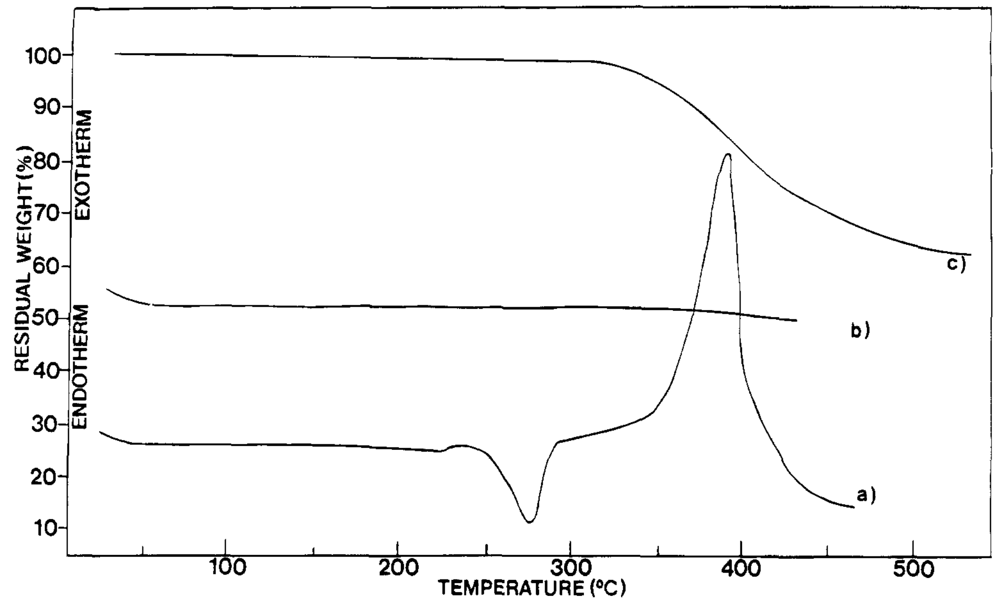


Figure 4. DSC scanns of poly(enaryloxynitrile) **8** obtained from disodium salts of 1,4-bis[(4-hydroxybenzoyl)oxy]butane and **2**: (a) first scan, (b) second scan, and (c) TGA trace.

Table 2. Thermal Properties of Poly(enaryloxynitriles) Containing Ester Units

		temp (°C)				residual weight (%)	
polymer	diols	T_g	endo	exo	10% weight loss	400 °C	500 °C
6	EG	230	322	361	381	85.1	70.1
7	1,3-PD		277	350	374	75.6	68.1
8	1,4-BD	225	271	363	370	80.0	63.9
9	1,6-HD	170		377	381	80.3	62.4
10	1,8-OD	105		362	380	83.0	66.3
11	1,4-CHD			330	379	79.1	60.8
12	DEG	142	268	349	367	70.1	58.0
13	HQ			396	396	88.9	80.2

polymer **9**, **10**, **11**, and **13** showed no endothermic peak attributable to polymer melting. Especially, polymers **9** and **10** with flexible long carbon chains showed the fully amorphous state. The absence of the sharp reflection between 10 < θ < 30° is the evidence of the noncrystalline state in the X-ray diffractogram. More experiments are needed to understand the causes of the thermal transition observed for the polymers in detail. These polymers showed interesting thermal behavior, as evidenced by calorimetry showing exotherms which do not appear on scanning the samples, as shown in Figure 4b. After the exotherm had occurred, the previously soluble sample was completely insoluble in THF and DMF. On the basis of these results, the chemical structure of the polymers must have changed during heating to 370 °C. However, decomposition of the polymer seemed to occur simultaneously with the chemical change of the dicyanovinyl group.

A large exotherm appeared at 370 °C, which is almost comparable to that reported in the literature.[10,11] These polymers began to lose weight around 370 °C, which correlated well with the exothermic peak observed in the DSC curves, Figure 4a. Thermal gravimetric analysis results are listed in Table 2. The polymers sustained a 10% weight loss at 380 °C at a heating rate of 10 °C/min in nitrogen and gave a residual weight varying from 60 to 80% at 500 °C. The polymer prepared from hydroquinone showed greater thermal stability than those obtained from aliphatic ester units. The thermal decomposition of polymers begin at a temperature of 325 °C and showed a sudden weight loss at around 350 °C. The lower decomposition temperature of polymers **6**–**12** is mainly due to alkyl units in the main chain while the poly(enaryloxynitriles) containing aromatic diols decomposed at 400 °C.

As the chain length of alkyl ester units in the polymer increased, the residual weight of polymer at 500 °C decreased. It was expected that the incorporation of aromatic rings in the polymer would give a high char yield. Thermal curing was conducted at the beginning of the exotherm at 320 °C to monitor the chemical change during the curing process. A sample of heated polymer displayed gradual changes in its IR spectrum as it was heated for 1 h at a temperature of 320 °C. The bands of uncured polymer at 2235 cm^{-1} corresponding to the nitrile group were reduced, while the absorption bands at around 1580 cm^{-1} were broadened, as shown in Figure 2c. It may be due to the change of dicyanovinyl group by various chemical reactions. The thermal stabilities were related to the existence of the dicyanovinyl group in the polymer chain.

Insolubility in solvent after curing, disappearance of the exotherm during the second DSC scan, reduction of the nitrile group intensity in the IR spectrum, and enhancement of thermal stability are all evidence of intermolecular and/or intramolecular cyclization and cross-linking reactions of the dicyanovinyl groups.[4-8]

Experiments designed to clarify the chemical processes during thermally initiated curing are needed and now in progress.

Conclusion

Poly(enaryloxynitriles) with flexible alkyl units were synthesized from the difunctional dicyanovinyl chloride *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) and disodium salts of α,ω-bis[(4-hydroxybenzoyl)oxy]alkanes by interfacial polymerization. These polymers are soluble in common organic solvents such as THF and acetone as well as polar aprotic solvents such as DMF, DMSO, DMAc, and NMP. They show a large exotherm in the DSC scan and undergo a curing reaction around 350 °C to form insoluble material. Moreover, thermally curable and stable polymers were formed to give 60–80% residual weight at 500 °C in nitrogen. Extension to the synthesis of poly(enaryloxynitriles) with flexible alkyl units by solution polymerization to promote the molecular weight is needed and now in progress.

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