

# Rheo-kinetic Evaluation on the Formation of Urethane Networks Based on Hydroxyl-Terminated Polybutadiene

V. SEKKAR, K. AMBIKA DEVI, K. N. NINAN

Vikram Sarabhai Space Centre, Thiruvananthapuram, India, 695 022

Received 28 December 1999; accepted 16 May 2000

**ABSTRACT:** Rheo-kinetic studies on bulk polymerization reaction between hydroxyl-terminated polybutadiene (HTPB) and di-isocyanates such as toluene-di-isocyanate (TDI), hexamethylene-di-isocyanate (HMDI), and isophorone-di-isocyanate (IPDI) were undertaken by following the buildup of viscosity of the reaction mixture during the cure reaction. Rheo-kinetic plots were obtained by plotting  $\ln(\text{viscosity})$  vs. time. The cure reaction was found to proceed in two stages with TDI and IPDI, and in a single stage with HMDI. The rate constants for the two stages  $k_1$  and  $k_2$  were determined from the rheo-kinetic plots. The rate constants in both the stages were found to increase with catalyst concentration and decrease with NCO/OH equivalent ratio ( $r$ -value). The ratio between the rate constants,  $k_1/k_2$  also increased with catalyst concentration and  $r$ -value. The extent of cure reaction at the point of stage separation ( $x_i$ ) increased with catalyst concentration and  $r$ -value. Increase in temperature caused merger of stages. Arrhenus parameters for the uncatalyzed HTPB-isocyanate reactions were evaluated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1869–1876, 2001

**Key words:** hydroxyl-terminated polybutadiene; toluene diisocyanate; hexamethylene diisocyanate; isophorone diisocyanate; viscosity buildup; kinetics

## INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) is extensively used as a binder for composite solid propellants in advanced launch vehicles and rockets.<sup>1</sup> The urethane network formed through the crosslinking reaction of HTPB with isocyanate curatives provides the continuous polymeric matrix, which accommodates the inorganic oxidizer and metallic fuel, while providing the required structural integrity. Uniform distribution of the solid particles in the propellant grain ensures reproducible mechanical and ballistic properties. Sufficiently long pot life for the propellant paste is a favorable condition to enhance the ease of pro-

cessability, and thereby to manufacture defect-free propellant grains. Processability characteristics of solid propellant mixing are greatly dependent on the kinetics of binder network formation. Functionality distribution of the prepolymer and the reactivity of the functional groups play a very crucial role in the network formation kinetics. Thus, understanding the kinetics of the urethane network formation can help to arrive at optimum conditions with regard to acceptable pot lives for propellant slurries.

The kinetics of urethane formation has been extensively studied in the solvent media.<sup>2–6</sup> However, the studies on the kinetics in the bulk polymerization mode will be of more relevance to the propellant processing, and hence, more desired. It may further be noted that the kinetics in the bulk will be quite different from that in solution.<sup>7,8</sup> However, extremely high viscosity of the curing

---

Correspondence to: V. Sekkar.

*Journal of Applied Polymer Science*, Vol. 79, 1869–1876 (2001)  
© 2001 John Wiley & Sons, Inc.

polymer in the bulk could be an impediment to satisfactory estimation of functional groups,<sup>9,10</sup> and in such instances spectroscopic methods, are best suited.<sup>4,9</sup> Because the conventional chemical and spectroscopic analytical methods can only reveal the extent of functional group consumption during the cure reaction, they have limited applicability in estimating the branching status of the crosslinking system, which essentially determines the pot life. Viscosity of the curing polymer, on the other hand, can be a very convenient, and the most pertinent parameter for following the network formation in the pregel stage, as it is a direct effect of both chain extension and chain branching.<sup>11</sup> Thus, an understanding of the role of various factors that influence the viscosity buildup kinetics, is not only crucial in controlling the pot life but also offers a method to conveniently predict its magnitude.<sup>11</sup>

The aim of the present work is to evaluate the kinetic parameters associated with the urethane network formation based on HTPB and various diisocyanate compounds with reference to viscosity buildup during the cure reaction.

## EXPERIMENTAL

### Materials

Hydroxyl-terminated polybutadiene (HTPB) prepolymer, was prepared in the Vikram Sarabhai Space Centre (VSSC) by H<sub>2</sub>O<sub>2</sub>-initiated free radical polymerization of butadiene in a 2-propanol-water mixed-solvent system.<sup>12</sup> The di-isocyanates used were a 80 : 20 mixture of 2,4 and 2,6 isomers of toluene diisocyanate, TDI (A. G. Bayer, Germany), hexamethylene diisocyanate, HMDI, and isophorone diisocyanate, IPDI (Fluka Co., Switzerland). The isocyanate compounds were used as such without further purification after assessing the isocyanate content. Dibutyl-tin-dilaurate (DBTDL) procured from Fluka was used as the cure catalyst.

### Determination of Equivalent Weight of HTPB

Equivalent weight of HTPB ( $E_{\text{HTPB}}$ ) is calculated from hydroxyl value of HTPB using the expression,

$$E_{\text{HTPB}} = 56100 \div \text{hydroxyl value of HTPB}$$

where, hydroxyl value is expressed in terms of milligrams of KOH per gram of HTPB. The hy-

droxyl value of HTPB was determined by the acetylation method employing an acetic anhydride-pyridine mixture (1 : 8 by volume) as the acetylating agent as per the procedure elaborated elsewhere.<sup>13</sup>

### Isocyanate Content in the Diisocyanate Compound

The isocyanate content in the diisocyanate compounds was estimated by reacting the isocyanate compound with a known excess of *n*-butyl amine. The excess amine was back titrated with standard HCl solution. The isocyanate content was calculated from the amount of *n*-butyl amine consumed. The procedure is detailed elsewhere.<sup>14</sup>

### Viscosity Measurement

An RVDV II<sup>+</sup> model Brookfield viscometer was used to measure the viscosity during the cure reaction. The prepolymer and the diisocyanates were mixed at various NCO/OH equivalent ratios (*r*-value) with varying amounts of DBTDL. The mixture was degassed under vacuum before charging into the sample cell. The sample cell used was a small sample adapter of 2-mL capacity (Model CP-14). Measurements were made under isothermal conditions at temperatures varying from 25 to 70°C.

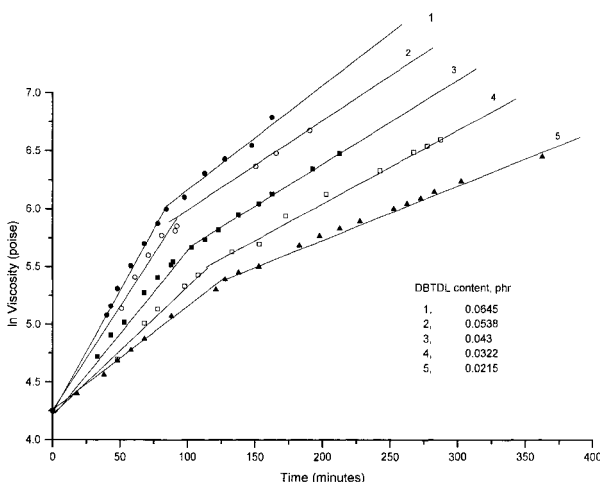
### FTIR Studies

The advancement of urethane formation was followed by monitoring the absorbance by the NCO group using a NICOLETE-510-P model FTIR spectroscope. A drop of the curing polymer was smeared between two polypropylene sheets and the % absorption by the residual NCO at 2250 cm<sup>-1</sup> was measured at different time intervals.

## RESULTS AND DISCUSSION

### Determination of the Rate Constants for Viscosity Buildup

The viscosity of the curing mixture increases with time as the urethane formation advances. The viscosity buildup during the cure process can be attributed chiefly to two factors: (1) an increase in molecular weight as a result of polymer chain growth; (2) chain branching due to the presence of tri- or higher functional moieties present in the prepolymer or in the additives. In our previous publication,<sup>11</sup> it was shown that the viscosity ( $\eta_t$ )



**Figure 1** Plots of  $\ln$  viscosity vs. time for HTPB-IPDI-DBTDL systems;  $r = 1$ ; 25°C.

of the curing system at any given time  $t$ , could be related to time in the form of an exponential function as given below:

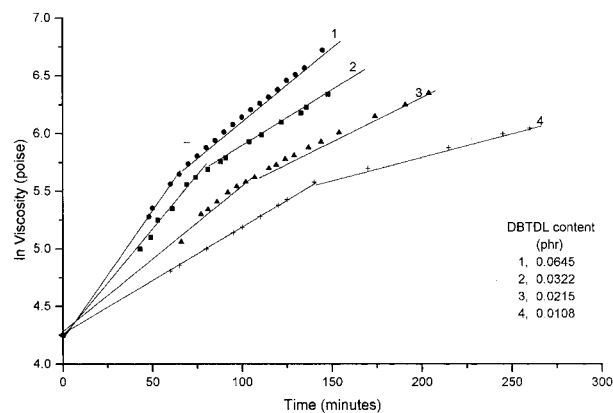
$$\eta_t = \eta_0 e^{kt} \quad (1)$$

where,  $\eta_0$  is the viscosity at  $t = 0$ , and  $k$  is the rate constant for viscosity buildups. Taking logarithm

$$\ln \eta_t = \ln \eta_0 + kt \quad (2)$$

Thus, plotting  $\ln \eta_t$  against  $t$  should yield a straight line, the slope of which is the rate constant for the viscosity buildup. The viscosity buildup is thus a first-order process with respect to the viscosity of the curing mixture.

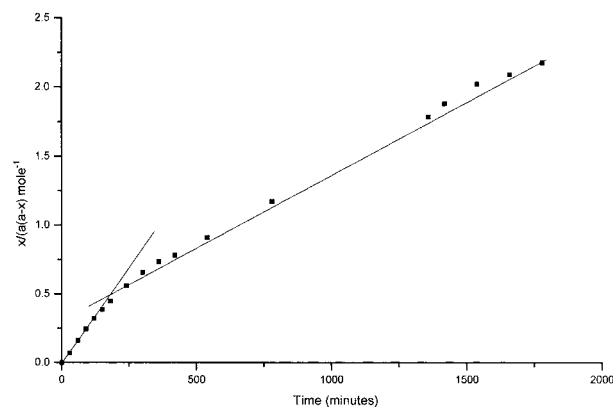
The plots of  $\ln \eta_t$  vs.  $t$  for HTPB-IPDI and HTPB-TDI systems at  $r = 1$  and at 25°C with varying catalyst contents are shown in Figures 1 and 2. The straight-line plots in both cases exhibit a distinct break in continuity. The second-order chemical kinetic plots for the reaction between HTPB and IPDI at 25°C and  $r = 1$  and at a catalyst (DBTDL) concentration of 0.0215 g of DBTDL/100 g HTPB, based on residual NCO content estimation using the FTIR technique also showed a well-pronounced break in continuity (Fig. 3). A similar kind of discontinuity in the conventional second-order kinetic plots was reported earlier as well<sup>3,6,15-17</sup> for the HTPB-TDI/IPDI systems. Such a discontinuity can arise because of two considerations: (1) the difference in the reactivity of the functional groups (kinetic



**Figure 2** Plots of  $\ln$  viscosity vs. time for HTPB-TDI-DBTDL systems at  $r = 1$  and 25°C.

control process), (2) the increased viscosity of the medium causing retardation in the reaction rates due to reduced freedom in chain mobility (diffusion controlled process). Coutinho<sup>15</sup> ruled out diffusion control possibility based on the fact that the kinetic plots involving diisocyanates of similar reactivity did not exhibit discontinuity. For example, dodecyldiisocyanate (DDI), in which the two isocyanates have similar reactivity, did not show any break in the kinetic plots on its bulk-polymerization reaction with HTPB.<sup>15</sup> In the present work also,  $\ln \eta - t$  plots for the HTPB-HMDI system did not show any break (Fig. 6). It is to be noted that in HMDI, the two isocyanates are similar in reactivity.

One of the two NCO groups of IPDI is primary, and the other is secondary in nature. Primary NCO is more reactive than the secondary one, owing to steric considerations. Further, IPDI mol-



**Figure 3** Second-order kinetic plot for the HTPB-IPDI system at  $r = 1$  and 25°C based on FTIR data; DBTDL content—0.0215 phr.

**Table I** Rheo-kinetic Parameters for the System HTPB-IPDI,  $r = 1$ , 25°C

System	DBTDL Content g of Cat per 100 g HTPB	$k_1 \times 10^2$ min <sup>-1</sup>	$k_2 \times 10^2$ min <sup>-1</sup>	$k_1/k_2$	$\eta_I$ (poise)	$t_I$ (min)	$x_I$
HTPB-IPDI	0.0215	0.84	0.48	1.74	194.4	121.1	0.243
	0.0322	1.06	0.61	1.73	234.9	112.8	0.304
	0.043	1.45	0.74	1.94	287.1	96.9	0.348
	0.0538	1.71	0.86	2.01	342.7	92.2	0.404
	0.0645	2.07	1.08	1.92	403.4	84.5	0.415
HTPB-TDI	0.0108	1.28	0.72	1.78	277.3	111.5	0.340
	0.0215	1.74	1.01	1.72	287.1	81.0	0.348
	0.0322	2.14	1.28	1.67	299.6	68.0	0.358
	0.0645	4.33	2.54	1.70	—	—	—

ecule can exist in two configurations, viz: *cis* and *trans*.<sup>17,18</sup> The *cis* and *trans* forms in the commercial IPDI are estimated to be in the ratio of 72 : 28.<sup>17,18</sup> The isocyanate groups in the *cis* and *trans* forms differ in their reactivity.<sup>17,18</sup> It is well known that the isocyanate groups in the *ortho* position of TDI molecule are less reactive than the one in the *para* position due to steric hindrance at the *ortho* position caused by the 1-methyl group.<sup>19</sup> Both *o*- and *p*-NCO groups are activated by each other through mesomeric electron withdrawing effect. So the depletion of *p*-NCO groups in the initial phase of the cure reaction may further cause deactivation of the *o*-NCO groups in addition to the steric hindrance. In HTPB, all the OH groups are allylic in nature,<sup>9</sup> and are similar in reactivity and are not likely to cause the break in the rheo-kinetic plots.

Hence, it is quite obvious that the break in the kinetic plots is mainly due to the differential reactivity of the the isocyanate groups of IPDI and TDI and not due to the operation of diffusion control mechanism. It can further be held that the more reactive isocyanate dominates stage I and the less reactive one stage II. The rate constants for the two stages  $k_1$  (stage I) and  $k_2$  (stage II) were evaluated from the slopes of the plots for the HTPB-IPDI and HTPB-TDI systems at  $r = 1$  and 25°C with varying DBTDL content, and are listed in Table I. A very significant aspect associated with the rate constants obtained through the rheo-kinetic method is that the values of the rate constants depend not only on the relative reactivity of the functional groups but also on the chain-branching probability. It is to be noted that the

branching probability relies essentially on the functionality spectrum of the prepolymer system.

#### Effect of Catalyst Concentration on the Viscosity Buildup

Greater insight of viscosity build up during the cure reaction can be obtained by analyzing the trend in the parameters associated with the point of digression in the  $\ln \eta - t$  plots such as: viscosity ( $\eta_i$ ), time ( $t_i$ ), the extent of reaction ( $x_i$ ).  $\eta_i$  and  $t_i$  were evaluated from the least-square fit on  $\ln \eta - t$  data. The values of  $x_i$  were deduced from FTIR data. The results are given in Table I.

It can be seen from Table I that the rate constants  $k_1$  and  $k_2$  for both the HTPB-IPDI and HTPB-TDI systems increase with the catalyst concentration. The ratio between the two rate constants  $k_1/k_2$  shows an increasing trend with the catalyst concentration for the HTPB-IPDI system, while it remains nearly the same for the TDI-cured system. In the case of conventional second-order kinetic analysis, the ratio of the rate constant for the first stage to that for the second stage showed the opposite trend. The said ratio decreased with catalyst content,<sup>3</sup> indicating that the less reactive NCO is more preferentially activated by the catalyst to the more reactive NCO group. Rise in the reaction temperature has a similar effect on the ratio<sup>2-7,15-17</sup> in the conventional kinetic analysis. This discrepancy between the conventional and the rheo-kinetic modes seems to suggest that branching plays a pivotal role in the kinetics of viscosity buildup, while it has no relevance in the conventional kinetic anal-

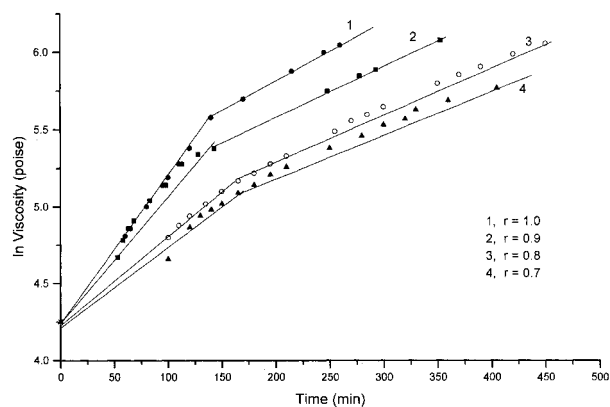
ysis. The conventional chemical kinetics is based on estimation of functional groups by the methods that are totally independent of the branching status of the curing polymer. The viscosity buildup data (Table I) further indicate that while  $t_i$  varies from 121.1 min to 84.5 min, the  $\eta_i$  changes from 194.4 to 403.4 poises. The varied values of  $\eta_i$  suggest that the point of deviation in  $\ln \eta$ -time plots occurs at different stages of conversion. In fact, the extent of reaction at the break point ( $x_i$ ), calculated from FTIR data, also increases from a value of 0.24 to 0.42, as the catalyst content is increased from 0.0215 to 0.0645 phr. This indicates that the discontinuity in the kinetic plots is not due to diffusion control mechanism but is essentially based on kinetic considerations. Had the diffusion control mechanism been the reason for the discontinuity, the break should occur at nearly the same  $x_i$  values.

A common strategy adopted when differential reactivity is encountered is to consider the entire reaction as a set of two consecutive reactions.<sup>3,5,6</sup> It is thus assumed that while the conversion with more reactive groups advances, virtually no reaction involving the less reactive group occurs. But a more appropriate and acceptable approach could be considering a set of simultaneous and competitive reactions; one faster and the other slower.<sup>8,9</sup> The use of catalyst and rise in reaction temperature would, however, narrow down the difference in the rate constants of the two reactions. The effect of the slower reaction on the overall rate may depend on the numerical difference between the rate constants of the two sets of reaction and its relative population. The smaller the difference in the reaction rates, the more the effect will be felt in the latter part of the conversion. An increase in the catalyst concentration narrows down the difference in the reactivity between the two isocyanate groups and eventually pushes the point of deviation to a higher  $x_i$ . A very large difference in the numerical values would, however, render the set of two reactions consecutive.

Further, as DBTDL content increases, the range of reaction covered in stage II decreases, because the break in the reaction is shifted to a higher extent of the reaction. This means that the number of branching events in stage II decreases with the catalyst concentration. Hence, the contribution of chain branching to the viscosity buildup in stage II is expected to decrease with catalyst concentration. It is to be noted that chain-branching component to viscosity buildup

is more significant, compared to the contribution to the same by chain extension. Thus, the reduction in the number of branching events in stage II at high DBTDL contents might have engineered a small reduction in the magnitude of  $k_2$ . Thus, it can be visualized that the increment in the catalyst content, while enhancing the rates both in stages I and II and preferentially activating the less reactive NCO group, it, nevertheless, causes a decrease in the contribution of chain branching to the viscosity buildup in stage II. This could be a probable reason for the increasing trend in  $k_1/k_2$  with catalyst concentration.

In the case of TDI, the values of  $\eta_i$ ,  $x_i$ , and  $k_1/k_2$  do not vary significantly with catalyst content, while  $t_i$  varies substantially. One could be tempted to arrive at the conclusion that diffusion control mechanism operates when TDI is used as the curative; however, it is unlikely for the reasons cited earlier. Higher reactivity of the aromatic NCO groups may be a probable reason for the above-stated behavior. The  $x_i$  values at various catalyst concentrations range from 0.34 to 0.36. Incidentally, the ratio of the *p*-NCO and *o*-NCO groups in TDI (80 : 20 mixture of 2,4 and 2,6 isomers) is 1 : 2. Thus, the fraction of *p*-NCO groups (0.33) matches well with the extent of reaction at the break point. This seems to suggest that the *o*-NCO groups start to take part in the reaction more probably after near complete consumption of the *p*-NCO groups. This could be due to a larger numerical difference in the reactivities between the *o*- and *p*-NCO groups under the present reaction conditions.



**Figure 4** Plots of  $\ln$  viscosity vs. time for the HTPB-TDI system at different  $r$ -values;  $T = 25^\circ\text{C}$ ; no catalyst.



**Table II** Effect of  $r$ -Value on Rheo-kinetic Parameters for the System HTPB-TDI at 25°C

$r$ -Value	$k_1 \times 10^2$ min <sup>-1</sup>	$k_2 \times 10^2$ min <sup>-1</sup>	$k_1/k_2$	$\eta_I$ (poise)	$t_I$ (min)	$x_i$
0.7	0.41	0.27	1.52	138.4	166.1	0.176
0.8	0.56	0.32	1.75	160.8	149.5	0.207
0.9	0.79	0.34	2.32	202.4	133.9	0.256
1.0	0.94	0.40	2.35	261.1	139.3	0.324

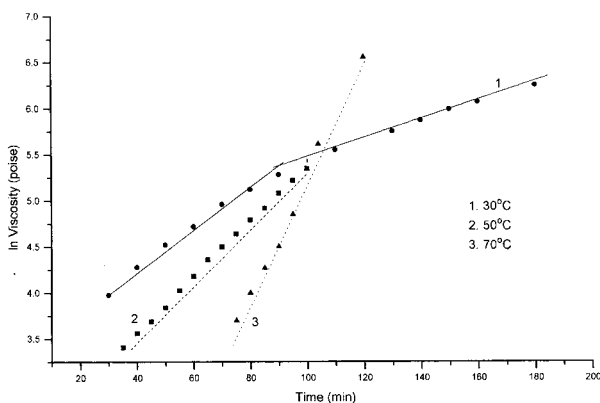
### Effect of $r$ -Value on the Viscosity Buildup

Viscosity build up was studied for uncatalyzed bulk polymerization reaction between HTPB and TDI at 25°C and at four different  $r$ -values, viz: 0.7, 0.8, 0.9, and 1.0. Stage separation was evident at all  $r$ -values (Fig. 4), and the rate constants for both the stages ( $k_1$  and  $k_2$ ),  $k_1/k_2$ ,  $\eta_i$ ,  $t_i$ ,  $x_i$  are listed in Table II. It can be seen from the table that both  $k_1$  and  $k_2$  increase with the  $r$ -value, which is obviously in accordance with the law of mass action and also due to a reduction in the branching activity at low  $r$ -values. Also, it can be noted the effect of  $r$ -value on  $k_1$  is more pronounced than on  $k_2$ . Stage II is marked by depleted quantity of NCO groups and mostly involve in the less reactive  $o$ -NCO groups. Hence, the branching probability in stage II is expected to be less at lower  $r$ -values. In view of these reasons, the ratio  $k_1/k_2$  is expected to increase with the  $r$ -value that is actually observed. The values of  $\eta_i$  and  $x_i$  also increase significantly with the  $r$ -value. The lower value of  $x_i$  at the small  $r$ -values is due to the depletion of more reactive  $p$ -NCO at earlier stages of reaction. The value of  $k_1/k_2$  at  $r = 1$  is significantly higher than the corresponding value

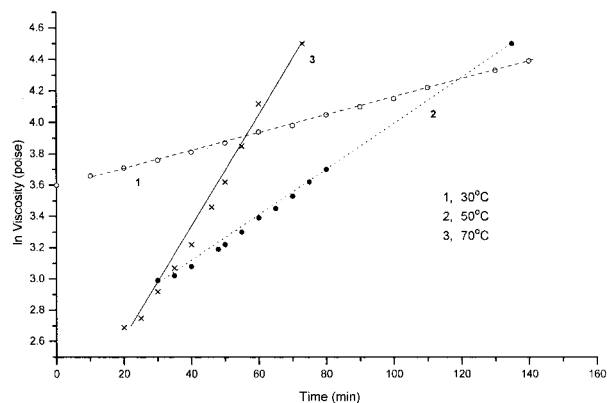
obtained with DBTDL, indicating preferential activation of  $o$ -NCO over  $p$ -NCO by the catalyst.

### Effect of Temperature on Viscosity Buildup

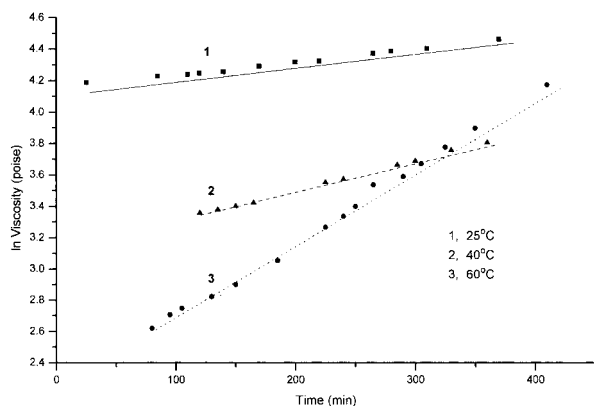
Viscosity buildup was studied for uncatalyzed reactions between HTPB and the diisocyanate compounds (TDI, HMDI, IPDI) at various temperatures. The rheo-kinetic plots are shown in Figures 5–7, and the corresponding rate constants are listed in Table III. Two-stage viscosity buildup was observed for the HTPB–TDI system at 30°C, but at 50 and 70°C the stage separation was not evident. At higher temperatures, reactivity of both the isocyanates would be enhanced. However, the activation received by the less reactive isocyanate will be greater compared to the more reactive one.<sup>2–7,15–17</sup> This would probably reduce the reactivity difference at higher temperatures and eventually make the stages to coalesce. Further, as expected, the rate constants for uncatalyzed reactions are smaller than those obtained when the catalyst was employed. As mentioned earlier, HTPB–HMDI curing reaction yielded only single-stage  $\ln \eta - t$  plots as a result



**Figure 5** Plots of  $\ln$  viscosity vs. time at different temperatures for the HTPB–TDI system;  $r = 1$ ; no catalyst.



**Figure 6** Plots of time vs.  $\ln$  viscosity at different temperatures for the HTPB–HMDI system;  $r = 1.0$ ; no catalyst.



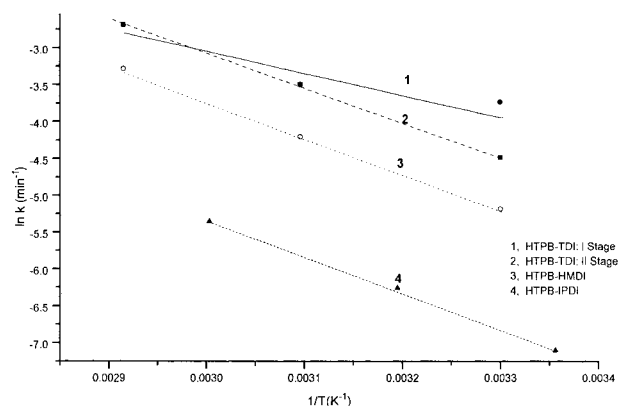
**Figure 7** Plots of  $\ln$  viscosity vs. time for the HTPB-IPDI system at different temperatures;  $r = 1.0$ ; no catalyst.

of similarity in the reactivity of the two NCO groups. HTPB-IPDI reaction in the absence of a catalyst was extremely sluggish even at elevated temperatures. Even after 7 h, the extent of reaction was very low (within the domains of stage I) and the rate constants obtained under such conditions could be attributed only to the stage I of the reaction.

From the magnitude of the rate constants for viscosity buildup, the reactivity of the diisocyanates, when not catalyzed, can be arranged in the following order: TDI > HMDI > IPDI, which is in the expected lines.<sup>7,11</sup>

#### Evaluation of Arrhenius Parameters

Arrhenius plots were obtained by plotting  $\ln k$  vs.  $1/T$  (Fig. 8), with  $T$  expressed on the Kelvin scale



**Figure 8** Arrhenius plots for the HTPB-TDI, HMDI, IPDI systems; no catalyst.

and the activation energies were calculated from the slopes of the straight lines thus obtained. In evaluating the Arrhenius parameters for TDI, because there was no stage separation at 50 and 70°C, the values obtained at these temperatures were taken as the overall value for both the stages. The activation energies calculated are listed in Table III. It is to be noted that the activation energy calculated for IPDI is for stage I only. The activation energies obtained from rheo-kinetic analysis are found to be in the same range as reported elsewhere.<sup>8,19</sup> The calculated activation energy for stages I and II of the HTPB-TDI cure reaction are 22.1 kJ mol<sup>-1</sup> and 38.7 kJ mol<sup>-1</sup>, indicating that the *p*-NCO is more reactive than *o*-NCO, and that the increase in temperature tends to narrow down the difference in the reactivity of the two isocyanate groups, suggesting that the hindrance effect of the 1-methyl

**Table III** Effect of Temperature on the Rheo-kinetic Parameters for HTPB-Diisocyanate Systems at  $r = 1$ ; No Catalyst

Isocyanate Type	Temperature °C	$k_1 \times 10^2$ (min <sup>-1</sup> )	$k_2 \times 10^2$ (min <sup>-1</sup> )	Activation Energy (kJ/mol)
TDI	30	2.41	1.13	22.1 (I stage)
	50	3.03	—	38.7 (IIstage)
	70	6.78	—	
HMDI	30	0.56	—	37.1
	50	1.50	—	
	70	3.77	—	
IPDI	25	0.0823	—	45.2
	40	0.191	—	
	60	0.472	—	

group on the *o*-NCO site becomes less significant at elevated temperatures.<sup>3</sup>

## CONCLUSIONS

The important conclusions that can be drawn from the present study are:

1. The cure reaction between HTPB and diisocyanate compounds takes place in two stages with TDI and IPDI and in the single stage with HMDI; the first stage is faster than the second stage.
2. The stage separation is essentially caused by kinetic considerations and not due to the operation of diffusion control mechanism
3. The factors such as catalyst content and *r*-value significantly influence the rate constants and the ratio between the rate constants corresponding to the different stages. The increase in the catalyst content increases the  $k_1/k_2$ , ratio which is contrary to the observation made in the conventional chemical kinetics. Increase in the temperature causes merger of the stages.
4. Based on the rate constants for the viscosity buildup during the cure reaction involving HTPB, the reactivity of the isocyanates can be arranged in the following order, TDI > HMDI > IPDI, when catalysts are not employed.

The authors wish to express their gratitude to the Director, VSSC, Thiruvananthapuram for kindly granting permission to undertake this research program. The authors also express profound thanks to Dr. M. Kanakavel and Mrs. R. Sadhana for providing the IR spectral data.

## REFERENCES

1. Boyors, C.; Klager, K., Eds. *Propellants, Manufacture, Hazards and Testing*; American Chemical Society: Washington, DC, 1969.
2. Coutinho, F. M. B.; Rocha, M. C. G. *J Polym Sci Polym Chem Ed* 1988, 26, 3167.
3. Kothandaraman, H.; Nasar, A. S. *J Appl Polym Sci* 1993, 50, 1611.
4. Pham, Q. T.; Ghafi, M. E. *Makromol Chem* 1985, 186, 527.
5. Coutinho, F. M. B.; Cavalheiro. *J Appl Polym Sci Appl Polym Symp* 1991, 49, 29.
6. Coutinho, F. M. B.; Rezende, L. C.; Quijada, R. *J Polym Sci Polym Chem* 1986, 24, 727.
7. Saunders, J. H.; Frisch, K. C. *Polyurethanes Chemistry and Technology, Part-I, Chemistry*; Interscience Publishers: New York, 1962.
8. Dubois, C.; Disilets, S.; Ait-kadi, A.; Tanguy, P. *J Appl Polym Sci* 1995, 58, 827.
9. Aranguren, M. I.; William, R. J. *J. Polymer* 1986, 27, 425.
10. Kamal, M. R. *Polym Eng Sci* 1974, 14, 231.
11. Sekkar, V.; Krishnamurthy, V. N.; Jain, S. R. *J Appl Polym Sci* 1997, 66, 1795.
12. Brosse, J. C.; Derouet, D.; Epailard, F.; Soutif, J. C.; Legeay, G.; Dusek, K. *Advances in Polymer Science*; Springer-Verlag: Berlin, 1987, 81, 167.
13. Siggia, S. *Quantitative Organic Analysis via Functional Groups*; John Wiley & Sons Inc.: New York, 1963, p 15.
14. Siggia, S. *Quantitative Organic Analysis via Functional Groups*; John Wiley & Sons Inc.: New York, 1963, p. 558.
15. Coutinho, F. M. B.; Rezende, L. C.; Quijada, R.; Petrobras, C. *J Polym Sci Polym Chem* 1986, 24, 3021.
16. Ajitkumar, S.; Kansara, S. S.; Patel, N. K. *Eur Polym J* 1998, 34, 1273.
17. Coutinho, F. M. B.; Rocha, M. C. G. *Eur Polym J* 1991, 27, 213.
18. Cunliffe, A. V.; Davis, A.; Farey, M.; Wright, J. *Polymer* 1985, 26, 301.
19. Descheres, I.; Pham, Q. T. *Makromol Chem* 1986, 187, 1963.