Effect of Catalysts on the Reaction Between A Cycloaliphatic Diisocyanate (H-MDI) and *n*-Butanol

İSKENDER YILGÖR and JAMES E. MCGRATH, *Department of Chemistry and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

Synopsis

Kinetics of the reaction between bis(4-isocyanatocyclohexyl)methane, H-MDI, and *n*-butanol was studied in toluene at 100°C. Effects of various catalysts, such as $Hg(CH_3COO)_2$, $Zn(CH_3COO)_2 \cdot 2H_2O$, $SnCl_4 \cdot 5H_2O$, and dibutyltindilaurate on the reaction rate and kinetics were also investigated. Reactions were followed by determining the unreacted isocyanate as a function of reaction time, using the standard dibutylamine back titration method. All catalysts seem to be very effective in increasing the rate of the reaction compared to the uncatalyzed system. Depending on the initial stoichiometric ratio of (NCO) to (OH) and the concentration of the catalyst used, it seems possible to have preferential catalysis of the primary reaction between (NCO) and (OH) over the side reactions.

INTRODUCTION

The reactions between isocyanates and alcohols have been studied very extensively for a very long time due to their importance in polyurethane technology.[1-3] Many aspects of these reactions, including the type and structure of the isocyanate, alcohol, and the solvent used, the effect of reaction temperature and time and most importantly, the role of a wide range of catalysts on these reactions have been investigated.[1-5] In most of these studies the isocyanates utilized were mainly aromatic in nature, such as diphenylmethane diisocyanate (MDI) or tolylene diisocyanate (TDI), probably due to their widespread application in the manufacture of various commercial polyurethanes.

It has been observed that the rate of the reactions between aromatic diisocyanates and primary alcohols were much faster than that of aliphatic diisocyanates and alcohols under the same reaction conditions. Another important observation was the difference in the reactivity of second (NCO) group on the same molecule after the first one has reacted. This decrease in the reactivity towards the alcohol is mainly attributed to resonance effects in the aromatic ring and is very well documented in the literature.[1,2]

In the presence of a catalyst, the reaction between an isocyanate and a primary alcohol follows a second-order kinetics. On the other hand, a number of side reactions are also possible and may even become important as the urethane formation reaction reaches high conversion.[1,2] These side reactions, which also consume isocyanates, produce a deviation from second-order to higher-order kinetics, and the overall rate equation becomes very complicated.[6] These secondary reactions give rise to branching and sometimes even crosslinking and therefore contribute significantly to the phys-

ical and mechanical properties of the polyurethanes obtained. Several investigators have studied the role of the catalyst employed on the relative acceleration of the primary and secondary reactions and have found that in some cases there is a preferential catalysis of only the isocyanate–alcohol (primary) reaction, but not the side (secondary) reactions.[7-10]

There has also been a strong interest in the polyurethanes based on aliphatic or cycloaliphatic diisocyanates, such as hexamethylene diisocyanate (HDI) or bis(4-isocyanatocyclohexyl)methane (H-MDI), mainly due to their UV resistance and weatherability. Most of the research on these systems has been directed towards the synthesis of novel polyurethanes for possible applications, with only a limited interest on the kinetics of the reactions.[1,10,11] In this study we have investigated the effect of various catalysts on a model reaction between H-MDI and n-butanol in toluene at 100°C. The reactions were followed by determining the unreacted isocyanate as a function of reaction time, using the standard dibutylamine back titration method.[12] Experimental results were later analyzed according to the second-order reaction kinetics. The catalysts utilized were also evaluated with respect to their selective catalysis of the primary isocyanate–alcohol reaction relative to the possible side reactions.

EXPERIMENTAL

Materials

Bis(4-isocyanatocyclohexyl)methane, (Hylene W, H-MDI) was a product of E. I. du Pont de Nemours. It was distilled under high vacuum ($\sim10^{-3}$ mm Hg) before use. Its purity as determined by isocyanate analysis was better than 99.7%.

n-Butanol was a product of Merck A. G. It was dried over calcium oxide, refluxed over sodium, and fractionally distilled before use.

Toluene was purified by shaking with cold, concentrated sulfuric acid and distilled water, followed with dilute aqueous potassium carbonate and distilled water. It was dried over anhydrous calcium chloride and phosphorous pentoxide (P_2O_5) and was fractionally distilled from P_2O_5.

Catalysts, utilized were $Hg(CH_3COO)_2$, $Zn(CH_3COO)_2 \cdot 2H_2O$, $SnCl_4 \cdot 5H_2O$, and dibutyltindilaurate (T-12). They were all reagent grade and were used without further purification. During the reactions standard solutions of catalysts in toluene were used. Table I provides the data on the catalyst solutions and their concentrations employed during the kinetic studies.

Procedure

Reactions were conducted in a 250-mL round bottom, four-neck flask, fitted with a mechanical stirrer, nitrogen inlet, condenser, and pipette outlet. All reactions were carried out in a constant temperature bath at 100 $\mp$ 0.1°C. Standard n-butanol and catalyst solutions were first introduced into the reactor and heated to the reaction temperature. Standard H-MDI solution was also heated to 100°C in a separate flask. Then, the H-MDI solution was added into the reactor and the time was marked as $t = 0$. At

desired time intervals 10.0 mL of reaction solution were withdrawn with a pipette from the reactor and quenched in an Erlenmayer flask containing di-*n*-butylamine solution in toluene at 0°C. The unreacted isocyanate content was determined by the standard back titration method.[12] Volume (and concentration) corrections were made due to the expansion of solvent at 100°C. Duplicate reactions were conducted for each system, including the blank titrations. Reactions were studied at two different initial concentrations, where the ratios of [NCO] to [OH] were 0.95 and 1.90, respectively.

Two control reactions were also conducted. In the first reaction H-MDI solution in toluene was heated to 100°C for 24 h, and at various times samples were withdrawn and titrated. No change in NCO content was observed over a 24-h period. Another control reaction was carried out between H-MDI and *n*-butanol in toluene at 100°C, without any catalyst.

RESULTS AND DISCUSSION

The model reaction between a cycloaliphatic diisocyanate [bis(4-isocyanatocyclohexyl)methane, H-MDI] and *n*-butanol was studied in toluene at 100°C. The effect of various catalysts on these urethane forming reactions were investigated. Consumption of isocyanate groups during the reactions were monitored and the results were analyzed according to second-order reaction kinetics. As a result of the analyses, the catalysts studied were compared with each other according to their relative catalytic activities and also with regard to their preferential catalysis of the primary reaction between isocyanate and alcohol relative to possible side reactions.

The experimental results were first tabulated in terms of percent (NCO) consumed against reaction time. Then, since the initial stoichiometric ratio of (NCO) to (OH) was different than 1.00, the results were analyzed according to the following equation, given for second order reactions:

$$\frac{1}{a - b} \ln \frac{b(a - x)}{a(b - x)} = kt$$

where a and b are the initial molar concentrations of NCO and OH and x is the concentration of NCO that has reacted at time t. k is the apparent second-order rate constant for the reaction. When the left-hand side of the above equation is plotted against time, one obtains a straight line for a second-order reaction. A deviation from linearity is due to the side reactions, which change the order of the overall reaction.

In the analysis of our experimental data, we estimated the "apparent" rate constants (k) for each reaction from the slope of the linear portion of the second-order plot. We also determined the percent conversion where deviation from the linearity was observed for each system, which seems to be a useful parameter to detect the contribution of the secondary reactions on the overall reaction. Catalysts which lead to deviation at higher conversion values may be considered as better candidates for the production of linear, high molecular weight polyurethanes based on H-MDI and glycols.

Table I provides the data on the type of the catalysts used and their concentrations during the kinetic studies. As we have mentioned before,

TABLE I
Catalysts and Their Molar Concentrations Used during Kinetic Studies

Catalyst	$[M] \times 10^5$
$Hg(CH_3COO)_2$	580
$Zn(CH_3COO)_2 \cdot 2H_2O$	86
$SnCl_4 \cdot 5H_2O$	5.8
T-12(I)	15.6
T-12(II)	1.56

we have also tried, what may be called a "blank reaction," by simply heating an H-MDI solution in toluene at 100°C. We titrated samples from this system at various times over a period of 24 h to determine whether there was any change in NCO content, probably as a result of cyclization or oligomerization among H-MDI molecules, which is generally observed for MDI and other isocyanates. In our system we did not observe any detectable decrease in NCO content over the reaction period studied.

Conversion–time curves for the reactions, where the initial ratio of NCO to OH is 0.95, are given in Figure 1. This provides a good comparison between different systems although the catalyst concentrations are different in each case. Figure 2 gives the second-order plots for these reactions, including the uncatalyzed reaction. As can be seen easily, in most of these systems a deviation from linearity is observed after a certain conversion, indicating the contribution of important side reactions. The results obtained from these plots are summarized in Table II. When we compare the values of k, the "apparent" second-order rate constant in the reaction between NCO and OH, it is clear that all catalysts are very effective when compared with
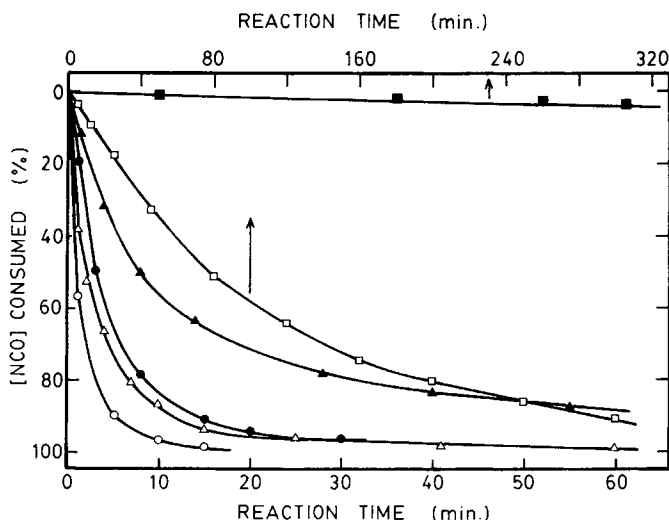

Fig. 1. Effect of various catalysts on the rate of isocyanate consumption in the reaction between H-MDI and n-butanol in toluene at 100°C, [NCO]/[OH] = 0.95: (■) no catalyst; (□) $Zn(CH_3COO)_2 \cdot 2H_2O$; (△) $Hg(CH_3COO)_2$; (▲) $SnCl_4 \cdot 5H_2O$; (○) T-12(I); (●) T-12(II).

TABLE II
Comparison of the Effect of Various Catalysts on the Reaction between H-MDI and
n-Butanol in Toluene at 100°C, [NCO]/[OH] = 0.95

Catalyst	$[C] \times 10^5$ (mol/L)	$k \times 10^2$ (l/meq · min)	% Conv. at devn.	Time to 90% conv. (min)
None	—	~0.06	7	>4000
Hg(CH$_3$COO)$_2$	580	53	85	13
Zn(CH$_3$COO)2 · 2H$_2$O	86	1.2	40	300
SnCl$_4$ · 5H$_2$O	5.8	13	90	73
T-12(I)	15.6	170	—	5
T-12(II)	1.56	34	30	14

uncatalyzed reaction. As expected, T-12 has the highest efficiency, even though it was used in lower concentrations than the others. In terms of the selective catalysis of the NCO–OH reaction, Hg(CH$_3$COO)$_2$ and SnCl$_4$ · 5H$_2$O seem to be very good, since the deviation from linearity only begins around 90% conversion for each of these catalysts. Other workers[10] have also demonstrated that, for the reaction between hexamethylene diisocyanate and n-butanol in dimethylacetamide at 100°C, Hg, Zn, and Sn salts enhanced only the primary reaction. For our system T-12 also seems to be selective at high concentration, but the reaction is too fast to follow by titration, and thus it may not be very reliable. On the other hand, at lower concentration of T-12, deviation is observed around 30% conversion. Zn(CH$_3$COO)$_2$ · 2H$_2$O also does not seem to be very selective for this system.

Conversion–time curves for the reactions, where the initial ratio of NCO to OH was 1.90, were reproduced in Figure 3. If there were no side reactions, these curves would be expected to level off around 52.6% conversion with
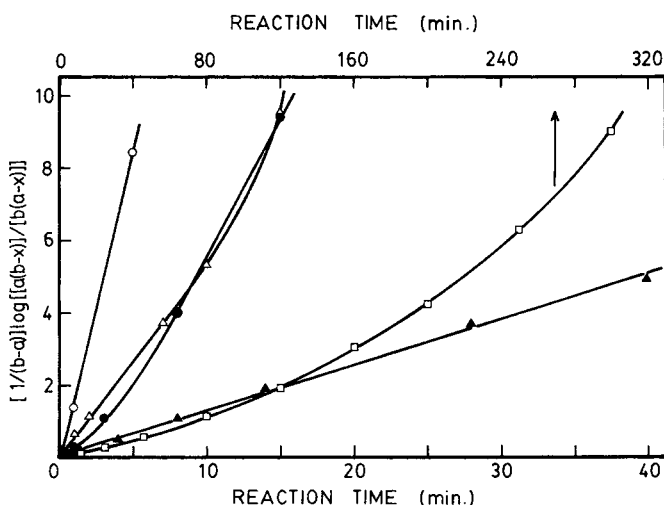

Fig. 2. Catalyst effect on the second-order kinetic plots for the reaction between H-MDI and n-butanol in toluene at 100°C, [NCO]/[OH] = 0.95: (□) Zn(CH$_3$COO)$_2$ · 2H$_2$O; (△) Hg(CH$_3$COO)$_2$; (▲) SnCl$_4$ · 5H$_2$O; (○) T-12(I); (●) T-12(II).
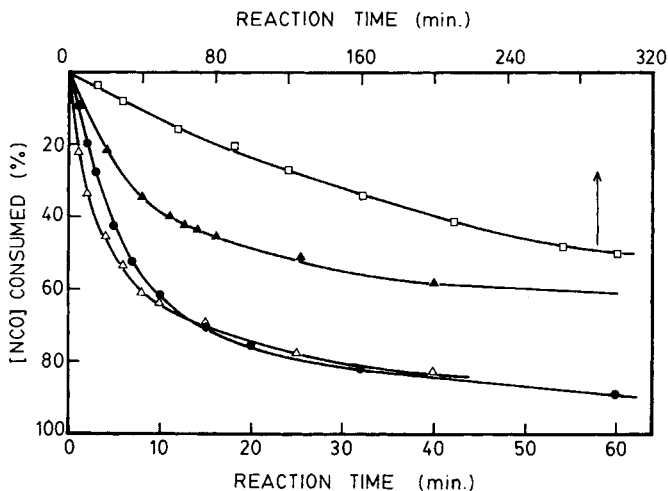
REACTION TIME (min.)

Fig. 3. Effect of various catalysts on the rate of isocyanate consumption in the reaction between H-MDI and n-butanol in toluene at 100°C, [NCO]/[OH] = 1.90: (□) $Zn(CH_3COO)_2 \cdot 2H_2O$; (△) $Hg(CH_3COO)_2$; (▲) $SnCl_4 \cdot 5H_2O$; (●) T-12(II).

respect to NCO, (100/1.90 = 52.6). As can be seen from Figure 3, only the $Zn(CH_3COO)_2 \cdot 2H_2O$ catalyzed system tends to level off around this value in the period studied. $SnCl_4 \cdot 5H_2O$ catalyzed reaction goes slightly beyond this value, to 60–65% conversion. However when $Hg(CH_3COO)_2$ or T-12 are used, all excess NCO present in the system has also been consumed as the result of side reactions.

Second-order plots for these systems are given in Figure 4. When we analyze the results, we observe that in all reactions deviation from linearity starts at fairly low conversions. Similar to the results observed in Figures
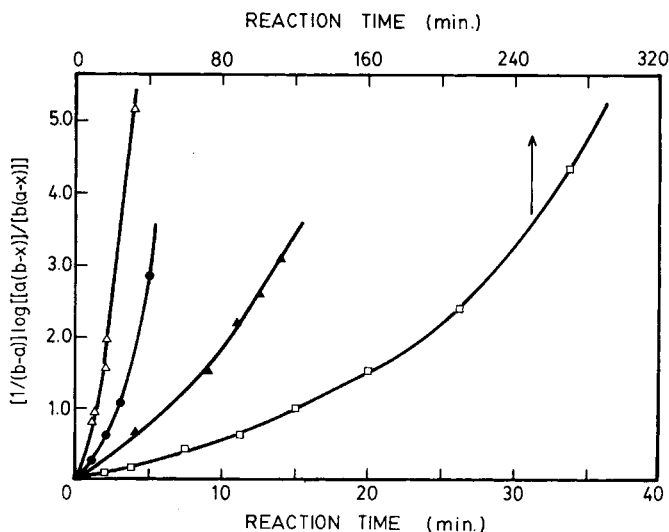
REACTION TIME (min.)

Fig. 4. Catalysts effect on the second-order kinetic plots for the reaction between H-MDI and n-butanol in toluene at 100°C, [NCO]/[OH] = 1.90: (□) $Zn (CH_3COO)_2 \cdot 2H_2O$; (△) $Hg(CH_3COO)_2$; (▲) $SnCl_4 \cdot 5H_2O$; (●) T-12(II).

1 and 2, T-12 and Hg(CH₃COO)₂ seem to be accelerating these reactions more than the other catalysts employed. However, since we have a large excess of NCO groups relative to the OH present in the reactions, probability of the side reactions is much higher when compared with stoichiometric reactions. Therefore, in the presence of effective catalysts and excess NCO, side reactions are also promoted and reaction kinetics deviate from second-order, early during the processes.

CONCLUSIONS

Our preliminary investigation of the kinetics of the reactions between bis(4-isocyanatocylohexyl)methane (H-MDI) and *n*-butanol, in toluene, at 100°C, have shown that the uncatalyzed reactions are extremely slow. In order to achieve 90% conversion, the reactions must be carried out for more that 72 h. Several organic or inorganic salts of Sn, Hg, and Zn are effective catalysts for these reactions. It also seems to be possible to have preferential catalysis of primary reaction between NCO and OH over side reactions, depending on the stoichiometric ratio of NCO/OH and also the concentration of the catalyst used. In order to find the optimum system and the conditions for these reactions, the investigations will be continued using a wider concentration range of the catalysts [especially Hg(CH₃COO)₂ and SnCl₄ · 5H₂O]. Effects of reaction solvent and temperature will also be studied.

References

1. J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology,* High Polymer Series, XVI, Wiley-Interscience, New York, Part I, 1962, and Part II, 1964.

2. R. W. Lenz, *Organic Chemistry of Synthetic High Polymers,* Wiley-Interscience, New York, 1967.

3. C. Hepburn, *Polyurethane Elastomers,* Applied Science, London, 1982.

4. D. C. Allport and W. H. Janes, *Block Copolymers,* Applied Science, London, 1973.

5. D. J. Lyman, *J. Polym. Sci.,* **45,** 49 (1960).

6. M. Sato, *J. Am. Chem. Soc.,* **82,** 3893 (1960).

7. H. L. Heiss, F. P. Combs, P. G. Gemeinhardt, J. H. Saunders, and E. E. Hardy, *Ind. Eng. Chem.,* **51,** 929 (1959).

8. J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.,* **1947,** 713.

9. J. W. Baker and J. Gaunt, *J. Chem. Soc.,* **1949,** 19.

10. G. Anzuino, A. Pirro, G. Rossi, and L. Polo Friz, *J. Polym. Sci., Polym. Chem. Ed.,* **13,** 1667 (1975).

11. İ. Yilgör, E. H. Orhan, and B. M. Baysal, *Makromol. Chem.,* **179,** 109 (1978).

12. D. J. David and H. B. Staley, *Analytical Chemistry of Polyurethanes,* High Polymer Series, XVI, Part III, Wiley-Interscience, New York, 1969.