Synthesis of Poly(enaryloxynitriles) Containing Schiff Bases and Their Thermal Properties

Sang-Gon Kim, Yang-Kyoo Han[†], and Myoung-Seon Gong*

Department of Chemistry, Dankook University, Cheonan, Chungnam 330-714, Korea
[†]Division of Polymer Research, Korea Institute of Science and Technology, P.O. Box 131,
Cheongryang, Seoul 130-650, Korea

Poly(enaryloxynitriles) containing Schiff bases were prepared from *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (2) and various aromatic diols having Schiff base moiety by interfacial polymerization. The chemical structure of the polymers was confirmed through syntheses of their corresponding model compounds. All the polymers were soluble in polar aprotic solvents and their brittle films were cast from DMF solution. They showed a large exotherm around 340 ℃ attributable to the chemical change of dicyanovinyl group. Especially, curing of azomethine group was observed to occur at 390 ℃ by differential scanning calorimetry. According to the thermogravimetric analyses, they exhibited excellent thermal stability with 60-90% residual weight at 500 ℃ in nitrogen.

Introduction

In recent years, there have been increasing considerable interests in the synthesis of a variety of high performance polymers with good thermal and mechanical properties which are useful for structural applications. Among them, however, most of high-temperature structural materials have several difficulties in processing due to the evolution of volatile compounds, and insolubility and/or infusibility. Thus many researchers are focusing their efforts on improving the processessibility of thermally stable polymers.[1] The approaches primarily involves incorporating more flexible moieties in the polymer backbone to permit processing as thermoplastics or placing reactive groups on the polymer chain that could be thermally reacted to result in chain extension. Among the functional groups, biphenylene, nadimide, acetylene, maleimide, styryl, N-cyanourea and phthalonitrile have been most frequently employed for the preparation of thermally curable and stable polymers.[2,3] Although the curing mechanism has not been clearly examined, the dicyanovinyl group should be one of the thermally curable functions.

Recently, new class of novel poly(enaminonitriles)[4~10] and poly(enaryloxynitriles),[11~13] which are thermally curable without evolution of volatile compounds, have been prepared by a vinylic nucleophilic substitution reaction and they show an excellent thermal stability. The incorporation of dicyanovinyl group into polyurethane[14,15] and polyester[16~18] enhances the solubility in common organic solvents as well as the thermal stability.

The dicyanovinyl chloride is reactive to nucleophiles such as amines and phenoxide anions possessing pK_a value around 10.[19,20] Especially, disodium salts of diphenol derivatives show a good reactivity to *p*-bis(1-chloro-2,2-dicyanovinyl) benzene (2) to produce various poly(enaryloxynitriles).[20] Therefore poly(enaryloxynitriles) containing Schiff bases can be easily prepared by a reaction of dichloride 2 with sodium salts of aromatic diols having Schiff bases and their properties were of considerable interest.

[†]Current address: Department of Chemistry, Colledge of Natural Science, Hanyang University, Seoul 133-791, Korea

In this paper, we report the synthesis of new poly(enaryloxynitriles) incorporated with Schiff bases in the main chain and their thermal properties will be discussed.

Experimental

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 coworkers.[4] *p*-Hydroxybenzaldehyde, *o*-hydroxybenzaldehyde, *p*-phenylenediamine, terephthaldehyde, *m*-phenylenediamine, *o*-aminophenol, *p*-aminophenol, hydrazine and 4-aminophenyl ether were used without further purification. Dichloromethane and 1,2-dichloroethane were purified by conventional purification method.

All melting points were determined on a Aldrich Mel-Temp II melting points apparatus using capillary tubes and are uncorrected. ¹H NMR spectra were recorded on a Varian 360A spectrometer. FT-IR spectra were taken on a Midac spectrphotometer. Thermal analyses of polymers were carried out on a DuPont 2100 and a Mettler thermal analyzer. Inherent viscosities of polymer solution were measured in a Cannon-Ubbelohde viscometer at 25 ℃. The polymer solutions for the viscosity measurements were filtered through sintered glass filter. Gel permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (10², 10³ and 10⁴ Å) in THF and calibrated with polystyrene standards. Elemental analyses were carried out with a Yanaco MT-3, CHN-analyzer.

Preparation of 1-(4-phenyliminomethyl)phenoxy-1-phenyl-2,2-dicyanoethene (3). 4-Phenyliminomethyl phenol (1.05 g, 5.32 mmol) was quickly dissolved in a solution of sodium hydroxide (0.26 g, 6.5 mmol) in 20 mL of water. The resulting solution was tansferred to the blender jar. Monochloride 1 (1 g, 5.32 mmol) dissolved in 20 mL of 1,2-dichloroethane was poured into the jar, in one portion, and then stirred at full speed for 5 min. After the organic layer was separated and evaporated, the solid product was filtered and washed with water twice. The yellow solid product was recrystallized from methanol.

Table 1. Structure and Properties of Diol Monomers Containing Azomethine Group

Diol	Structure	Yield(%)	mp(°C)	Color
6	HO–⟨ ⟩–CH=N-Ph-N=CH–⟨ ⟩–OH	92	273	yellow
7	⟨ ⟩–CH=N-Ph-N=CH–⟨ ⟩ (OH, HO)	71	235	orange
8	HO–⟨ ⟩–CH=N–⟨ ⟩–N=CH–⟨ ⟩–OH	62	–	orange
9	⟨ ⟩–CH=N–⟨ ⟩–N=CH–⟨ ⟩ (OH, HO)	59	101	brown
10	HO–⟨ ⟩–CH=N-Ph-O-Ph-N=CH–⟨ ⟩–OH	45	159	yellow
11	⟨ ⟩–CH=N-Ph-O-Ph-N=CH–⟨ ⟩ (OH, HO)	78	209	yellow
12	HO–⟨ ⟩–CH=N-N=CH–⟨ ⟩–OH	58	293	yellow
13	⟨ ⟩–CH=N-N=CH–⟨ ⟩ (OH, HO)	72	229	yellow
14	HO–⟨ ⟩–N=CH-Ph-CH=N–⟨ ⟩–OH	64	276	yellow
15	⟨ ⟩–N=CH-Ph-CH=N–⟨ ⟩ (OH, HO)	60	232	yellow
16	HO–⟨ ⟩–CH=N–⟨ ⟩–OH	80	210	brown
17	HO–⟨ ⟩–CH=N–⟨ ⟩ (HO)	60	132	brown
18	⟨ ⟩–CH=N–⟨ ⟩–OH (OH)	87	138	brown
19	⟨ ⟩–CH=N–⟨ ⟩ (OH, HO)	72	185	orange

The similar procedures were applied to the synthesis of other model compounds *p*-bis[1-(4-phenyliminomethyl)phenoxy-2,2-dicyanovinyl]benzene (4) and bis[4'-(1-phenyl-2,2-dicyanovinyloxy)benzal]-1,4-phenylenediamine (5).

3: 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; ¹H NMR (DMSO-d₆) δ 8.0 (s, 1H, -CH=N-), 7.4 (m, 5H, -Ph), 7.4-6.8 (m, 9H, -O-Ph- and =N-Ph); UV (THF, λ_max) 207, 222, 235, 288 nm. Anal. Calcd for C₂₃H₁₅N₃O₁: C, 76.88; H, 4.18; N, 14.48. Found: C, 75.92; H, 4.02; N, 14.21.

4: 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; ¹H NMR (DMSO-d₆) δ 8.2 (s, 2H, -N=CH-), 7.8 (s, 4H, -Ph-), 7.4-6.8 (m, 8H, 2 -Ph-O-), 7.0 (m, 5H, =N-Ph); UV (THF, λ_max) 215, 236, 276, 319 nm. Anal. Calcd for C₄₀H₂₄N₆O₂: C, 77.42; H, 3.87; N, 13.55. Found: C, 76.82; H, 3.79; N, 13.29.

5: Yield 85%; mp 340 °C ; IR (KBr) 3270 (aromatic C-H), 2210 (C≡N), 1620 (CH=N), 1565 (C=C), 1260-1150 (C-O) cm⁻¹; ¹H NMR (DMSO-d₆) δ 8.4 (s, 2H, -CH=N-), 7.7-6.8 (m, 8H, 2 -O-Ph-), 7.5 (m, 10H, 2 -Ph), 7.0 (s, 4H, =N-Ph-N=); UV (THF, λ_max) 235, 285, 342 nm. Anal. Calcd for C₄₀H₂₄

N₆O₂: C, 77.42; H, 3.87; N, 13.55. Found: C, 76.89; H, 3.72; N, 13.39.

Representative Preparation of Aromatic Diols Containing Schiff bases. Aromatic diols containing Schiff bases were prepared by the modified method reported by Hatt.[22] In a 500 mL of round bottomed flask, *p*-hydroxybenzaldehyde (10 g, 81.9 mmol) and *p*-phenylenediamine (4.43 g, 40.97 mmol) were dissolved in methanol (200 mL). After the reaction mixture was refluxed for 10 hr and cooled, the precipitated solid powder was filtered and washed with methanol. The yellowish green powder was recrystallized from ethylacetate to give bis(4'-hydroxybenzal)-1,4-phenylenediamine.

Similar synthetic procedures were applied to the preparation of the other diols containing Schiff bases 7-19. Their physical properties were listed in Table 1.

6: Yield 92%; mp 272-274 °C ; IR (KBr) 3472 (O-H), 3279 (aromatic C-H), 1610 (CH=N), 1590 (C=C), 1245-1090 (C-O) cm⁻¹; ¹H NMR (Acetone-d₆) δ 8.1 (s, 2H, 2 -CH=N-), 6.8 (m, 4H, =N-Ph-N=), 6.5-7.4 (2d, 8H, 2 -O-Ph-); UV (THF, λ_max) 236, 289, 359 nm. Anal. Calcd for C₁₅H₁₆N₂O₆: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.02; H, 5.98; N, 10.47.

Polymerization of *p*-Bis(1-chloro-2,2-dicyanoviny)benzene (2) with Aromatic diol. Bis(4'-hydroxybenzal)-1,4-phenylenediamine (1.05 g, 3.34 mmol) was dissolved quickly in sodium hydroxide (0.33 g, 8.25 mmol) in 20 mL of water. The resulting solution was transferred to the blender jar. Dichloride 2 (1 g, 3.34 mmol) in 20 mL of 1,2-dichloroethane was added into the jar, in one portion, and the reaction mixture was stirred at full speed for 5 min. The precipitated powdery polymer was filtered and then washed with water several times. The polymer was washed with methanol again and dried *in vacuo* at 50 °C for 12 h.

Other poly(enaryloxynitriles) containing Schiff bases were prepared by reacting 2 and various diols containing Schiff bases according to the similar synthetic procedures described above. The spectral data were consistent with their assigned structure and corresponded well with those of model compounds.

P₆: Yield 76%; IR (KBr) 3210 (aromatic C-H), 2232 (C≡N), 1614 (CH=N), 1581 (C=C), 1261-1050 (C-O) cm⁻¹; ¹H NMR (DMSO-d₆) δ 8.4 (m, 2H, -CH=N-), 7.8 (s, 4H, -Ph-), 7.6-6.8 (m, 8H, 2 -Ph-O-), 7.0 (m, 4H, =N-Ph-N=); UV (THF, λ_max) 288, 340 (br) nm. Anal. Calcd for (C₃₄H₁₈N₆O₂)ₙ: C, 75.28; H, 3.32; N, 15.50. Found: C, 75.01; H, 3.28; N, 14.97.

P₈: Yield 84%; IR (KBr) 3120-3010 (C-H), 2224 (C≡N), 1610 (CH=N), 1580 (C=C), 1300-1030 (C-O) cm⁻¹; ¹H NMR (DMSO-d₆+CDCl₃) δ 8.5 (m, 2H, -CH=N-), 7.8 (s, 4H, -Ph-), 7.6-6.9 (m, 8H, 2 -Ph-O-), 7.0 (m, 4H, =N-Ph-N=). Anal. Calcd for (C₃₄H₁₈N₆O₂)ₙ: C, 75.28; H, 3.32; N, 15.50. Found: C, 74.32; H, 3.21; N, 14.92.

P₁₀: Yield 91%; IR (KBr) 3230 (C-H), 2238 (C≡N), 1610 (CH=N), 1580 (C=C), 1335-1100 (C-O) cm⁻¹; ¹H NMR (DMSO-d₆) δ 8.4 (m, 2H, -CH=N-), 8.0-7.8 (s, 4H, -Ph-), 7.6-6.8 (m, 16H, 2 -O-Ph- and =N-Ph-O-Ph-N=). Anal. Calcd for (C₄₆H₂₂N₆O₃)ₙ: C, 78.19; H, 3.12; N, 11.90. Found: C, 77.92; H, 3.08; N, 12.01.

P₁₂: Yield 97%; IR (KBr) 3077 (C-H), 2238 (C≡N), 1610 (CH=N), 1589 (C=C), 1325-1165 (C-O) cm⁻¹; ¹H NMR
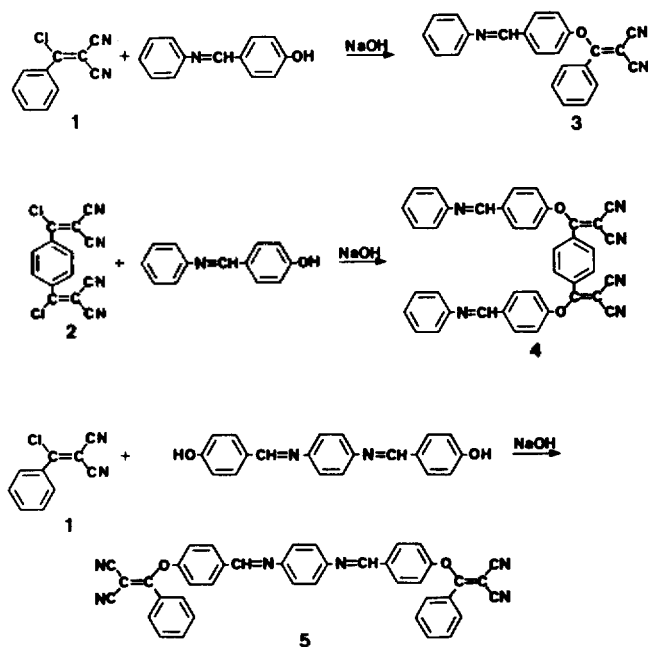
Scheme 1.

(DMSO-d_6) δ 8.8 (m, 2H, -C$\underline{H}$=N-), 7.8 (s, 4H, -$\underline{Ph}$-), 7.8-6.8 (m, 8H, 2 -$\underline{Ph}$-O). Anal. Calcd for ($C_{28}H_{14}N_6O_2)_n$: C, 72.10; H, 3.00; N, 18.2. Found: C, 72.41; H, 2.92; N, 17.78.

P_{14}: Yield 96%; IR (KBr) 3237 (C-H), 2220 (C≡N), 1612 (CH=N), 1580 (C=C), 1330-1100 (C-O) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.4 (m, 2H, -C$\underline{H}$=N-), 7.8 (s, 4H, -$\underline{Ph}$-), 7.6 (s, 4H, =CH-$\underline{Ph}$-CH=), 7.6-6.9 (m, 8H, 2 =N-$\underline{Ph}$-O-). Anal. Calcd for ($C_{34}H_{18}N_6O_2)_n$: C, 75.18; H, 3.32; N, 15.50. Found: C, 74.98; H, 3.28; N, 15.32.

Results and Discussion

Polymers containing Schiff bases have been generally prepared by the condensation reaction of diamines with dicarboxaldehyde derivatives.[21] But the poly(enaryloxynitriles) having Schiff base moieties can be obtained by interfacial polymerization techniques, which provide a convenient method for the preparation of various poly(enaryloxynitriles).[11]

As shown in Scheme 1, three Schiff bases model compounds, 1-(4-phenyliminomethyl)phenoxy-1-phenyl-2,2-dicyanoethene (3), p-bis[1-(4-phenyl iminomethyl)phenoxy-2,2-dicyanovinyl]benzene (4) and bis[4'-(1-phenyl-2,2-dicyano vinyloxy)benzal]-1,4-phenylenediamine (5), were prepared to examine the feasibility of the interfacial polymerization and to confirm the structure of the resulting polymers.

Poly(enaryloxynitriles) were prepared by reacting difunctional dicyanovinyl chloride, p-bis(1-chloro-2,2-dicyanovinyl) benzene (2), with various disodium salts of diphenol derivatives having Schiff bases according to the Scheme 2. The interfacial polymerizations were carried out in 1,2-dichloroethane as an organic medium using a high-speed blender. The conditions and results of polymerization are summarized in Table 2. The polymerizability of sodium salts of aromatic diol monomers might be depending on the nucleophilicity of phenoxide anion. Azomethine substituted phenol (pK_a value 9.2) showed a lower pK_a value than phenol itself (pK_a value 10).[19] Thus the sodium salts of diphenol derivatives
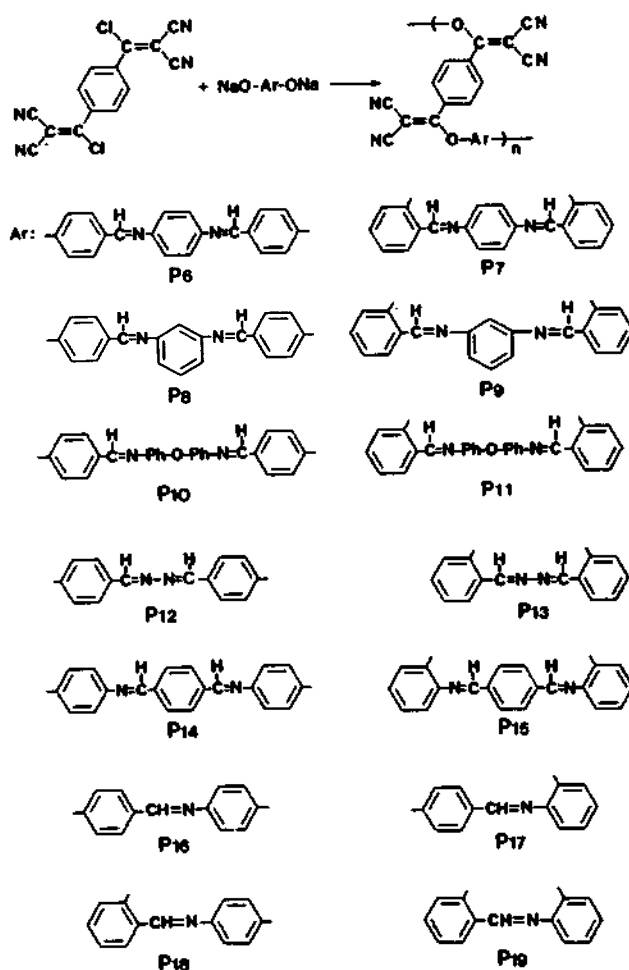
Scheme 2.

Table 2. Results from the Polymerization of 2 and Disodium Salts of Diphenol Derivatives Containing Schiff Bases[a]

Polymer	η_{inh}	M_n[b]	M_w[b]	Conversion (%)
P_6	0.27	4700	12800	76
P_7	0.24	7200	14500	78
P_8	0.17	3700	9700	81
P_9	0.28	4200	15000	59
P_{10}	0.29	2800	12100	91
P_{11}	0.14	4300	9500	78
P_{12}	0.12	2700	8600	97
P_{13}	0.26	4500	11600	78
P_{14}	0.27	2800	11300	99
P_{15}	0.12	4200	9400	71
P_{16}	0.22	2700	11000	72
P_{17}	0.13	2500	9600	90
P_{18}	0.10	4200	6700	54
P_{19}	0.21	3300	11200	90

[a] Polymerization was carried out at 20 ℃ for 5 min. [b] Molecular weights were measured by GPC from the soluble portion in THF.

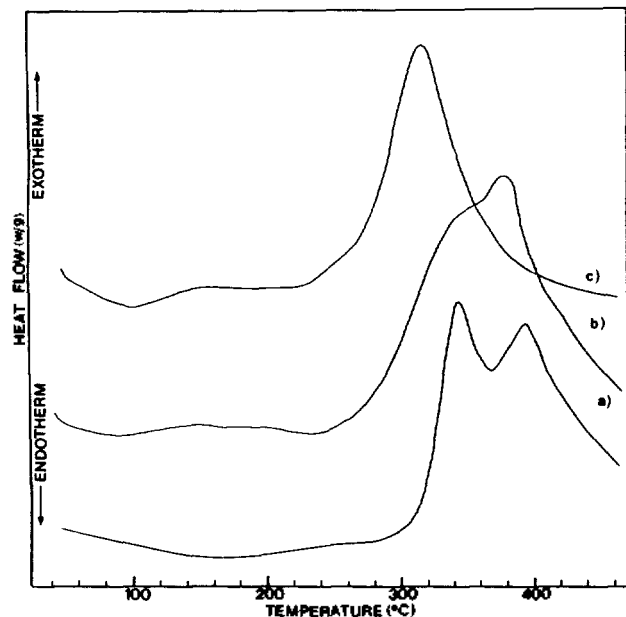containing azomethine group bestow an appreciable reactivity to dicyanovinyl chloride.

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Figure 1. Differential scanning calorimograms of polyenaryloxy-nitriles: a) P_4, b) P_{16} and c) P_9.

Figure 2. Differential scanning calorimogram and thermogravimogram of polymer P_{14}: a) Thermogravimogram, b) first scan, c) second scan after heating at 310 $^\circ$C and d) 2nd scan after heating at 390 $^\circ$C.

The polymers are incorporated with the different position and sequence of oxygen and nitrogen in the backbone. The polymers P_4, P_8, P_{10}, P_{12}, P_{14} and P_{16} contain para position of phenoxy group while P_7, P_9, P_{11}, P_{13}, P_{15} and P_{19} contain ortho position. Polymers P_{14} and P_{15} possess a changed sequence of azomethine group -CH=N- instead of -N=CH-. Although the central diamine is p-phenylenediamine in most polymers, P_8, P_{10} and P_{12} are composed of other aromatic diamines such as m-phenylenediamine, hydrazine and 4-aminophenyl ether, respectively.

Aromatic diol monomers containing Schiff bases show an unique diestuff color due to the high conjugation of azomethine group with aromatic ring. Thus the polymers derived from such diols displayed deep brown (P_4), black (P_8), yellow (P_{10}) and brown (P_{12}) color, respectively. Moreover, the solution of most polymers in DMF and NMP exhibited a dark brown color.

Poly(enaryloxynitriles) having azomethine group were confirmed by comparing their IR and NMR spectra with those of the model compounds 4, 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. The ^1H NMR spectrum clearly showed the broad singlet signal at 8.1-8.5 ppm corresponding to the azomethine proton, the multiplet signal around 7.8-6.8 ppm indicating the fragment of 2 and aromatic protons in diphenol units. These data support the structure of the synthesized poly(enaryloxynitriles) containing azomethine group. These observations were consistent with the results of model compounds and corresponded to their assigned chemical structure. Elemental analysis also supported the formation of the expected poly(enaryloxynitriles) and agreed well with the calculated data.

The most polymers exhibited virtually poor solubilities in polar protic solvents and fairly good solubilities in polar aprotic solvents such as NMP, DMF DMSO and DMAc. The polymers derived from the ortho phenoxy group showed bet-
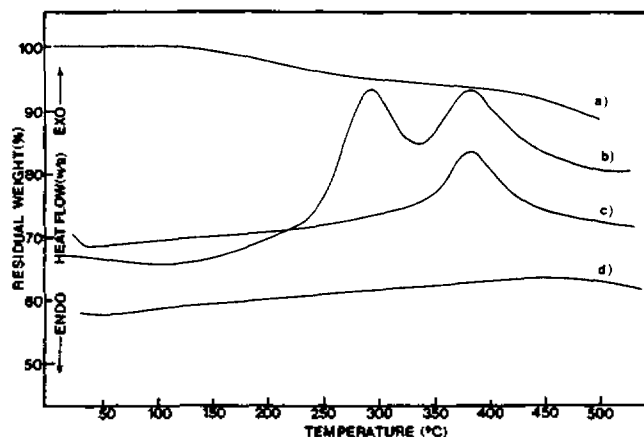
ter solubility than those of para position. It is considered that the distorted structure causes the decrease in crystallinity with better solubility in solvent. Meta position of diamine also prevents close packing of the macromolecular chains which results in a better solubility than para position of diamine. The inherent viscosities of polymers are between 0.10-0.25 dL/g in N,N-dimethylformamide solution. The M_n and M_w obtained from the soluble portion by GPC in THF were in the range of 3000-7500 and 9000-15000, respectively, which were not high molecular weight judging from the results of viscosity and GPC measurements. Molecular weights did not increase by changing monomer concentration during interfacial polymerization. It may be due to the partial hydrolysis of azomethine groups during the formation of disodium salts of diphenols. A poor solubility of growing polymer chains in the organic phase under interfacial polymerization is considered to be another reason for the formation of low molecular weight polymer.

In general, the azomethine exhibits maximum values at $\lambda = 172$ nm and $\lambda = 238$ nm in its UV absorbance spectrum, where $\lambda = 172$ nm peak is more intense and has been assigned to a $\pi \to \pi^*$ transition.[23] On the other hand, the model compounds 3, 4 and 5 showed the maxima at $\lambda = 288$, $\lambda = 319$ and $\lambda = 342$, respectively. The absorbance of model compound 5 shifted into a longer wave length than other model compounds 3 and 4 due to the high conjugation with aromatic ring. Polymer P_4 exhibited a broad UV absorption band with maximum value at $\lambda = 288$ and a shoulder from 340 nm to 440 nm.

Poly(enaryloxynitriles) containing Schiff bases exhibit interesting thermal behavior as evidenced by the calorimogram as shown in Figure 1. Most of polymers did not show noticeable glass transition temperature in differential scanning calorimetry. On the contrary the polymers with o-positioned phenoxy group exhibited the endothermic temperature attributable to the melting of polymer. Thus the polymers P_7 and P_{15} showed endotherm at 210 $^\circ$C and 150 $^\circ$C, respectively. However, polymers with p-position of phenoxy group will retain a more rigid backbone, and this effect may partially result in a high melting temperature. Thus the resulting

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Table 3. Thermal Properties of Poly(enaryloxynitriles) Containing Schiff Bases

Polymer	Exo (°C)	Endo (°C)	10% wt loss (°C)	residual weight (%) 400 °C	residual weight (%) 500 °C
P_6	340, 390	—	410	92	88
P_7	320	210	250	68	51
P_8	313	—	335	81	71
P_9	304	—	337	83	76
P_{10}	320	—	400	93	84
P_{11}	334	202	385	79	78
P_{12}	332	—	440	91	84
P_{13}	340	235	375	87	79
P_{14}	301	—	494	93	87
P_{15}	328	150	356	82	64
P_{16}	350, 373	—	521	96	92
P_{17}	272, 390	—	408	92	83
P_{18}	348	—	557	97	95
P_{19}	310	120	375	88	80

Figure 3. Thermogravimograms of polyenaryloxynitriles: a) P_{18}, b) P_{16}, c) P_{14}, d) P_6, e) P_{12} and f) P_{10}.

polymers had no melting endotherm, but showed an exothermic peak near 350 °C. In the case of most polymers, the temperature required to obtain sufficient intermolecular mobility may be higher than the curing temperature of the polymer. DSC analysis did detect a broad, large exothermic transition for all the poly(enaryloxynitriles) starting near 300 °C and reaching maximum intensity near 340 °C. This peak was completely absent when the sample was cooled and rescanned. In the case of polymer P_6, two consecutive exotherms appeared (Figure 1(a)), while polymer P_{16} and P_{18} showed a broad peak with a shoulder indicating that two exotherms are overlapped as shown in Figure 1(b). On the other hand, polymer P_9 showed 1st exotherm at relatively lower temperature than 340 °C as indicated in Figure 1(c). DSC curve of polymers P_{14} and P_{17} was analogous to that of P_9. When the polymers were heated around 340 °C, the polymers were no longer soluble in the solvents such as N,N-dimethylformamide and N-methylpyrrolidinone. When a sample of polymer P_6 was heated around 340 °C, its IR spectrum changed gradually. The nitrile band at 2232 cm⁻¹ decreased apparently and also peaks at 1580-1600 cm⁻¹ broadened. At the same time, a new band around 3400 cm⁻¹ appeared. The insolubility of the cured polymers after heating may be due to the stiffness of the rearranged chain or cross-linking of dicyanovinyl group. It was reported that the intramolecular cyclization involved the generation of an imine function in the case of poly(enaminonitriles).[4,8] Although the curing process of poly(enaryloxynitriles) has not been clearly elucidated, similar curing reaction pathways are expected.

Poly(enaryloxynitriles) with azomethine moieties showed second exotherm at 380-400 °C attributable to further cross-linking of dicyanovinyl group and conjugated azomethine groups. Polymer P_{14} also showed two exotherms at 300 and 390 °C in DSC thermogram in Figure 2(b). They, however, did not reappear upon cooling and rescanning the sample at the corresponding temperature as shown in Figure 2(c) and 2(d). More experiments are needed to understand the causes of the thermal transition observed for the polymers
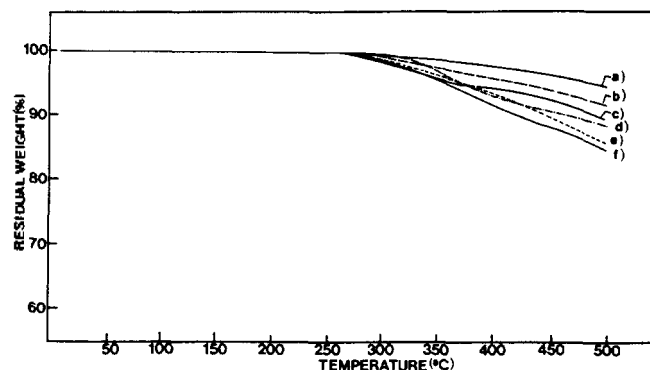
in detail.

The thermal stability data are listed in Table III and TGA traces are exhibited in Figure 3. The polymers sustained a 10% weight loss between 300-420 °C at a heating rate of 10 °C/min under nitrogen. They had residual weights of 60-90% at 500 °C. Especially, P_{16} abd P_{18} showed a 90% residual weight at 500 °C. Their excellent thermal stabilities result from the successive curing of dicyanovinyl group followed by azomethine group.

In the series of poly(enaryloxynitriles), the thermal stability could not be related with the structure of polymers derived from various diphenol drivatives. However the oxygen in an ortho position in the polymer backbone causes lower thermal stability than that of a para position. One of the reasons for such a low thermal stability is likely due to the molecular weight of the polymers formed during interfacial polymerization. Therefore, the synthesis of polyenaryloxynitriles containing Schiff bases by solution polymerization is necessary to increase their molecular weights and now in progress.

Conclusion

New poly(enaryloxynitriles) with Schiff bases moieties were prepared from p-bis(1-chloro-2,2-dicyanovinyl)benzene and aromatic diols having azomethine group. All the polymers were soluble in polar aprotic solvents such as DMF, DMSO and NMP and brittle films were cast from DMF solution. They were cured around 340 °C to form insoluble material via the chemical change of dicyanovinyl group. Especially further curing of azomethine group was observed to occur at 390 °C and enhanced a thermal stability. They exhibited excellent thermal stability with 60-90% residual weight at 500 °C.

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Estimation of Redox Potentials of Cytochrome C₃

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¹H NMR Estimation of Multi-Redox Potentials of Cytochrome c₃ from *Desulfovibrio vulgaris* Hildenborough

Jang-Su Park*, **Shin Won Kang, and Sung Nak Choi**

Department of Chemistry, College of Natural Sciences, Pusan National University, Pusan 609-735, Korea
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The macroscopic and microscopic redox potentials of tetrahemoprotein, cytochrome c_3 from *Desulfovibrio vulgaris* (Hildenborough) (*Dv*H) were estimated from ¹H NMR and differential pulse polarography (DPP). Five sets of NMR resonances were confirmed by a redox titration. They represent cytochrome c_3 molecules in five macroscopic redox states. The electron transfer in cytochrome c_3 involves four consecutive one-electron steps. The saturation transfer method was used to determine the chemical shifts of eight heme methyl resonances in five different oxidation states. Thirty two microscopic redox potentials were estimated. The results showed the presence of a strong positive interaction between a pair of particular hemes. Comparing the results with those of *Desulfovibrio vulgaris* Miyazaki F (*Dv*MF), it was observed that the two proteins resemble each other in overall redox pattern, but there is small difference in the relative redox potentials of four hemes.

Introduction

Cytochrome c_3 isolated from the sulfate-reducing bacteria *Desulfovibrio vulgaris* Hildenborough (*Dv*H) is a tetraheme electron transfer protein which plays an impotant role in the metabolism of sulfur compounds and hydrogen.[1] It was independently identified by Postgate in England and Ishmoto in Japan in 1954.[2-7] Cytochrome c_3 has a molecular weight of approximately 13,000 with 107 amino acid residues in a single polypeptide chain. The amino acid sequences of cytochrome c_3 show no homology with mammalian cytochrome c except for four sequences: two Cys-x-y-Cys-His, and two Cys-w-x-y-z- Cys-His which resemble the Cys-x-y-Cys-His sequences of cytochrome c. These four sequences provide

thioether attachments of the heme to the polypeptide chain and the histidine ligand to the heme iron atom.[8]

Extensive investigations of cytochrome c_3 from several genera have been carried out. Amino acid sequences of cytochrome c_3 from *Desulfovibrio vulgaris*, Miyazaki F (*Dv*MF), *Desulfovibrio vulgaris* Hildenborough (*Dv*H), *D. gigas*, *D. salexigens*, *D. desulfuricans* and *D. desulfuricans* Norway (*DdN*) have been determined.[9] Comparisons of their primary structures show rather poor homology among the six cytochromes c_3 above. The closest pair is *Dv*H and *Dv*MF. They differ by 14 out of 107 amino acid residues.[9] The complete three dimensional structures of *Dv*MF and *Dv*H have been obtained.[10-12]

The redox potential of cytochrome c_3 is an important parameter in understanding its physiological role.

Since cytochrome c_3 has four redox centers, four macro-

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*To whom correspondences should be addressed.