

NOTES

Preparation and Thermal Properties of Poly(enaryloxynitrile)s

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Amines as a nucleophile can readily replace the chlorine of dicyanovinyl compounds, 1-chloro-1-phenyl-2,2-dicyanoethene (**1**) and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) to form enamionitriles.¹

Moore and coworkers first synthesized poly(enaminonitrile)s based on the reaction of difunctional dicyanovinyl compound, **2** with aromatic²⁻⁴ or aliphatic diamines.⁵ Aromatic diamines underwent solution polymerization in aprotic polar solvent in the presence of acid acceptor, whereas aliphatic diamines underwent interfacial polymerization.^{5,6} The resulting polymers showed a good thermal stability and insolubility in the solvent for the untreated polymer, after heat curing without evolution of small molecules. These flexible polymeric precursor which cyclizes to produce the final thermal stable, rigid rod polymer have been compared with polyimides as a thin film without void and contraction caused by emission of volatile product.

The more strongly nucleophilic phenoxide anion possessing a pK_a value of 10 has an appreciable reactivity to **2**. Recently, it has been reported that poly(enaryloxynitrile)s prepared from **2** and disodium salts of bisphenol-A showed excellent thermal stability.⁷

In the present paper, we report details of a successful synthesis of a new class of thermal

curable poly(enaryloxynitrile)s derived from **2** and aromatic diols such as catechol, resorcinol, hydroquinone and various dihydroxynaphthalenes. In addition, thermal properties of poly(enaryloxynitrile)s are investigated and presented.

EXPERIMENTAL

1-Chloro-1-phenyl-2,2-dicyanoethene (**1**) and monomer (**2**) were synthesized by the modified method previously reported by Moore *et al.*⁴ Catechol, resorcinol, hydroquinone and dihydroxynaphthalene derivatives were purchased from Aldrich Chemical Co. and used without further purification.

The IR spectra were obtained with a Perkin-Elmer Model 1310 spectrophotometer and ¹H and ¹³C NMR spectra were recorded on a Bruker Am-300 spectrometer. GPC data were obtained by Waters HPLC using three columns (μ -styragel 10², 10³, and 10⁴ Å) in THF at 25°C, and polystyrene standards were used for calibration. Elemental analyses data were obtained with a Yanaco MT-3, CHN-Analyzer. Thermal analyses were performed with a Dupont 910 and 961 thermal analyzer.

Preparation of p-Bis(1-phenyl-2,2-dicyanovinyl-oxyl)benzene

0.55 g (5.0 mmol) of hydroquinone was dissolved in the solution of 0.23 g (5.8 mmol) of sodium hydroxide in 20 ml of water with gentle swirling for 4 hours and the reaction mixture was transferred to the blender. A mixture of 1.89 g (10 mmol) of **1** in 20 ml of 1,2-dichloroethane was poured in one portion into the blender. After the blender was stirred at full speed for 2 minutes, the organic layer was separated and the solvent was evaporated. The greenish solid product was filtered and recrystallized from acetone.

A similar procedure was applied to the synthesis of model compound **4** by reaction two equivalents of sodium β -naphthoxide with **2**.

3. Yield 90%; mp 282°C.

IR (KBr): 3050, 2250, 1590, 1500, 1330, and 1180 cm^{-1} .

^1H NMR (CDCl_3): $\delta = 7.3\text{--}7.7$ (m, 10H, aromatic H's in **1**), and 7.0–6.8 ppm (m, 4H, aromatic H's in hydroquinone).

^{13}C NMR: $\delta = 71.9$ ($=\text{C}(\text{CN})_2$), 110.5, 113.5 ($-\text{CN}$), 122.5, 128.0, 129.2, 130.0, 132.8, 151.5 (aromatic C's), and 180.5 ppm ($=\text{C}-\text{O}-$).

Anal. Calcd: C, 77.2%; H, 1.0%; N, 13.9%.

Found: C, 76.8%; H, 1.0%; N, 14%.

4. Yield 87%; mp 302–304°C.

IR (KBr): 3040, 2220, 1595, 1327, and 1165 cm^{-1} .

^1H NMR (CDCl_3): $\delta = 7.3\text{--}7.7$ (s, 4H, aromatic H's in fragment of **2**), and 6.8–7.2 ppm (m, 14H, naphthyl H's).

^{13}C NMR (CDCl_3): $\delta = 71.0$ ($=\text{C}(\text{CN})_2$), 111.5, 112.9 ($-\text{CN}$), 12.9, 127.4, 128.7, 129.6, 133.1, 151.2 (aromatic C's), and 181.0 ppm ($=\text{C}-\text{O}-$).

Anal. Calcd: C, 79.4%; H, 3.5%; N, 10.9%.

Found: C, 79.1%; H, 3.6%; N, 10.7%.

Representative Polymerization of 2 with Disodium Salts of Aromatic Diol in Homogeneous Solution

A solution of 0.99 g (9.0 mmol) of hydro-

quinone and 0.72 g (18.0 mmol) of powdered sodium hydroxide in 20 ml of dimethylformamide was stirred with nitrogen inlet for 8 hours. 2.69 g (9.0 mmol) of **2** in 10 ml of dimethylformamide was added and the temperature was raised to 50°C and maintained for 2 hours. The pale yellow solution was allowed to cool and was poured into a large amount of water to precipitate the polymer **5**.

A similar polymerization procedures were applied to prepare other polymers.

Representative Polymerization of 2 with Disodium Salts of Aromatic Diol by Interfacial Techniques

A solution of 1 g (3.3 mmol) of **2** in 20 ml of 1,2-dichloroethane was transferred to the blender. A hydroquinone (0.36 g, 3.3 mmol) in 20 ml of water was added to the blender at full speed for 2 minutes. The polymer was collected and washed with water. The polymer was dried at 60°C under vacuum for 5 hours.

A similar procedures were applied to prepare other polymers. In the case of dihydroxynaphthalene-derived polymers, nitrobenzene was used as a organic solvent in place of 1,2-dichloroethane.

7. Yield 95%.

IR (KBr): 3010, 2820, 2220, 1595, 1490, 1400, 1310, and 1210 cm^{-1} .

^1H NMR (CD_3CN): $\delta = 7.3\text{--}7.6$ (m, 4H aromatic H's in fragment in **2**), and 6.5–6.9 ppm (m, aromatic H's in Hydroquinone).

^{13}C NMR: $\delta = 72.0$ ($=\text{C}(\text{CN})_2$), 110.1, 113.8, ($-\text{CN}$), 121.8, 128.0, 128.9, 129.3, 133.4, 134.1, 152.1 (aromatic C's), and 180.1 ppm ($=\text{C}-\text{O}-$).

Anal. Calcd: C, 71.4%; H, 2.4%; N, 16.7%.

Found: C, 71.7%; H, 2.5%; N, 16.5%.

12. Yield 92%.

IR (KBr): 3040, 2210, 1600, 1510, 1330, 1250, and 1160 cm^{-1} .

^1H NMR ($\text{DMSO}-d_6$): $\delta = 7.2\text{--}7.6$ (s, 4H, aromatic H's in fragment in **2**), and 7.3–6.6 ppm (6H, aromatic H's in naphthalene).

^{13}C NMR ($\text{DMSO}-d_6$): $\delta = 71.3$ ($=\text{C}(\text{CN})_2$),

110.9, 113.0 ($-\underline{C}N$), 121.8, 126.9, 128.6, 129.6, 130.3, 133.0, 151.2 (aromatic C's), and 181.2 ppm ($=\underline{C}-O-$).

Anal. Calcd: C, 74.6%; H, 2.6%; N, 14.5%,
Found: C, 75.0%; H, 2.7%; N, 14.7%.

RESULTS AND DISCUSSION

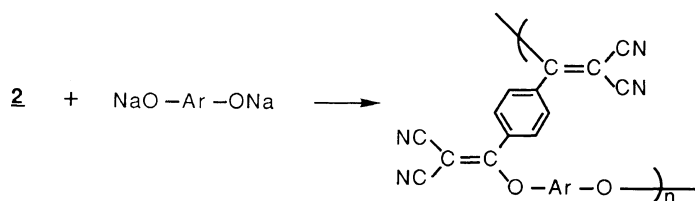
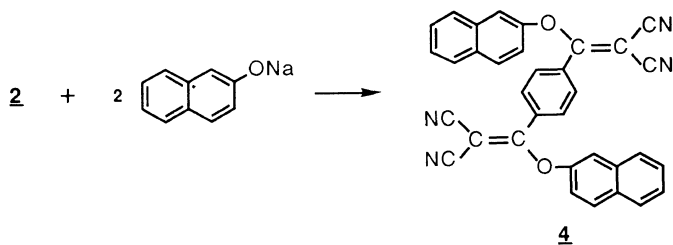
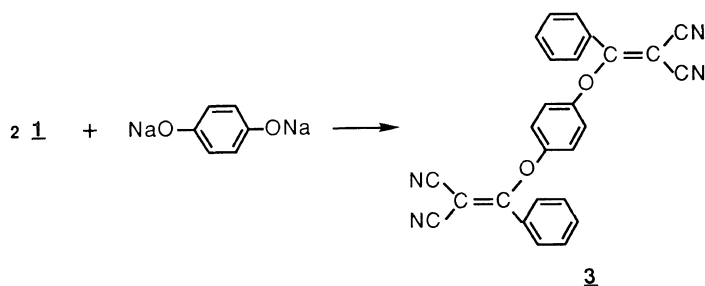
Two different model compounds, *p*-bis(1-phenyl-2,2-dicyanovinyl) benzene (**3**) and *p*-bis[1-(β -naphthyl-2,2-dicyanovinyl)]benzene (**4**) were prepared by reacting the

aryloxide anion derived from hydroquinone and β -naphthol with dicyanovinyl compounds, **1** and **2**.

The model products, **3** and **4** were identified to be enaryloxynitrile by IR, 1H and ^{13}C NMR spectroscopy and characterized by satisfactory elemental analysis.

The polymerization of **2** with disodium salts of aromatic diols could proceed by both solution and interfacial polymerization techniques.

Aromatic diols such as catechol, resorcinol,



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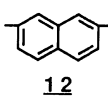
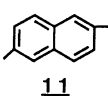
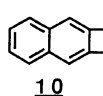


Table I. Polymerization results of **2** and disodium salts of aromatic diols

Polymer	Diol ^c	Solvent	Temp/°C	Time/min	Yield/%	η_{inh}^d	M_n^e	M_w
5 ^a	Ca	C ₂ H ₄ Cl ₂ /H ₂ O	25	2	90	0.28	5160	12400
5 ^b	Ca	DMF	50	300	93	0.30	3880	13500
6 ^a	Re	C ₂ H ₄ Cl ₂ /H ₂ O	25	2	92	0.32	6220	15500
7 ^a	Hy	C ₂ H ₄ Cl ₂ /H ₂ O	25	2	95	0.31	5440	15000
7 ^b	Hy	DMF	50	300	92	0.27	4820	13800
8 ^a	1,5-DhNa	Nitrobenzene/H ₂ O	20	2	85	0.10	4780	11240
9 ^a	1,6-DhNa	Nitrobenzene/H ₂ O	20	2	89	0.17	5700	12000
10 ^a	2,3-DhNa	Nitrobenzene/H ₂ O	20	2	87	0.12	4800	12440
11 ^a	2,6-DhNa	Nitrobenzene/H ₂ O	20	2	92	0.16	4540	11200
12 ^a	2,7-DhNa	Nitrobenzene/H ₂ O	20	2	91	0.21	6100	11500
12 ^b	2,7-DhNa	DMF	60	300	89	0.28	4200	13200

^a Interfacial polymerization.

^b Solution polymerization.

^c Ca, catechol; Re, resorcinol; Hy, hydroquinone; DhNa, dihydroxynaphthalene.

^d Measured at a concentration of 1 g dl⁻¹ in *N*-methyl-2-pyrrolidone at 25°C.

^e M_n and M_w of polymers, which is partially soluble in acetonitrile, were obtained by using three columns (μ -styrigel 10², 10³, and 10⁴ Å) in THF at 25°C, and polystyrene standards were used for calibration.

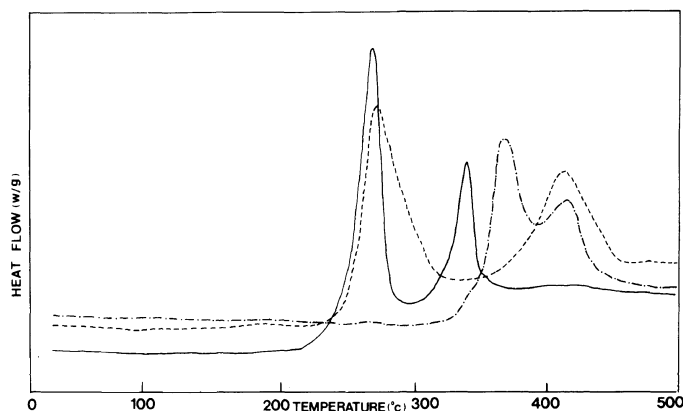


Figure 1. DSC thermogram of polymers from catechol (—), resorcinol (-----), and hydroquinone (-·-·-) with *p*-bis(1-chloro-2,2-dicyanovinyl)benzene.

hydroquinone and various dihydroxynaphthalene derivatives were selected and their disodium salts were readily polymerized with **2** to give the corresponding polymers **5**–**12** in high conversion. The polymerization results are summarized in Table I.

When polymer **7** and **12** were compared with the model compound **3** and **4**, respectively, the spectral data of polymers matched well with

those of the model compounds.

In the case of polymer **7**, the ¹H NMR peaks of the aromatic protons in hydroquinone are shown as a multiplet at 6.5–6.9 ppm, whereas those of **2** unit are seen as a broad singlet between 7.3–7.6 ppm. The characteristic bands of poly(enaryloxynitrile) in its IR spectra are exhibited at 2220, 1595, and 1160–1210 cm⁻¹ corresponding to C≡N, C=C, and C–O

bands, respectively. The proposed structures of polymer were also confirmed by ^{13}C NMR spectra. The peak at 180.5 ppm indicated the presence of the enaryloxy linkage ($=\text{C}-\text{O}-$) apparently.

Polymers **8**–**12** derived from dihydroxynaphthalene were also identified as poly(enaryloxynitrile) by comparison with their IR,

^1H and ^{13}C NMR spectra with different kind of model compound **4**.

All the polymers were soluble in polar aprotic solvents such as DMF, DMSO, DMAc, and *N*-methyl-2-pyrrolidinone, and partially soluble in acetonitrile, nitrobenzene and THF. Polymers **8**–**12** were less soluble than polymers **5**–**7** in such solvent.

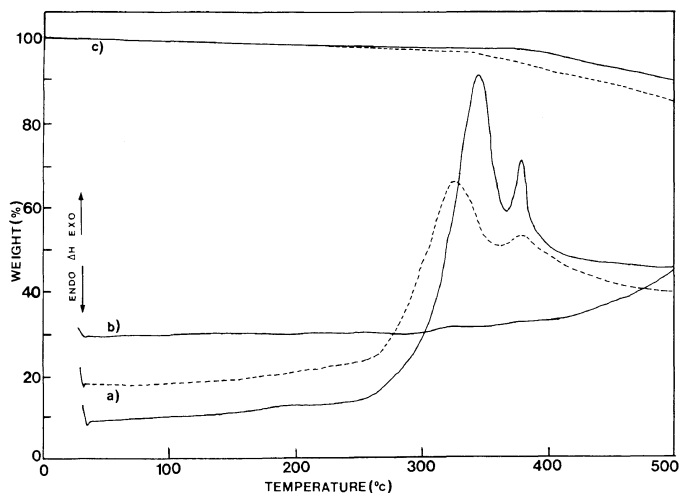


Figure 2. DSC thermogram of (a) 1st heating, (b) 2nd heating, and (c) TGA thermogram of polymers obtained from 1,6-dihydroxy naphthalene (-----) and 2,7-dihydroxy naphthalene (—) with *p*-bis(1-chloro-2,2-dicyanovinyl)benzene.

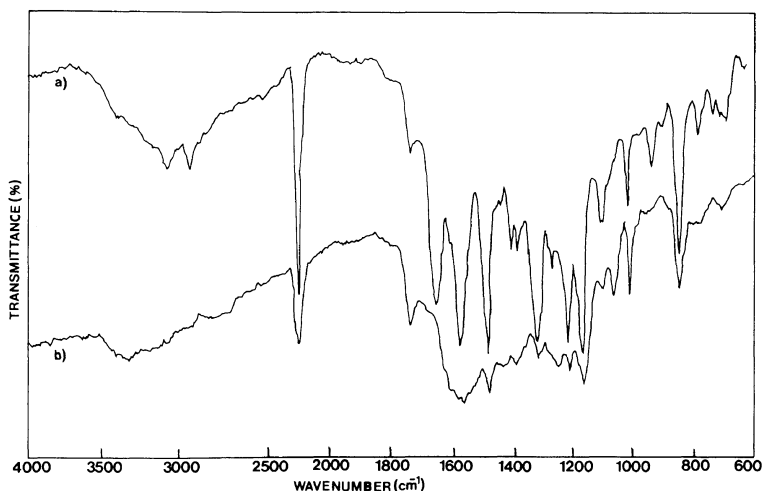


Figure 3. Infrared spectra poly(enaryloxynitrile) from disodium salts of hydroquinone and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene after (a) 0 h and (b) 1.5 h at 350°C under nitrogen.

The polymers of soluble portion in acetonitrile, **5–7** appeared to possess molecular weight of $M_n=4000–6000$ and $M_w=12000–15000$. However, these are not high molecular weight judging from viscosity and GPC data, but the clear and hard films were cast from the N-MP solution on a glass. Films of these polymers adhered very strongly to glass surfaces. Poly(ennaphthoxy-nitrile)s, **8–12** exhibited lower molecular weight than corresponding polymer **5–7**. These polymers with inherent viscosity of more than 0.1 could be cast from DMF into transparent films but were somewhat brittle and fingernail-creasable.

As can be seen from Figures 1 and 2(a), all

the polymers show interesting differential scanning calorimetry (DSC) curves with two consecutive large exotherms. The calorigrams of these polymers did not show any traces of glass transition temperature.

The first exothermic peak appears at 272, 274, and 363°C for polymers **5**, **6**, and **7**, respectively. In the case of poly(ennaphthoxy-nitrile)s incorporating naphthalene unit, the temperatures of first exotherm are between 320 and 350°C, and second exotherm peak is smaller and 40°C–50°C higher than the first exotherm. They disappear upon cooling and rescanning the samples as illustrated in Figure 2(b). After these polymers have been heated

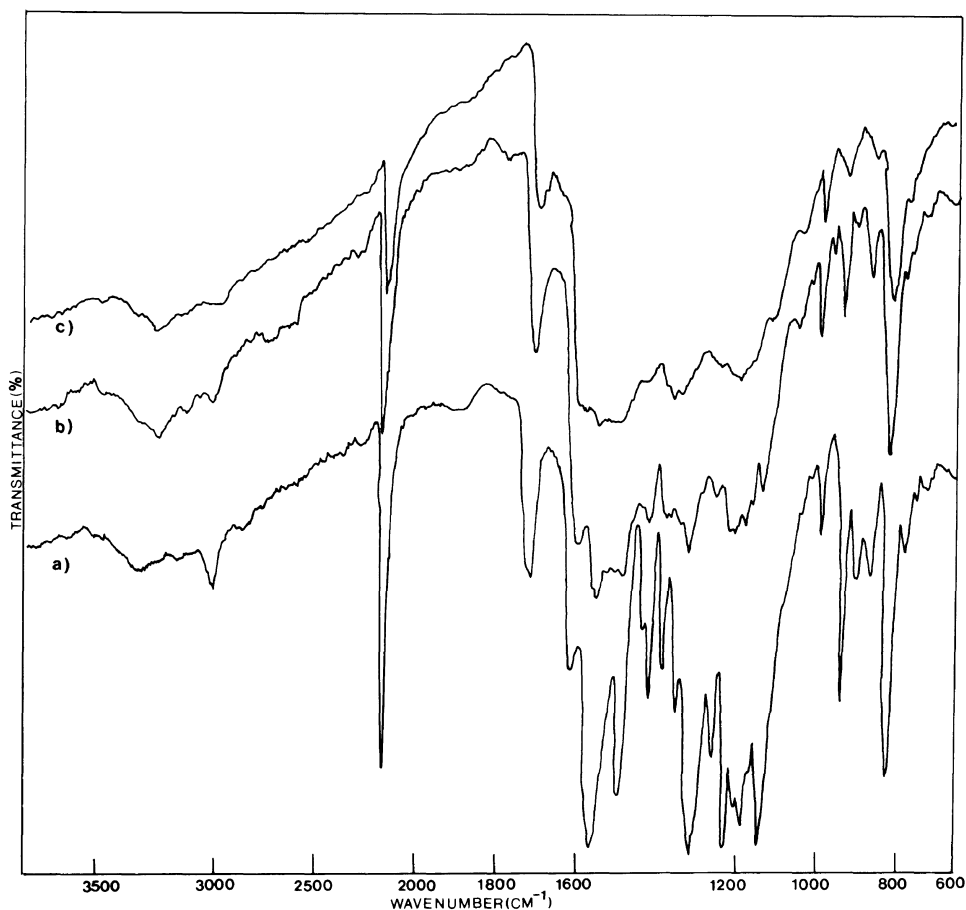


Figure 4. Infrared spectra of poly(enyaryloxynitrile) derived from disodium salts of 2,7-dihydroxy naphthalene and *p*-bis(1-chloro-2,3-dicyanovinyl)benzene after (a) 0 h, (b) 1 h, and (c) 2 h at 350°C under nitrogen.

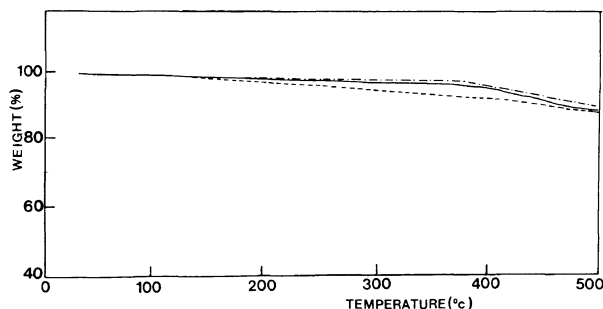


Figure 5. TGA thermogram of polymers obtained from cathecol (-----), resorcinol (—), and hydroquinone (-·-·-) with *p*-bis(1-chloro-2,2-dicyanovinyl)benzene with a heating rate of $10^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere.

beyond the temperature of first exotherm, solubility of solvent, from which the films were cast, decreased or they were no longer soluble in the solvent for the untreated polymers.

Polymer **7** heated to 320°C changed color from yellowish green to orange and displayed a gradual change in their IR spectra as they were heated. The nitrile band at 2220 cm^{-1} decreased apparently and broad strong band between 1700 and 1560 cm^{-1} attributable to $\text{C}=\text{C}$ or $\text{C}=\text{N}$ double bond appeared as shown in Figure 3.

For the polymers **8–12**, the nitrile stretching band was also reduced after curing over 2 hours at 350°C , while the absorption bands at $1650\text{--}1580\text{ cm}^{-1}$ appeared (Figure 4).

Besides the phenomena mentioned above, a slight loss of weight in their TGA curves at corresponding temperature also indicated that the structure of polymer changed without decomposition or evolution of small molecules. It might be happened that rearrangement or cross-linking of the dicyanovinyl group occurred during heating at the temperature of its first exotherm. It is difficult to confirm at this point the curing mechanism causing this exotherm.

All the polymers show excellent thermal stability as shown in Figure 2(c) and Figure 5.

Thermogravimetric analysis results are listed in Table II. The polymers **5–7** gave **6–7%** weight loss in nitrogen over a temperature

Table II. Residual weight and thermal properties of poly(enyaryloxynitrile)s by DSC and TGA

Polymer	Residual weight (%)			1st exotherm/ $^{\circ}\text{C}$	2nd exotherm/ $^{\circ}\text{C}$
	300°C	400°C	500°C		
6	94.5	93.3	88.3	272	340
7	94.6	93.4	89.2	274	419
8	95.3	94.7	90.0	364	421
9	93.7	89.9	80.4	347	— ^a
10	96.9	91.1	86.9	324	380
11	94.7	91.3	82.2	338	373
12	92.1	88.9	80.2	334	395
12	98.5	97.6	90.5	345	378

^a Two exothermic temperatures are superimposed around at 350°C .

range of 400°C and 10% weight at 500°C . Poly(ennaphthyloxynitrile)s, **8–12** showed 10% to 20% weight loss at 500°C , which were less stable than dihydroxybenzene-derived polymers. In the series of naphthalene-derived polymers, the thermal stability might not be related with the structure of polymer synthesized from various kinds of dihydroxynaphthalenes.

In the experiment of thermal reaction of model compound **3** and **4**, the chemical process causing such exotherm cannot be elucidated. Further works on the other model compound to investigate the curing mechanism are now in progress.

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