

## Preparation and Thermal Properties of Poly(enaminonitriles-ester)s Derived from Dicyanovinyl-Containing Bis-Hydroxy Monomers

Jong-Tae Kim and Myoung-Seon Gong\*

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

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Dicyanovinyl-containing bis-hydroxy monomers, *p*-bis[1-(4-hydroxypiperidinyl)]-2,2-dicyanovinyl]benzene (**2**), *p*-bis[1-[1-(2-hydroxyethyl)piperazinyl]-2,2-dicyanovinyl]benzene (**3**), *p*-bis[1-(4-hydroxyphenylamino)-2,2-dicyanovinyl]benzene (**4**) and *p*-bis[1-[*N*-methyl-(*N*-hydroxyethyl)amino]-2,2-dicyanovinyl]benzene (**5**) were prepared from *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**1**) and the corresponding amino alcohol. The poly(enaminonitriles-ester)s with a variety of chemical structures in the main chain were prepared from them. The chemical structure of polymers was confirmed through the syntheses of their corresponding model compounds. The polymers are easily soluble in polar aprotic solvents such as DMF, DMSO and NMP. Brittle and hard films can be cast from DMF solutions of polymers. Most polymers showed a large exotherm in DSC analyses and undergo a curing reaction around 350 °C to form insoluble materials. The polymers consisting of rigid aromatic moieties show 80-88% residual weight at 500 °C under nitrogen.

### Introduction

Recently, considerable effort was made to modify chemical structure of high-temperature polymers, essentially in order to improve their thermal and mechanical properties which are useful for structural applications.<sup>1,2</sup> The widely used thermally curable reactive functions were maleimide, nadimide, acetylene, phenylacetylene, *N*-cyanourea and phthalonitriles, and they have been applied to the synthesis of aromatic oligomers or prepolymers capped with reactive end groups.<sup>3,4</sup> Potential applications include their use as matrix materials for advanced composites and molding materials for the fabrication of electronic devices.<sup>1</sup>

The incorporation of dicyanovinyl group into polymer chain enhances the solubility in common organic solvents as well as the thermal stability.<sup>5-15</sup> The presence of dicyanovinyl group in the backbone of polymers also makes them susceptible to cross-linking reaction which may be initiated by heat. It has been also reported that dicyanovinyl group is employed for the synthesis of oligomers consisting rigid rod units capped at both ends with curable dicyanovinyl group.<sup>16</sup>

Obtaining a curable polymer by direct synthesis from functionalized monomers is an attractive approach since the number of curing function on the polymer backbone can be controlled. The advantage of dicyanovinyl group is that they can be readily transformed into dicyanovinyl-containing difunctional monomers owing to their good reactivity of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene.<sup>17</sup> Also the polymers could be easily prepared from the reaction of corresponding dicyanovinyl-containing monomers, allowing the careful tuning of the thermal and mechanical properties through copolymerization.<sup>18</sup>

In this article, four types of new dicyanovinyl-containing bis-hydroxy monomers were prepared and polymerized to synthesize several thermally curable poly(enaminonitriles-ester)s, and the thermal properties were examined.

### Experimental

*p*-Bis(1-chloro-2,2-dicyanovinyl)benzene (**1**) was synthesized according to the method described in the literature.<sup>5</sup> *p*-Bis[1-[*N*-methyl-(*N*-hydroxyethyl)amino]-2,2-dicyanovinyl]benzene (**5**) was also prepared by the method previously reported.<sup>13</sup> *p*-Aminophenol, 4-piperidinol, 1-(2-hydroxy ethyl) piperazine were used without further purification. Adipoyl chloride and succinyl chloride were used after distillation under reduced pressure. Terephthaloyl chloride was purified by sublimation under reduced pressure. *N*-Methyl-2-pyrrolidinone (NMP) was purified by distillation under reduced pressure after drying by azeotropic distillation of benzene mixture and stored over 4 Å molecular sieves. Triethylamine and THF were purified by distillation over calcium hydride. The solubility behavior was tested by dissolving 5 mg of powdery polymer sample in 1 mL of solvent. All melting points were determined on a Aldrich Mel-Temp II melting points apparatus using capillary tubes and are uncorrected. The gel fraction was obtained by weighing the insoluble portion after filtering the NMP solution of the cured sample at 310 °C.

Infrared (FT-IR) spectra were taken on a Midac Model M-1200 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Varian Gemini-2000 spectrometer. Differential scanning calorimetry of polymers were carried out on a DuPont 2100 and thermal gravimetric analyses were obtained with a Mettler thermal analyzer. Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (10<sup>2</sup>, 10<sup>3</sup> and 10<sup>4</sup> Å) in THF and calibrated with polystyrene standards. Inherent viscosities of polymer solution were measured in a Cannon-Fenske viscometer at 25 °C. Elemental analyses were carried out with a Yanaco MT-3, CHN-analyzer.

***p*-Bis[1-(4-hydroxypiperidinyl)]-2,2-dicyanovinyl]benzene (**2**).** To a solution of compound **1** (2.0 g, 6.6 mmol) in 30 mL of methylene chloride, a solution of 4-hy-

droxypiperidine (2.7 g, 26.6 mmol) in 20 mL of methylene chloride was poured slowly at room temperature with vigorous stirring. The reaction mixture was maintained at 40 °C for 5 h. After the reaction was completed, the yellow powdery product was filtered. The crude product was washed with 0.1 N sodium hydroxide and distilled water, and dried under vacuum. Finally the powdery product was recrystallized in dry acetonitrile to give 2.25 g of white crystal.

**2:** Yield 75%. mp 312 °C. IR (KBr) 3450 (O-H), 3180 (aromatic C-H), 2950 (aliphatic C-H), 2220 (C≡N), 1580 (C=C), 1260-1105 (C-O and C-N) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 7.6 (s, 4H, -Ph-), 4.7 (m, 2H, OH), 4.0 (m, 2H, CH-OH), 3.4 (m, 8H, CH<sub>2</sub>-N-CH<sub>2</sub>), 1.8 (m, 8H, -CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-). Anal. Calcd for C<sub>24</sub>H<sub>24</sub>N<sub>6</sub>O<sub>2</sub>: C, 67.28; H, 5.60; N, 19.63. Found: C, 66.93; H, 5.39; N, 19.49.

**p-Bis[1-[1-(2-hydroxyethyl)piperazinyl]-2,2-dicyanovinyl]benzene (3).** To a solution of compound 1 (2.0 g, 6.6 mmol) in 30 mL of acetonitrile, a solution of 1-(2-hydroxyethyl)piperazine (5.46 g, 26.6 mmol) in 20 mL of acetonitrile was poured slowly at room temperature with vigorous stirring. The reaction mixture was maintained at 40 °C for 5 h. The yellow powdery product was filtered and washed with 0.1 N sodium hydroxide several times. The yellow solid product was washed with distilled water and recrystallized in dry acetonitrile.

**3:** Yield 84%. mp 274 °C. IR (KBr) 3450 (O-H), 3150 (aromatic C-H), 2980-1870 (aliphatic C-H), 2220 (C≡N), 1580 (C=C), 1260-1105 (C-O and C-N) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 7.6 (s, 4H, -Ph-), 4.5 (m, 2H, OH), 4.0-3.4 (m, 8H, HO-CH<sub>2</sub>-CH<sub>2</sub>-N-), 3.4 (m, 8H, N-CH<sub>2</sub>-CH<sub>2</sub>-N-). Anal. Calcd for C<sub>26</sub>H<sub>30</sub>N<sub>8</sub>O<sub>2</sub>: C, 66.20; H, 6.17; N, 23.04. Found: C, 66.23; H, 5.98; N, 22.89.

**p-Bis[1-(4-hydroxyphenylamino)-2,2-dicyanovinyl]benzene (4).** In a 100 mL of round-bottomed flask, compound 1 (2.0 g, 6.6 mmol) was dissolved in 20 mL of acetonitrile. To this solution, a solution of *p*-aminophenol (4.5 g, 38.6 mmol) in 20 mL of acetonitrile was added dropwise with vigorous stirring under nitrogen. The reaction mixture was maintained at 70 °C with stirring for 24 h. The yellow powdery product was filtered and washed with distilled water and 2-propanol to remove excess *p*-aminophenol and solid quaternary ammonium salts several times. The crude solid product was recrystallized from *N,N*-dimethylacetamide to produce yellow crystals and dried in vacuo at 50 °C for 12 h.

**4:** Yield 83%. mp 324 °C. IR (KBr) 3450 (O-H), 3380 (N-H), 3180 (aromatic C-H), 2220 (C≡N), 1582 (C=C), 1260-1105 (C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) 9.1 (s, 2H, -OH), 7.6 (s, 4H, -Ph-), 7.2-6.8 (m, 8H, NH-Ph-O). Anal. Calcd for C<sub>26</sub>H<sub>16</sub>N<sub>6</sub>O<sub>2</sub>: C, 70.27; H, 3.60; N, 18.92. Found: C, 69.92; H, 3.48; N, 18.79.

**p-Bis[1-[4-(2-benzoyloxyethyl)piperazinyl]-2,2-dicyanovinyl]benzene (6).** A mixture of compound 2 (2.43 g, 5.0 mmol) and triethylamine (5 g, 50 mmol) in 20 mL of NMP was placed in a 100 mL three-necked flask equipped with a dropping funnel, a condenser and a nitrogen inlet. After 0.70 g (5.0 mmol) of benzoyl chloride in 10 mL of freshly distilled THF was added to the reaction flask for 30 min with a flush of nitrogen, the reaction mixture was stirred for 8 h. The temperature was raised to 70

°C and maintained for an additional 24 h. The pale yellow solution was evaporated and the yellow residue was dispersed in aqueous sodium hydroxide solution and filtered. The powdery product was washed with distilled water and recrystallized in acetonitrile.

Other model compound *p*-bis[1-[4-(benzoyloxy)phenylamino]-2,2-dicyanovinyl]benzene (7) was prepared by the similar procedures described above.

**6:** Yield 75.4%. mp 245 °C. IR (KBr) 3150 (aromatic C-H), 3000-1870 (aliphatic C-H), 2220 (C≡N), 1738 (C=O), 1580 (C=C), 1260-1105 (C-O and C-N) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) 7.6 (s, 4H, -Ph-), 7.8-7.2 (m, 10H, -Ph), 4.0-3.4 (m, 8H, -COO-CH<sub>2</sub>-CH<sub>2</sub>-N-), 3.4 (m, 16H, N-CH<sub>2</sub>-CH<sub>2</sub>-N-). Anal. Calcd for C<sub>36</sub>H<sub>38</sub>N<sub>8</sub>O<sub>4</sub>: C, 66.87; H, 5.88; N, 17.34. Found: C, 66.53; H, 5.71; N, 17.19.

**7:** Yield 86%. mp 247 °C. IR (KBr) 3380 (N-H), 3180 (aromatic C-H), 2220 (C≡N), 1735 (C=O), 1580 (C=C), 1275-1100 (C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 7.6 (s, 4 H, -Ph-), 7.6-7.2 (m, 10H, Ph-), 7.2-6.8 (m, 8 H, NH-Ph-O). Anal. Calcd for C<sub>40</sub>H<sub>24</sub>N<sub>6</sub>O<sub>4</sub>: C, 73.62; H, 3.68; N, 12.88. Found: C, 73.46; H, 3.58; N, 12.77.

**Representative polymerization of 2, 3, 4 and 5 with acid chlorides.** Terephthaloyl chloride (0.80 g, 3.9 mmol) dissolved in 10 mL of THF was added dropwise to a solution of compound 4 (1.73 g, 3.9 mmol) in 20 mL of NMP and 1.0 g of triethylamine. The reaction mixture was stirred vigorously at room temperature under nitrogen atmosphere for 8 h and then the temperature was raised to 70 °C, and maintained for an additional 24 h. When the reaction was completed, a viscosity increase was observed and the precipitation of triethyl ammonium chloride occurred. After the solution was precipitated into water, the polymer was isolated by filtration, and washed with 0.1 N NaOH solution and distilled water. The polymers were purified by reprecipitation from NMP solution into methanol.

The similar synthetic procedures were applied to the preparation of other polyesters from monomers 2, 3 and 5.

**P2S:** Yield 82%; IR (KBr): 3120-2980 (aromatic C-H), 2980-2850 (aliphatic C-H), 2222 (C≡N), 1735 (C=O), 1580 (C=C), 1320-1110 (C-O and C-N) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>+CDCl<sub>3</sub>) 7.6 (s, 4H, aromatic H's in 2), 4.1 (m, 2H, 2-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-), 2.7 (m, 8H, -CH<sub>2</sub>-N-CH<sub>2</sub>-), 2.3 (s, 4H, -CO-CH<sub>2</sub>-CO-), 1.8 (m, 8H, -CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-). Anal. Calcd for (C<sub>28</sub>H<sub>26</sub>N<sub>6</sub>O<sub>4</sub>)<sub>n</sub>: C, 65.88; H, 5.10; N, 16.47. Found: C, 66.25; H, 4.89; N, 15.95.

**P3T:** Yield 76%; IR (KBr): 3150, 2875 (aromatic and aliphatic C-H), 2220 (C≡N), 1736 (C=O), 1580 (C=C), 1320-1110 (C-N and C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 7.8 (s, 4H, -COPhCO-), 7.6 (s, 4H, aromatic H's in 3), 4.0-3.4 (m, 8H, -O-CH<sub>2</sub>-CH<sub>2</sub>-N-), 3.4 (m, 16H, N-CH<sub>2</sub>-CH<sub>2</sub>-N-). Anal. Calcd for (C<sub>34</sub>H<sub>32</sub>N<sub>6</sub>O<sub>4</sub>)<sub>n</sub>: C, 66.23; H, 5.19; N, 18.18. Found: C, 65.75; H, 4.89; N, 17.97.

**P4A:** Yield 92%; IR (KBr): 3375 (N-H), 3150, 2875 (aromatic and aliphatic C-H), 2220 (C≡N), 1735 (C=O), 1580 (C=C), 1272-1115 (C-N and C-O) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 8.8 (br, 2H, 2 N-H), 7.6 (s, 4H, aromatic H's in 1), 7.2-6.8 (m, 8H, -O-Ph-NH), 2.4 (t, 4H, -CO-CH<sub>2</sub>-), 1.8 (m, 8H, -CO-CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for (C<sub>32</sub>H<sub>22</sub>N<sub>6</sub>O<sub>4</sub>)<sub>n</sub>: C, 69.31; H, 3.97; N, 15.16. Found: C, 68.75; H, 3.79; N, 15.21.

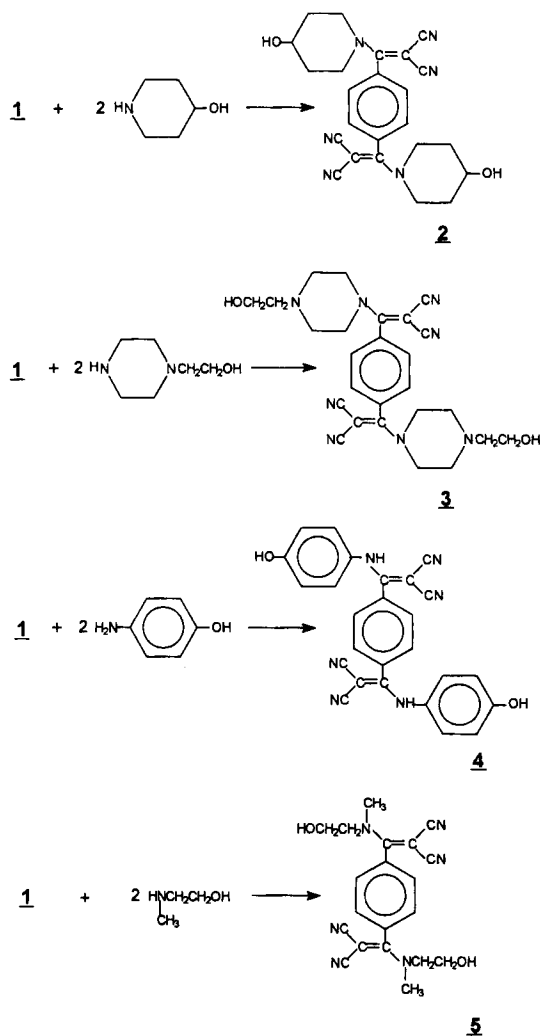
**P4T:** Yield 98%; IR (KBr): 3380 (N-H), 3120 (C-H),

2220 (C≡N), 1737 (C=O), 1580 (C=C), 1280-1120 (C-N and C-O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (DMSO- $d_6$ )  $\delta$  9.0 (br, 2H, N-H), 8.0 (s, 4H, -CO-Ph-CO-), 7.6 (s, 4H, aromatic H's in **2**), 7.2-6.9 (m, 8H, -O-Ph-NH). Anal. Calcd for (C<sub>34</sub>H<sub>18</sub>N<sub>6</sub>O<sub>4</sub>)<sub>n</sub>: C, 71.08; H, 3.14; N, 14.63. Found: C, 70.87; H, 3.09; N, 14.41.

**P5T**: Yield 92%; IR (KBr): 3000 (C-H), 2210 (C≡N), 1740 (C=O), 1210-1110 (C-O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (DMSO- $d_6$ ) 8.0 (s, 4H, -CO-Ph-CO-), 7.8 (s, 4H, aromatic H's in **1**), 4.0-3.8 (m, 4H, -O-CH<sub>2</sub>-), 3.7-3.4 (m, 10H, -CH<sub>2</sub>N(CH<sub>3</sub>)-). Anal. Calcd for (C<sub>28</sub>H<sub>22</sub>N<sub>6</sub>O<sub>4</sub>)<sub>n</sub>: C, 66.40; H, 4.35; N, 16.60. Found: C, 66.28; H, 4.28; N, 16.57.

## Results and Discussion

**Monomer synthesis.** Dicyanovinyl-containing bis-hydroxy monomers, *p*-bis[1-(4-hydroxypiperidinyl)]-2,2-dicyanovinyl]benzene (**2**), *p*-bis[1-[1-(2-hydroxyethyl)piperazinyl]-2,2-dicyanovinyl]benzene (**3**), *p*-bis[1-(4-hydroxyphenylamino)-2,2-dicyanovinyl]benzene (**4**) and *p*-bis[1-[*N*-methyl-(*N*-hydroxyethyl)amino]-2,2-dicyanovinyl]benzene (**5**) were prepared from *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**1**) and excess hydroxyl-containing amine compounds such as



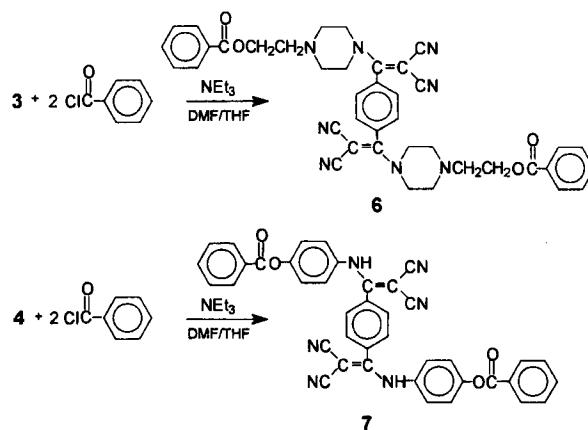
Scheme 1.

4-piperidinol, 1-(2-hydroxyethyl)piperazine, *p*-aminophenol and 2-(*N*-methylamino)ethanol, respectively, as illustrated in Scheme 1. Vinylic nucleophilic substitution reactions have been effectively exploited in the synthesis of several class of monomers. The IR spectrum showed strong absorption in the region 3500-3400  $\text{cm}^{-1}$  attributable to O-H stretching frequencies. In the  $^1\text{H NMR}$  spectrum, the hydroxyl protons of monomer **2**, **3** and **5** appear around 4.2 ppm, whereas those of **4** occur at 9.6 ppm indicating that the hydroxyl protons attached to the phenyl ring are highly acidic. The dihydroxy monomers were obtained as a pure material after recrystallization from acetonitrile or DMAc.

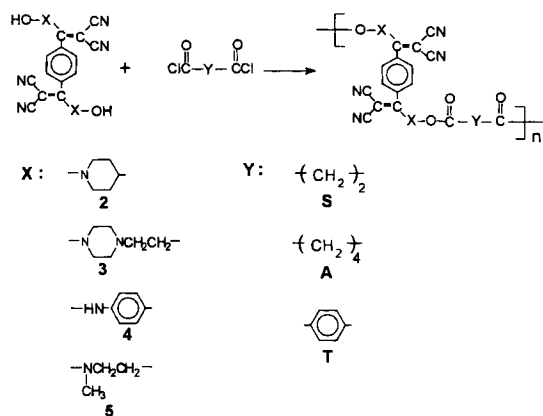
**Model compounds.** For examination of the reactivity of monomer and also for possible structural identification of the resulting polymers, two model compounds, *p*-bis[1-[4-(2-benzoyloxyethyl)piperazinyl]-2,2-dicyanovinyl]benzene (**6**) and *p*-bis[1-[4-(benzoyloxy)phenylamino]-2,2-dicyanovinyl]benzene (**7**) were prepared by reacting dicyanovinyl-containing bis-hydroxyl monomers **3** and **4** with benzoyl chloride as shown in Scheme 2. In the case of monomer **3** possessing tertiary amine moiety in the piperazine ring, the model compound **6** can accept the hydrochloric acid to form in part quaternary ammonium salts.

**Polymer synthesis.** In order to ascertain the optimum medium of polymerization, the reaction of the monomer **2** with terephthaloyl chloride was carried out first in THF, but the yields and the molecular weight were rather low due to the partial precipitation of polymer during polymerization. When the polymerization of dicyanovinyl-containing bis-hydroxy monomers with terephthaloyl chloride have been conducted in THF/NMP (50/50) mixed solvent in the presence of triethyl amine as an acid acceptor, the powdery polymers were obtained after precipitation into methanol. However, the higher portion of THF caused an early precipitation of low molecular weight polymer during polymerization. Aliphatic diacid chlorides adipoyl chloride and succinyl chloride were also chosen for the polycondensation with monomers **2**, **3**, **4** and **5** to give the corresponding polyesters in high conversion as shown in Scheme 3. The polymerization results are summarized in Table 1 along with the viscosity and molecular weight data. Polymer **P2T** represents poly(**2**, dicyanovinyl-containing bis-hydroxy monomer; T, acid chloride).

**Polymer characterization.** The polymers obtained in



Scheme 2.



Scheme 3.

this experiment were identified as poly(enaminonitriles-esters) by comparing their IR and NMR spectra with those of model compounds **6** and **7**. In the IR spectra of all the polymers, characteristic absorption bands of  $C\equiv N$ ,  $C=O$  and  $C=C$  were exhibited around 2220, 1735 and 1580  $cm^{-1}$ , respectively. The representative FT-IR spectra of model compound **7** and poly(enaminonitriles-arylate) **P4T** also matched to their assigned chemical structures. In the  $^1H$  NMR spectra, polymers showed a singlet peak at 7.8 ppm corresponding to the terephthaloyl moiety or multiplet peaks around 2.3 ppm assignable to methylene proton adjacent to the carbonyl group of adipoyl- and succinyl group. On the other hand, another broad singlet signal around 7.8-7.4 ppm corresponding to the fragment of **1** units clearly indicated that the poly(enaminonitriles-ester)s were prepared. In the NMR spectra of model compound **7** and poly(enaminonitriles-arylate) **P4T**, the aromatic proton in fragment of **1** appeared at 7.6 ppm, whereas those of aromatic protons in aminophenol at 7.2-6.8 ppm. Elemental analyses also supported the formation of the model compounds and polymers matched well with the calculated data.

**Polymer solubility and Molecular weight.** Qualitative solubility tests of these poly(enaminonitriles-esters) in excess solvent were carried out with fibrous or powdery samples. As was expected from the structure, the polymers were found to be soluble in several polar aprotic solvents such as NMP, DMF, DMSO and DMF, but insoluble in common organic solvents such as ethanol, ethylacetate and dichloromethane. On the other hand the polymers were partially soluble in THF and 1,2-dimethoxyethane. The polymers derived from adipoyl chloride showed better solubilities than those obtained from terephthaloyl chloride or succinyl chloride. It is considered that the flexible long alkyl units cause an increase of solubility in the solvent. Especially, the low solubility in NMP was found for the polymers derived from piperidinol-containing monomer **2**. One possible explanation is a reduced mobility of monomer **2** due to the direct bond of nitrogen-containing ring and dicyanovinyl group.

The polymers obtained from solution polymerization possess intrinsic viscosities of 0.26-0.65 dL/g. The weight average molecular weights were in the range of 11,600-14,500. GPC data were obtained from the soluble portion in THF, however, THF is not a good solvent for poly(enaminonitri-

**Table 1.** Results of Polymerization of Dicyanovinyl-Containing bis-hydroxyl Monomers with Acid chlorides

Polymer	Monomers <sup>a</sup>	Mw <sup>b</sup> (g/mol)	[ $\eta$ ] <sup>c</sup> (dL/g)	Yield (%)	Gel Fraction <sup>e</sup> (%)
<b>P2S</b>	2, SC	- <sup>d</sup>	0.26	82	82
<b>P2T</b>	2, TC	- <sup>d</sup>	0.28	86	73
<b>P3A</b>	3, AC	12400	0.31	63	80
<b>P3T</b>	3, TC	13700	0.34	76	69
<b>P4S</b>	4, SC	12200	0.37	96	87
<b>P4A</b>	4, AC	14500	0.39	92	79
<b>P4T</b>	4, TC	- <sup>d</sup>	0.29	98	92
<b>P5T</b>	5, TC	- <sup>d</sup>	0.65	81	84

<sup>a</sup>SC, succinyl chloride; AC, adipoyl chloride; TC, terephthaloyl chloride. <sup>b</sup>Weight average molecular weights were obtained by GPC from the soluble portion of polymers in THF. <sup>c</sup>Intrinsic viscosities were measured in DMF in 1 g/dL at 25 °C. <sup>d</sup>Insoluble in THF. <sup>e</sup>The gel fraction was obtained by weighing the insoluble portions after filtering the NMP solution of the cured sample at 310 °C.

**Table 2.** Thermal Properties of Polymers Prepared from Dicyanovinyl-Containing Monomers

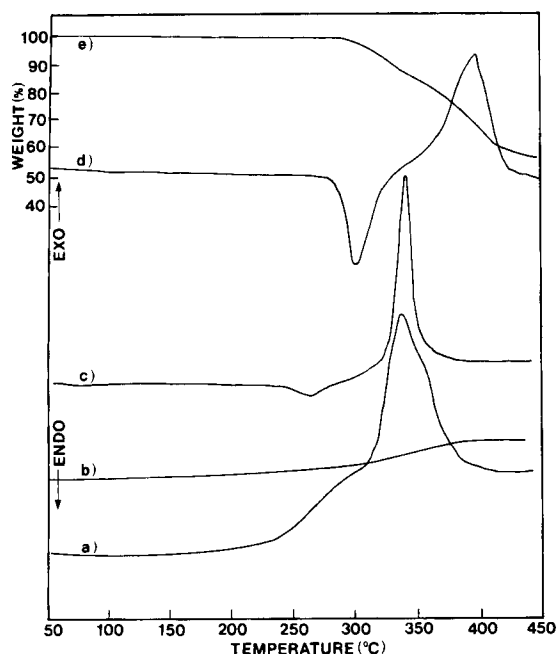
Polymer	Monomers <sup>a</sup>	$T_g^a$	$T_{endo}^b$	$T_{exo}^c$	$T_{100}^d$	Residual Weight (%)		
						400 °C	500 °C	500 °C <sup>e</sup>
<b>P2S</b>	2, SC	-	302	392	335	54	44	69
<b>P2T</b>	2, TC	-	296	385	360	64	57	72
<b>P3A</b>	3, AC	212	276	341	310	75	66	72
<b>P3T</b>	3, TC	245	-	335	374	80	59	68
<b>P4S</b>	4, SC	-	-	319	461	92	85	88
<b>P4A</b>	4, AC	-	-	332	395	89	80	82
<b>P4T</b>	4, TC	-	-	333	472	95	88	91
<b>P5T</b>	5, TC	270	-	330	368	82	63	67

<sup>a</sup> $T_g$ : glass transition temperature. <sup>b</sup> $T_{endo}$ : temperature of endotherm. <sup>c</sup> $T_{exo}$ : temperature of exotherm. <sup>d</sup> $T_{100}$ : temperature determined at a weight loss of 10%. <sup>e</sup>Residual weight of cured samples at 310 °C.

les-ester)s. These are moderate molecular weights judging from the data of viscosity and GPC.

**Thermal properties.** Polymers exhibit interesting thermal behavior as evidenced by the data of Table 2. The typical DSC traces of polymers involve a large exotherm between 320 °C and 390 °C at a heating rate of 10 °C/min.

Glass transition temperature of the polymers from the aliphatic acid chloride were determined by the differential scanning calorimetry (DSC), however, the polymers derived from the aromatic acid chloride showed no distinct transition points in DSC or it was difficult to determine them. The polar character of the cyano group increase dipole-dipole interaction, thereby increasing both the chain stiffness and increasing  $T_g$ . Only the polymers derived from **P3A** melted on heating in the capillary tubes, but those from other monomers showed no melting behavior in the capillary tubes below the decomposition temperature. However polymers **P2S** and **P2T** showed a large endotherm at 302 and 296 °C, respectively, as shown in Figure 1(d). It did not seem to be a melting temperature because weight loss occurred at the beginning temperature of endotherm. The TGA



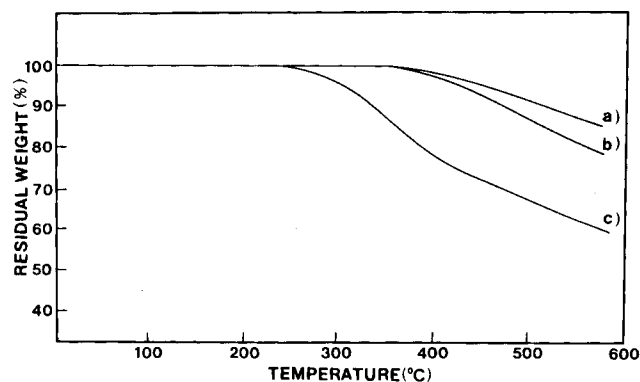
**Figure 1.** Differential scanning calorimograms of a) polymer **P4T** (1st scan), b) **P4T** (2nd scan), c) **P3T**, d) **P2T** and e) TGA trace of polymer **P2T**.

values exhibited a 10% weight loss at a temperature of their endothermic peak at 302 or 296 °C in Figure 1(e). Though it is not clearly understood at present stage, the polymer seems to decompose with absorption of heat.

Specially, polymers obtained from **2** showed an endothermic peak as well as exothermic peak at 382 °C and 392 °C which is higher than those obtained from other monomers in Figure 1(d). On the other hand, other polymers showed a broad exotherm starting 310 °C and reaching maximum intensity at 330-350 °C as shown in Figure 1(a) and 1(c). The exotherm does not reappear upon cooling and rescanning the sample as illustrated in Figure 1(b). This might be due to the chemical change of dicyanovinyl moiety, when the sample was heated around its exothermic temperature.

When the polymer **P4T** was compared with the poly(enaminonitriles) with same chemical structure, prepared from **1** and 4,4'-bis(*p*-aminophenyl)terephthalester in the previous paper,<sup>16</sup> the similar thermal stabilities showing a large exotherm at 350 °C and a 90% residual weight at 500 °C resulted. After the polymer sample was heated in a sealed tube under vacuum at 310 °C, the solubility in THF and DMF, in which the untreated samples were soluble, was reduced apparently. This observation may be due to the chemical change of dicyanovinyl group by intramolecular cyclization or intermolecular cross-linking reaction. The results of the gel fraction data are shown in Table 2. The polymers derived from alkyl-containing enaminonitriles or alkyl diacid chloride displayed a lower gel fraction ranging 69-73% than those of aromatic ones ranging 84-92%.

At the temperature of a large exotherm, detectable weight loss for the polymer **P4T** is not observed in Figure 2(b). This result indicates that the polymer **P4T** was cured thermally at a temperature of its exotherm without evolution of



**Figure 2.** Thermogravimetric analysis of a) cured polymer **P4T**, b) uncured polymer **P4T** and c) **P3A**.

any volatile byproduct. The thermal stability data are listed in Table 2. The polymers **P4S** and **P4T** sustained a 10% weight loss over a temperature of 450 °C at a heating rate of 10 °C/min, and gave a residual weight 85 and 88% at 500 °C in nitrogen. When the samples were heated at the beginning of its exothermic temperature, the thermal stabilities including residual weight were improved for all the polymers in Figure 2(a). On the other hand, the polymers **P2S**, **P2T**, **P3A** and **P3T** possess low thermal stabilities with 10% weight loss around 350 °C and 44-66% residual weight at 500 °C. Especially, polymer **P2S** show the lowest thermal stability showing a 44% residual weight at 500 °C in Figure 2(c). However, they show more improved thermal stability than that of polyesters consisting of the corresponding alkyl monomer without dicyanovinyl group as a curing reaction. Poly(enaminonitriles-ester)s derived from aromatic monomers showed good thermal stability, which may result from the curing of the dicyanovinyl group.

## Conclusions

1. Novel dicyanovinyl-containing bis-hydroxy monomers, *p*-bis[1-(4-hydroxypiperidinyl)-2,2-dicyanovinyl]benzene (**2**) *p*-bis[1-[1-(2-hydroxyethyl)piperazinyl]-2,2-dicyanovinyl]benzene (**3**), *p*-bis[1-(4-hydroxyphenylamino)-2,2-dicyanovinyl]benzene (**4**) and *p*-bis[1-[*N*-methyl-(*N*-hydroxyethyl)amino]-2,2-dicyanovinyl]benzene (**5**) were prepared.
2. New poly(enaminonitriles-ester)s were prepared by reacting various acid chlorides such as succinyl chloride, adipoyl chloride and terephthaloyl chloride with dicyanovinyl-containing bis-hydroxy monomers.
3. They are easily soluble in polar aprotic solvents such as DMF, DMSO and NMP and hard and brittle films can be cast from DMF solutions of polymers.
4. Most polymers show a large exotherm between 320 and 390 °C in DSC thermogram and undergo a curing reaction around 350 °C to form insoluble materials.
5. Especially, poly(enaryloxynitriles) derived from **P4T** showed excellent thermal stabilities with 90% residual weight at 500 °C under nitrogen.

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