

NOTES

Synthesis of Polyurethanes Containing a Dicyanovinyl Group and Thermal Properties

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A close analogy of chemical reactivity between dicyanovinylidene group ($=C(CN)_2$) and carbonyl group has been proposed by Wallenfels.^{1,2}

Dicyanovinyl chloride is readily attacked by nucleophiles and the resulting carbanion enhances expulsion of chloride anions by mesomeric electron donation of the cyano group.^{3,4)}

1-Chloro-2,3-dicyanoethene (**1**) is reactive toward nucleophiles such as water, alcohols, and amines. 1-Chloro-1-phenyl-2,2-dicyanoethene (**2**) reacts only with amine group of aminol to form the alcohol derivatives containing enaminonitrile moiety.⁵

Poly(enaminonitrile)s⁶⁻¹¹ and poly(enaryloxynitrile)s¹² prepared from *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**3**) with diamines and aromatic diols showed good thermal stability after curing without releasing of volatile byproduct.

Polyurethane which undergoes heat curing has become a subject of considerable interest. We previously reported that *p*-bis[1-*N*-methyl-*N*-hydroxyethylamino]-2,2-dicyanovinyl]benzene (**4**) containing enaminonitrile unit was polymerized with diisocyanates and the resulting polyurethanes showed good thermal stability.⁵

In this paper, polyurethanes with dicyanovinyl group, which is partially distributed in the main chain of polymer back bone, are prepared by the copolymerization of diisocyanates with **4** and 1,4-butanediol and their thermal properties are investigated.

EXPERIMENTAL

p-Bis(1-chloro-2,2-dicyanovinyl)benzene was synthesized by the method previously reported.⁸ 1,4-Butanediol, diphenylmethane-4,4'-diisocyanate (MDI), hexamethylenediisocyanate (HDI), and tolylene-2,4-diisocyanate (TDI) were purified by conventional purification method. *N*-Methyl-2-pyrrolidinone (N-MP) and triethylamine were purified by drying over calcium hydride and distillation.

IR spectra were taken on a Perkin-Elmer Model 1310 spectrometer and ¹H NMR spectra were recorded on a Bruker Am-300 spectrometer. Size exclusion chromatography data were obtained by Waters HPLC using three columns (μ -Styragel 10², 10³, and 10⁴ Å) in THF at 25°C, and calibrated with polystyrene standard. Elemental analyses were obtained with a Yanaco MT-3, CHN-Analyzer. Thermal analyses were performed with a Mettler thermal analyzer at a heating rate of

10°C min⁻¹ in nitrogen.

Representative Polymerization of Diisocyanate with 1,4-Butanediol and **4**

A solution of 1 g (2.9 mmol) of **4** and 0.26 g (2.9 mmol) of 1,4-butanediol in 10 ml of N-MP was added to a mixture of 3.7 μ l (0.01 mmol) of triethylamine and 1.40 g (5.8 mmol) of MDI in 5 ml of N-MP in nitrogen atmosphere. The temperature was raised to 70°C and maintained for 2 hours. The resulting yellow solution was poured into a large amount of methanol to precipitate the polymer. The precipitate was filtered and dried *in vacuo* (0.1 Torr) at 80°C for 12 hours.

Similar procedures were followed by the polymerization of different compositions of **4** and 1,4-butanediol units in the polyurethane.

8 Yield 95%.

IR (KBr): 3317, 2953, 2210, 1712, 1527, 1222, and 1100 cm⁻¹.

¹H NMR (DMSO-*d*₆): 9.3 (s, 2H, 2NH), 7.1–7.8 (m, 10H, aromatic H's in MDI and 1/2 **4**), 4.0 (m, 6H, 2 –O–CH₂–CH₂–N–CH₃ and 1/2 –OCH₂CH₂CH₂CH₂O–), 3.6–3.3 (m, 5H, –CH₂–N–CH₃), 2.2 (s, 2H, 1/2 –O–CH₂CH₂CH₂CH₂O–).

Anal. Calcd for (C₂₇H₂₅N₅O₄)_n: C, 67.08%, H, 5.18%; N, 14.49%. Found: C, 66.02%; H, 5.07%; N, 13.91%.

11 Yield 89%.

IR (KBr): 3319, 2955, 2208, 1722, 1550, 1226, and 1064 cm⁻¹.

¹H NMR (DMSO-*d*₆): 9.5 (s, 2H, 2 –NH–), 7.1–7.8 (m, 5H, aromatic H's in TDI and 1/2 **4**), 4.0–4.2 (m, 6H, 2 –O–CH₂CH₂–NCH₃ and 1/2 –OCH₂CH₂CH₂CH₂O–), 3.5–3.8 (m, 5H, –CH₂–NCH₃), 3.0 (s, 3H, ph-CH₃), 2.0 (m, 2H, 1/2 –O–CH₂CH₂CH₂CH₂O–).

Anal. Calcd for (C₂₀H₂₁N₅O₄)_n: C, 60.76%; H, 5.32%; N, 17.72%. Found: C, 60.37%; H, 5.17%; N, 17.48%.

12 Yield 87%.

IR (KBr): 3358, 2937, 2780, 2270, 1712, 1556, 1440, 1249, and 1138 cm⁻¹.

¹H NMR (DMSO-*d*₆): 9.0 (s, 2H, 2 –NH–),

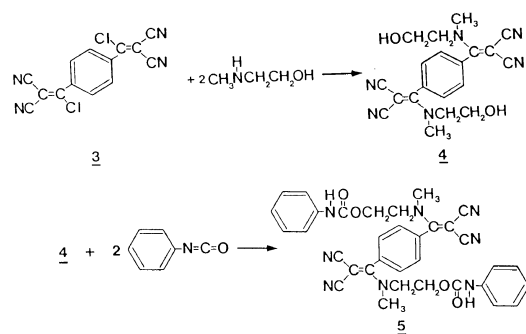
7.0–7.6 (m, 2H, 1/2 aromatic H's in **4**), 4.0 (m, 6H, 2 –O–CH₂CH₂–N–CH₃ and 1/2 –OCH₂CH₂CH₂CH₂O–), 3.0–3.8 (m, 9H, –CH₂NCH₃ and –HNCH₂–(CH₂)₄–CH₂–NH–), 2.0 (m, 10H, 1/2 –O–CH₂CH₂CH₂–CH₂–O– and –HNCH₂–(CH₂)₄–CH₂–NH–).

Anal. Calcd for (C₂₀H₂₇N₅O₄)_n: C, 59.85%; H, 6.73%; N, 17.46%. Found: C, 58.92%; H, 6.29%; N, 17.23%.

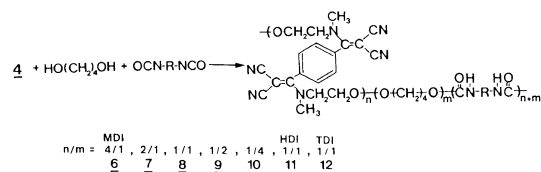
RESULTS AND DISCUSSION

Diol monomer, *p*-bis[1-[*N*-methyl-*N*-(hydroxyethyl)amino]-2,2-dicyanovinyl]benzene (**4**) was prepared by reacting *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**3**) with 2-(*N*-methylamino)ethanol.

Preparation of model compound, **5**, from phenylisocyanate was performed to demonstrate the feasibility of polymerization and obtain a model urethane compound for the characterization of polymers.



The polymerization of different contents of **4** and 1,4-butanediol with diisocyanates such as MDI, HDI, and TDI was attempted to obtain a controlled amount of enamionitrile unit in the main chain of polyurethane.



The conditions and results of copolymerization of 1,4-butanediol and **4** with diisocyanates

Table I. Results of polymerizations of **4** and 1,4-butanediol with diisocyanates

Polymer ^a	1,4-BD/4	Diisocyanate	Yield	η_{inh}^b	M_w^c
			%		
6	1/4	MDI	96	0.31	12,800
7	1/2	MDI	97	0.23	11,200
8	1/1	MDI	95	0.34	21,000
9	2/1	MDI	95	0.26	11,800
10	4/1	MDI	95	0.21	8,400
11	1/1	HDI	87	0.19	7,420
12	1/1	TDI	85	0.27	12,400

^a Polymerizations were performed at 70°C for 2 hours in all cases.

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

^c Weight average molecular weights were obtained with Waters HPLC in tetrahydrofuran and calibrated with polystyrene standard.

are summarized in Table I.

Polyurethanes, **6–12**, were obtained by solution polymerization in *N*-methyl-2-pyrrolidinone at 70°C for 2 hours. The yellow powdery polymers were obtained after precipitation into methanol in good yield. The chemical structures of copolymers were characterized by spectroscopies.

In the case of IR spectrum of polymer with the same content of **4** and 1,4-butanediol units, characteristic bands at 3320, 2210, 1710, 1530, and 1220–1100 cm⁻¹ assignable to N–H, C≡N, C=O, C=C, and C–O, respectively, appeared.

Compared to the IR spectra of polymers with different contents of **4** and 1,4-butanediol, as the component of **4** in polymer increased, the intensity of the C≡N stretching band at 2210 cm⁻¹ in contrast to C=O band at 1710 cm⁻¹ increased.

¹H NMR spectrum showed aromatic protons of a fragment of **4** at 7.8 ppm, whereas those of MDI appeared at 7.1–7.5 ppm as a multiplet. The higher content of 1,4-butanediol unit in polymer exhibited the gradual increase of methylene protons at 2 ppm. The proposed structure of polymer was also confirmed by

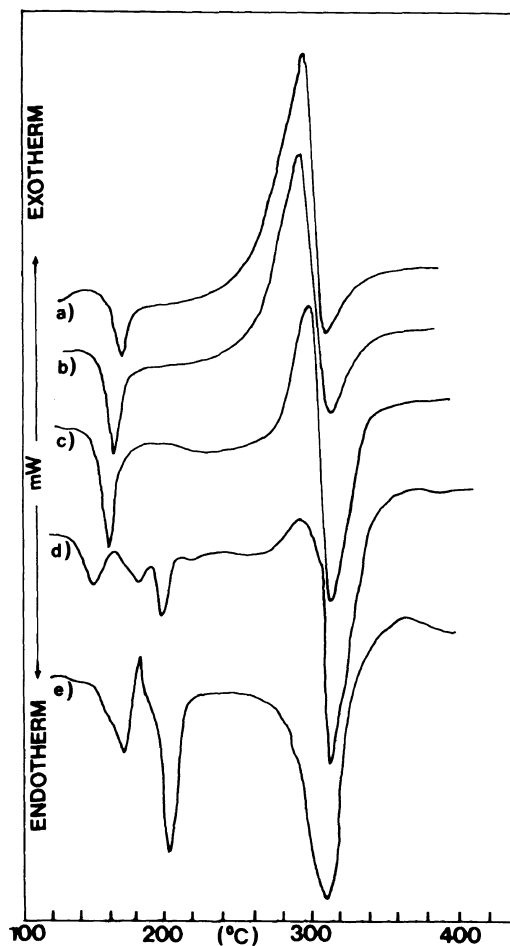


Figure 1. DSC thermograms of polyurethanes, a) **6**, b) **7**, c) **8**, d) **9**, and e) **10**, obtained from **4** and 1,4-butanediol with MDI at a heating rate of 10°C min⁻¹ in nitrogen.

elemental analysis. The spectroscopic data of other polyurethanes obtained from TDI and HDI matched well with the corresponding chemical structures.

Polyurethanes, **6–12** exhibit good solubility in common organic solvents such as DMF, DMSO, acetonitrile and THF, and slightly soluble in methylene chloride and acetone. After these polymers have been heated near the temperature of exotherm, they are no longer soluble or are reduced in solubility in the solvent for the untreated polymers.

The polymers appeared to possess an in-

herent viscosity of 0.2–0.3, and $M_n = 3,800$ – $5,200$ and $M_w = 8,600$ – $21,000$. These are not high molecular weights judging from the size exclusion chromatography data. When the film was cast from the DMF solution of polymer after evaporation of solvent, the clear and tough film was formed.

In DSC thermograms as shown in Figure 1, polyurethanes **6**, **7**, and **8** showed an endotherm at 170°C , 162°C , and 160°C , respectively, which corresponds to the melting of polymer. Higher transition temperatures were observed for the polymer incorporating more than **4** units.

In the case of polymers, **9** and **10**, three or two consecutive endotherms appeared. This might be due to the liquid crystalline behavior of the polymer.

The polymers except **10** exhibit large

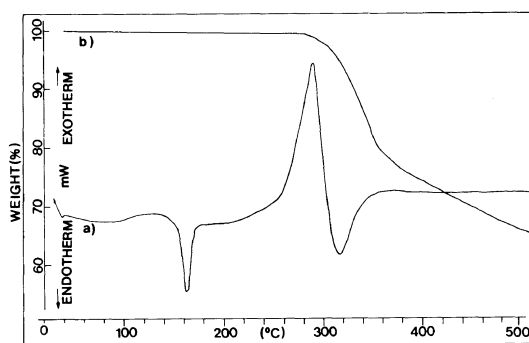


Figure 2. (a) DSC thermogram and (b) TGA trace of polyurethane, **6**.

exothermic peaks at 290°C and endothermic peak at 320°C . As the content of **4** in polymer increased, exothermic peak intensity increased and endothermic peak intensity decreased. In the case of polymer **10**, a large endotherm appeared alone at 320°C . At the temperature of the exotherm, slight weight loss was detected and a sudden weight loss begun at 320°C .

Thermogravimetric analysis of polymers are shown in Figure 2 and the data are summarized in Table II. Any detectable loss of weight is not observed at the beginning of a large exotherm temperature. This indicates that the polyurethanes containing dicyanovinyl group were cured without decomposition or elimination of volatile a byproduct.

The polymers showed a 10% weight loss in nitrogen over a temperature range of 300 – 320°C and gave a weight residual varying from 40–66% at a temperature of 500°C . The higher content of **4** in the polymer showed greater thermal stability than those with higher content of 1,4-butanediol. Within each series, greater thermal stability was associated with the content of enamionitrile units in the polymer. In addition, all polymers displayed rapid change at the temperature of exotherm in the IR spectra. The urethane N–H, $\text{C}\equiv\text{N}$, and C=O bands at 3330 , 2210 , and 1710 cm^{-1} disappeared gradually and the bands at 1520 – 1580 cm^{-1} , characteristic C=N bands, appeared as illustrated in Figure 3.

In the curing mechanism, poly(enaminoni-

Table II. Thermal properties of polyurethanes obtained from **4** and 1,4-butanediol with diisocyanates

Polymer	1,4-BD/ 4	T_m	Exo	Endo	Residual weight/%	
		$^\circ\text{C}$	$^\circ\text{C}$	$^\circ\text{C}$	400°C	500°C
6	1/4	170	295	308	74	56
7	1/2	162	291	310	69	62
8	1/1	160	298	312	57	51
9	2/1	150, 184, 197	295	310	50	40
10	4/1	169, 205	—	310	47	35
11	1/1	140	302	370	55	42
12	1/1	—	300	320	63	52

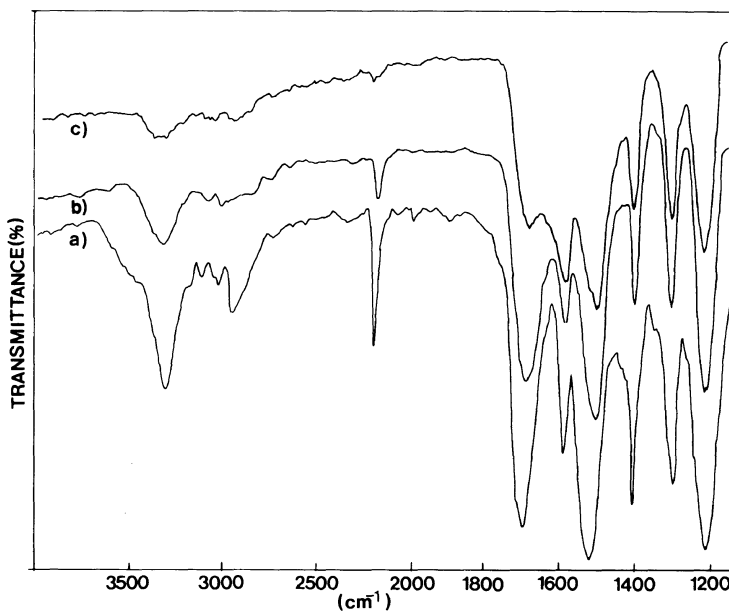


Figure 3. Superimposed IR spectra of polyurethane, **8**, after (a) 0 h, (b) 0.5 h, and (c) 1 h at 265°C under nitrogen.

trile)s undergo intramolecular cyclization to polyquinoline.⁶⁻⁸ However, curing reactions of polyurethanes are assumed to proceed largely by intermolecular addition of the dicyanovinyl group.¹² Upon comparison with poly(enaminonitrile)s⁸ and poly(enaryloxynitrile)s,¹³ polymers **6-12** showed less thermal stability, probably due to the presence of aliphatic hydrocarbon units in the chain.

REFERENCES

1. K. Wallenfels, *Chemia*, **20**, 303 (1966).
2. K. Wallenfels, K. Friedrich, J. Rieser, and W. Ertel, *Angew. Chem., Int. Ed. Engl.*, **15**, 261 (1976).
3. Z. Rappoport and R. Ta-Shma, *J. Chem. Soc., B*, 871 (1971).
4. Z. Rappoport and A. Topol, *J. Chem. Soc., Perkin Trans. 2*, 1823 (1972).
5. M. S. Gong, H. S. Moon, and S. T. Kim, *Macromolecules*, **25**, 7392 (1992).
6. J. A. Moore and D. R. Robello, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **27**(2), 127 (1986).
7. J. A. Moore and D. R. Robello, *Macromolecules*, **19**, 2667 (1986).
8. J. A. Moore and D. R. Robello, *Macromolecules*, **22**, 1084 (1989).
9. J. A. Moore and P. G. Mehta, *Polym. Mater. Sci. Eng.*, **63**, 351 (1990).
10. J. A. Moore and P. G. Mehta, *Polym. Mater. Sci. Eng.*, **64**, 835 (1991).
11. M. S. Gong, J. O. Lee, and S. T. Kim, *Polymer (Korea)*, **15**, 95 (1991).
12. G. B. Buttler and J. E. Kresta, "Cyclopolymerization and Polymers with Chain-Ring Structures," ACS Symp. Ser. 195, American Chemical Society, Washington D.C., 1982, pp 285-295.
13. H. S. Moon, S. T. Kim, and M. S. Gong, *Makromol. Chem. Rapid Commun.*, **12**, 591 (1991).