

Reaction Kinetics of Dicyclohexylmethane-4,4'-Diisocyanate with 1- and 2-Butanol: A Model Study for Polyurethane Formation

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ABSTRACT: Reactions of dicyclohexylmethane-4,4'-diisocyanate (H_{12} MDI) with 1- or 2-butanol in *N,N*-dimethylformamide using dibutyltin dilaurate (DBTDL), stannous octoate (SnOct), or triethylamine (TEA) as catalyst were conducted in stirred reactors at 40°C. Reactor contents were circulated through an external loop containing a temperature-controlled FTIR transmission cell; reaction progress was monitored by observing decrease in height of the isocyanate peak at 2266 cm^{-1} . Catalyzed reactions were second order as indicated by linear $1/[NCO]$ plots; uncatalyzed reactions yielded nonlinear plots. In all cases, the reaction with a primary alcohol was faster than that with a secondary alcohol. DBTDL dramatically increased the reaction rate with both primary and secondary al-

hols. For $[DBTDL] = 5.3 \times 10^{-5}$ mol/L (300 ppm Sn) the second-order rate constant, k , was 5.9×10^{-4} (primary OH) and 1.8×10^{-4} L/(mol s) (secondary OH); for both alcohols, this represents an increase in initial reaction rate on the order of 2×10^1 when compared with the uncatalyzed reactions. The second-order rate constant was observed to increase linearly with DBTDL concentration in the range 100–700 ppm Sn. SnOct and TEA showed little to no catalytic activity with the primary alcohol and only a slight increase in reaction rate with the secondary alcohol. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3101–3107, 2008

Key words: urethane kinetics; dicyclohexylmethane-4,4'-diisocyanate (H_{12} MDI); FTIR; catalysis; polyurethanes

INTRODUCTION

Polyurethanes are an important and versatile class of polymeric materials, with many uses within the fields of coatings, foams, sealants, adhesives, elastomers, and biomaterials.^{1,2} They are conveniently divided into two classes depending upon whether having been derived from aromatic or aliphatic isocyanates. Recently, a number of reports have been issued concerning biodegradable polyurethanes containing hydrolytically unstable polyester soft segments, for example, poly(ϵ -caprolactone), poly(*D,L*-lactide), poly(glycolide), and/or copolymers therefrom.^{3–9} For these materials, aliphatic isocyanates are overwhelmingly preferred due to the toxicity of aromatic amines, which are the presumed degradation products of an aromatic polyurethane. However, the reaction of an aliphatic isocyanate with an alcohol is kinetically slower than the corresponding reaction of

an aromatic isocyanate, particularly when secondary alcohols are involved, such as those present in poly(*D,L*-lactide)-based polyols. The present investigation attempts to address this issue through study of the kinetics of catalyzed urethane formation of dicyclohexylmethane-4,4'-diisocyanate (H_{12} MDI), a cycloaliphatic diisocyanate, with model primary and secondary alcohols.

Kinetics of the urethane-forming reaction has been extensively studied, with most of the earlier studies focused on the reactions of aromatic diisocyanates.^{10–17} With few exceptions, these studies have shown that the catalyzed reaction of an isocyanate with an alcohol is a second-order reaction as indicated by linearity on a $1/[NCO]$ versus time plot.^{10–16} In addition, it has been shown that the important factors that effect reaction kinetics are the type of isocyanate, i.e., aromatic versus aliphatic, and the nature and concentration of the catalyst. The two major types of catalysts commonly used are tertiary amines and organometallic compounds. Tertiary amines catalyze both isocyanate-hydroxyl and isocyanate-water reactions, and are commonly used for reactions involving aromatic isocyanates. Organometallic catalysts such as dibutyltin dilaurate (DBTDL) and stannous octoate (SnOct) are generally preferred for aliphatic isocyanates, since they promote the isocya-

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nate-hydroxyl reaction of aliphatic isocyanates more effectively than tertiary amines.¹⁸

Several investigations have been directed specifically toward the reaction kinetics of H₁₂MDI. Yilgor et al. determined the rate constants of the reaction between H₁₂MDI and poly(ethylene glycol) in bulk.¹⁷ Later, Yilgor et al. studied the effects of different catalysts on the reaction of H₁₂MDI and *n*-butanol in toluene at 100°C.¹⁶ Seneker et al. observed a rate constant of 4.1×10^{-4} kg/(mol min) at 40°C for the reaction of H₁₂MDI and *n*-butanol in *N*-methyl-2-pyrrolidone (NMP), catalyzed with 1.05×10^{-5} mol/kg dibutyltin dilaurate (DBTDL).¹⁴

Kinetics of the isocyanate/alcohol reaction has been traditionally monitored by analysis of aliquots removed from the reaction at various times. The instantaneous isocyanate concentration was determined by quenching the aliquot with a known excess of amine, and then back-titrating unreacted amine with an acid to determine the concentration of isocyanate within the aliquot.^{10,11,14,16,17,19,20} In at least one case, isocyanate concentration was determined through FTIR spectroscopic analysis of the reaction aliquots.²¹

More recently, *in situ* FTIR spectroscopy has been used to monitor alcohol/isocyanate reaction kinetics in real-time, without the need for removal of aliquots.²² This increasingly popular technique has proven to be very useful not only for monitoring kinetics of urethane reactions^{21–24} but also for various other types of polymerizations.^{22,25–30} Real-time data collection greatly facilitates the monitoring of conversion and the ability to perform kinetic analyses, including determination of reaction order and rate constants. The reaction mixture may be sampled by insertion of an ATR or transmission probe into the reactor, or the reactor contents may be circulated through an external loop containing a flow-through transmission cell.

The isocyanate peak ($2260\text{--}2270\text{ cm}^{-1}$) is easily identified and monitored in the IR spectrum allowing for straightforward calculation of reaction progress. However, careful attention must be paid to the crystal used to collect IR spectra. NaCl and KBr have very good IR transparency and very little spectral interference, but suffer from sensitivity to water. Diamond composite ATR crystals have the benefit of excellent durability, but depending on the other components of the composite crystal, may or may not be suitable for observing the isocyanate region of the spectra. ZnSe crystals have good IR transparency in the isocyanate region as well as no inherent susceptibility to water.

In this study, we have employed real-time FTIR spectroscopic analysis to study the kinetics of the reaction of H₁₂MDI with model primary and secondary alcohols in *N,N*-dimethylformamide (DMF) solu-

tion, using either DBTDL, stannous 2-ethylhexanoate (SnOct), or triethylamine (TEA) as catalyst.

EXPERIMENTAL

Materials

Anhydrous *N,N*-dimethylformamide (DMF), anhydrous 1-butanol, anhydrous 2-butanol, tin (II) 2-ethylhexanoate (SnOct), dibutyl tin dilaurate (DBTDL), and triethylamine (TEA, Aldrich, Milwaukee, WI) were all used as received. Dicyclohexylmethane-4,4'-diisocyanate (H₁₂MDI) (Desmodur W, Bayer, Pittsburgh, PA) was distilled under vacuum and collected in three fractions, using only the second fraction. This was later compared with a new bottle of as received H₁₂MDI by ¹³C NMR and determined to be of equal purity.

Procedures

H₁₂MDI kinetics monitoring

Isocyanate reactions were monitored using a Bruker Equinox 55 FTIR spectrometer set at a spectral resolution of 4 cm^{-1} . A schematic representation of the reaction vessel and flow cell setup is displayed in Figure 1. The flow cell assembly (A) (64401-2, New Era Enterprises, Vineland, NJ) possessed a 20-mm diameter aperture equipped with ZnSe windows and 0.20 mm Teflon spacers (see detail B). The intensity of the IR signal was controlled by spacer thickness between windows (path length) and IR beam intensity (controlled with adjustable iris aperture). The flow cell temperature was controlled using an Ace Glass temperature controller (12111-15, Vineland, NJ). The reaction vessel temperature was controlled with a silicone oil bath (C) and a Therm-O-

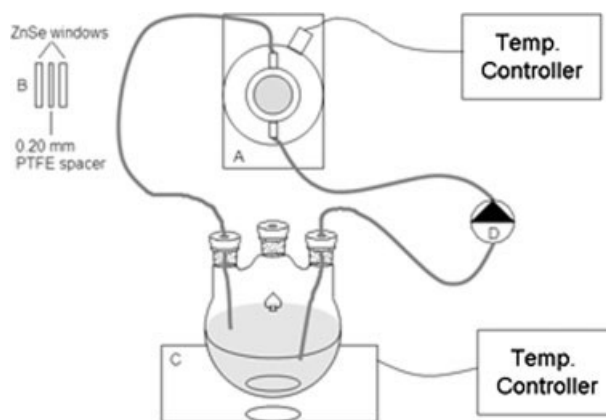


Figure 1 Schematic representation of FTIR flow cell system utilized for data collection. (A) Temperature controlled flow cell, (B) flow cell window setup, (C) temperature controlled oil bath, (D) pump.

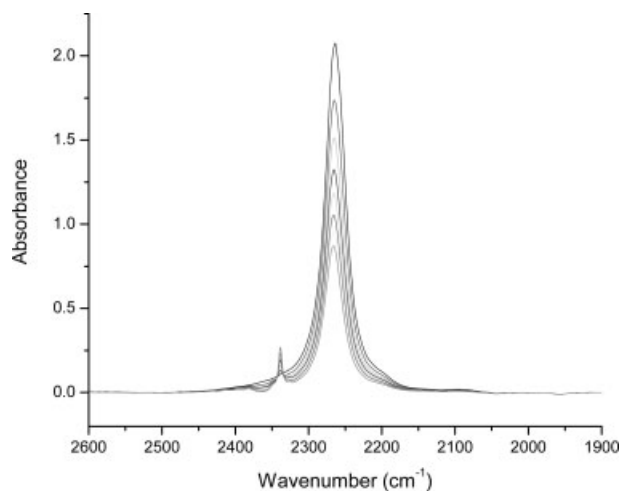


Figure 2 Partial FTIR spectrum for the reaction of H₁₂MDI with 2-BuOH using DBTDL (300 ppm Sn) catalyst showing the progression of isocyanate consumption (Table I, Exp. 4).

Watch L6-1000SS temperature controller (Instruments for Research and Industry, Cheltenham, PA). The reaction vessel consisted of a three-necked 100-mL round bottom flask, equipped with a magnetic stir bar and suction and discharge tubes (6-mm O.D. PTFE) passing through rubber septa fitted to the necks of the flask. The suction tube was submerged below the liquid level in the flask. The reaction vessel contents were continuously pumped through the flow cell using a Cole Parmer Master Flex PTFE Tubing Pump Head (D) connected to a digital Cole Parmer Master Flex Drive, using 6-mm O.D. PTFE tubing and a pump head speed of 75 RPM. The system was designed with materials, such as PTFE, that would not interfere with the reactions being monitored and were easily cleaned after each reaction. To prevent contamination from one reaction to the next, the flow cell was completely disassembled, cleaned, and reassembled between reactions.

A representative procedure for the reaction was as follows: within a Vacuum Atmospheres Dri-Lab glovebox under inert N₂ atmosphere, a three-necked 100 mL round bottom flask equipped with a magnetic stir bar was charged with 74.440 g (~ 80 mL) of anhydrous DMF. The flask was capped with rubber septa, taken out of the glove box, and connected to a dry N₂ purge. After connecting the flask to the PTFE tubing, the N₂ purge was removed, the pump was turned on, and air was removed from the tubing by first elevating the pump and then the flow cell until all air had been displaced from the tubing. The flask was then lowered into the 40°C oil bath and the flow cell temperature controller was also set to 40°C. The system was then allowed to equilibrate for ~ 20 min, after which a 32 scan solvent background was col-

lected using OPUS 4.2 software. Then, 1.053 g (4.0 mmol) H₁₂MDI was added to the flask via syringe, and spectra (average of 8 scans) were collected every 5 min. Once the isocyanate peak at 2266 cm⁻¹ had equilibrated (~ 20 min), 0.595 g (8.0 mmol) 1- or 2-BuOH (1 : 1 OH : NCO) was added along with the desired amount of catalyst. The reaction was allowed to continue until 30–50% conversion of isocyanate was observed as shown by a reduction in the 2266 cm⁻¹ peak.

Peak integration and regression analysis

Spectral analysis was performed on the calibration and real-time FTIR data with respect to the 2266 cm⁻¹ peak. Upon completion of the reaction, the data set collected was converted into a GC (3D) file using OPUS 4.2. The peak height was measured between 2330 and 2180 cm⁻¹ with a straight baseline from 2450 to 2175 cm⁻¹ (OPUS method L). Linear regressions were calculated with Origin 7.0 graphing software.

RESULTS AND DISCUSSION

FTIR spectroscopy was used to monitor kinetics of the isocyanate/alcohol reaction in real time. The urethane system studied consisted of H₁₂MDI and either 1- or 2-BuOH in DMF solvent, using SnOct, DBTDL, or TEA as catalyst. This system was designed as a model for polyurethane systems consisting of mixed polyols, which may have primary or secondary hydroxyl functionality or in some cases both.⁶ The reaction was monitored by following the disappearance of the isocyanate peak centered at 2266 cm⁻¹. Figure 2 shows partial FTIR spectra col-

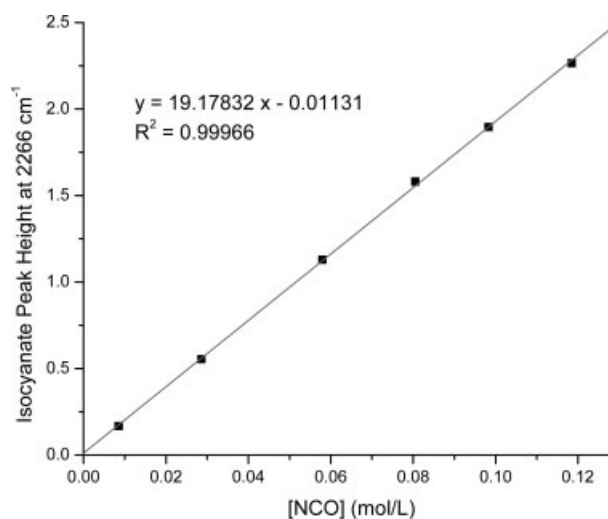


Figure 3 Isocyanate peak height at 2266 cm⁻¹ versus isocyanate concentration for H₁₂MDI in DMF at 40°C.

TABLE I
Reaction Formulations and Second-Order Rate Constants for Isocyanate/Alcohol Reactions in *N,N*-Dimethylformamide^a at 40°C with [NCO]/[OH] = 1.00

Exp.	[H ₁₂ MDI] (mol/L)	1-BuOH [OH] (mol/L)	2-BuOH [OH] (mol/L)	Catalyst, [Catalyst] (mol/L × 10 ⁵)	<i>k</i> [L/(mol s) × 10 ⁴]
1	0.051	0.10	–	–	^c
2	0.052	–	0.10	–	^d
3	0.051	0.10	–	DBTDL, ^b 5.3	5.90
4	0.051	–	0.10	DBTDL, ^b 5.3	1.79
5	0.051	0.10	–	SnOct, ^b 5.3	0.23
6	0.051	–	0.10	SnOct, ^b 5.3	0.13
7	0.051	0.10	–	TEA, 5.1	0.31
8	0.050	–	0.10	TEA, 5.2	0.11

^a About 0.08 L of DMF was contained in each reaction vessel.

^b 300 ppm Sn.

^c Nonlinear second order plot; initial rate = 2.6×10^{-7} mol/(L s).

^d Nonlinear second order plot; initial rate = 7.8×10^{-8} mol/(L s).

lected during a representative reaction of H₁₂MDI and 2-BuOH with DBTDL catalyst (300 ppm Sn). In theory, the reaction could also be quantified by the appearance of the urethane peak, but the isocyanate peak is of much greater intensity and is less affected by neighboring peaks. However, there is a small peak that develops at 2339 cm⁻¹ that does affect the area of the isocyanate peak. For this reason, the reaction was quantified using peak height, rather than peak area. To correlate peak height to an absolute concentration of isocyanate, a calibration using solutions of H₁₂MDI of known concentrations was performed. Figure 3 shows the calibration plot of peak height at 2266 cm⁻¹ versus concentration. The calibration equation used for the analysis of each reaction was

$$H = 19.17832[\text{NCO}] - 0.01131 \quad (1)$$

where *H* is the 2266 cm⁻¹ peak height. As predicted from the Beer-Lambert Law, there is a linear relationship between the isocyanate concentration and the observed peak height. For each reaction, the actual isocyanate concentration was calculated from the peak height using the calibration equation (1). A plot of 1/[NCO] versus time was linear over a broad range of conversion for the catalyzed isocyanate/alcohol reactions studied, and from these plots a second order rate constant, *k*, was extracted. For the two uncatalyzed (control) reactions, the second-order plots were nonlinear, and in these cases, the initial reaction rate was measured.

The reaction of H₁₂MDI with 1- or 2-BuOH was evaluated with three different catalysts, DBTDL, SnOct, and TEA. The experimental formulations are listed in Table I. The effect of each catalyst can be seen in Figure 4, which shows the normalized isocyanate concentration versus time plot for all of the experiments listed in Table I. Normalized [NCO]

was plotted to compensate for slight variations in [NCO]₀ among the various experiments. As would be expected, in all systems the primary alcohol reaction was faster than the corresponding secondary alcohol reaction. DBTDL, one of the most commonly used organometallic urethane catalysts, showed the greatest increase in reaction rate when compared with the control (no catalyst) as indicated by the highest conversion in the shortest time. Both SnOct and TEA caused a slight increase in reaction rate of the secondary alcohol; however, TEA showed no significant catalysis in the reaction with the primary alcohol, and SnOct appeared to have slightly retarded the reaction, presumably due to the introduction of 2-ethylhexanoic acid. These last two reactions, along with the uncatalyzed 1-BuOH reaction, were repeated to ensure their reproducibility. The duplicate reactions yielded the same results; the TEA-catalyzed reaction was similar to the uncatalyzed reaction and the SnOct-catalyzed reaction was slightly

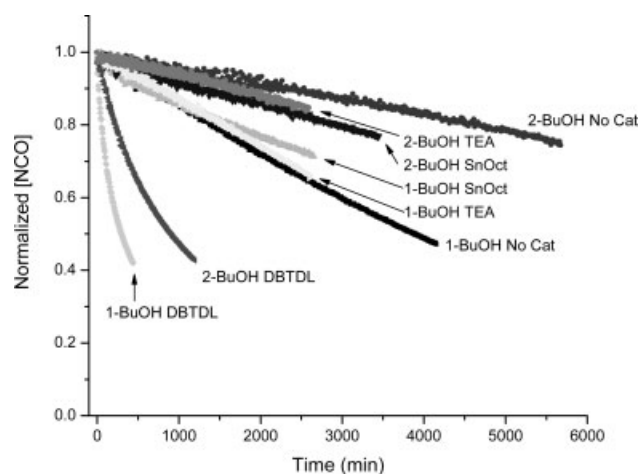


Figure 4 Normalized isocyanate concentration ([NCO]/[NCO]₀) versus time for the experiments listed in Table I.

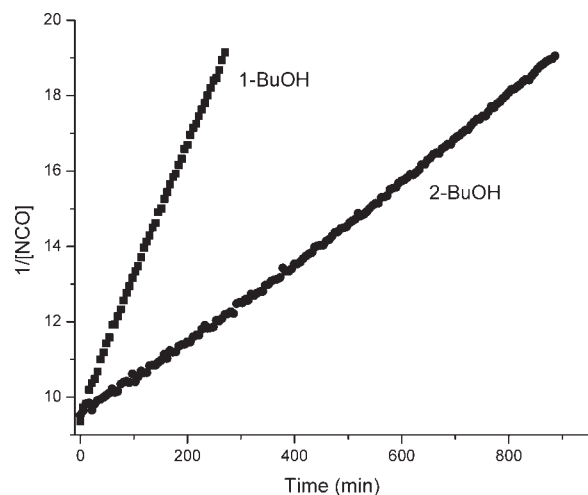


Figure 5 Second-order rate plot of H_{12} MDI and BuOH in DMF with DBTDL catalyst (300 ppm Sn; Table I, Exp. 3 and 4).

retarded. Figure 5 shows second-order plots of the DBTDL-catalyzed reaction, which are representative. The second-order rate constant, k , was determined as the slope of the linear plot, and these are listed in Table I for all of the catalyzed reactions. The catalyzed reactions had $k_{\text{primary OH}}/k_{\text{secondary OH}}$ rate constant ratios of 3.3, 1.8, and 2.8 for DBTDL, SnOct, and TEA, respectively. Second-order plots for the uncatalyzed reactions (not shown) displayed upward curvature, presumably due to autocatalysis as a result of the formed urethane linkages. Thus, for these two reactions, only the initial reaction rates are listed (footnote to Table I). Comparison of initial rates showed that for both alcohols, 5.3×10^{-5} mol/L (300 ppm Sn) DBTDL caused an increase in initial reaction rate on the order of 2×10^1 when compared with the uncatalyzed reactions.

Additionally, a series of reactions of H_{12} MDI and 1-BuOH was carried out in which the DBTDL con-

centration was varied from 25 to 800 ppm as listed in Table II. This set of experiments was designed to determine the relationship between [DBTDL] and rate constant as well as to probe the time scale limitations of the flow cell apparatus. Figure 6 shows the second-order rate plots. As would be expected, the rate of reaction increased with increasing catalyst concentration. Second-order rate constants were calculated by linear regression of the kinetic data in Figure 6 and were plotted as a function of [DBTDL] in Figure 7. The resulting plot has an apparent positive y -intercept, consistent with a finite rate for the uncatalyzed reaction. The rate constant increased linearly with increasing [DBTDL] in the concentration range of 100–700 ppm Sn. This linear behavior indicates that the overall rate of the urethane forming reaction is governed by the catalyzed reaction of the isocyanate and alcohol; whereas the uncatalyzed and/or urethane catalyzed reactions do not significantly contribute to the overall rate. However, between 0 and 100 ppm Sn the data displayed downward curvature, with earlier catalyst increments causing disproportionately greater increases in the value of the rate constant. This is consistent with a change in mechanism, and possibly reaction order, from an uncatalyzed or self-catalyzed reaction to the DBTDL-catalyzed reaction characteristic of the broad linear region from 100 to 700 ppm Sn. There is a deviation from linearity above 700 ppm Sn, which may indicate the upper limit of reaction rate that can be monitored using this specific flow cell apparatus.

Lastly, to examine the precision of our method, the reaction of H_{12} MDI with 1-BuOH catalyzed by DBTDL at a concentration of 500 ppm Sn was performed in triplicate. The rate constants observed were 7.72 (initial experiment as listed in Table II), 7.54, and 7.83×10^{-4} L/(mol s). The observed rate constants showed a variation of less than 2.4% as

TABLE II
Reaction Formulations and Second-Order Rate Constants for Isocyanate/Alcohol Reactions in *N,N*-Dimethylformamide^a at 40°C with [NCO]/[OH] = 1.00 with Varying [DBTDL]

Exp.	[H_{12} MDI] (mol/L)	1-BuOH [OH] (mol/L)	[DBTDL] (mol/L $\times 10^5$), (ppm Sn)	k [L/(mol s) $\times 10^4$]
9	0.052	0.10	0.4, 25	1.90
10	0.051	0.10	0.9, 50	2.53
11	0.052	0.10	1.8, 100	3.72
12	0.051	0.10	3.6, 200	4.84
3	0.051	0.10	5.3, 300	5.90
13	0.051	0.10	7.0, 400	6.71
14	0.051	0.10	8.9, 500	7.72
15	0.051	0.10	10.7, 600	8.83
16	0.051	0.10	12.4, 700	9.54
17	0.051	0.10	14.1, 800	9.12

compared with the initial value or less than 2.6% as compared with the average value of 7.63×10^{-4} L/(mol s). These results indicate that the results are precise and reproducible.

CONCLUSIONS

These experiments demonstrate the importance of the configuration of reagents used in urethane and poly(urethane) systems. The urethane reaction with a primary alcohol is much faster than that of a secondary alcohol in all cases and is quantified by the second-order rate constant ratio, $k_{\text{primary OH}}/k_{\text{secondary OH}}$ which was 3.3 in the case of DBTDL at 300 ppm Sn. The difference in reactivity was also apparent in the time to reach 50% conversion of isocyanate groups. The reactions catalyzed by DBTDL at 300 ppm Sn were 240 and 860 min to reach 50% conversion of isocyanate for reaction with 1- and 2-BuOH, respectively. Additionally, DBTDL was shown to be the most effective catalyst, whereas SnOct and TEA showed similar catalytic activity that was minimal when compared with DBTDL. This difference in reactivity must be addressed when using a system that contains both primary and secondary alcohols. Previous work⁶ demonstrates the importance of alcohol structure, where a polyurethane formulated with a polyol having primary end groups was of higher molecular weight than a mixed polyol system of primary and secondary polyols synthesized under the same reaction conditions. Lastly, the overall rate of the urethane forming reaction with [DBTDL] of less than 100 ppm Sn was affected by the rates of the uncatalyzed, urethane catalyzed, and DBTDL catalyzed reactions. However, above 100 ppm Sn, the rate of the uncatalyzed and urethane catalyzed reactions were insignificant when compared with the

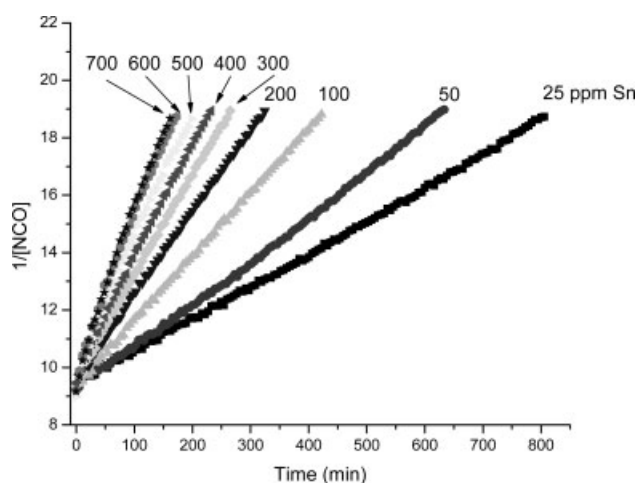


Figure 6 Second-order rate plot of H_{12}MDI and 1-BuOH in DMF with varying concentrations of DBTDL catalyst at 40°C .

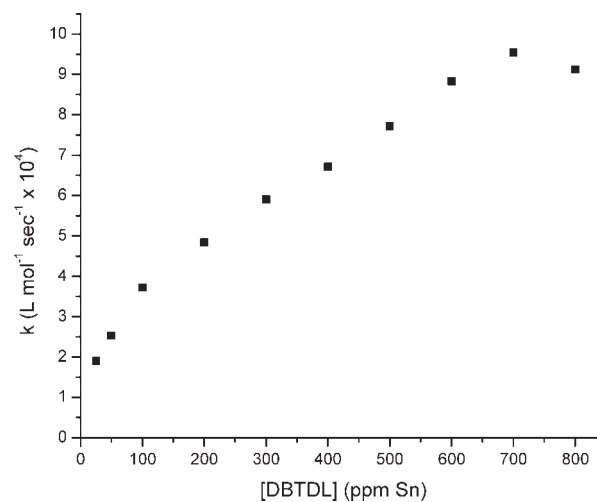


Figure 7 Second-order rate constant versus [DBTDL], for reaction of H_{12}MDI with 1-BuOH in DMF at 40°C .

DBTDL catalyzed reaction, whereby [DBTDL] controlled the overall rate.

References

1. Holden, G.; Quirk, R. P.; Kricheldorf, H. R. *Thermoplastic Elastomers*; 3rd ed.; Hanser Gardner Publications: Munich, 2004.
2. *The Polyurethanes Book*; Randall, D.; Lee, S., Eds.; Wiley: New York, 2003.
3. Asplund, J. O. B.; Bowden, T.; Mathisen, T.; Hilborn, J. *Biomacromolecules* 2007, 8, 905.
4. Guan, J.; Fujimoto, K. L.; Sacks, M. S.; Wagner, W. R. *Biomaterials* 2005, 28, 3961.
5. Hassan, M. K.; Mauritz, K. A.; Storey, R. F.; Wiggins, J. S. *J Polym Sci A* 2006, 44, 2990.
6. Moravek, S. J.; Cooper, T. C.; Hassan, M. K.; Wiggins, J. S.; Mauritz, K. A.; Storey, R. F. *Div Polym Chem Polym Prep* 2007, 48, 568.
7. Tatai, L.; Moore, T. G.; Adhikari, R.; Malherbe, F.; Jayasekara, R.; Griffiths, I.; Gunatillake, P. A. *Biomaterials* 2007, 28, 5407.
8. Van Minnen, B.; Stegenga, B.; van Leeuwen, M. B. M.; van Kooten, T. G.; Bos, R. R. M. *J Biomed Mat Res A* 2006, 76A, 377.
9. Yeganeh, H.; Lakouraj, M. M.; Jamshidi, S. *J Polym Sci A* 2005, 43, 2985.
10. Majumdar, K. K.; Kundu, A.; Das, I.; Roy, S. *Appl Organomet Chem* 2000, 14, 79.
11. Rand, L.; Thir, B.; Reegen, S. L.; Frisch, K. F. *J Appl Polym Sci* 1965, 9, 1787.
12. Saunders, J. H.; Frisch, K. F. *Polyurethanes: Chemistry and Technology, Part 1*; Wiley-Interscience: New York, 1962.
13. Willeboordse, F. *J Phys Chem* 1970, 74, 601.
14. Seneker, S. D.; Potter, T. A. *J Coat Technol* 1991, 63, 19.
15. Turri, S.; Trombetta, T.; Levi, M. *Macromol Mater Eng* 2000, 283, 144.
16. Yilgor, I.; McGrath, J. E. *J Appl Polym Sci* 1985, 30, 1733.
17. Yilgor, I.; Orhan, E. H.; Baysal, B. M. *Makromol Chem* 1978, 179, 109.
18. Silva, A. L.; Bordado, J. C. *Catal Rev* 2004, 46, 31.
19. Bialas, N.; Hocker, H. *Makromol Chem* 1990, 191, 1843.
20. Schwetlick, K.; Noack, R.; Stebner, F. *J Chem Soc Perkin Trans* 1994, 2, 599.
21. Gorna, K.; Polowinski, S.; Gogolewski, S. *J Polym Sci A* 2002, 40, 156.

22. Yilgor, I.; Mather, B. D.; Unal, S.; Yilgor, E.; Long, T. E. *Polymer* 2004, 45, 5829.
23. Thomson, M. A.; Melling, P. J. *In Situ Spectroscopy of Monomer and Polymer Systems*; Kluwer Academic/Plenum Publishers: New York, 2003.
24. Xu, L.; Li, C.; Simon Ng, K. Y. *J Phys Chem A* 2000, 104, 3952.
25. Hofmann, M.; Puskas, J. E.; Weiss, K. *Eur Polym Mater* 2002, 38, 19.
26. Messman, J. M.; Scheuer, A. D.; Storey, R. F. *Polymer* 2005, 46, 3628.
27. Messman, J. M.; Storey, R. F. *J Polym Sci A* 2004, 42, 6238.
28. Pasquale, A. J.; Long, T. E. *Macromolecules* 1999, 32, 7954.
29. Shaikh, S.; Puskas, J. E. *Polym News* 2003, 28, 71.
30. Storey, R. F.; Donnalley, A. B.; Maggio, T. L. *Macromolecules* 1998, 31, 1523.