The Kinetics of the Polymerization Reaction of Toluene Diisocyanate with Polyether Polyols

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THE KINETICS OF THE POLYMERIZATION REACTION OF TOLUENE DIISOCYANATE WITH POLYETHER POLYOLS

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ABSTRACT

·The uncatalyzed and catalyzed polymerization of polypropylene glycols (MW 400–2000) with toluene diisocyanate has been studied in toluene solution at three different temperatures. Discontinuity was observed in the second-order plots of uncatalyzed reactions in contrast to the catalyzed reactions which showed straight-line plots. The rate constants (k_1, k_2) and the activation parameters (Ea_1, Ea_2, $\Delta S_1^{\#}$, $\Delta S_2^{\#}$) for the isocyanate groups in the 4- and 2-positions were calculated. In the uncatalyzed and diethylcyclohexylamine-catalyzed reactions, the rate constants were found to decrease with increasing molecular weight of the polyols, whereas in the dibutyltin-dilaurate-catalyzed reactions the rate constants and the activation parameters were found to be independent of the molecular weight of the polyols.

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INTRODUCTION

About 90% of the polyols used in polyurethane manufacture are hydroxyl-terminated polyethers. Among them, most of the polyols are based on propylene oxide [1]. Toluene diisocyanate (80/20 mixture of 2,4- and 2,6-isomers) is most widely used as a curing agent in polyurethane synthesis. The isocyanate groups in the 2- and 4-positions have different reactivities [2].

The kinetics of the model urethane formation reaction between isocyanates and alcohols has been extensively studied [3–8]. However, comparatively little information has been reported on the diisocyanate–diol reaction kinetics [2, 9–13]. Reports on the kinetics of the polypropylene glycols–toluene diisocyanate reaction are particularly scarce [10]. The difficulty is mainly due to the increase of viscosity during the polymerization reaction. Aranguren and his coworkers [13] studied the reactivity of ortho and para isocyanate groups of toluene diisocyanate with a sorbitol-based polyether polyol. Wissman and his coworkers [10] investigated the reactivity of the isocyanate group in the 4-position of a 80/20 mixture of 2,4- and 2,6-toluene diisocyanate with some polypropylene glycol employing tin catalyst and excess diisocyanate. Some reports [14–16] on the reaction of toluene diisocyanate with polypropylene glycols were recently published, but they do not describe the reactivity of both isocyanate groups in the toluene diisocyanate molecule.

The properties of a polyurethane depend on the molecular weight of the polyol and the presence and nature of the catalyst [17]. The aim of the present kinetic study of commercial polyether polyol (MW 400–2000)–toluene diisocyanate reaction is to determine:

1. The effect of the molecular weights of the polyols in the polyurethane formation reaction.
2. The effect of the temperature and catalyst on the reactivity of isocyanate groups in the 2- and 4-positions of the toluene diisocyanate molecule.

EXPERIMENTAL

Materials

The polypropylene glycols (PPG) used in this study were obtained from UB Petroproducts Ltd. The specifications for each polyol are listed in Table 1. Toluene diisocyanate (TDI), obtained from Fluka, contained 80% 2,4-TDI and 20% 2,6-TDI isomers and was distilled at reduced pressure before use. Dibutyltin dilaurate (DBTDL) (Merck) was used as received. Diethylcyclohexylamine (DECHA) (Sigma) was distilled before use. Toluene was purified by a reported procedure [18].

Polymerization and Rate Measurement

Polymerizations for different time intervals were carried out in individual reactors. Conical flasks (100 mL) containing calculated amounts of polyol and toluene (total volume 15 mL) were fitted with a silicone rubber tube attached to the nitrogen inlet–outlet tube. These reactors were purged with nitrogen, closed with a

TABLE 1. Properties of Polyether Polyols

Identification	Equiv wt	Hydroxyl no., mg KOH/g	Brookfield viscosity at 25°C, cP	Water, maximum %	Applications
Vittacol-400[a]	200	260–280	90 ± 10	0.1	Elastomers
Vittacol-1000[a]	500	112.5	140 ± 20	0.1	Leather coatings, adhesive, sealant, etc.
Vittacol-2000[a]	1000	53–58	300 ± 20	0.1	Adhesive, sealant, castable elastomers, etc.

[a]Indian Trademark, UB Petroproducts Ltd. They are diols consisting primarily of propoxylates.
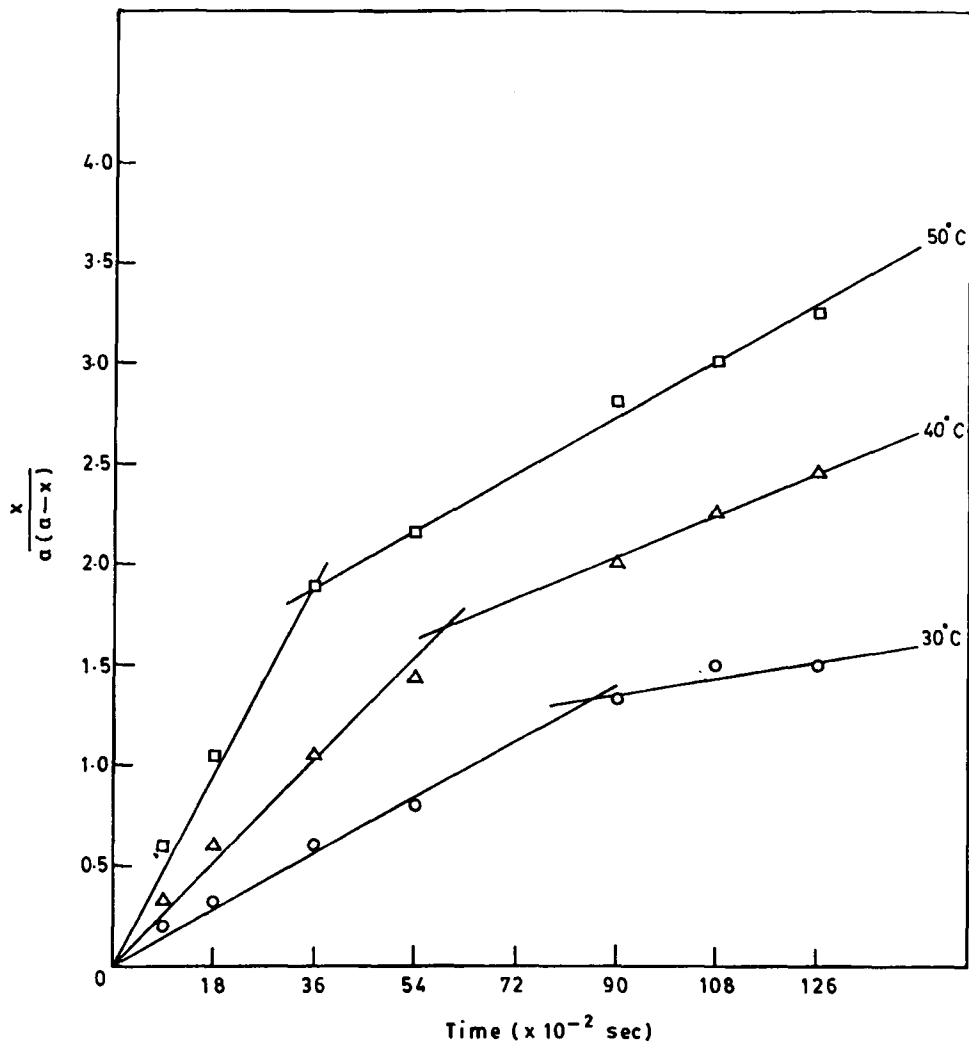
FIG. 1.   Uncatalyzed second-order TDI–Vittacol-400 reaction plots.

silicone rubber tube, and immersed in a constant temperature bath with stirring. A specially built magnetic multistirrer was employed. After thermal equilibrium was attained, 5 mL of 0.8 N TDI/toluene solution was injected through the rubber tube. The concentration of the reactants was 0.2 N and the −NCO/−OH ratio was unity. After each time interval, the reactor was removed from the bath and 5 mL of 2 N dibutylamine solution was added. The flask was kept at room temperature for 1 hour to ensure complete reaction of the unreacted isocyanate with the amine. The excess amine was measured by titration with 0.48 N alcoholic hydrochloric acid with a methyl red/methylene blue mixed indicator [19]. To study the effect of catalyst on the reaction rate, identical experiments were conducted in the presence of calculated amount of the catalysts, viz., DECHA or DBTDL. The titer values

TABLE 2. Second-Order Rate Constants and Activation Parameters for the Uncatalyzed Reaction between Toulene Diisocyanate and Polyols

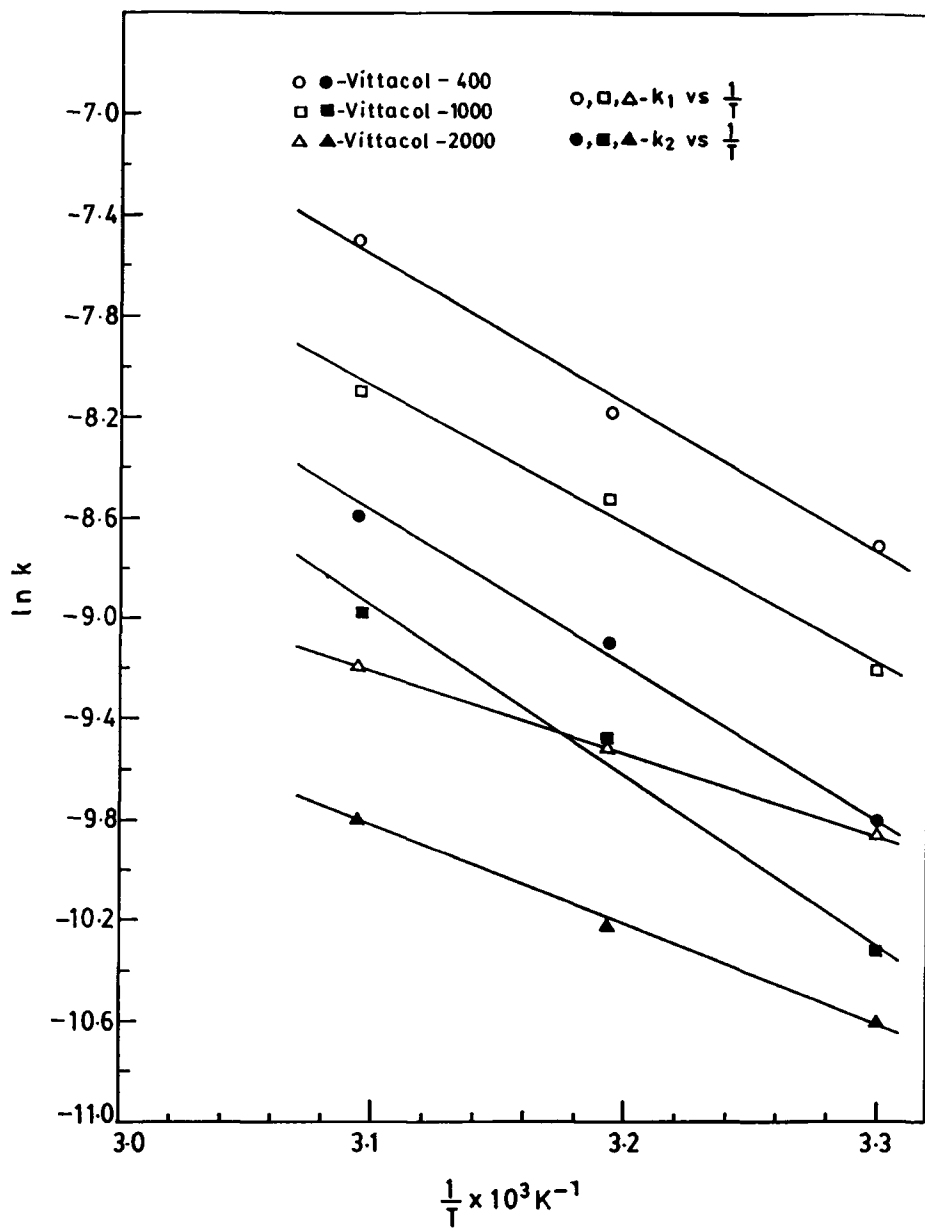| Polyol	Temperature, °C	$k_1 \times 10^4$ (4-NCO), $L \cdot mol^{-1} \cdot s^{-1}$	$k_2 \times 10^4$ (2-NCO), $L \cdot mol^{-1} \cdot s^{-1}$	Conversion, % (minutes)	k_1/k_2	Ea_1, kJ·mol^{-1}	Ea_2, kJ·mol^{-1}	$\Delta S_1^{\#}$, J·K^{-1}·mol^{-1}	$\Delta S_2^{\#}$, J·K^{-1}·mol^{-1}
Vittacol-400	30	1.667	0.556	24 (210)	3.00	45	49	−179	−177
	40	2.778	1.110	33 (210)	2.49				
	50	5.278	1.667	40 (210)	2.66				
Vittacol-1000	30	1.000	0.330	13 (210)	3.00	45	53	−182	−164
	40	2.000	0.778	23 (210)	2.57				
	50	3.000	1.220	31 (210)	2.45				
Vittacol-2000	30	0.527	0.250	10 (210)	2.11	27	34	−247	−231
	40	0.750	0.360	13 (210)	2.00				
	50	1.000	0.556	15 (210)	1.80				

FIG. 2.   Arrhenius plots for uncatalyzed TDI-Vittacol-400, Vittacol-1000, and Vitta-col-2000 reactions.

TABLE 3. Second-Order Rate Constants and Activation Parameters for the Diethylcyclohexylamine (2.5×10^{-3} M) Catalyzed Reaction between Toluene Diisocyanate and Polyols

Polyol	Temperature, °C	$k \times 10^4$, L·mol^{-1}·s^{-1}	Conversion, % (minutes)	E_a, kJ·mol^{-1}	$\Delta S^{\#}$, JK^{-1}·mol^{-1}
Vittacol-400	30	2.000	7 (35)		
	40	4.330	15 (35)	47.0	−169
	50	6.667	20 (35)		
Vittacol-1000	30	1.944	10 (42)		
	40	2.778	12 (42)	27.0	−236
	50	3.478	14 (42)		
Vittacol-2000	30	1.250	5 (42)		
	40	1.667	7 (42)	27.0	−241
	50	2.080	9 (42)		

are taken to represent the concentration of dibutylamine inasmuch as the concentration of the catalyst was negligible in comparison.

RESULTS AND DISCUSSION

All reactions reported in this paper were carried out at three different temperatures (30, 40, and 50°C). The data were treated according to a second-order rate equation for equal initial reactant concentrations. The second-order rate plots (Fig.

TABLE 4. Second-Order Rate Constants and Activation Parameters for the Dibutyltin Dilaurate (2.5×10^{-4} M) Catalyzed Reaction between Toluene Diisocyanate and Polyols

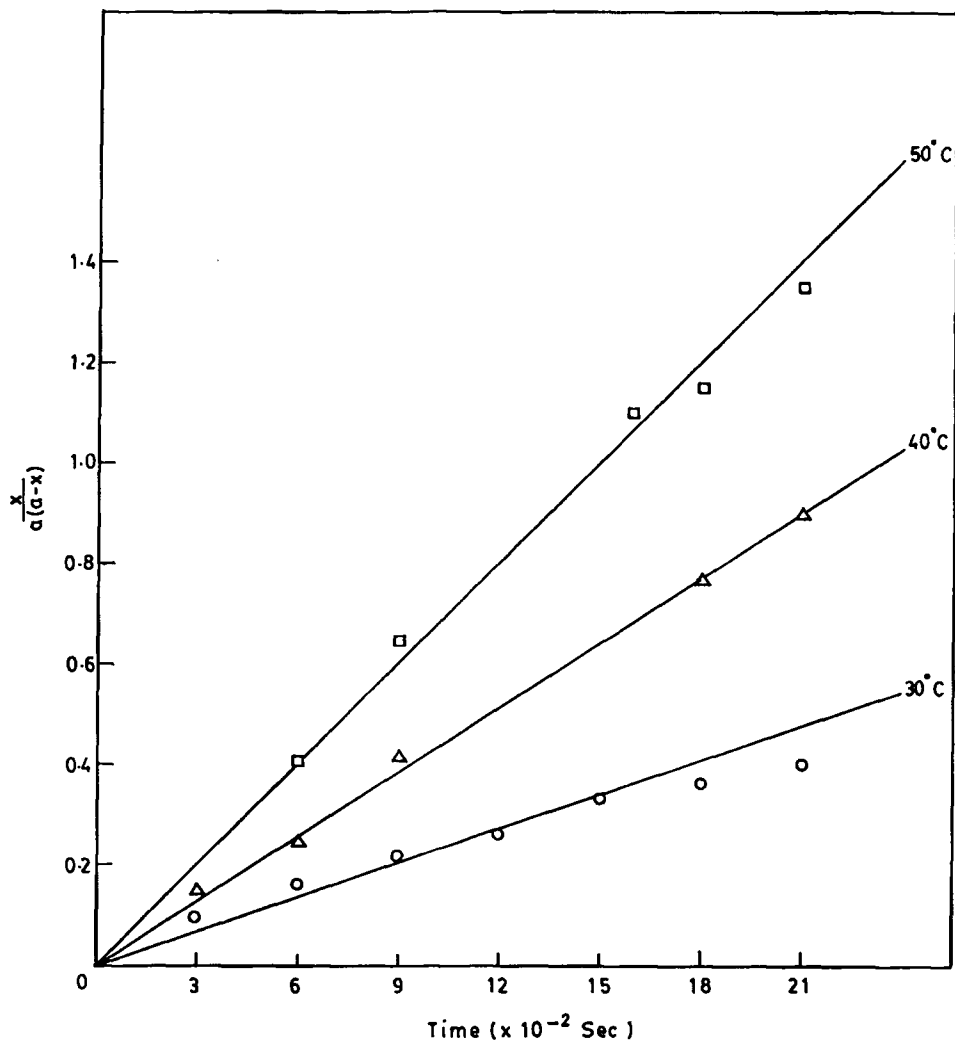| Polyol	Temperature, °C	$k \times 10^4$, L·mol^{-1}·s^{-1}	Conversion, % (minutes)	E_a, kJ·mol^{-1}	$\Delta S^{\#}$, JK^{-1}·mol^{-1}
Vittacol-400	30	12.000	34 (35)		
	40	22.220	46 (30)	47.0	−156
	50	42.220	52 (21)		
Vittacol-1000	30	13.330	40 (35)		
	40	21.667	52 (35)	45.0	−162
	50	41.667	55 (25)		
Vittacol-2000	30	13.330	40 (35)		
	40	23.330	53 (35)	45.0	−162
	50	40.000	60 (30)		

FIG. 3.   Diethylcyclohexylamine catalyzed second-order TDI–Vittacol-400 reaction plots.

1) for the uncatalyzed reactions of PPG-400, PPG-1000, and PPG-2000 with TDI show a very distinct break in continuity beyond 10% conversion. The authors [20] observed pronounced discontinuity at 13% conversion in the reaction of TDI with a prepolymer having primary hydroxyl groups. Thus, this behavior may be due to the difference in reactivity of the isocyanate groups in TDI molecules. The —NCO group in the 4-position should be more reactive than the —NCO group in the 2-position. Since the —NCO group in the 4-position is activated by the —NCO group in the 2-position, it is free from steric hindrance due to the methyl group in the 1-position. The —NCO group in the 2-position may react after consumption of the —NCO group in the 4-position. According to this argument, the breakpoint
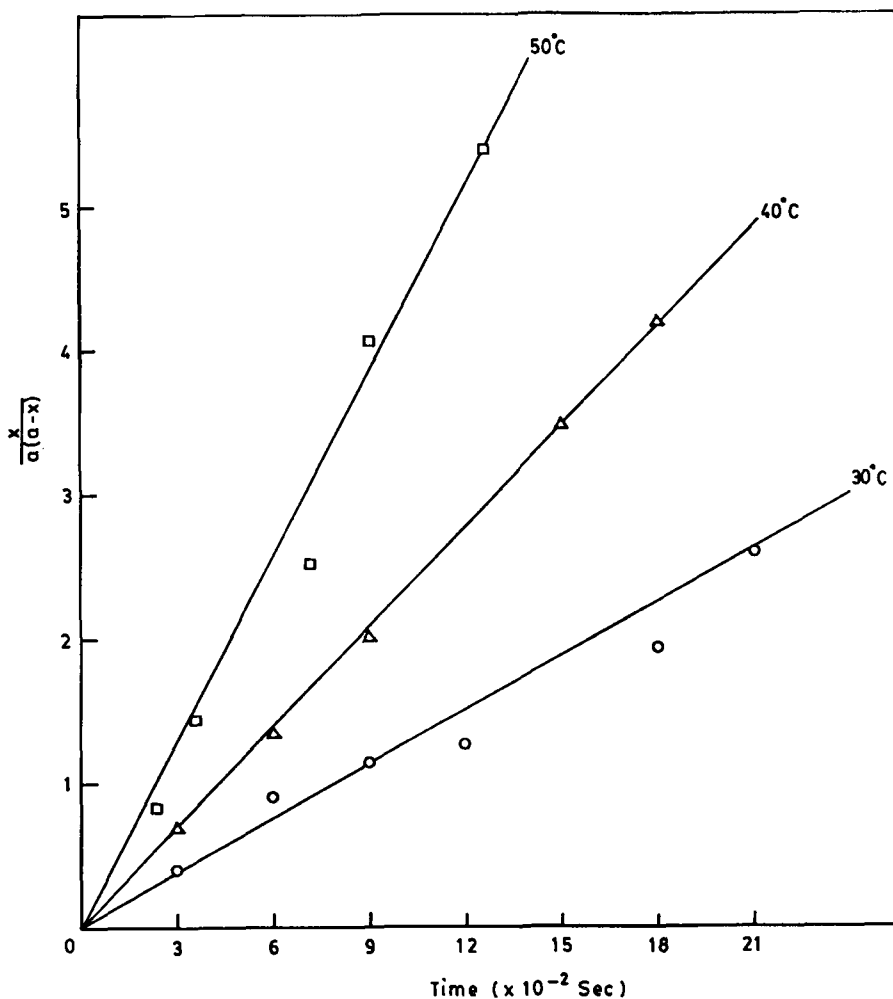
FIG. 4.   Dibutyltin dilaurate catalyzed second-order TDI–Vittacol-400 reaction plots.

should appear around 50% conversion, but it is observed at around 10% conversion. Thus, it may be concluded that the −NCO group in the 2-position can react simultaneously with the −NCO group in the 4-position after some extent of reaction [3].

Table 2 shows the rate constants and the activation parameters for the uncatalyzed reaction of TDI with polyols. The rate constants k_1 and k_2 for the isocyanate groups in the 4- and 2-position, respectively, were calculated from the slopes of the two distinct straight lines. This method is generally accepted for a reaction involving two isocyanate groups present in the same benzene ring [3]. The rate constants for both the isocyanate groups decreased with increasing molecular weight of the polyols. Farkans [21] observed that the reaction rate decreased with increasing carbon chain length of oligomer diols in the reaction with hexamethylene diisocyanate. It was also found that 40% conversion was achieved in the reaction with PPG-400 in

3½ hours at 50°C, whereas the conversion with PPG-2000 was only 15% under the same conditions.

The isocyanate group in the 4-position shows a 3 times higher reactivity than that in the 2-position. However, some authors [22, 23] have assumed that the reactivity of the para isocyanate group is about 10 times that of the ortho group, whereas Brock [24] calculated the reactivity of the para isocyanate group and found that it was about 2.67 times more reactive than the ortho group. The authors [20] calculated the reactivity of the isocyanate group in the 4-position; it was 4 times as reactive as the isocyanate group in the 2-position. The effect of temperature on the less reactive group can be understood by calculating the k_1/k_2 ratios for different temperatures. As can be observed from Table 2, the value decreases with increasing temperature. This trend indicates that the temperature enhances the reactivity of the isocyanate group in the 2-position rather than that in the 4-position.

The activation energies, Ea_1 and Ea_2, for the uncatalyzed reaction were calculated from the slopes of the Arrhenius plots (Fig. 2). The values of Ea_2 for the reaction of the isocyanate group in the 2-position are higher than the values of Ea_1 for the reaction of the isocyanate group in the 4-position of TDI molecules. This may be attributed to the inductive and steric effects provided by the neighboring methyl substituent in the 1-position. The entropy of activation was calculated from

$$\Delta S^{\#} = \left[\log \frac{k}{T} - \log \frac{K}{h} + \frac{\Delta H^{\#}}{2.303RT} \right] 2.303R$$

$\Delta H^{\#}$ in the above equation was obtained from the energy of activation by using the relation $\Delta H^{\#} = Ea - RT$.

The rate constants and the activation parameters for the DECHA- and DBT-DL-catalyzed reaction of TDI with polyols are listed in Tables 3 and 4, respectively. Representative rate plots (Figs. 3 and 4) do not show any break in continuity. In view of the enhanced rate of the reaction, the discontinuity in the plots due to the different reactivities of the two isocyanate groups is not manifest.

As previously mentioned, the rate constants decreased with increasing molecular weights of the polyols in the DECHA-catalyzed reactions. The apparent entropies of activation are highly negative due to the formation of a rigid complex between the catalyst and isocyanate in the transition state.

In contrast with DECHA-catalyzed reactions, the rate constants, percentage conversions, and the activation parameters derived from the DBTDL-catalyzed reaction of PPG-400, PPG-1000, and PPG-2000 with TDI are nearly independent of the molecular weight of the polyols. Wissman and his coworkers [10] reported that the rate constants of DBTDL-catalyzed polyether polyol–TDI reactions were found to be essentially independent of the chain length and the functionality of the polyols. When compared to uncatalyzed and DECHA-catalyzed reactions, the conversion is very high in the DBTDL-catalyzed reaction. Sixty percent conversion was achieved within 30 minutes in the reaction with PPG-2000 at 50°C, whereas only 15% conversion was achieved in 210 minutes under the same conditions in the uncatalyzed reaction. Also, the uniform rate constants and the activation parameters indicate that the reaction is not diffusion-controlled. The above observations can be explained on the basis of activation of both TDI and polyol by DBTDL. Smith [9] and Van der Weij [5] have also proposed a similar postulate.

CONCLUSION

1. Reactions of polypropylene glycols (Vittacol-400, Vittacol-1000, and Vittacol-2000) with TDI follow an apparent second-order rate law.
2. The uncatalyzed reactions show a break in continuity in second-order rate plots whereas the catalyzed reactions show straight line plots.
3. DBTDL was found to be a very efficient catalyst for the TDI–polyol reaction.
4. In the DBTDL-catalyzed systems, the reaction rates were found to be independent of the molecular weight of the polyols.

ACKNOWLEDGEMENT

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