

The Reaction of Glass Fiber with Diisocyanate and Its Application

RYUTOKU YOSOMIYA, *Department of Industrial Chemistry, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino-Shi, Chiba 275, Japan*, and KIYOTAKE MORIMOTO and TOSHIO SUZUKI, *Nisshin Spinning Co., Ltd. Nishiarai Laboratory, 1-18-1, Nishiarai Sakaecho, Adachi-ku, Tokyo 123, Japan*

Synopsis

The synthesis of reactive glass fiber having isocyanate groups was tried by reacting silanol groups on the surface of glass fiber with diisocyanate compounds. The effect of solvent, influence of the structure of diisocyanate, and effect of amine catalyst were examined, and results that the reactivity increased with increasing the polarity of solvent, when aromatic diisocyanate was used, and with increasing the basicity of amine catalyst were obtained. Further, glass fiber having isocyanate groups was addition-reacted with diol, and diol added glass fiber was synthesized.

INTRODUCTION

As trials to make functional glass fibers, the authors have already reported the synthesis and application of a glass fiber at its silanol surface groups introducing various highly functional groups.^{1,2}

The synthesis of reactive glass fiber having isocyanate groups which is formed by reaction of glass fiber and diisocyanate compounds has scarcely been reported, and only the reaction of silanol groups on the surface of silica with 2,4-tolylene diisocyanate (2-4TDI) was reported by Lange.³ Recently the authors investigated the mechanical properties of glass fiber-reinforced rigid polyurethane foam, and estimated the reaction of silanol groups on the surface of the glass fiber with isocyanate groups from a fact that behaviors of interlaminar shear strength of reinforced materials with coupling the agent-treated glass fiber and the non-treated one were not different from each other.⁴

In this paper, the reactivity of various diisocyanate compounds with silanol groups on the surface of glass fiber was examined, and polyester (polyether)-diols were reacted to form glass fiber-diols combinations as a trial in which the synthesized glass fibers with isocyanate were made functional.

EXPERIMENTAL

Materials. E-glass of Nitto Boseki Co., Ltd., was used and submitted to hydrothermal treatment under various conditions as previously reported.¹ Diphenylmethane 4,4'-diisocyanate (P-MDI), crude (polymeric) MDI (C-MDI), and hydrogenated MDI (H-MDI) of Sumitomo Bayer Urethane Co., Ltd., and xylene diisocyanate (XDI) of Takeda Chemical Industries Co., Ltd., were used without further purification. Dioxane, monochlorobenzene, *N,N*-dimethyl-

acetamide (DMAc), and dimethylsulfoxide (DMSO) used in this experiment as solvent were dehydrated with a desiccating agent, purified by distillation under reduced pressure, and immediately used. Quinoline, α -picoline, pyridine, triethylamine, *N,N*-dimethylaniline and 1,8-diaza-bicyclo (5,4,0) undecene-7 (DBU) of reagent grade were distilled and purified, and used as catalysts. Polyester-diol (polyadipate of ethylenglycol/butanediol = 1/1; Dainippon Ink and Chemical, Inc.) and polyether-diol (polypropylene glycol; Sanyo Chemical Industries, Inc.) were used without further purification.

Reaction of Glass Fibers with Diisocyanate Compounds. Prescribed amounts of glass fiber, solvent, and diisocyanate compound were added in order (a prescribed amount of catalyst was added last when the catalyst was used) into a dried air-tight reaction vessel soaked in a oil bath which was kept at a constant temperature, and reacted in a nitrogen atmosphere for a prescribed period. The reaction product was filtrated, washed sufficiently with dioxane to remove unreacted diisocyanate and solvent, and vacuum-dried with phosphorus pentoxide in a desiccator at room temperature. The reaction product was assigned by infrared absorption spectrum.

Analysis. (a) Infrared absorption spectrum was measured with IR spectrophotometer (SHIMAZU; IR-27) by KBr pellet method.

(b) The surface of the reaction product was observed with an electron microscope (AKASHI; Mini-SEM-MSM).

(c) Amount of combined diisocyanate compound measurement: glass fiber used for reaction and reaction product (glass fiber having isocyanate groups) were weighed, and the amount of combined diisocyanate compound was determined from the weight difference.

(d) Determination of free isocyanate group: 1g of glass fiber having isocyanate group and 50 mL of 0.2*N* *n*-butylamine-dioxane solution were added into a dried air-tight reaction vessel, the reaction was conducted at room temperature for 4 h with stirring, excess *n*-butylamine was titrated with 0.2*N* hydrochloric acid using bromophenol blue as an indicator, and the amount was calculated.

Addition Reaction of Diol with Glass Fiber Having Isocyanate Group: 1 g of glass fiber having isocyanate group, 50 mL of solvent, 1–5 g of polyester-diol

TABLE I
Solvent Effects on the Reaction of the Glass Fiber with P-MDI^a

Solvent	Dielectric constant (ϵ)	Dipole moment (μ)	Reaction temp. combined	30°C free NCO	Reaction temp combined	90°C free NCO
			NCO $\times 10^5$ (mol/g)	$\times 10^5$ (mol/g)	NCO $\times 10^5$ (mol/g)	free NCO $\times 10^5$ (mol/g)
Dioxane	2.21	0.45	0	0	0	0
Chloro-benzene	5.62	1.56	3.80	2.60	9.54	6.42
DMAc ^b	37.8	3.79	7.35	5.66	12.60	7.08
DMSO ^c	48.6	4.03	8.80	7.95	15.45	10.95

^a Reaction condition: glass fiber 2 g, P-MDI 1 g, solvent 50 mL, reaction time 60 min.

^b *N,N*-Dimethylacetamide.

^c Dimethylsulfoxide.

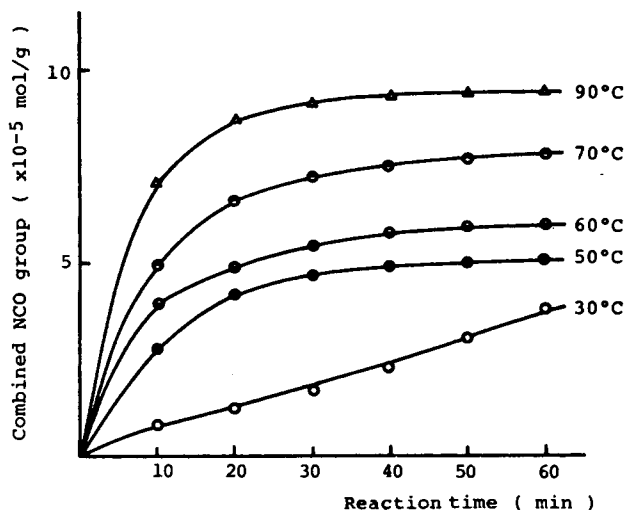


Fig. 1. Effect of temperature on the reaction of the glass fiber with P-MDI.

or polyether-diol, and a prescribed catalyst was added; the mixture was reacted at 30°C for prescribed period in a nitrogen flow atmosphere. The reaction mixture was washed sufficiently with dioxane to remove unreacted materials, and vacuum dried at 40°C. The reaction product was confirmed by weight change ratio and infrared spectrum.

RESULTS AND DISCUSSION

Solvent Effect on the Reaction of Glass Fiber with Diisocyanate. Reaction was carried out in various solvents to synthesize glass fibers having isocyanate group, and the solvent effect was investigated. Results in which P-MDI was used as a diisocyanate compound are shown in Table I. The weight of re-

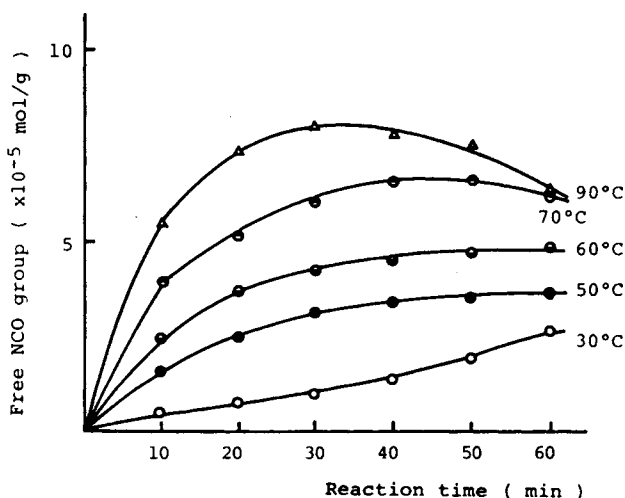


Fig. 2. Effect of temperature on the reaction of the glass fiber with P-MDI.

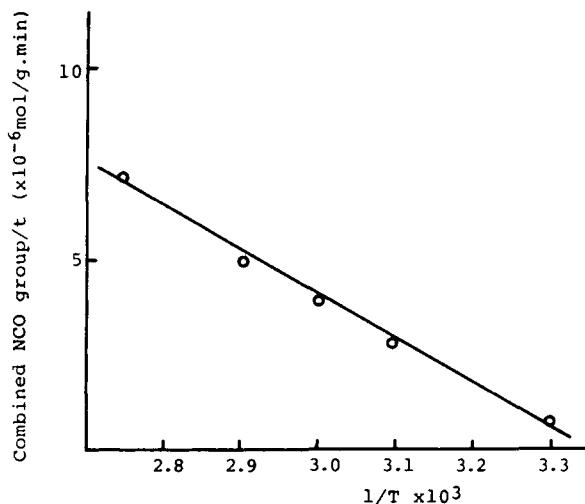


Fig. 3. Arrhenius plot of the reaction of the glass fiber with P-MDI.

action product in dioxane scarcely changed, and absorptions assigned to urethane bonding (1710 cm^{-1}) and isocyanate bonding (2250 cm^{-1})⁵ are not recognized entirely in the infrared absorption spectrum, and it can be said that the reaction will not proceed in this solvent.

Characteristic absorptions assigned to urethane bonding and isocyanate bonding are clearly recognized in infrared spectra of reaction products which were formed in monochlorobenzene, DMAc, and DMSO. From this result it is considered that reaction products formed in these solvents mean the synthesis of glass fiber having isocyanate groups. It is suggested from Table I that combined isocyanate and free isocyanate group content increase as a more polar solvent is used. In general, polar solvent solvates with the isocyanate group to increase the activity,⁶ accordingly less polar solvent solvates not sufficiently to activate, and it is considered that no reaction for dioxane is attributed to the nonsolvation.

Effect of Temperature on the Reaction of Glass Fiber with Diisocyanate.

Figure 1 shows the effect of temperature on the combined isocyanate. Combined isocyanate increases with increasing temperature, and attains a constant value after 1–2 hr. Figure 2 shows a relation to the free isocyanate group. The free

TABLE II
The Rate Constant and Apparent Activation Energy for the Reactions between the Glass Fiber and Diisocyanate

Diisocyanate	E (kcal/mol)	Rate constant $\times 10^6$ (mol/g.min)
P-MDI	8.25	7.2
C-MDI	8.44	7.0
XDI	8.90	5.4
H-MDI	10.5	2.5

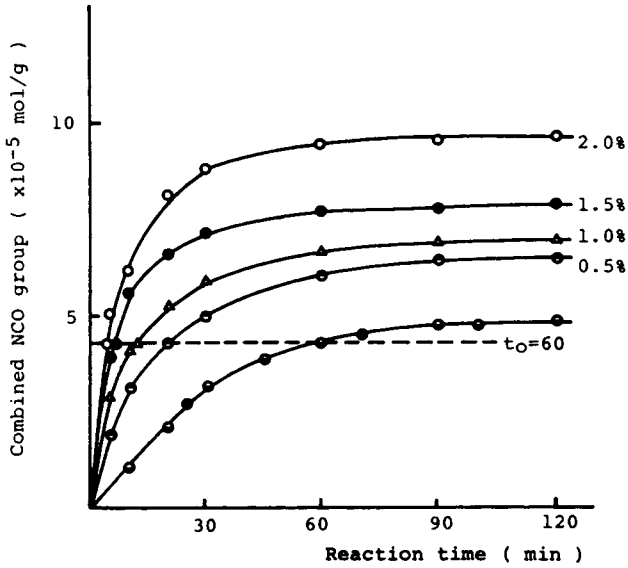


Fig. 4. Effect of amine on the reaction of glass fiber with P-MDI.

isocyanate group increases with increasing reaction period in lower temperatures, but in higher temperatures the free isocyanate group increases initially, but decreases later. This result suggests that silanol groups and isocyanate group are highly activated, and the crosslinking reaction between glass fiber and diisocyanate is accelerated.

Results of Figure 1 were expressed in the form of ordinary Arrhenius plot, and the result was shown in Figure 3. It is obvious that the rate of isocyanate bonding and the reciprocal of absolute temperature ($1/T$) satisfy approximately a linear relation. Similar relations are obtained for other diisocyanate compounds, and

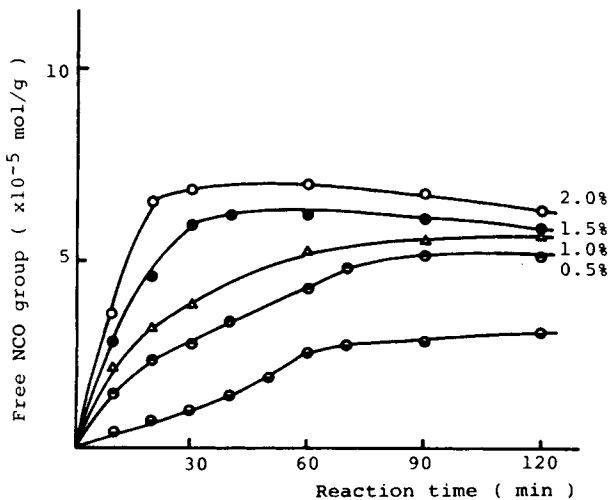


Fig. 5. Effect of amine on the reaction of glass fiber with P-MDI.

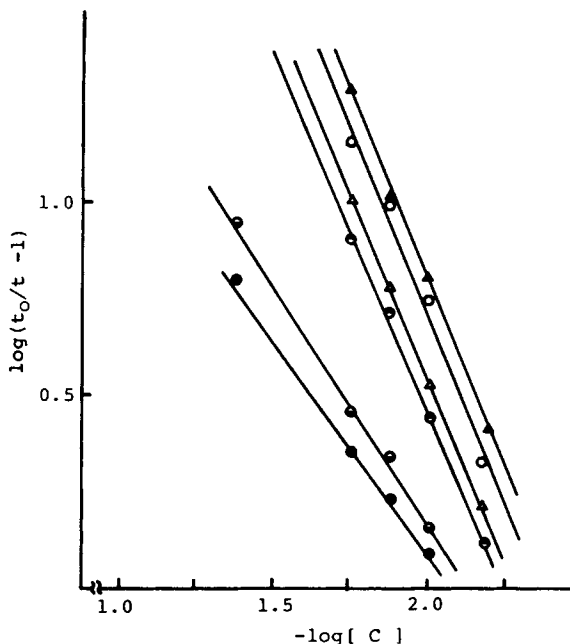


Fig. 6. Plots of catalysis law for various amine to glass fiber with P-MDI: (O) α -picoline; (Δ) pyridine; (\circ) quinoline; (\ominus) triethylamine; (\bullet) dimethylamine; (\blacktriangle) DBU.

the apparent activation energy is calculated for each case. Results are shown in Table II. The apparent activation energies of isocyanate bonding are 8–10 kcal/mole, and this values approximate the activation energy of reaction between ordinary alcohol and isocyanate.⁷

It is clear from Table II that the reactivity with silanol differs depending on the structure of diisocyanates. It is well known that in general aromatic isocyanates are more reactive than aliphatic isocyanates with hydroxy compounds,⁸ the order of reactivity obtained in this investigation is also P-MDI \div C-MDI > XDI > H-MDI, and it is considered that the reaction of silanol group with diisocyanate is very similar to the reaction of the ordinary hydroxy group with diisocyanate.

Effect of Amine Catalyst on the Reaction of Glass Fiber with Diisocyanates. It is well known that basic catalyst is effective on the reaction of isocyanate compounds with hydroxy compounds. The reaction behaviors in the presence of various amines were examined also in this investigation.

As an example, quinoline was added to reaction systems of P-MDI and glass fiber in various amounts, the combined isocyanate group and free isocyanate group were measured, and results are shown in Figures 4 and 5. As shown in Figure 4, the combined isocyanate group increases in proportion to the concentration of amine. As shown in Figure 5, the free isocyanate group also increases in proportion to the concentration of amine, but the free isocyanate group decreases with increasing reaction period in the increased amine concentration region. From this result it is obvious that amine exhibits the catalytic effect remarkably also on the reaction system of glass fiber–diisocyanate. Then the catalytic effect of amine is analyzed according to the theory of Weisfield.⁹ As-

TABLE III
 Catalytic Parameters for Various Amines

Catalyst	P-MDI		H-MDI		C-MDI		XDI		Ionization constant of amine at 25°C
	k_C/k_0	x	k_C/k_0	x	k_C/k_0	x	k_C/k_0	x	
Quinoline	698	1.0	824.5	1.2	1238	0.9	733.5	1.0	6.3×10^{-10}
Pyridine	995	1.0	1325	1.3	3404	1.0	1994	1.2	2.3×10^{-7}
α -Picoline	1921	1.0	2554	1.8	4685	1.1	3572	1.2	3×10^{-8}
Triethylamine	51.1	0.9	377.0	1.0	—	—	752.2	1.1	5.6×10^{-4}
<i>N,N</i> -Dimethylamine	2.52	0.8	—	—	484	1.1	—	—	1×10^{-9}
DBU ^a	2044	1.0	—	—	—	—	—	—	—

^a DBU = 1,8 diaza-bicyclo (5,4,0) undecene 7.

suming that the time required to form a certain intermediate in reaction is inversely proportional to the rate of reaction, then the following equations hold:

$$k/k_0 = t_0/t \quad (1)$$

where k and k_0 are the rate constants for the catalyzed and uncatalyzed reactions, respectively, and t and t_0 correspond to the times required for formation of the intermediate species in the catalyzed and uncatalyzed reactions. From the catalysis law,

$$k = k_0 + k_C[C]^x \quad (2)$$

where k_C is the catalytic coefficient, $[C]$ is the concentration of catalyst, and x is the order of catalysis. Dividing eq. (2) by k_0

$$k/k_0 - 1 = k_C/k_0[C]^x \quad (3)$$

or

$$\log(k/k_0 - 1) = \log(k_C/k_0) + x \log[C] \quad (4)$$

From these equations, the order of catalysis, x , and relative catalytic coefficient are derived by plotting $\log(k/k_0 - 1)$ or $\log(t_0/t - 1)$ against the logarithm of catalyst concentration $[C]$.

 TABLE IV
 The Yield of Reaction between the Glass Fiber Containing Isocyanate Group and Polyester-Diol or Polyether-Diol^a

	Molecular weight <i>M</i>	Yield of reaction (%)			
		P-MDI combined		H-MDI combined	
		Calcd	IR analysis	Calcd	IR analysis
Polyester-diol	1000	51.9 (80.5)	50.5 (79.0)	21.6 (66.9)	30.5 (61.4)
	1200	48.0	49.0	15.3	17.4
	1700	45.0	45.5	10.5 (62.7)	18.0 (55.5)
	2000	46.8 (78.0)	41.4 (72.8)	16.4	17.6
Polyether-diol	200	64.2	51.5	30.6	30.0
	400	50.8 (82.6)	52.0 (78.2)	38.1 (59.5)	31.5 (50.0)
	1000	42.5	48.3	17.2 (51.8)	20.8 (47.7)
	2000	46.8 (81.4)	39.7 (79.0)	10.8	11.5

^a Catalyst: DBU 1%/diol, reaction temp 30°C, reaction time 60 min; solvent: chlorobenzene, () DMSO.

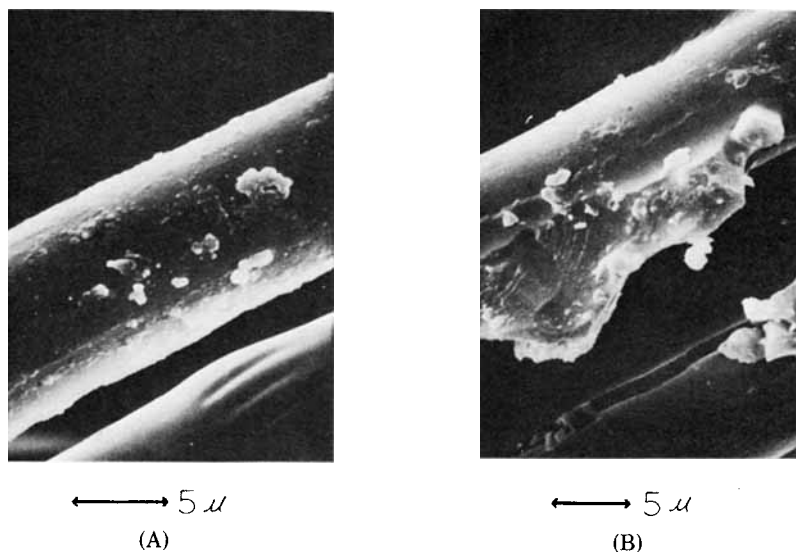


Fig. 7. Electron microscope photographs of P-MDI-combined glass fiber and diol-adduct of it: (A) glass fiber combined with P-MDI; (B) polyester-diol adduct of glass fiber combined with P-MDI.

Now as an example a result which used various amine catalysts for glass fiber-P-MDI systems is shown in Figure 6. The linear relationship holds invariably for all amine catalysts used. From the gradient and intercept of these straight lines, the order of catalyst and relative catalytic coefficient (k_C/k_0) are calculated for each amine catalyst. Similarly, results for reaction systems of glass fiber-C-MDI, -XDI, and -H-MDI are shown in Table III. The catalytic effect increases in proportion to the basicity of amine invariably for diisocyanate compounds used; this inclination agrees with that for the catalytic effect on the reaction of ordinary isocyanate compounds and alcohols. In the case of *N,N*-dimethylaniline, the catalytic effect is extremely low although the basicity of *N,N*-dimethylaniline is approximately equal to that of pyridine and α -picoline. It is considered that this result is caused from the steric hindrance¹⁰ of a complex formed of isocyanate and amine.

Addition Reaction of Diols (Polyester-diol, Polyether-Diol) with Glass Fiber Having Isocyanate Group. Polyester-diols and polyether-diols with various molecular weight were addition-reacted with glass fibers having isocyanate groups in chlorobenzene (or DMSO) at 30°C for 60 min using 1% of DBU based on diol as a catalyst. The yield of reaction obtained is shown in Table IV. The yield of reaction is approximately 50% for glass fiber combined with P-MDI and the yield of reaction decreases with increasing molecular weight of diol. The yield of reaction for glass fiber combined with H-MDI is lower than that for P-MDI generally, and decreases with increasing molecular weight of diol. Values in parentheses in Table IV represent the result which used DMSO as a solvent. In this case also, the yield of reaction increases with increasing the polarity of solvent.

Electron microscope photographs of diol-added glass fiber are shown in Figure 7. Figure 7(A) clearly indicate that, in the case of glass fiber treated with P-MDI,

glass fiber combined with diisocyanate was formed to the surface. Figure 7(B) shows the addition product of glass fiber having isocyanate group with polyester-diol. Their surface is deformed uneven and roughened.

Considering the result mentioned above that diol-added glass fiber can be easily synthesized, the synthesis of glass fiber combined with various amino acids and peptides must be possible. Properties and applications of diol-added and amino acid-added glass fibers will be reported in the next paper.

CONCLUSION

Various diisocyanates were reacted with glass fiber, the effect of solvents and amine catalysts on the reactivity was examined, and from the result obtained it becomes clear that the reaction of silanol group on the surface of glass fiber with diisocyanates exhibits the behavior similar to the reaction of compounds including hydroxy group with isocyanates. Further, diol-added glass fiber could be synthesized easily by reacting diol with glass fiber which was combined with isocyanate groups.

The authors wish to express their thanks to Professor A. Nakajima of Kyoto University for his continued advice and helpful discussions.

References

1. K. Hashimoto, T. Fujisawa, M. Kobayashi, and R. Yosomiya, *J. Appl. Polym. Sci.*, **27**, 4529 (1982).
2. T. Fujisawa, M. Kobayashi, K. Hashimoto, and R. Yosomiya, *J. Appl. Polym. Sci.*, **27**, 4849 (1982).
3. K. R. Lange, *Chem. Ind.*, **6**, 441 (1968).
4. K. Morimoto, T. Suzuki, and R. Yosomiya, *Polym. Plast. Tech. Eng.*, to appear.
5. M. L. Unland, *J. Phys. Chem.*, **79**, 610 (1975).
6. S. Ephrain, A. E. Woodward, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **80**, 1326 (1958).
7. J. H. Saunders and K. C. Frish, *Polyurethane* Wiley-Interscience, New York, 1961.
8. W. Cooper, R. W. Pearsan, and S. Darke, *Ind. Chem.*, (Mar), 122 (1960).
9. L. B. Weisfeld, *J. Appl. Polym. Sci.*, **5**, 424 (1961).
10. K. G. Flynn and D. R. Nenovtas, *J. Org. Chem.*, **28**, 3527 (1963).

Received April 18, 1983

Accepted August 9, 1983