

Polyisobutylene-based urethane foams

I. Comparative reactivities of hydroxyl-terminated polyisobutylene-diols and -triols and other hydroxyl-capped polyols with isocyanate

Masayuki Ako* and Joseph P. Kennedy

Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

Summary

The rates of urethane formation between linear and three-arm star hydroxyl-terminated polyisobutylenes (PIB-diols and-triols) and 4,4'-diphenylmethane diisocyanate (MDI) have been studied in the presence of triethylene diamine and stannous octoate catalysts in chlorobenzene at 25°C. The second order rate constants were determined and compared with those obtained with various polyether triols, hydroxyl-terminated polybutadiene and hydroxyl-terminated polyolefin. The rates of the normalized PIB-diol/MDI and PIB-triol/MDI reactions are essentially identical. In the presence of triethylene diamine, the rates of the PIB-diol and PIB-triol/MDI reactions are the same or much higher than that of the polyether-triol/MDI reaction. In contrast, in the presence of stannous octoate, the rates of the PIB-diol and PIB-triol/MDI reactions are much slower than that of the polyether-triol/MDI reaction. Differences in catalytic pathways are invoked to explain these observations. The reactivities of hydroxyl-terminated PIBs are similar to those of other hydroxyl-terminated polyhydrocarbons and sufficient for the synthesis of foams.

Introduction

The synthesis, characterization and some properties of polyurethane elastomers based on new linear and three-arm star hydroxyl-terminated polyisobutylenes (PIB) have recently been described (1-8). The excellent combination of properties of PIB-based polyurethane networks, such as barrier properties, and hydrolytic, oxidative, and thermal stabilities, would render these materials of interest for foam applications. Thus the kinetics of the reaction between a model alcohol for hydroxyl-terminated PIB and various isocyanates have been studied as a prelude for the synthesis of PIB-based polyurethane thermoplastic elastomers (3).

This paper concerns the kinetics of the reactions between various hydroxyl-terminated polymers including hydroxyl-terminated PIB-diols and-triols and a diisocyanate (MDI) with two catalysts, triethylene diamine and stannous octoate, in chlorobenzene at 25°C. The results of these studies show that hydroxyl-terminated PIBs are promising starting materials for polyurethane foams.

* Permanent address: Bridgestone Corporation, Totsuka-Ku, Yokohama, Japan

ExperimentalMaterials

PIB-diols and three-arm star triols (Akron Cationic Polymer Development Co.) have been synthesized by living carbocationic polymerization of isobutylene; the synthetic procedures have been described (9-11). The various other prepolymers have been obtained from commercial suppliers, i.e., the polyether triols Voranol 3010 and Multranol 3900 from Dow and Mobay, respectively, the hydroxyl-terminated polybutadiene R-45HT from ARCO, and the hydroxyl-terminated polyolefin Polytal HA from Mitsubishi Kasei. The characteristics of these polyols as provided by the manufacturers are shown in Table I.

TABLE I
Characteristics of Polyols Used

POLYOL (Trade Name and Manufacturer)	MAIN CHAIN STRUCTURE	TERMINAL OH GROUP	\bar{M}_n^a	\bar{F}^b	HYDROXYL VALUE (meq/g)
Polyether triol (Voranol 3010, Dow)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{CHO)}_n \end{array}$	Sec-OH	3000	3.0	1.00
Polyether triol (Multranol 3900, Mobay)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{CHO)}_n \end{array}$	Prim-OH (>70%) & Sec-OH	4800	3.0	0.62
Hydroxyl-terminated polybutadiene (R-45HT, ARCO)	$\text{-(CH}_2\text{CH=CHCH}_2\text{)}_n$	Prim-OH	2800	2.3	0.82
Hydroxyl-terminated polyolefin (Polytal HA, Mitsubishi Kasei)	Polyethylene- polypropylene copolymer	Prim-OH (?)	2000	1.6	0.80
Polyisobutylene diol (PIB-diol, Akron Cationic Polymer Dev. Co.)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CCH}_2\text{)}_n \\ \\ \text{CH}_3 \end{array}$	Prim-OH	2000	2.0 ^c	1.00
Polyisobutylene triol (PIB-triol, Akron Cationic Polymer Dev. Co.)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CCH}_2\text{)}_n \\ \\ \text{CH}_3 \end{array}$	Prim-OH	7000	3.0 ^c	0.43

a. by VPO b. \bar{F} = number average end functionality c. by IR

These starting materials were dried under reduced pressure. 4,4'-Diphenylmethane diisocyanate (MDI, Mobay) was vacuum distilled before use. Chlorobenzene, anhydrous (Aldrich), triethylene diamine (DABCO, Air Products and Chemicals), stannous octoate (Witco Chemical) and di-n-butylamine (Aldrich) were used as received. A ~ 0.1 N di-n-butylamine solution in chlorobenzene was prepared. Standard 0.1 N HCl was prepared by diluting a Fisher certified HCl solution in a volumetric flask with distilled water. Indicator solution (0.1 %) was prepared by dissolving bromophenol blue (Aldrich) in methanol.

Rate Measurements

Solutions of isocyanate in chlorobenzene ([NCO] = 0.05 mole/L), polyols in chlorobenzene ([OH] = 0.05 mole/L) and catalysts in chlorobenzene ([triethylene diamine] = 0.025

mole/L, [stannous octoate] = 0.00625 mole/L) were prepared in 50 mL volumetric flasks. Polyol solutions were transferred to stoppered 250 mL Erlenmeyer flasks equipped with magnetic stirrers in a dry box flushed with dry nitrogen gas at 25°C. Catalyst solutions were added by a pipet (5 mL) followed by the isocyanate solution.

Aliquots of 10 mL were removed by a pipet at the end of each time interval and immediately added to Erlenmeyer flasks containing 20 mL of di-n-butylamine in chlorobenzene solutions (0.1 N). The pipets were rinsed with 10 mL chlorobenzene into the same Erlenmeyer flasks. The flasks were shaken and kept at room temperature for 1 hour to assure complete reaction of the unreacted isocyanate with the di-n-butylamine. The excess di-n-butylamine was determined by titration with 0.1 N HCl, after adding 60 mL of methanol and 5 drops of indicator solution.

Results and Discussion

The polyether triol (V-3010) was reacted with MDI in chlorobenzene solution at 25°C before the reactions with the other polyols were carried out. The second order rate constant was calculated by the usual expression (12):

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad (1)$$

where a = initial concentration of -OH and -NCO (mole/L), $a-x$ = residual concentration of -OH and -NCO (mole/L), k = rate constant (L/mole·sec), t = time (sec). The k was determined graphically from data such as shown in Figure 1. While the reaction time was very long in the absence of catalyst ($k = 3.70 \times 10^{-6}$ L/mole·sec), in the presence of triethylene diamine the rate increased by about 65 fold ($k_c = 2.43 \times 10^{-4}$ L/mole·sec, see Figure 1). Similar series of experiments have been carried out with various polyols, i.e., polyether-triol (M-3900), hydroxyl-terminated polybutadiene (R-45HT), hydroxyl-terminated polyolefin (Polytal HA), PIB-diol and PIB-triol, in the presence of triethylene diamine and stannous octoate. Figures 2 and 3 show the data and the captions further define conditions.

With one exception all plots are linear over the ranges investigated. According to these results both isocyanate groups of MDI are equally reactive. In Table II are collected the rate constants for the six polyols. The rate constants for the PIB-diol and PIB-triol are very similar in the presence of the two catalysts used. Evidently the number or length of the PIB arms do not influence the rate constants. The rate constants for the amine and tin catalyzed reactions are quite different for the six polyols. In the presence of triethylene diamine the polyols with primary OH groups are much more reactive than those having secondary OH groups, such as V-3010. With stannous octoate, the polyether polyols are much more reactive than the other polyols, even if the polyether polyol contains secondary OH groups. These observations may be explained by assuming that the amine and stannous octoate catalyzed routes follow different paths. According to Baker et al. (13,14), the NCO/OH reaction catalyzed by

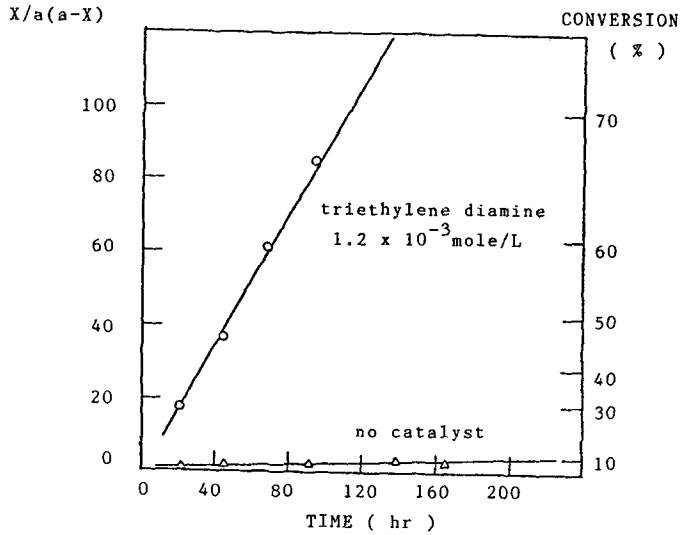


Figure 1. Second order plots for the V-3010/MDI reaction (chlorobenzene, 25°C, $[\text{NCO}]_0 = [\text{OH}]_0$)

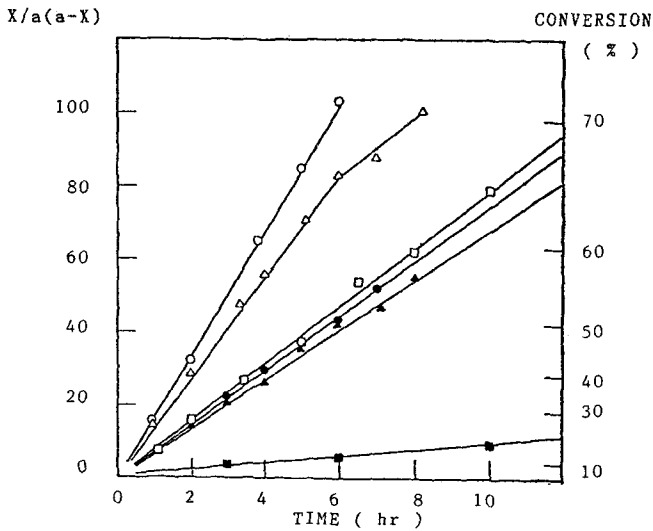


Figure 2. Second order plots for polyol/MDI reaction (chlorobenzene, 25°C) with triethylene diamine $[\text{NCO}]_0 = [\text{OH}]_0 = 0.0238$ mole/L, $[\text{amine}] = 1.2 \times 10^{-3}$ mole/L

O: Polytal HA, Δ: R-45HT, □: M-3900
 ●: PIB-diol, ▲: PIB-triol, ■: V-3010

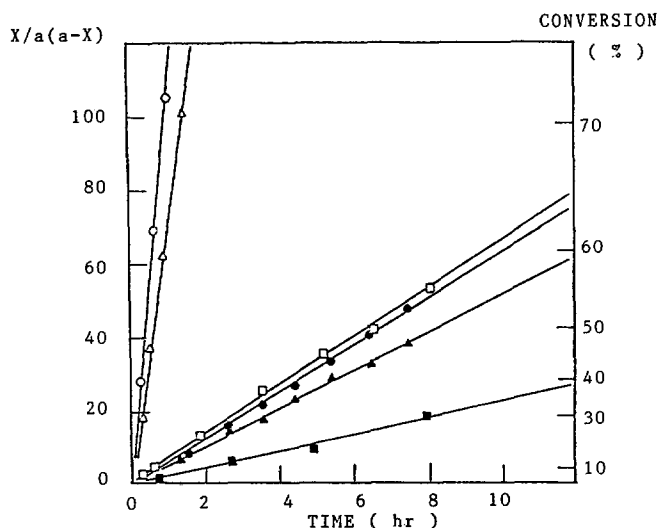


Figure 3. Second order plots for polyol/MDI reaction (chlorobenzene, 25°C) with stannous octoate $[\text{NCO}]_0 = [\text{OH}]_0 = 0.0238$ mole/L, $[\text{stannous octoate}] = 3.0 \times 10^{-4}$ mole/L
 O: M-3900, Δ : V-3010, \square : Polytal HA
 \bullet : PIB-diol, \blacktriangle : PIB-triol, \blacksquare : R-45HT

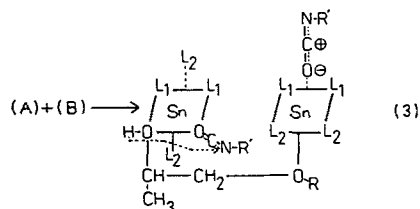
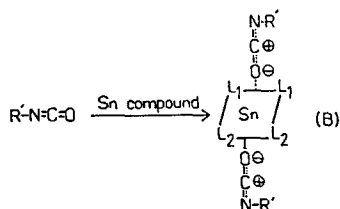
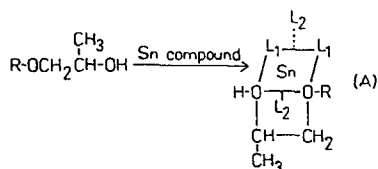
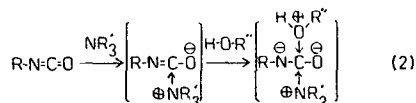
TABLE II

Rate Constants of Reactions of Polyols with 4,4'-Diphenylmethane Diisocyanate*

POLYOL	$k_c \times 10^4$ L/mole·sec	
	Triethylene diamine (1.2×10^{-3} mole/L)	Stannous octoate (3.0×10^{-4} mole/L)
Polyether triol (V-3010)	2.43	188
Polyether triol (M-3900)	22.20	295
Hydroxyl-terminated polybutadiene (R-45HT)	38.90	6.20
Hydroxyl-terminated polyolefin (Polytal HA)	48.70	18.10
Polyisobutylene diol (PIB-diol)	20.40	17.80
Polyisobutylene triol (PIB-triol)	20.30	13.90

* $[\text{NCO}]_0 = [\text{OH}]_0 = 2.38 \times 10^{-2}$ mole/L, Temp. 25°C, in chlorobenzene

tertiary amine proceeds by eq. (2), where as Smith et al. (15, 16) proposed that by stannous octoate follows eq. (3).



Bridge complex

L_1, L_2 : ligand

Thus, as suggested by eq. (2), the amine catalyst is not in direct contact with the -OH end group. The amine and the -OH end group approach the reactive steric carbon center from opposite sides. Under this scenario steric compression exerted by the polyol rest R'' may be rate determining and a secondary OH group, i.e., polyoxypropylene triol, V-3010, would be expected to be less reactive than a polymer with primary OH end group. In contrast, in the case of the stannous octoate catalysis eq. (3), the -OH groups may interact directly with the catalytic site. With polyether polyols the penultimate ether oxygen may also exhibit affinity to the metal site, illustrated by the complex (A) of eq. (3). This interaction may enhance the reactivity as compared with the hydrocarbon alcohols which contain only -OH end groups.

The reactivities of hydroxyl-terminated PIBs are sufficient for the preparation of flexible polyurethane foams. In amine catalyzed systems, the rate of reaction of PIB-alcohols with diisocyanate is much higher than that of V-3010 which is the conventional raw material for flexible polyurethane foams.

Acknowledgement

This material is based on research supported by the National Science Foundation (Grant DMR-84-18617). One of us (M. A.) is grateful to Bridgestone Corporation for a sabbatical leave.

References

1. V. S. C. Chang and J. P. Kennedy, *Polym. Bull.*, 8, 69 (1982)
2. P. H. Sung, S. J. Pan, J. E. Mark, V. S. C. Chang, J. E. Lackey and J. P. Kennedy, *Polym. Bull.*, 9, 375 (1983)
3. V. S. C. Chang and J. P. Kennedy, *Polym. Bull.*, 9, 479 (1983)
4. J. E. Lackey, V. S. C. Chang, J. P. Kennedy, Z.-M. Zhang, P.-H. Sung and J. E. Mark, *Polym. Bull.*, 11, 19 (1984)
5. T. A. Speckhard, P. E. Gibson, S. L. Cooper, V. S. C. Chang and J. P. Kennedy, *Polymer*, 26, 55 (1985)
6. T. A. Speckhard, K. K. S. Hwang, S. L. Cooper, V. S. C. Chang and J. P. Kennedy, *Polymer*, 26, 70 (1985)
7. T. Miyabayashi and J. P. Kennedy, *J. Appl. Polym. Sci.*, 31, 2523 (1986)
8. J. P. Kennedy and J. Lackey, *J. Appl. Polym. Sci.*, 33, 2449 (1987)
9. R. Faust and J. P. Kennedy, *Polym. Bull.*, 15, 317 (1986)
10. R. Faust and J. P. Kennedy, *J. Polym. Sci., Polym. Chem.*, 25, 1847 (1987)
11. M. K. Mishra, B. Wang and J. P. Kennedy, *J. Polym. Sci., Polym. Chem.*, Ed. (in press)
12. E. Dyer, H. A. Taylor, S. J. Mason and J. Samson, *J. Am. Chem. Soc.*, 71, 4106 (1949)
13. J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713, (1947)
14. J. W. Baker, M. M. Davies, and J. Gaunt, *J. Chem. Soc.*, 24, (1949)
15. H. A. Smith, *J. Appl. Polymer Sci.*, 7, 85 (1963)
16. K. C. Frisch, Sect. 1, "Fundamental Chemistry and Catalysis of Polyurethanes" in *Polyurethane Technology*, P. F. Bruius, Ed., Interscience Publishers, 1969, p. 23

Accepted December 1, 1987 K