Preparation and Properties of Poly(enaryloxy nitriles) Containing Schiff Bases

Sang-Gon Kim, Seung-Jae Lee, and Myoung-Seon Gong*

Department of Chemistry, Dankook University, Cheonan, Chungnam 330-714, Korea

Received December 7, 1994; Revised Manuscript Received May 2, 1995®

ABSTRACT: Poly(enaryloxy nitriles) containing Schiff bases were prepared by reacting *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) with *p*-hydroxybenzaldehyde, which were then polymerized with various aromatic diamines. The chemical structure of the polymers was confirmed through syntheses of their corresponding Schiff base-containing model compounds. All the polymers were soluble in polar aprotic solvents such as DMF, DMSO, DMAc, and NMP. Moderate molecular weight polymers possessing M_w in the range 11 000–21 000 were obtained, and brittle films were cast from DMF solution. They showed a large exotherm around 340 °C attributable to the chemical changes of the dicyanovinyl group. Especially, curing of the azomethine group was observed to occur at 390 °C by differential scanning calorimetry. According to the thermogravimetric analyses, the polymers exhibited excellent thermal stability with 80–95% residual weight at 500 °C under nitrogen.

Introduction

New organic polymer systems are in constant demand in the field of thermally stable polymers. High-temperature capability, low moisture absorption, and improved storage and processing properties are emphasized for new thermally stable polymers. Among the various functional groups, biphenylylene, nadimide, acetylene, maleimide, styryl, *N*-cyanourea, and phthalonitrile groups have been frequently employed for the preparation of thermally curable and stable polymers.[1] The dicyanovinyl group should also be one of the thermally curable functionalities.

In recent years, novel poly(enamino nitriles)[3–8] and poly(enaryloxy nitriles),[9–11] which are thermally curable without evolution of volatile compounds, have been prepared by a vinylic nucleophilic substitution reaction and they showed an excellent thermal stability. The incorporation of the dicyanovinyl group into polymers such as polyurethanes[12,13] and the polyesters[14,15] enhances the solubility in common organic solvents as well as the thermal stability.

The dicyanovinyl chloride group is reactive to nucleophiles such as amines as well as to phenoxide anions possessing pK_a values around 10.[16,17] Especially, disodium salts of diphenol derivatives show good reactivity to *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) to produce various poly(enaryloxy nitriles).

In the case of aromatic diols containing azomethine groups, the partial hydrolysis of the azomethine linkage occurred during salt formation by reaction of aromatic diols containing Schiff base moieties with sodium hydroxide. Therefore, interfacial polymerization techniques using disodium salts of diphenols and **2** were limited. In general, polyazomethines have been prepared from dialdehydes and diamines.[18] Poly(enaryloxy nitriles) containing Schiff bases can be easily prepared by condensation polymerization of enaryloxy nitriles with formyl groups and diamines, and their properties were of considerable interest.

In this paper, we report the synthesis of new poly(enaryloxy nitriles) incorporating Schiff bases in the main chain by solution polymerization and their thermal properties will be discussed.

Experimental Section

1-Chloro-1-phenyl-2,2-dicyanoethene (**1**) and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**2**) were synthesized according to the method previously reported by Moore and co-workers.[3] *p*-Hydroxybenzaldehyde, *p*-phenylenediamine, *m*-phenylenediamine, *o*-phenylenediamine, hydrazine, and 4-aminophenyl ether (Aldrich Chemical Co.) were used without further purification. 1,2-Bis(4-aminophenoxy)ethane was prepared by the literature procedure.[2] *N*,*N*-Dimethylformamide (DMF) and *N*-methyl-2-pyrrolidinone (NMP) were purified by conventional methods.

Solubilities were estimated by dissolving 5 mg of the corresponding powdery polymer in 1 mL of solvent after heating to 80 °C. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300 MHz. In all ^{1}H NMR experiments, the chemical shifts are recorded in ppm from tetramethylsilane as an internal standard. FT-IR spectra were taken on a Midac spectrophotometer. UV–vis spectra were obtained with a Shimadzu Model 2100S in tetrahydrofuran at 20 °C. Differential scanning calorimetry of polymers was carried out on a DuPont 2100 or a Mettler thermal analyzer at a heating rate of 10 °C/min under nitrogen. TGA thermograms were performed on a Perkin-Elmer System 7 analyzer interfaced with a Perkin-Elmer 500 computer. Gel permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (10^2, 10^3, and 10^4 Å) in tetrahydrofuran calibrated with polystyrene standards by using a UV detector (254 nm) at 20 °C. Intrinsic viscosities of the polymer solutions were measured with a Cannon-Ubbelohde viscometer at 25 °C in DMF. Elemental analyses were carried out with a Yanaco MT-3 CHN analyzer.

1-(4-Formylphenoxy)-1-phenyl-2,2-dicyanoethene (3). A mixture of *p*-hydroxybenzaldehyde (1.3 g, 10.6 mmol) dissolved in a solution of sodium hydroxide (0.52 g, 13.0 mmol) in 20 mL of water was poured into a solution of **1** (1.89 g, 10.0 mmol) in 20 mL of 1,2-dichloroethane in a blender jar and then stirred at full speed for 3 min. The reaction mixture was stirred for an additional 2 h with a magnetic stirrer at 50 °C. After the organic layer was separated and evaporated, the crude solid was filtered out with a glass filter, washed with water several times, and recrystallized from 2-propanol.

3: yield 73%; mp 123 °C; IR (KBr) 3102 (C–H), 2227 (C≡N), 1762 (C=O), 1580 (C=C), 1310–1120 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 9.4 (s, 1H, formyl), 7.4 (m, 5 H, –Ph), 7.4–6.8 (2 d, 4 H, –CO–Ph–O–). Anal. Calcd for $C_{17}H_{10}N_2O_2$: C, 74.45; H, 3.65; N, 10.22. Found: C, 73.93; H, 3.52; N, 10.03.

***p*-Bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (4).** *p*-Hydroxybenzaldehyde (1.3 g, 10.6 mmol) was dissolved in a solution of sodium hydroxide (0.52 g, 13.0 mmol) in 20 mL of water for 2 h with stirring at room temperature. The resulting solution was poured into a solution of **2** (1.58 g, 5.3

® Abstract published in *Advance ACS Abstracts*, June 15, 1995.

0024-9297/95/2228-5638$09.00/0

mmol) in 20 mL of 1,2-dichloroethane in a blender jar and then stirred at full speed for 5 min. The reaction mixture was stirred for an additional 2 h at low speed at 50 °C. The solid that precipitated was separated out, washed with water and methanol, and recrystallized from acetonitrile.

4: yield 59%; mp 286 °C; IR (KBr) 3094 (C−H), 2230 (C≡N), 1760 (C=O), 1585 (C=C), 1300−1120 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.1 (s, 2 H, 2 formyl), 7.6 (s, 4 H, −Ph−), 7.3−6.7 (2 d, 8 H, 2 −CO−Ph−O−). Anal. Calcd for $C_{28}H_{14}N_4O_4$: C, 71.49; H, 2.98; N, 11.91. Found: C, 71.36; H, 2.86; N, 11.83.

1-[4-[(Phenylimino)methyl]phenoxy]-1-phenyl-2,2-dicyanoethene (5). Into a 100 mL round-bottomed flask equipped with a nitrogen inlet system, condenser, and a drying tube was placed aniline (0.8 g, 8.6 mmol) dissolved in NMP (20 mL) under nitrogen. To this solution was added an equivalent weight of **3** (2.19 g, 8.0 mmol) with stirring. After standing overnight at 60 °C, the yellow solution was cooled and precipitated into a large amount of water and the precipitate was filtered off. The product was washed with water several times, recrystallized from methanol, and dried at 60 °C *in vacuo* for 10 h.

5: yield 86%; mp 154 °C; IR (KBr) 3230 (aromatic C−H), 2210 (C≡N), 1610 (CH=N), 1570 (C=C), 1260−1120 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8 .0 (s, 1 H, −CH=N−), 7.4 (m, 5 H, −Ph), 7.4−6.8 (m, 9 H, −O−Ph− and =N−Ph). Anal. Calcd for $C_{23}H_{15}N_3O$: C, 76.88; H, 4.18; N, 14.48. Found: C, 76.61; H, 4.13; N, 14.27.

***p*-Bis[1-[4-[(phenylimino)methyl]phenoxy]-2,2-dicyanovinyl]benzene (6).** Into a 100 mL round-bottomed flask equipped with a nitrogen inlet system, condenser, and a drying tube was placed aniline (0.8 g, 8.6 mmol) dissolved in NMP (20 mL). To this solution was added an equivalent weight of **4** (1.88 g, 4.0 mmol) with stirring under nitrogen. The reaction mixture was heated to 60 °C and maintained for 10 h. After the yellow solution was cooled and precipitated into a large amount of water, the precipitated solid was filtered off. The solid product was washed with water several times, recrystallized from acetonitrile, and dried at 60 °C *in vacuo* for 10 h.

6: yield 83%; mp 195 °C; IR (KBr) 3275 (aromatic C−H), 2215 (C≡N), 1620 (CH=N), 1574 (C=C), 1245−1120 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.2 (s, 2 H, 2 −N=CH−), 7.8 (s, 4 H, −Ph−), 7.4−6.8 (m, 8 H, 2 −Ph−O−), 7.0 (m, 5 H, =N−Ph). Anal. Calcd for $C_{40}H_{24}N_6O_2$: C, 77.42; H, 3.87; N, 13.55. Found: C, 76.98; H, 3.84; N, 13.32.

Polymerization of *p*-Bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (4) with Aromatic Diamines. *p*-Bis-[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (**4**) (1 g, 2.13 mmol) and *p*-phenylenediamine (0.23 g, 2.13 mmol) were dissolved in 20 mL of anhydrous *N*-methyl-2-pyrrolidinone. The solution turned yellowish brown and increased in viscosity within 1 h. The stirred mixture was maintained at 70 °C with stirring for 8 h under nitrogen. The reaction mixture was cooled and then poured into the large volume of water to precipitate the polymer. The precipitated polymer as a fine powder was dissolved in DMF and reprecipitated into methanol. The polymer was filtered off and dried *in vacuo* at 50 °C for 12 h.

Other poly(enaryloxy nitriles) containing Schiff bases were prepared by reacting **4** and 4-aminophenyl ether, hydrazine, *m*-phenylenediamine, *o*-phenylenediamine, and 1,2-bis(4-aminophenoxy)ethane by using similar synthetic procedures.

7: yield 76%; IR (KBr) 3210 (aromatic C−H), 2232 (C≡N), 1614 (CH=N), 1581 (C=C), 1261−1050 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.4 (m, 2 H, 2 −CH=N−), 8.0−7.8 (s, 4 H, −Ph−), 7.6−6.8 (m, 8 H, 2 −Ph−O−), 7.0 (m, 4 H, =N−Ph−N=). Anal. Calcd for $(C_{34}H_{18}N_6O_2)_n$: C, 74.28; H, 3.32; N, 15.50. Found: C, 73.01; H, 3.28; N, 14.97.

8: yield 84%; IR (KBr) 3120−3010 (C−H), 2224 (C≡N), 1610 (CH=N), 1580 (C=C), 1300−1030 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6 + $CDCl_3$) δ 8.5 (m, 2 H, 2 −CH=N−), 7.8−7.6 (s, 4 H, −Ph−), 7.6−6.9 (m, 8 H, 2 −Ph−O−), 7.0 (m, 4 H, =N−Ph−N=). Anal. Calcd for $(C_{34}H_{18}N_6O_2)_n$: C, 75.28; H, 3.32; N, 15.50. Found: C, 73.32; H, 3.28; N, 14.97.

9: yield 87%; IR (KBr) 3218 (aromatic C−H), 2227 (C≡N), 1618 (CH=N), 1580 (C=C), 1255−1050 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.4 (m, 2 H, 2 −CH=N−), 8.0−7.8 (s, 4 H, −Ph−), 7.6−6.7 (m, 8 H, 2 −Ph−O−), 6.9 (m, 4 H, =N−Ph−N=). Anal. Calcd for $(C_{34}H_{18}N_6O_2)_n$: C, 74.28; H, 3.32; N, 15.50. Found: C, 73.37; H, 3.29; N, 15.27.

10: yield 97%; IR (KBr) 3077 (C−H), 2238 (C≡N), 1610 (CH=N), 1589 (C=C), 1325−1165 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.8 (m, 2 H, 2 −CH=N−), 8.0−7.8 (s, 4 H, −Ph−), 7.8−6.8 (m, 8 H, 2 −Ph−O−). Anal. Calcd for $(C_{28}H_{14}N_6O_2)_n$: C, 72.10; H, 3.00; N, 18.2. Found: C, 71.41; H, 2.92; N, 17.78.

11: yield 91.0%; IR (KBr) 3230 (C−H), 2238 (C≡N), 1610 (CH=N), 1580 (C=C), 1335−1100 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.4 (m, 2 H, 2 −CH=N−), 8.0−7.8 (s, 4 H, −Ph−), 7.6−6.8 (m, 16 H, 2 −O−Ph− and =N−Ph−O−Ph−N=). Anal. Calcd for $(C_{46}H_{22}N_6O_3)_n$: C, 78.19; H, 3.12; N, 11.90. Found: C, 76.92; H, 3.08; N, 12.01.

12: yield 92%; IR (KBr) 3120−3015 (aromatic C−H), 2930−2850 (aliphatic C−H), 2220 (C≡N), 1615 (CH=N), 1582 (C=C), 1310−1105 (C−O) cm^{-1}; ^{1}H NMR (DMSO-d_6 + $CDCl_3$) δ 8.7 (m, 2 H, 2 −CH=N−), 7.6 (s, 4 H, −Ph−), 7.3−6.8 (2 d, 8 H, 2 −CO−Ph−O−), 4.0 (s, 4 H, $-OCH_2CH_2O-$). Anal. Calcd for $(C_{40}H_{26}N_6O_4)_n$: C, 73.39; H, 3.98; N, 2.84. Found: C, 71.93; H, 4.07; N, 12.36.

Results and Discussion

Polymers containing Schiff bases have been generally prepared by the condensation reaction of diamines with dicarboxaldehyde derivatives.[18] Poly(enaryloxy nitriles) containing Schiff bases can also be synthesized by an analogous vinyl substitution reaction of dicyanovinyl chlorides with disodium salts of diphenols containing the azomethine group. Interfacial polymerization techniques[9,10] have provided a convenient method for the preparation of various poly(enaryloxy nitriles). However, interfacial polymerization yielded polymers of rather limited molecular weights. Hence a conventional condensation polymerization method was chosen for the preparation of poly(enaryloxy nitriles) containing Schiff bases by using enaryloxy nitriles containing formyl groups. Enaryloxy nitriles containing formyl groups were prepared from **1** or **2** and the sodium salt of *p*-hydroxybenzaldehyde, but the yield was low because of the low pK_a value of *p*-hydroxybenzaldehyde (pK_a value 7.62).[17] 1-(4-Formylphenoxy)-1-phenyl-2,2-dicyanoethene (**3**) and *p*-bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (**4**) were obtained in 59 and 73% yields, respectively. As shown in Scheme 1, two model compounds, 1-[4-[(phenylimino)methyl]phenoxy]-1-phenyl-2,2-dicyanoethene (**5**) and *p*-bis[1-[4-[(phenylimino)-methyl]phenoxy]-2,2-dicyanovinyl]benzene (**6**) were prepared by reacting the dicyanovinyl compounds containing formyl groups, **3** and **4**, with aniline to examine the feasibility of the polymerization and also to confirm the structure of the resulting polymers.

The conditions and results of polymerization are summarized in Table 1. Poly(enaryloxy nitriles) containing Schiff bases were prepared by reacting aromatic diamines with *p*-bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (**4**) in *N*-methyl-2-pyrrolidinone, as shown in Scheme 2. Several poly(enaryloxy nitriles) were prepared by condensation polymerization of **4** with various aromatic diamines such as *o*-, *m*-, *p*-phenylenediamine, hydrazine, 4-aminophenyl ether, and 1,2-bis-(4-aminophenoxy)ethane. Polymers **7** and **10**−**12** contained para-linked diamine groups, while **8** and **9** possess meta and ortho linkages, respectively.

The polymers displayed colors such as deep brown (**7**), black (**8**), brown (**10**), and yellow (**11**), respectively, because of the extensive conjugation of the azomethine group with aromatic rings. Moreover, the solution of

Scheme 1

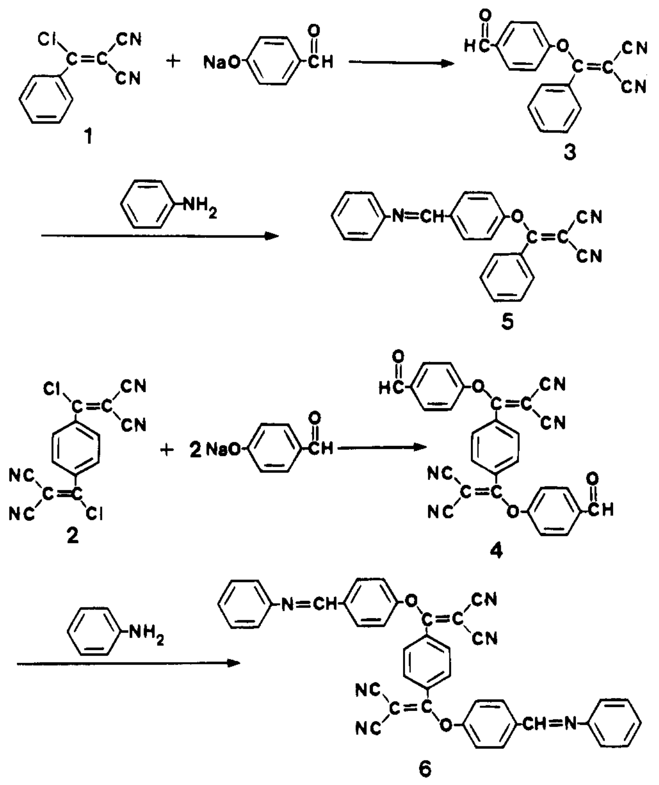
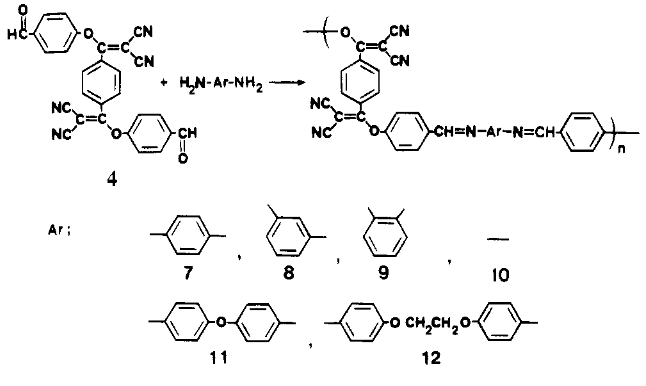


Table 1. Conditions and Results of Polymerization of Various Aromatic Diamines with 4

polymer	diamines[a]	M_n	M_w	$[\eta]^b$ (dL/g)	yield (%)
7	*p*-PDA	4700	15 400	0.58	73
8	*m*-PDA	5300	17 500	0.49	84
9	*o*-PDA	3500	10 600	0.22	87
10	HYD	6300	13 600	0.45	97
11	APE	3500	21 000	0.60	91
12	BAE	4650	20 500	0.52	92

[a] *p*-PDA, *p*-phenylenediamine; *m*-PDA, *m*-phenylenediamine; *o*-PDA, *o*-phenylenediamine; HYD, hydrazine; APE, 4-aminophenyl ether; ABE, 1,2-bis(4-aminophenoxy)ethane. [b] Intrinsic viscosity was measured in DMF in 1 g/dL at 25 °C.

Scheme 2



most polymers in DMF and NMP exhibited a deep brownish color.

The polymers obtained here were identified as poly(enaryloxy nitriles) having azomethine groups by comparing their IR and NMR spectra with those of model compounds **5** and **6**. In the IR spectra, characteristic absorption bands of $C\equiv N$, CH=N, and C=C were exhibited at 2225, 1625, and 1580 cm^{-1}, respectively. In the ^1H NMR spectrum, the presence of a broad singlet signal at 8.5 ppm corresponding to the azomethine proton, and the multiplet signal around 7.8–6.8 ppm corresponding to the fragment of **2** and aromatic protons in the diphenol units clearly indicated that the poly(enaryloxy nitriles) containing azomethine groups were synthesized. This observation was consistent with the results for model compounds and corresponded to their assigned chemical structures. Elemental analysis also supported the formation of the model compounds and matched well with the calculated data. In the case of polymers, it has been observed that this class of polymers tends to form thermally stable chars at high temperatures which result in elemental analyses which are low in carbon values.

Table 2. Thermal Properties of Poly(enaryloxy nitriles) Containing Schiff Bases

			residual weight (%)	
polymer	exo (°C)	10% wt. loss (°C)	400 °C	500 °C
7	340, 390	610	98	96
8	325, 380	570	96	90
9	336	500	92	86
10	342, 385	520	96	92
11	320, 393	650	99	96
12	335	450	94	85

The solution polymerization of **4** with aromatic diamines produced polymers of moderate molecular weight. When the solubility behavior of polymers containing Schiff bases was investigated, most polymers exhibited virtually no solubility in polar protic solvents such as methanol and ethanol, while they displayed fairly good solubilities in several polar aprotic solvents such as NMP, DMF, dimethyl sulfoxide, and *N,N*-dimethyl acetamide.

The polymers derived from ortho and meta diamines showed better solubilities than para diamines. It is considered that the distorted structure, which prevents a closer packing of the macromolecular chains, causes a decrease of crystallinity and an increase in solubility. The polymers obtained from solution polymerization have intrinsic viscosities of 0.22–0.60 dL/g. The M_n and M_w were in the range of 3500–7500 and 11 500–22 500. These are moderate molecular weights judging from the data of viscosity and GPC. It may be due to the ease of formation of the azomethine linkage from diamines and dialdehydes in the course of solution polymerization. In general, the azomethine group exhibits maximum values at λ_{max} = 172 nm and λ_{max} = 238 nm in its UV absorbance spectrum, where the 172 nm peak is more intense and has been assigned to a $\pi \rightarrow \pi^*$ transition.[19] On the other hand, for model compounds **5** and **6**, the maxima are at λ_{max} = 288 nm and λ_{max} = 342 nm, respectively. Model compound **6** absorbs at a longer wavelength than model compound **5** because of the increased conjugation with aromatic rings. Polymer **7** exhibited a broad UV absorption with a maximum value at λ_{max} = 288 nm and a shoulder from 340 to 440 nm.

These polymers exhibit interesting thermal behavior, as evidenced by the data of Table 2. The typical DSC traces of polymers **7**, **8**, **10**, and **11** involve two consecutive exotherms around 340 and 390 °C, respectively, as shown in Figures 1a and 2a. On the other hand, polymers **9** and **12** showed a broad exotherm starting near 300 °C and reaching maximum intensity at 335 °C with a shoulder at 375 °C, indicating two overlapping exotherms. The first exotherm does not reappear upon cooling and rescanning the sample, as shown in Figure 1b. When the polymers were heated to 340 °C in a nitrogen atmosphere, the polymers were no longer soluble in solvents such as NMP and DMF even at an

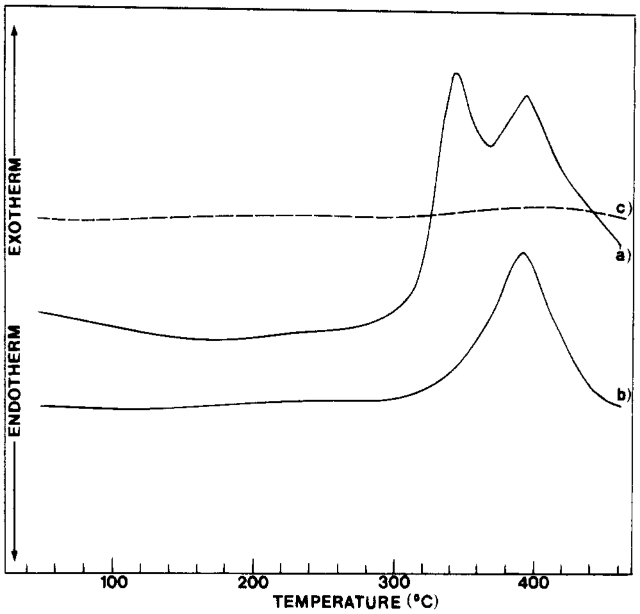


Figure 1. Differential scanning calorimograms of polymer **7**: (a) first scanning; (b) second scanning after heating to 350 °C; (c) second scanning after heating to 400 °C at a heating rate of 10 °C/min in nitrogen.

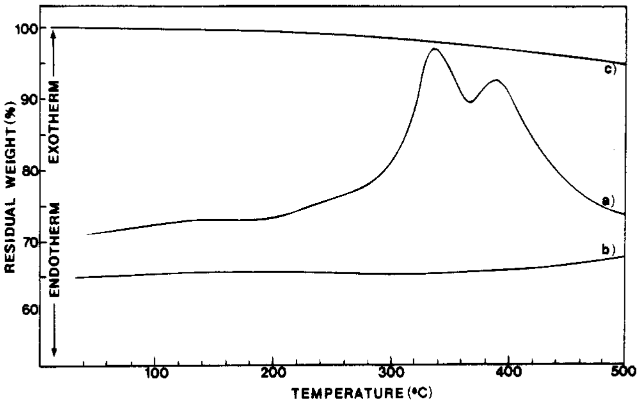


Figure 2. Differential scanning calorimograms: (a) first scanning; (b) second scanning after heating up 400 °C; (c) TGA thermogram of polymer **11**.

elevated temperature (80 °C). The IR spectrum of the cured material indicated that the nitrile band at 2232 cm^{-1} decreased in intensity and peaks at 1580−1600 cm^{-1} broadened. At the same time a new band at 3400 cm^{-1} appeared. In the case of poly(enaryloxy nitriles), the chemical pathways of curing of the dicyanovinyl group have not been clearly elucidated. When the 1-phenoxy-1-phenyl-2,2-dicyanoethane as a model compound for curing was heated at 350 °C under nitrogen, 70% polymeric residue was obtained. The curing of poly(enaryloxy nitriles) might proceed via the cross-linking of the dicyanovinyl group. According to experiments on the poly(enamino nitriles) reported by Moore and co-workers, it might happen that intramolecular cyclization or cross-linking of the dicyanovinyl group occur during heating at the temperature of the first exotherm.[4,7,20] More experiments on model compounds are required to explicate the curing mechanism. In addition, the polymers with azomethine moieties showed a second exotherm at 380−400 °C attributable to further cross-linking of this system, which may be attributed to the presence of conjugated azomethine groups. When a sample of polymer **7** was heated to 390 °C (DSC) in a sealed DSC pan at a heating rate of 10 °C/min, this peak was completely absent when the sample was cooled and rescanned in Figure 1c. No melting endotherm was noted below the exotherm near 350 °C. The polymer may melt higher than 350 °C or an insufficient amount of crystalline material may be formed during the measurement to exhibit a melting peak. A glass transition temperature was not also detected by DSC for most polymers. The Schiff base polymers contain a more rigid backbone, and this effect may partly result in a glass transition temperature that is higher than the curing temperature. Polymers **11** derived from 4-aminophenyl ether showed thermal behavior similar to that seen in Figure 2a,b At the temperature of the first and second exotherms, detectable weight loss of the polymer is not observed (Figure 2c). This result indicates that the poly(enaryloxy nitriles) cured thermally without release of volatile byproducts.

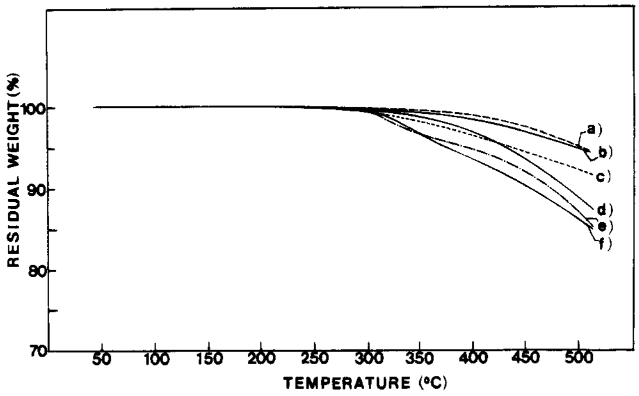


Figure 3. Thermograms of poly(enaryloxy nitriles): (a) **11**; (b) **7**; (c) **10**; (d) **8**; (e) **9**; (f) **12**.

The thermal stability data are listed in Table 2, and TGA traces are exhibited in Figure 3. The polymers sustained a 10% weight loss over a temperature range of 500 deg at a heating rate of 10 °C/min and gave a residual weight varying from 85 to 96% at 500 °C in nitrogen. From the data in Table 2, para-substituted polymer **7** shows improved thermal stability over the meta- or ortho-substituted poly(enaryloxy nitriles) **8** and **9**. A structural difference between polymers **7** and **12** is the presence of flexible alkyl groups in the main chain. The latter polymer showed lower thermal stability.

Poly(enaryloxy nitrile) **11** derived from 4-aminophenyl ether showed excellent thermal stability (96% residual weight at 500 °C and 80% at 800 °C), which may result from the successive curing of the dicyanovinyl group and azomethine groups.

References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.
(2) Spinelli, H. J.; Harris, F. W. *Reactive oligomers*; ACS Symposium Series 282; American Chemical Society: Washington, D.C., 1985; p 89.
(3) Robello, D. R.; Moore, J. A. *Macromolecules* **1989**, *22*, 1084.
(4) Robello, D. R.; Moore, J. A. *Macromolecules* **1986**, *19*, 2667.
(5) Mehta, P. G.; Moore, J. A. *Macromolecules* **1993**, *26*, 916.
(6) Mehta, P. G.; Moore, J. A. *Polym. Mater. Sci. Eng.* **1990**, *63*, 351.
(7) Kim, S. Y.; Mehta, P. G.; Moore, J. A. *Macromolecules* **1994**, *27*, 3504.
(8) Gong, M. S.; Kim, S. T.; Lee, J. O.; Kim, Y. S. *Polymer (Korea)* **1991**, *15*, 95.
(9) Gong, M. S.; Kim, S. T.; Moon, H. S. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 591.
(10) Gong, M. S.; Moon, H. S.; Kim, J. S.; Kim, C. B. *Polym. J.* **1993**, *25*, 193.
(11) Gong, M. S.; Kim, T. M.; Shin, J. C. *Macromolecules* **1995**, *28*, 2212.

(12) Gong, M. S.; Kim, J. S.; Kim, S. T.; Choi, S. H. *Polym. J.* **1993**, *25*, 763.

(13) Gong, M. S.; Kim, S. T.; Moon, H. S. *Macromolecules* **1992**, *25*, 7392.

(14) Gong, M. S.; Cho, H. G.; Choi, S. H.; Kim, B. G. *Macromolecules* **1993**, *26*, 6654.

(15) Gong, M. S.; Kim, Y. S.; Kim, B. G. *Polym. J.* **1994**, *26*, 1910.

(16) Dean, J. A. *Lange Handbook of Chemistry*, 13th ed.; McGraw Hill: New York, 1985; pp 5−18~60.

(17) Gong, M. S.; Kim, T. M.; Moon, S. H.; Kim, S. G. *Bull. Korean Chem. Soc.* **1994**, *15*, 901.

(18) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromoleules* **1987**, *20*, 729.

(19) Stern, E. S.; Timmons, C. J. *Electronic Absorption Spectroscopy in Organic Chemistry*, 3rd ed.; Edward Anord Ltd.: London, 1976.

(20) Moore, J. A.; Kaur, S.; Perry, R. J. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1994**, *35* (1), 385.

MA946506H