

Dicyanovinyl기를 가지는 Poly(Schiff bases)와 그들의 공중합체들의 합성과 열적 성질

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Synthesis and Thermal Properties of Poly(Schiff bases) Containing Dicyanovinyl Group and Their Copolymers

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요약: 주쇄에 dicyanovinyl기를 가진 새로운 poly(Schiff bases)와 그의 공중합체를 dicyanovinyl기를 포함한 단량체인 *p*-bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (**4**)와 TA를 4-aminophenyl ether (ODA)와 용액 중합에 의하여 합성하였다. 생성된 중합체들 **P(1/0) ~ P(2/1)**은 고유 점도가 0.42~0.20 dL/g이었다. ODA와 **4**의 호모 중합체의 경우 극성 비양자성 용매에 매우 잘 녹았으나 중합체에 TA의 비율이 증가하면 NMP에 대한 용해도가 현저히 감소하였다. TA가 많이 포함된 중합체들은 중합중에 용매에 침전되어 분자량이 증가하지 않는 것으로 보여진다. DSC 분석에서 중합체들은 350°C에서 커다란 발열 피크를 보여주며 이온도에서 열화 반응이 진행되어 용매에 불용성 물질이 형성되었다. 거의 모든 중합체들이 480~540°C 사이에서 10% 중량 감량을 나타내 주었으며, 500°C에서 잔사량은 88~95%로서 열안정성을 보여주었다.

ABSTRACT: Poly(Schiff bases) and their copolymers incorporating dicyanovinyl group in the main chain were prepared by the solution polymerization of a dicyanovinyl-containing monomer, *p*-bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (**4**), and terephthalaldehyde (TA) with 4-aminophenyl ether (ODA). The resulting polymers possess intrinsic viscosities 0.42~0.20 dL/g in the case of polymers **P(1/0) ~ P(2/1)**. The homopolymer derived from **4** and ODA is easily soluble in polar aprotic solvents. However, the solubility of the polymers in NMP decreased apparently with the increase of the content of TA in the polymer chain. Attempts to prepare high-molecular weight polymers from higher content of TA were unsuccessful, probably due to the precipitation of polymer during polymerization. The polymers show a large exotherm in differential scanning calorimetry and undergo a curing reaction around 350°C to form insoluble material in solvent. Almost all the poly(Schiff bases) exhibited 10% weight loss between 480~540°C and 88~95% residual weight at 500°C in a nitrogen atmosphere.

Keywords: dicyanovinyl group, poly(Schiff bases), thermally stable polymers, thermally curable polymers.

INTRODUCTION

Recently thermally stable polymers have been extensively explored to achieve a high-temperature stability with good mechanical properties which are essential for the structural applications. Most of the high-temperature materials have difficulties in processing due to the evolution of volatile compounds, and insolubility and/or infusibility, resulting in limited applications.¹ Much efforts have been focused on the structural modification of thermally stable polymers to improve the processibility.^{1,2} Among these works, introduction of thermally curable functional groups such as biphenylene, nadimide, acetylene, maleinide, *N*-cyanourea and phthalonitrile have been noted by many researchers.^{3,4} Recently, new class of novel poly(enaminonitriles),⁵⁻¹⁰ which are thermally curable without release of volatile compounds, have been prepared by a vinylic nucleophilic substitution reaction and they show an excellent thermal stability. The dicyanovinyl group is one of the thermally curable functionalities. It was also reported that poly(enaryloxynitriles) could be produced by interfacial polymerization of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene with aromatic diols such as bisphenol A, dihydroxy benzenes¹¹ and dihydroxy naphthalenes.¹² The resulting polymers also showed a good thermal stability without evolution of volatile byproduct after thermal curing. The incorporation of dicyanovinyl group into polyurethane^{13,14} and polyester¹⁵⁻¹⁷ enhanced the solubility in common organic solvents as well as the thermal stability through cyclization. Interfacial polymerization techniques^{11,12,18-21} have been a convenient route to the synthesis of various poly(enaryloxynitriles), but yielded polymers of rather low molecular weight.¹⁹ Therefore the solution polymerization was often adopted for the prepa-

ration of poly(enaryloxynitriles) containing Schiff bases, which may undergo curing reaction. Since the poly(Schiff bases) containing dicyanovinyl group possess two functionalities in the polymer backbone, they are of considerable interest.

In this paper, we report the synthesis of new poly(enaryloxynitriles) and their copolymers containing Schiff bases in the main chain. Their thermal properties are also be discussed.

EXPERIMENTAL

1-Chloro-1-phenyl-2,2-dicyanoethene (**1**) and *p*-bis(1-chloro-2,2-dicyanovinyl) benzene (**2**) were prepared according to the procedures as described in the literature.^{5,6} 1-(4-Formylphenoxy)-1-phenyl-2,2-dicyanoethene (**3**) and *p*-bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (**4**) were prepared by the method reported by Gong and co-workers.²²

4-Aminophenyl ether (4,4'-oxydianiline, ODA, Aldrich Chemical Co.) and terephthaldehyde were purified by sublimation under vacuum. *N,N*-Dimethylformamide (DMF), dimethylsulfoxide (DMSO), *m*-cresol, toluene and *N*-methyl-2-pyrrolidinone (NMP) were purified by conventional methods.

Solubilities were estimated by dissolving 5 mg of the corresponding powdery polymer sample in 1 mL of solvent after heating to 80°C. ¹H NMR spectra were recorded on a Varian EM-360A spectrometer operating at 60 MHz. In all ¹H NMR experiments the chemical shifts are recorded in ppm from tetramethylsilane as an internal standard. FT-IR spectra were taken on a Midac Model M-1200 spectrophotometer. Differential scanning calorimetry of polymers was carried out on a DuPont 2100 thermal analyzer at a heating rate of 10°C/min under nitrogen. TGA was performed on a Perkin-Elmer System 7 thermal ana-

lyzer. Intrinsic viscosities of polymer solution were measured with a Cannon-Fenske viscometer at 25°C in DMSO. Elemental analyses were carried out with a Yanco MT-3, CHN analyzer.

***p*-Bis[4-(2,2-dicyanovinyl)oxy] benzalimino] phenyl ether (5).** In a 100 mL round bottomed flask equipped with a nitrogen inlet, a condenser and a dropping funnel was placed a solution of ODA (0.8 g, 4.0 mmol) dissolved in 20 mL of NMP. After the solution was purged with nitrogen, two equivalents weight of **3** (2.19 g, 8.0 mmol) was added dropwise with stirring at room temperature. The reaction mixture was heated to 60°C and maintained overnight. After 20 mL of anhydrous toluene was added, the mixture was heated to reflux. The toluene azeotrope was collected between 110~120°C. When most of toluene had been removed, the yellow solution was cooled to room temperature. The reaction mixture was precipitated into a large amount of methanol and the precipitate was filtered. The product was washed with methanol twice and recrystallized from 1,2-dichloroethane, and dried at 60°C *in vacuo* for 10 h.

5: Yield 92%. mp 235°C. IR (KBr) 3400~3350 (br, N-H), 3230 (aromatic C-H), 2220 (C≡N), 1620, 1615 (CH=N), 1578 (C=C), 1260~1120 (C-O) cm⁻¹. ¹H NMR (DMSO-d₆) δ 8.5 (s, 2 H, 2 -CH=N-), 7.4 (m, 10 H, 2 -Ph), 7.4~6.8 (m, 8 H, 2 -O-Ph-CH=), 7.2~6.7 (m, 8 H, =N-Ph-O-Ph=N). Anal. Calcd for C₄₂H₂₈N₆O₃: C, 75.90; H, 4.22; N, 12.65. Found: C, 75.37; H, 4.18; N, 12.41.

***p*-Bis[1-(4-phenyliminomethyl)phenoxy-2,2-dicyanovinyl]benzene (6).** In a 100 mL round bottomed flask equipped with a nitrogen inlet, a condenser and a dropping funnel tube was placed aniline (0.8 g, 8.6 mmol) dissolved in NMP (20 mL) under nitrogen. To this solution was added an half equivalent weight of **4** (1.88 g, 4.0 mmol) with stirring. The reaction mixture was

heated to 60°C and maintained overnight. After 20 mL of toluene was added, the mixture was heated to 110°C with vigorous stirring. The water evolved from the reaction mixture was removed by azeotropic distillation. After most of the water removed, the yellow solution was cooled and precipitated into a large amount of water. The precipitated solid was filtered. The solid product was washed with water several times, recrystallized from acetonitriles 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. ¹H NMR (DMSO-d₆) δ 8.2 (s, 2 H, -N=CH-), 7.8 (s, 4 H, -Ph-), 7.4~6.8 (m, 8 H, 2 O-Ph-CH=), 7.0 (m, 10 H, 2=N-Ph) Anal. Calcd for C₄₀H₂₄N₆O₂: C, 77.42; H, 3.87; N, 13.55. Found: C, 76.82; H, 3.79; N, 13.29.

Representative Copolymerization of *p*-bis [1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene and Terephthaldehyde with ODA.

p-Bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (0.50 g, 1.06 mmol), terephthaldehyde (0.14 g, 1.06 mmol) and ODA (0.23 g, 2.13 mmol) were dissolved in 20 mL of anhydrous *N*-methyl-2-pyrrolidinone and *m*-cresol (1/1, v/v) mixed solvent. The solution turned yellow and increased in viscosity. The precipitation of polymer occurred within 1 h. The stirred mixture was maintained at 70°C with stirring for 8 h under nitrogen. After the 20 mL of toluene was added, the mixture was heated to 110°C with stirring. The water evolved from the reaction mixture was removed by azeotropic distillation and an additional 20 mL of toluene was added. The additional toluene was then removed by increasing the temperature to 120°C. The reaction mixture was cooled and then poured into a large volume of methanol to precipitate the polymer. The polymer precipitated as a fine powder was filtered and dried in

vacuo at 50°C for 12 h.

Other copolymers containing Schiff bases were prepared by reacting different content of **4** and TA with ODA by similar synthetic procedures. In the case of polymers with the ratios of **4** and TA, 1:0, 5:1, 3:1 and 2:1, the solution polymerizations were carried out in NMP, while the other copolymers with higher content of TA were prepared in NMP and *m*-cresol (1/1=v/v) mixed solvent to prepare **P(1/0)**, **P(5/1)**, etc.

P(1/0): Yield 91.0%. IR (KBr) 3230 (C-H), 2214 (C≡N), 1610 (CH=N), 1580 (C=C), 1492, 1335~1100 (C-O) cm⁻¹. ¹H NMR (DMSO-d₆) δ 8.4 (m, 2 H, -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 (C₄₆H₂₂N₆O₃)_n: C, 78.19; H, 3.12; N, 11.90. Found: C, 76.92; H, 3.08; N, 12.01.

P(5/1): Yield 90%. IR (KBr) 3210 (aromatic C-H), 2214 (C≡N), 1610 (CH=N), 1575 (C=C), 1491, 1248~1050 (C-O) cm⁻¹. ¹H NMR (DMSO-d₆) δ 8.7 (m, 2 H, -CH=N-), 7.8 (s, 10/3 H, 5/6 -Ph-), 7.8~6.8 (m, 15.3 H, 5/6 2 -O-Ph-, 1/6 =CH-Ph-CH= and =N-Ph-O-Ph-N=). Anal. Calcd for (C_{43.33}H_{25.66}N_{5.33}O_{2.66})_n: C, 78.43; H, 3.87; N, 11.26. Found: C, 77.87; H, 3.79; N, 11.19.

P(3/1): Yield 91%. IR (KBr) 3120~3010 (C-H), 2220 (C≡N), 1612 (CH=N), 1574 (C=C), 1491, 1248~1030 (C-O) cm⁻¹. ¹H NMR (DMSO-d₆) δ 8.7 (m, 2 H, -CH=N-), 7.8 (s, 3 H, 3/4 -Ph-), 7.8-6.8 (m, 15 H, 3/4 2 -O-Ph-, 1/4 CH-Ph-CH and N-Ph-O-Ph-N). Anal. Calcd for (C₄₁H_{16.5}N₅O_{2.5})_n: C, 79.54; H, 2.67; N, 11.32. Found: C, 79.32; H, 2.57; N, 11.22.

P(2/1): Yield 90%. IR (KBr) 3120~3045 (C-H), 2218 (C≡N), 1610 (CH=N), 1576 (C=C), 1491, 1244~1065 (C-O) cm⁻¹. ¹H NMR (DMSO-d₆) δ 8.7 (m, 2 H, -CH=N-), 7.8 (s, 2 H, 1/2 -Ph-), 7.8-6.8 (m, 14 H, 1/2 2 -O-Ph-, 1/2 CH-Ph-CH and N-Ph-O-Ph-N). Anal. Calcd for (C₃₀H₁₈N₄O₂)_n: C, 77.92; H, 3.03; N, 12.12. Found: C, 77.41; H, 2.97; N, 11.88.

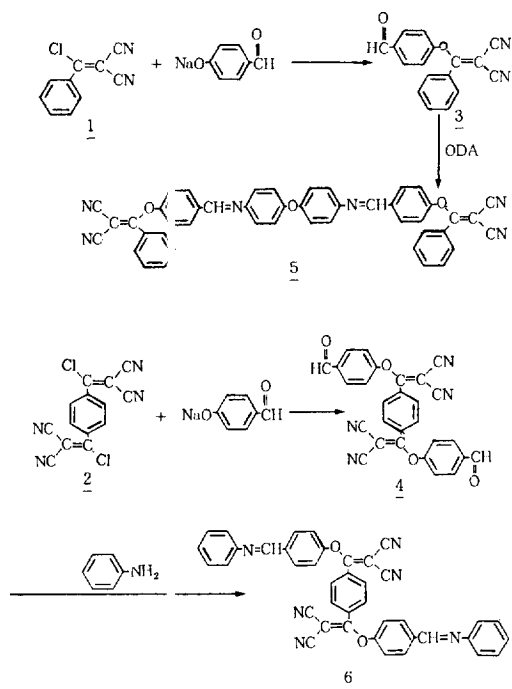
P(1/1): Yield 90%. IR (KBr) 3120~3041 (aromatic C-H), 2220 (C≡N), 1613 (CH=N), 1578 (C=C), 1491, 1246~1105 (C-O) cm⁻¹. Anal. Calcd for (C₂₀H₁₄N₂O₁)_n: C, 80.54; H, 4.76; N, 9.40. Found: C, 79.87; H, 4.57; N, 9.36.

RESULTS AND DISCUSSION

Poly(Schiff bases) have been prepared by the condensation polymerization reaction of aromatic diamines with terephthaldehyde.²³ Alternative route for the poly(Schiff bases) containing enaryloxynitriles moiety is a vinylogous substitution reaction of *p*-bis(1-chloro-2,2-dicyanovinyl) benzene (**2**) with sodium salts of diphenols containing azomethine group by interfacial polymerization technique. However, this method gave polymers of rather limited molecular weight because of hydrolysis of azomethine group during salt formation in aqueous sodium hydroxide solution. Therefore conventional solution condensation polymerization techniques were chosen for the preparation of poly(enaryloxynitriles) containing Schiff bases.

Monomer and Model Compounds. Enaryloxynitriles containing formyl group, 1-(4-formylphenoxy)-1-phenyl-2,2-dicyanoethene (**3**) and *p*-bis[1-(4-formylphenoxy)-2,2-dicyanovinyl] benzene (**4**) were prepared in high yield by the phase transfer reaction of **1** or **2** with sodium salt of *p*-hydroxybenzaldehyde. As shown in Scheme 1, two model compounds, *p*-bis[4-[(2,2-dicyanovinyl)oxy]benzal]imino]phenyl ether and *p*-bis[1-(4-phenyliminomethyl)phenoxy-2,2-dicyanovinyl] benzene (**6**) were synthesized and used for the conditions of polymer formation and the identification of chemical structure of polymers.

The effectiveness of this condensation reaction was expected by easy formation of azomethine linkage by elimination of water from aldehyde and amine.


Scheme 1

Polymerization. The conditions and results of copolymerization are summarized in Table 1. Polymerizations of different contents of **4** and terephthaldehyde units were attempted to obtain a controlled amount of enaryloxinitrile units in the main chain of polymers as shown in Scheme 2. They were readily copolymerized to give the corresponding polymers in high yield. The polycondensation of **4** and TA with diamines was carried out by solution polymerization techniques in a polar aprotic solvent such as NMP. The polymerization was found to take place fairly rapidly at 60°C and a gradual increase in viscosity was observed within 30 min. However the precipitation of polymer occurred with the increase of molecular weight. When the higher content of **4** was used, relatively high molecular weight polymer formation could be achieved in NMP in homogeneous solution judging from the viscosity data.

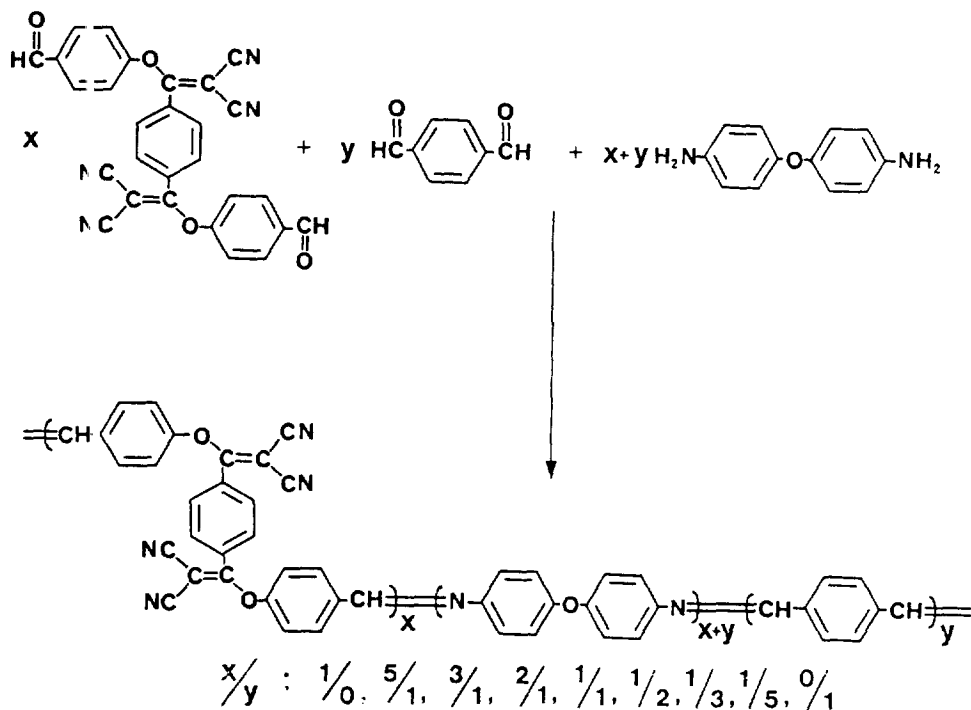
Table 1. The Conditions and Results of Copolymerization of **4** and Terephthaldehyde with ODA

Polymer	4/TA ^a	Solvent	η_{inh}^b	Yield (%)
P(1/0)	1/0	NMP	0.42	88
P(5/1)	5/1	NMP	0.40	90
P(3/1)	3/1	NMP	0.20	91
P(2/1)	2/1	NMP	0.37	90
P(1/1)	1/1	NMP ^c	0.24	89
P(1/2)	1/2	NMP ^c	-	92
P(1/3)	1/3	NMP ^c	-	93
P(1/5)	1/5	NMP ^c	-	89
P(0/1)	0/1	NMP ^c	-	90

^aTA : terephthaldehyde ; ^bMeasured in dimethylsulfoxide in 1 g/dL at 25°C ; ^cPolymerizations were carried out in NMP and *m*-cresol mixed solvent at 60°C for 12 hr.

On the other hand, in the case of polymers with lower content of **4**, the polymers were precipitated during polymerization, resulting in limited molecular weight of the copolymers. The attempts to prepare high-molecular weight polymers from higher content of TA was unsuccessful in the NMP and *m*-cresol mixed solvent, even the mixed solvent has higher solvating power to dissolve the copolymers of **4** and TA.

Solubility and Viscosity. Poly(Schiff bases) composed of **4** and ODA, **P(1/0)** was soluble in polar aprotic solvents such as NMP, DMF, DMSO and DMAc but insoluble in acetone and ethylacetate. On the other hand, polymers with higher content of TA units were partially soluble in NMP, DMF, DMSO and DMAc. The solubility in DMF and DMSO decreased with the increase of the content of TA. Table 1 exhibits the inherent viscosities of the resulting polymers **P(1/0)** ~ **P(1/1)**. The polymers obtained from solution polymerization have intrinsic viscosities of 0.20-0.42 dL/g. The viscosities of other polymers **P(1/2)** ~ **P(0/1)** with higher content of TA were not obtainable because of poor solubility in NMP. In the case of polymers **P(1/1)** and **P(1/3)**, about 50% and 30% of samples were soluble in hot NMP solvent, respectively. The various dicyanovinyl-con-



Scheme 2

taining polymers were readily soluble in amide-type polar aprotic solvents and DMSO. However the rigid double-bonded azomethine backbone lowers the solubility in solvent. The most polymers displayed the dye stuff colors such as deep brown or yellow due to the high conjugation of azomethine group with aromatic ring. Moreover, the solution of polymers **P(1/0)**, **P(5/1)** and **P(3/1)** in DMF and NMP exhibited a deep brownish color.

Characterization. The polymers obtained here were identified as poly(enaryloxynitriles) having azomethine group by comparing their IR and NMR spectra with those of the model compounds **5** and **6**. In the IR spectra, characteristic absorption bands of $C\equiv N$, $CH=N$ and $C=C$ were exhibited around 2220 , 1620 and 1580 cm^{-1} , respectively. The polymers with more content of **4** showed a stronger absorption band at 2220 cm^{-1}

attributable to higher content of nitrile group in the polymer chain. In the ^1H NMR spectrum of polymer **P(1/0)**, the broad singlet signal around 8.5 ppm corresponding to the azomethine proton and the multiplet signal around $7.8\sim 6.8\text{ ppm}$ corresponding to aromatic protons attached to **2** and diamine clearly indicated the poly(enaryloxynitriles) with azomethine group were also synthesized. The copolymer **P(3/1)** exhibited a peak around 7.8 ppm indicating existence of TA moiety in NMR spectrum, whereas it possessed a reduced peak at 2220 cm^{-1} attributable to nitrile group in its IR spectrum. 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(Schiff bases) containing enaryloxynitriles moieties and matched well with the proposed chemical structure and composition

of copolymers.

Thermal Properties. All the poly(Schiff bases) were subjected to DSC measurements at a heating rate and a cooling rate of 10°C/min under nitrogen. Polymers exhibit interesting thermal behavior as evidenced by the data of Table 2. The typical DSC traces of poly(Schiff bases) composed of only **4** and various aromatic diamines such as **P(1/0)** possess two consecutive exotherms around 350 and 400°C, respectively.²² But, DSC thermograms of copolymers involve a broad large exotherm starting near 300°C and reaching maximum intensity around 350°C. The exotherm does not reappear upon cooling and rescanning the sample as shown in Fig. 1(b). On the other hand, **P(1/1)** and **P(2/1)** showed exotherm at 350°C with a small shoulder around 410°C, indicating two overlapping exotherms. The exothermic peaks were reduced in intensity according to the decrease of the amount of **4**. In addition, the heat (ΔH) evolved per gram of polymer decreased in proportion to the content of TA at a temperature of its exotherm. These values were roughly proportional to the amount of the component of the dicyanovinyl function in the polymer chain. To demonstrate that curing of the poly(Schiff bases) proceed with chemical change of dicyanovinyl group, a sample of polymer **P(3/1)** was heated at 340°C for 30 min in a sealed tube under vacuum. The heated polymers were no longer soluble in the solvents such as NMP and DMI, which were good solvents for the uncured polymers. The IR spectrum of the cured material indicated that the intensity of nitrile band at 2220 cm^{-1} reduced apparently in intensity and peaks at 1530~1600 cm^{-1} broadened, in comparison with the spectrum of the starting material. At the same time, a new bands around 3400 cm^{-1} were broadened because of generation of imine function by the intermolecular addition reaction of dicyanovinyl group. **P(0/1)**, which does not have any enaryloxynitriles unit, did not

Table 2. Thermal Properties of Poly(Schiff bases) and Copolymers Containing Dicyanovinyl Group

Polymer	Exo(°C)	ΔH (J/g)	10% Wt. Loss (°C)	Residual Weight (%) 400°C	500°C
P(1/0)	342,390	82	610	98	96
P(5/1)	348	78	540	96	93
P(3/1)	349	64	532	98	94
P(2/1)	358,415	48	525	96	92
P(1/1)	358,410	32	520	99	92
P(1/2)	363	23	488	98	89
P(1/3)	361	15	500	97	90
P(1/5)	355	11	490	98	89
P(0/1)	-	-	480	98	88

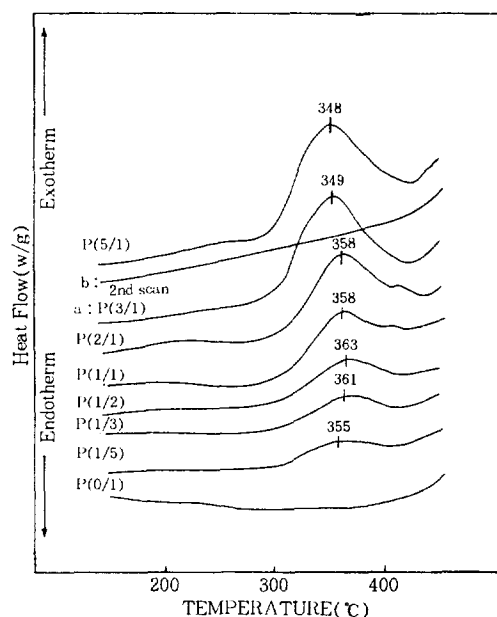


Fig. 1. DSC thermograms of poly(Schiff bases) and their copolymers containing dicyanovinyl group and **P(3/1)** (2nd scan) at a heating rate of 10°C/min.

exhibit exothermic behavior in DSC measurement within 450°C. This result supported that the curing reaction occurred at enaryloxynitriles units. However, in the case of poly(enaryloxynitriles), the chemical pathways of curing of dicyanovinyl group have not been clearly elucidated. According to the experiments on the poly(enaminonitriles) reported by Moore and coworkers, it might hap

pen that intramolecular cyclization or cross-linking of the dicyanovinyl group occurred during heating at the temperature of its first exotherm.^{8,6,10,24} Interestingly, some of the poly(Schiff bases) showed additional exothermic peak around 400°C which was not observed with poly(enaminonitriles) and poly(enaryloxynitriles). These DSC results implied that some curing reaction occurred through azomethine units in the polymer chain. More experiments on model compounds are required to elucidate the curing mechanism. 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 formed during the measurement to exhibit a melting peak. Glass transition temperature was not also detected by DSC for most polymers. The Schiff bases polymers retain a more rigid backbone, and this effect may partly result in a higher glass transition temperature than curing temperature. All the polymers exhibited excellent thermal

stability, losing no mass below 420°C in nitrogen (Fig. 2). This result indicates that the poly(enaryloxynitriles) cured thermally without release of volatile byproduct. The thermal stability data are listed in Table 2 and TGA traces are shown in Fig. 2. The polymers sustained a 10% weight loss at a temperature of 500°C with a heating rate of 10°C/min in nitrogen. The residual weight varied from 88 to 95% at 500°C. According to the data compiled in Table 2, the homopolymer **P(1/0)** shows better thermal stability than any other poly(Schiff bases) copolymerized with TA. A structural difference between polymers **P(1/0)** and **P(1/1)** is the existence of TA moieties in the main chain. Poly(enaryloxynitriles) **P(1/0)** derived from 4-aminophenyl ether showed an excellent thermal stability of 95% residual weight at 500°C. When a loss of weight of 5% is taken as standard for comparison of various polymers, it turns out that most of poly(Schiff bases) are thermally stable at a temperature of 500°C. Furthermore most

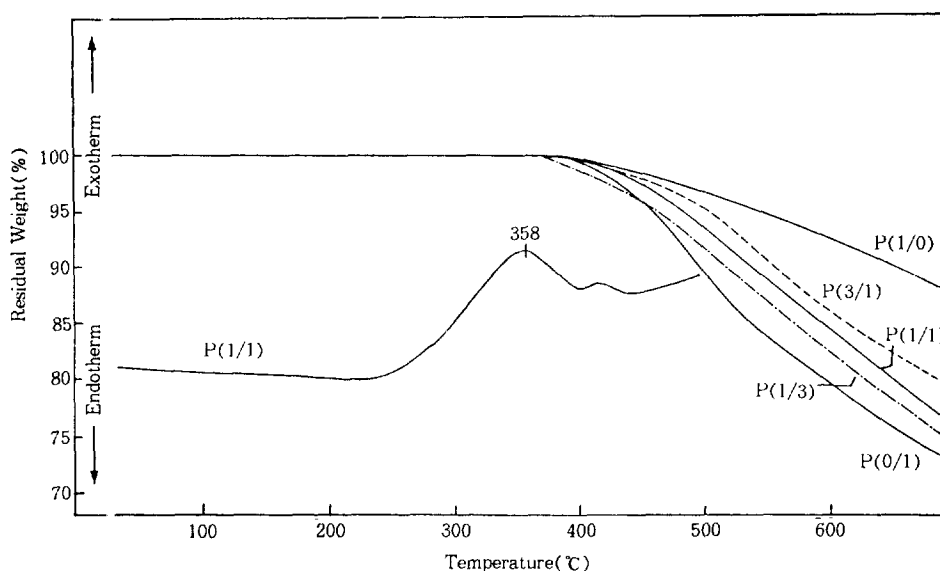


Fig. 2. TGA traces of poly(Schiff bases) and their copolymers containing dicyanovinyl group and DSC curve of **P(1/1)** at a heating rate of 10°C/min.

polymers exhibited over 70% residual weight at a temperature of 700°C. The polymers with more content of **4** showed better thermal stabilities at 700°C. These results were caused by the successive curing of dicyanovinyl group, followed by azomethine moieties.

CONCLUSIONS

1. Poly(Schiff bases) and their copolymers containing dicyanovinyl group were prepared from dicyanovinyl-containing monomer *p*-bis[1-(4-formylphenoxy)-2,2-dicyanovinyl] benzene (**4**) and terephthaldehyde with ODA by solution polymerization in NMP and *m*-cresol.

2. The polymer containing only **4** is soluble in polar aprotic solvents such as DMF, DMSO, DMAc and NMP. The solubility in NMP decreased with the increase of the content of terephthaldehyde moiety in the polymer backbone.

3. The polymers show a large exotherm in DSC thermograms and undergo a curing reaction around 350°C to form insoluble material. The polymers were cured thermally without release of volatile byproduct at a temperature of its exotherm.

4. Thermally curable and stable poly(Schiff bases) showed 83~95% residual weight at 500°C.

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