

NOTES

Synthesis and Thermal Properties of Polyester Containing Dicyanovinyl Groups in the Main Chain

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In recent years, new polymers of special physical properties have been developed through the syntheses and studies of thermally stable polymers. The most promising method of synthesis of such polymer is the incorporation of thermal curing function into polymer chain. Among the functional groups, nadimide, acetylenic, biphenylenic, maleimide, styryl, and *N*-cyanourea are most frequently employed for the preparation of thermally cross-linkable polymers.^{1,2} On heating, they are converted to thermally stable network polymers. The chemical process of network polymer formation usually involves cycloaddition or addition reaction. Although thermal curing mechanisms have not been clearly elucidated, the dicyanovinyl group is a curable function.³⁻⁶

This study presents new classes of thermally curable polymers based on the dicyanovinyl group, which is useful as a cross-linking agent for various polymers. The introduction of the dicyanovinyl group as an enaminonitrile or enaryloxynitrile moiety enhances the thermal stability through curing in the case of polyurethanes or polyesters.⁷⁻⁹ These systems are of special interest since enaminonitrile or enaryloxynitrile groups are readily introduced by copolymerization.

This paper reports the successful synthesis of a new polyesters and copolyesters containing

enaminonitrile units as a dicyanovinyl group by reacting common diols and *p*-bis[1-[*N*-methyl-(*N*-hydroxyethyl)amino]-2,2-dicyanovinyl]benzene (**2**) with terephthaloyl chloride and their thermal properties.

EXPERIMENTAL

p-Bis[1-[*N*-methyl-(*N*-hydroxyethyl)amino]-2,2-dicyanovinyl]benzene (**2**) was synthesized by the method previously reported.⁸ Ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, hydroquinone, and Bisphenol A were purified by vacuum distillation or recrystallization. Tetrahydrofuran and triethylamine for solution polymerizations were used after distillation over calcium hydride and sodium metal.

¹H NMR spectra were recorded on a Bruker Am-300 spectrometer and FT-IR spectra were taken on a Midac spectrophotometer. Thermal analyses of polymers were carried out on a Du Pont 2100 and a Mettler thermal analyzer with a heating rate of 10°C min⁻¹ under nitrogen atmosphere. GPC data were obtained with a Waters HPLC using three columns (μ -Styragel 10², 10³, and 10⁴ Å) and a UV detector at 254 nm in tetrahydrofuran and calibrated with polystyrene standards. Inherent viscosities of the polymer solution were measured in a

Cannon-Ubbelode viscometer in dimethyl formamide (DMF) solvent at 25°C. The polymer solutions for viscosity measurement were filtered through a micro-porous filter. Elemental analyses were performed with a Yanaco MT-3 CHN-Analyzer.

Preparation of Bis[1-(2-benzoyloxyethyl)-2,2-dicyanovinyl]benzene (3)

A solution of 2.0 g (5.4 mmol) of **2** and 0.64 g of triethylamine in 20 ml of tetrahydrofuran was placed in a 100 ml of three-necked flask equipped with a dropping funnel, a condenser and a nitrogen inlet. After 1.50 g (10.4 mmol) of benzoylchloride in 10 ml of freshly distilled tetrahydrofuran were added to the reaction flask for 30 minutes with a flush of nitrogen, the reaction mixture was stirred for 24 hours. The temperature was raised to 70°C and maintained for an additional 24 hours. The pale yellow solution was evaporated and the soil crystal was washed with distilled water several times and recrystallized in acetonitrile to give 2.62 g of the model compound **3**.

3. Yield 85%; mp 225°C (uncorrected).

¹H NMR (DMSO-*d*₆): δ = 7.8 (s, 4H, aromatic H's in **2**) 7.6–7.2 (m, 10H, 2 Ph-CO-O-). 4.0 (m, 4H, 2 -O-CH₂) and 3.4–3.7 (m, 10H, 2 -CH₂-N(CH₃)-).

IR (KBr): 2980 (C-H), 2230 (C≡N), 1760 (C=O), 1210–1090 (C-O and C-N) cm⁻¹.

Anal. Calcd for (C₃₄H₂₈N₆O₄)_n: C, 69.86%; H, 4.79%; N, 14.38%. Found: C, 70.01%; H, 4.81%; N, 14.36%.

Representative Polymerization of 2 and diol with Terephthaloyl Chloride

Terephthaloyl chloride (0.54 g, 2.64 mmol) dissolved in 10 ml of tetrahydrofuran was added dropwise to a solution of ethylene glycol and **2** (total amount: 2.64 mmol of the two components) in 20 ml of tetrahydrofuran containing 0.64 g of triethylamine. The reaction mixture was stirred vigorously at room temperature under nitrogen atmosphere for 24 hours and the temperature was raised to 70°C

and maintained for 24 hours.

When the reaction was completed, viscosity increase was observed and partial precipitation of polymer occurred. After 200 ml of *n*-hexane were added the polymer was isolated by filtration, and washed with water several times.

A similar procedure was applied to prepare other polymers, **4–16** with different content of **2** and ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, hydroquinone and Bisphenol A.

7. Yield 77%.

¹H NMR (dimethyl sulfoxide-*d*₆): δ = 8.0 (s, 4H, -CO-Ph-CO-), 7.8 (s, 2H, 1/2 aromatic H's in **2**), 4.0 (m, 4H, 1/2 2 -OCH₂CH₂-N(CH₃)- and 1/2 -OCH₂CH₂-O-), 3.8–3.4 (m, 5H, 1/2 2 -CH₂CH₂-N(CH₃)-).

IR (KBr): 3020 (C-H), 2220 (C≡N), 1710 (C=O), 1580 (C=C), 1100–1300 (C-N and C-O) cm⁻¹.

Anal. Calcd for (C₁₉H₁₅N₃O₄)_n: C, 65.33%; H, 4.30%; N, 12.03%. Found: C, 65.25%; H, 4.19%; N, 12.11%.

10. Yield 81%.

¹H NMR (DMSO-*d*₆): δ = 8.0 (s, 4H, -CO-Ph-CO-), 7.8 (s, 2H, 1/2 aromatic H's in **2**), 4.0–3.8 (m, 4H, 2 -O-CH₂-), 3.7–3.4 (m, 10H, 2 -CH₂N(CH₃)-).

IR (KBr): 3000 (C-H), 2210 (C≡N), 1710 (C=O), 1210–1110 (C-O) cm⁻¹.

Anal. Calcd for (C₂₈H₂₂N₆O₄)_n: C, 66.40%; H, 4.35%; N, 16.60%. Found: C, 66.28%; H, 4.28%; N, 16.57%.

15. Yield 90%.

¹H NMR (DMSO-*d*₆): δ = 8.0 (s, 4H, -CH-Ph-CO-), 7.8 (s, 2H, 1/2 aromatic H's in **2**), 7.5–6.8 (m, 4H, 1/2 aromatic H's in Bisphenol A), 4.1–3.8 (m, 2H, 1/2 2 -OCH₂-), 3.7–3.4 (m, 5H, 1/2 -CH₂N(CH₃)-), 1.8 (s, 3H, 1/2 -Ph-C(CH₃)₂-Ph-).

IR (KBr): 3010 (C-H), 2230 (C≡N), 1720 (C=O), 1100–1300 (C-N and C-O) cm⁻¹.

Anal. Calcd for (C_{24.5}H₁₆N₃O₄)_n: C, 70.67%; H, 3.85%; N, 10.10%. Found: C, 70.62%; H, 3.81%; N, 10.07%.

RESULTS AND DISCUSSION

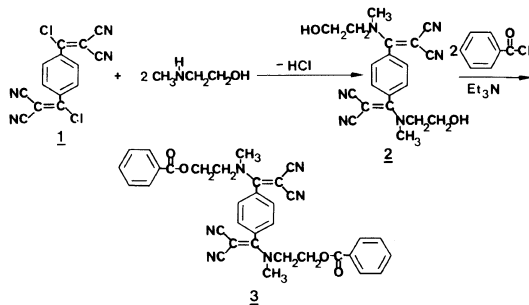
Diol monomer, *p*-bis[1-(*N*-methyl-(*N*-hydroxyethyl)amino)-2,2-dicyanovinyl]benzene (**2**) was prepared from the reaction of *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**1**) with excess 2-(*N*-methylamino)ethanol in methylene chloride at room temperature as described previously.⁸

The conditions and feasibility of ester formation were investigated by preparation of the model compound, *p*-bis[1-(*N*-methyl-(*N*-benzoyloxyethyl)amino)-2,2-dicyanovinyl]benzene (**3**), obtained by reacting **2** with benzoylchloride in the presence of triethylamine in 85% yield according to Scheme 1.

The IR spectrum of the model compound exhibited bands at 2230, 1760, 1580, and 1300–1100 cm⁻¹ assignable to C≡N, C=O, C=C, and C–O stretching absorption. In the NMR spectrum, the aromatic peaks of **2** and benzoate appeared at 7.8 and 7.5–8.2 ppm, respectively. The aliphatic protons attached to oxygen and nitrogen were shown as broad multiplets between 3.0 and 4.4 ppm. On the basis of these results, the model compound is presumed to be an enaminonitrile containing ester moiety.

The polymerizations of different contents of **2** and ethylene glycol with terephthaloyl chloride were conducted to obtain controlled amounts of enaminonitrile units in the main chain of polyesters.

Polyesters and copolyesters were prepared with **2** and ethylene glycol in the following mole



ratios: 0/1, 1/4, 1/2, 1/1, 2/1, 4/1, and 1/0. Copolyesters containing enaminonitrile units were also obtained from 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, hydroquinone, and Bisphenol A with terephthaloyl chloride in Scheme 2.

The results and conditions of copolymeriza-

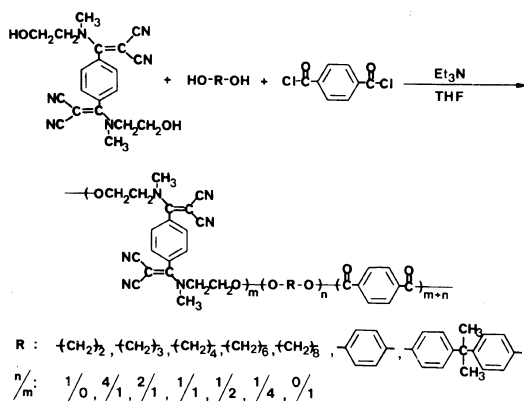


Table 1. Results and conditions of the polymerization of **2** and diol with terephthaloyl chloride

Polymer ^a	Diol ^b	Diol:2	Yield		
			%	<i>M_w</i> ^c	η_{inh} ^d
4	ED	1:0	80	—	—
5	EG	5:1	76	12000	0.12
6	EG	2:1	81	14500	0.11
7	EG	1:1	77	10600	0.11
8	EG	1:2	89	15000	0.21
9	EG	1:4	91	13700	0.17
10	EG	0:1	81	17000	0.19
11	1,3-PD	1:1	95	11500	0.12
12	1,4-BD	1:1	95	13500	0.17
13	1,6-HD	1:1	98	12000	0.13
14	1,8-OD	1:1	98	11100	0.12
15	HQ	1:1	92	12000	—
16	BPA	1:1	90	12500	—

^a Polymerizations were performed in tetrahydrofuran for 48 hours in all cases.

^b EG, ethylene glycol; 1,3-PD, 1,3-propanediol; 1,4-BD, 1,4-butanediol; 1,6-HD, 1,6-hexanediol; 1,8-OD, 1,8-octanediol; HQ, hydroquinone; BPA, Bisphenol A.

^c Weight average molecular weights were obtained in tetrahydrofuran solvent.

^d Measured in *N,N*-dimethylformamide in 1 g dl⁻¹ at 25°C.

tion are summarized in Table I. The solution polymerization resulted in white powdery polyesters in high conversion in all cases. The chemical structures of the polyesters were characterized by spectroscopy and matched well with the model compound.

In the IR spectrum of copolyester, **7** with equimolar ratio of **2** and ethylene glycol, the characteristic bands at 2220, 1710, 1580, and 1300–1100 cm^{-1} attributable to $\text{C}\equiv\text{N}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$, and $\text{C}-\text{O}$, respectively, appeared.

In the ^1H NMR spectrum, the aromatic protons of fragment of **2** appeared at 7.6 ppm as a singlet, whereas those of terephthalate, at 8.0 ppm.

The NMR integration ratio of two monomer units in the copolymers were variable according to the ratio of monomer in the feed. Thus, the integration of the peak at 4.1 ppm assignable to methylene protons attached to ester bond increased with the content of ethylene glycol

in the polymer chain. The polymer with more content of **2** showed a stronger band at 2210 cm^{-1} attributable to nitrile group in the IR spectrum. These results were also confirmed by elemental analyses.

The copolyesters containing enamionitrile units were soluble in polar aprotic solvents such as DMF, dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), and *N*-methylpyrrolidone (N-MP), and even soluble in 1,2-dichloroethane and tetrahydrofuran. The solubility of copolyester derived from Bisphenol A and hydroquinone in DMF and DMSO decreased apparently because of rigid structure of the aromatic moiety. As the amount of **2** in the polymer increased, solubility in DMF increased.

However, homopolyester composed only of ethylene glycol or **2** was insoluble in such a solvent. The increased solubility of other copolyesters in common organic solvents is mainly due to the incorporation of the

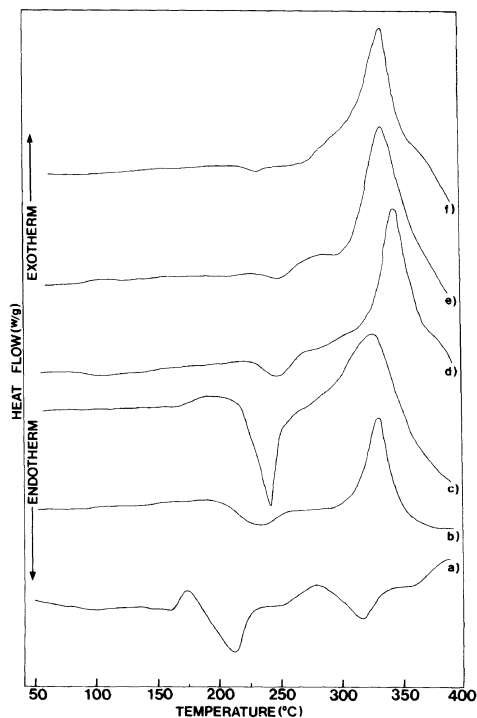


Figure 1. DSC thermogram of polyesters, a) **4**, b) **6**, c) **7**, d) **8**, e) **9**, and f) **10** obtained from **2** and ethylene glycol with terephthaloyl chloride under nitrogen.

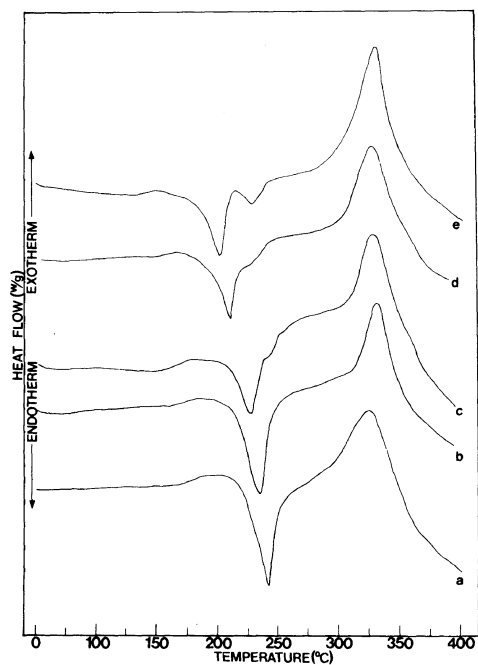


Figure 2. DSC thermograms of copolyesters, a) **7**, b) **11**, c) **12**, d) **13**, and e) **14** obtained from **2** and various diols with terephthaloyl chloride.

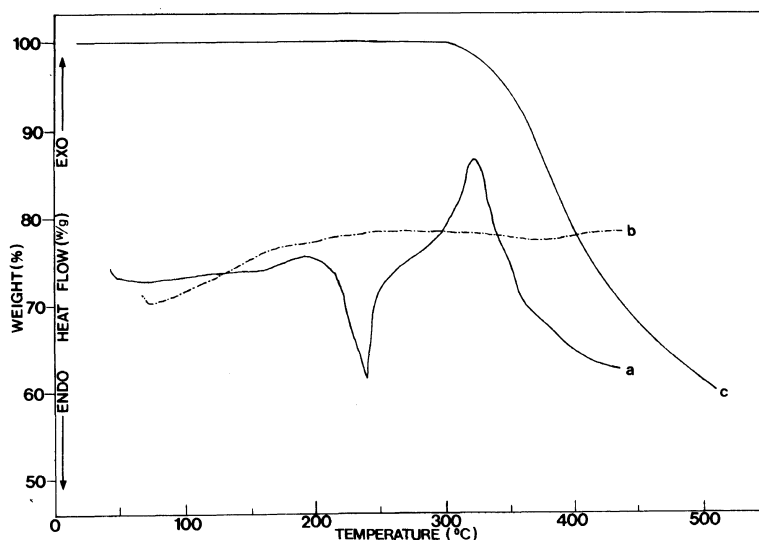


Figure 3. DSC thermograms, a) 1st scan, b) 2nd scan, and c) TGA traces of copolyester, 7 obtained from equimolar ratio of 2 and ethylene glycol with terephthaloyl chloride.

enaminonitriles moiety into the polyesters. When the polymers were heated at 320°C, the polymers were no longer soluble in the solvents for untreated polymers. This indicates that the polymers were changed in chemical structure during heating.

The polymers have inherent viscosities of 0.1–0.2 dl g⁻¹ with M_n in the range of 4000–5600 and M_w in the range of 12000–15000. Although the polyesters are not of high molecular weight judging from the viscosity and GPC data, hard films were cast from DMF solution.

In DSC thermograms as shown in Figures 1 and 2, copolyester 8, 9, and 10 with higher content of 2 showed no endotherm, while the copolyester 7 with lower content of 2 showed endotherm attributable to melting of polymer at 242°C.

The homopolyester of 2 shows only a large exotherm, which corresponds to changes in chemical structure, followed by decomposition.

On the other hand, polymers incorporated with other diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and 1,8-octanediol,

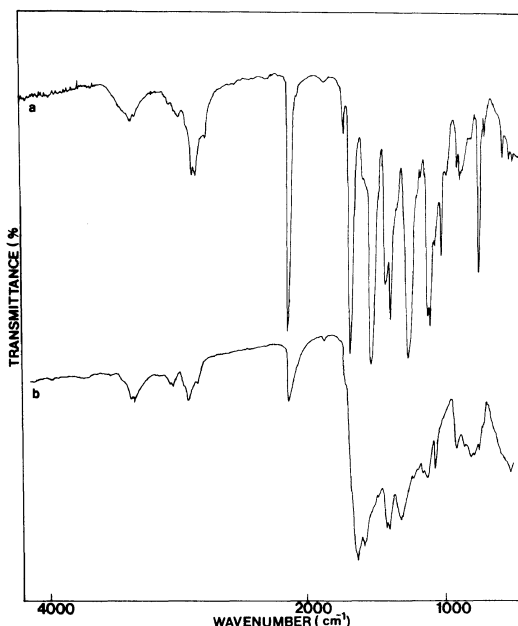


Figure 4. FT-IR spectra of polyester, 7 a) before and b) after curing 310°C for 1 h under nitrogen.

the clear endotherm appeared between 220–250°C as shown in Figure 2. The endotherm attributable to the melting temperature decreased regularly as the length of flexible

alkylenic chain increased.

Most copolyesters containing enamionitrile units showed an exotherm beginning at around 310°C. The exothermic peak disappeared upon cooling and rescanning the sample as exhibited in Figure 3(b), which may be due to change in chemical structure of polymer in the course of heating to 320°C. At the beginning of an exothermic temperature of 310°C, slight loss of weight was observed as exhibited in Figure 3(a) of DSC and 3(c) of TGA. Examination of the IR spectra of a sample of cured or uncured at 310°C for 1 hour showed that the bands at

2957 and 2212 cm⁻¹ corresponding to C–H and C≡N stretching have reduced apparently and bands at 1721 and 1558 cm⁻¹ broadened as shown in Figure 4.

The curing of the dicyanovinyl group thus obviously occurs. At the temperature of the highest peak of the exotherm at around 330°C, the weight loss was within 6% of their mass and decomposition of alkylenic unit of polymer accelerated.

Thermal stability data are listed in Table II and TGA traces are shown in Figure 5. The polymers showed a 10% weight loss in ni-

Table II. Thermal properties of polyesters containing enamionitrile units

No.	T_g	Endo	Exo	10% wt loss	Residual weight/%		
		°C	°C		°C	300°C	400°C
4	—	212	287	367	96	78	20
5	241	363	—	330	92	74	24
6	142	—	332	350	98	77	60
7	175	242	325	365	99	74	61
8	—	—	345	370	97	77	62
9	—	—	330	368	99	82	63
10	258	—	325	342	97	86	70
11	165	231	330	360	97	63	55
12	165	226	327	363	98	60	50
13	—	213	325	375	98	85	50
14	—	208	330	362	98	70	49
15	—	238	335	342	98	72	71
16	—	213	313	365	96	72	59

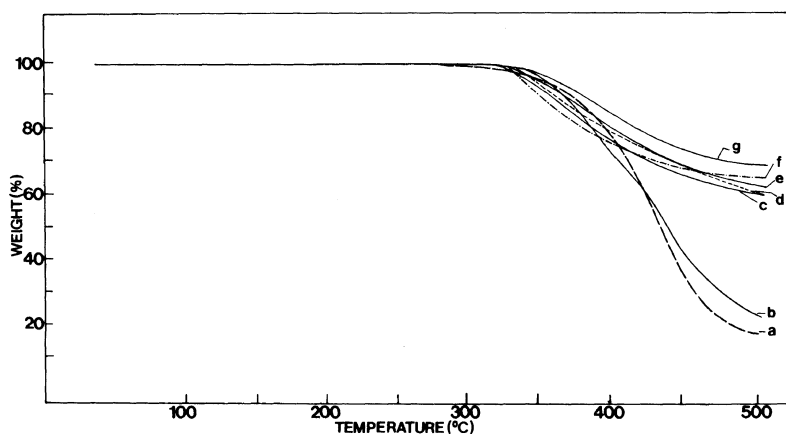


Figure 5. Thermogravimograms of polyesters, a) 4, b) 5, c) 6, d), 7, e) 8, f) 9, and g) 10 obtained from 2 and ethylene glycol with terephthaloyl chloride.

trogen over a temperature of 350–380°C and gave a residual weight varying from 50 to 70% at 500°C. But the homopolymer, **4** and copolymer, **5** with lower content of **2** showed 20–25% residual weight at 500°C. The higher content of enaminonitrile units in polymer showed greater thermal stability than those with higher content of ethylene glycol. This thermal stability was related to the content of the dicyanovinyl group in the polymer chain.

Insolubility in solvent after curing, disappearance of an exotherm during 2nd scanning of DSC, reduction of nitrile band in IR spectra and enhancement of thermal stability are evidence of inter- or intramolecular addition or cross-linking reactions of the dicyanovinyl group.

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