

Kinetics of Glycidyl Azide Polymer-Based Urethane Network Formation

S. K. Manu,¹ V. Sekkar,² K. J. Scariah,³ T. L. Varghese,⁴ S. Mathew⁵

¹PFC, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala, India 695 022

²APD, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala, India 695 022

³ANLD, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala, India 695 022

⁴PSCG, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala, India 695 022

⁵School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India 686 560

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ABSTRACT: Reactions between hydroxyl-terminated glycidyl azide polymer (GAP) and different isocyanate curatives such as toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), and methylene diisocyanate (MDCI) at various temperatures viz. 30, 40, 50, and 60°C were followed by Fourier transform infra red spectroscopy. The reactions were found to follow second-order kinetics. With TDI and IPDI at 30°C, a two-stage reaction was observed. For GAP-TDI system, the second stage was slower than the first while for GAP-IPDI system, the second stage was faster than the first indicating dominance of autocatalytic effect. The stage separation occurred due to the difference in reactivity of the isocyanate groups and was found to narrow down with increase in temperature. The viscosity

build up due to the curing reaction was followed for GAP-TDI system for comparison. The stage separation was evident in the viscosity build up also. Rheokinetic analysis done based on data generated showed a linear correlation between viscosity build up and fractional conversion. The kinetic and activation parameters evaluated from the data showed the relative difference in reactivity of the three diisocyanates with GAP. Both the approaches suggested that the reactivity of the isocyanates employed for the present study could be arranged as TDI > IPDI ≫ MDCI. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 908–914, 2008

Key words: GAP; cure kinetics; viscosity build up; rheokinetics

INTRODUCTION

In the recent times, polyurethane networks based on glycidyl azide polymer (GAP) have attracted much attention as an advanced propellant binder system.^{1–4} Extra high premium in the energetics, thermochemical stability, and low viscosity are a few among important advantages of GAP over other currently used propellant binder systems. Low viscosity for GAP binder ensures favorable processability characteristics for propellant slurry. Pot-life or the time within which the propellant slurry can be conveniently cast is critically dependant on the functionality of the binder polymer and the chemical kinetics involved in the network forming chemical reaction.^{5–7} Tracking viscosity build up during the cure is a reasonable means of pot-life evaluation. However, viscosity build up is a composite effect of chain propagation due to urethane linkage formation and chain branching which results from functionality higher than two. Thus, it is imperative to acquire

knowledge on the network formation kinetics with regards to viscosity build up and chemical kinetics, and such knowledge may render correlation between viscosity build up and conventional chemical kinetics feasible. The said correlation may eventually lead to a possibility of prediction of pot life for the propellant slurry and thus help to avoid much of material and time wastage. Thus, an attempt is made in this study to arrive at an understanding on the effect of the extent of cure reaction on the viscosity of the curing polymer.

For simple compounds, reaction kinetics can be evaluated conveniently in solution medium employing conventional quantitative functional group estimation techniques.^{8–10} But, in the case of polymers, especially for a curing system, traditional titrimetric methods are of little use as the polymer becomes insoluble beyond the gel point. In such cases, infrared spectroscopy will be a very useful tool, as the specific absorptions can be observed even after the incipient gel point as absorption frequency and extinction coefficients are not much sensitive to the gelation status. At the same time, spindle type viscometers allow the determination of viscosities of the crosslinking polymer only below the gel point.

Correspondence to: S. K. Manu (skmpillai@rediffmail.com).

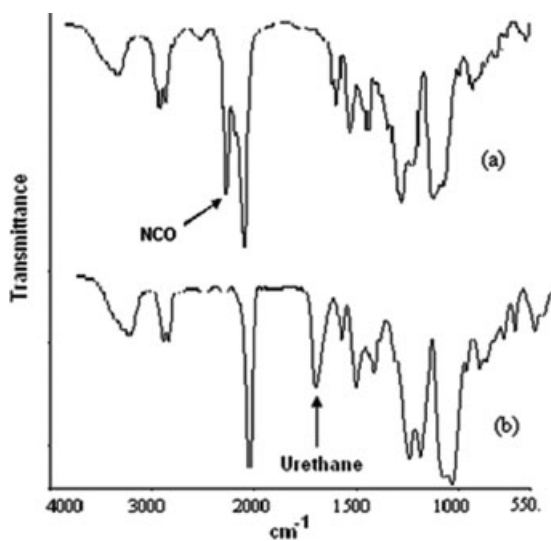
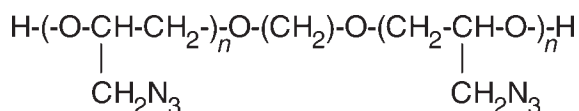


Figure 1 FTIR spectra of the DSC sample (a) immediately after mixing the ingredients and (b) after 3 h.

However, viscosity data below gelation are sufficient for pot life evaluation.

The GAP resin used for the study was prepared by a two-step process involving cationic ring opening polymerization of epichlorohydrin, followed by condensation with sodium azide under specific conditions. The structure of GAP diol used for the study is shown below. The polymer has only hydroxyl end groups which are predominantly



secondary in nature (>98%). Because of the secondary nature of the hydroxyl functional groups, reactivity of GAP with isocyanate is lower compared to telechelic binder like HTPB, which have primary hydroxyl functional. In the present study, the cure reaction between hydroxyl telechelic GAP and various isocyanate curatives was studied using both FTIR and spindle viscometer. FTIR data supported the calculation of the extent of reaction at various time periods and the same was correlated to viscosity at the corresponding period of time. Also, rate constants for the chemical reaction leading to the crosslinking and the viscosity build up were computed at various temperatures. Arrhenius and Eyring parameters were calculated for both chemical reaction path as well as for the viscosity build up.

EXPERIMENTAL

FTIR studies

The course of urethane formation reaction was followed by monitoring the changes in the absorbance

of NCO group at 2273 cm^{-1} using Perkin-Elmer Spectrum GX model FTIR spectrometer. The kinetic analysis was done one line with a drop of the curing polymer smeared between two sodium chloride windows and the % absorption by the residual NCO at 2273 cm^{-1} was measured at different time intervals.

Viscosity measurement

A RVDV II⁺ model Brookfield viscometer was used to measure the viscosity during the cure reaction. The curing mixture was degassed under vacuum before charging into the sample cell. The sample cell used was a small sample adapter of 10 mL capacity and the spindle used was S-21. The sample adapter was placed in a constant temperature hot water circulation jacket. Viscosity of the curing polymer was measured at various intervals of time. The viscosity build up studies were undertaken at different temperatures.

Materials

GAP resin with molecular weight close to 2000 (by VPO) produced in Vikram Sarabhai Space Centre (VSSC), Thiruvananthapuram was used for the study. Toluene diisocyanate (TDI) supplied by M/s. Bayer, Germany, isophorone diisocyanate (IPDI) supplied by M/s. Merck, Germany and methylene diisocyanate (MDCI) supplied by M/s Sigma-Aldrich (Bangalore, India) were used as curatives.

RESULTS AND DISCUSSION

Evaluation of the II order reaction rate constants

The reaction between hydroxyl-terminated GAP (GAP) and isocyanate curative can be represented

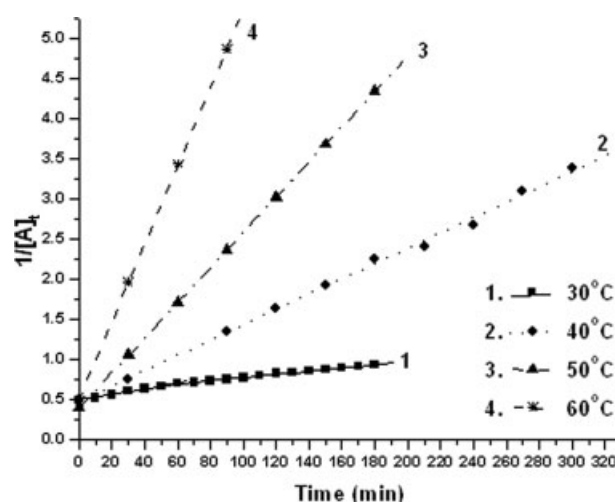


Figure 2 Second-order kinetic plots for GAP-TDI system.

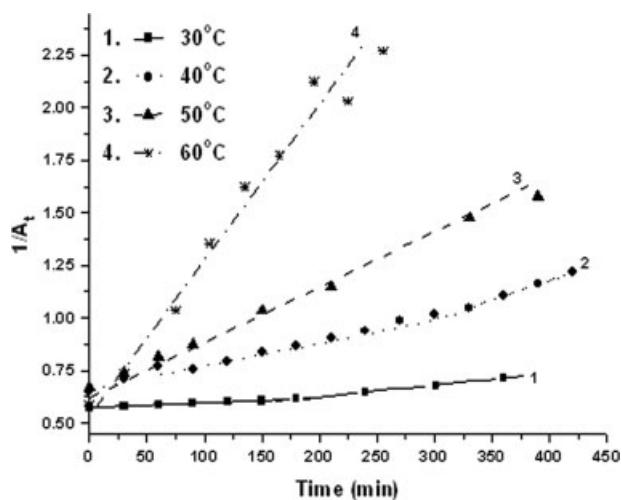
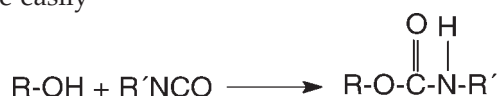


Figure 3 Second-order kinetic plots for GAP-IPDI system.

by the following scheme. The path of such a reaction can be easily



followed by recording FTIR spectra of the curing mixture at various time intervals. For instance, the spectra of GAP-TDI mixture immediately mixing and after 3 h are shown in Figure 1. It can be observed that there is a sharp reduction in the absorbance of NCO peak (2273 cm^{-1}) after 3 h of mixing.

Reduction in the intensity of the peak at 2273 cm^{-1} corresponds to the consumption of NCO groups, while increase in the intensity of the peak at 1726 cm^{-1} indicate the formation of urethane groups due to reaction between hydroxyl and isocyanate groups. The absorption bands at 2100 cm^{-1} due to stretching of azide group and CH stretching at 2930 cm^{-1} remain almost unaffected throughout the course of reaction. For this reason the ratio between the absorbance of NCO (2273 cm^{-1}) and that of CH stretching (2930 cm^{-1}) is taken as a measure of con-

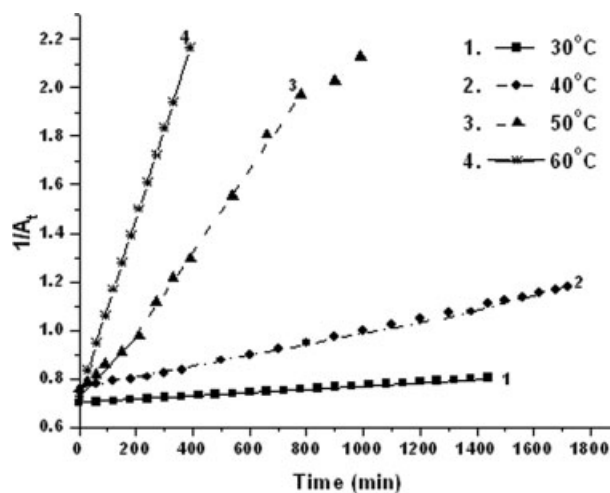


Figure 4 Second-order kinetic plots for GAP-MDCI system.

centration of isocyanate groups for the purpose of evaluating kinetic parameters.

It has been established that the reaction between hydroxyl and isocyanate groups follow 2nd order kinetics.⁸ When the ratio between the equivalents of NCO and OH groups is below unity the kinetic expression can be written as shown in eq. (1).

$$1/[\text{C}_{\text{NCO}}]_t = kt + 1/[\text{C}_{\text{NCO}}]_0 \quad (1)$$

where, $[\text{C}_{\text{NCO}}]_0$ and $[\text{C}_{\text{NCO}}]_t$ are concentrations of NCO groups at the start of the reaction and at any given time t , and k is 2nd order rate constant. When the absorbance is considered for concentration term, the kinetic equation may take the form as

$$1/[A]_t = kt + 1/[A]_0 \quad (2)$$

where,

$$[A]_0 = \frac{\text{Absorbance of NCO (2273 cm}^{-1}) \text{ at the start of the reaction}}{\text{Absorbance of CH}_3(2930 \text{ cm}^{-1}) \text{ at the start of the reaction}}$$

TABLE I
Kinetic Data for GAP Crosslinking from IR Spectroscopic Study

Diisocyanate	Second-order rate constant at different temperatures (min^{-1})			
	30°C	40°C	50°C	60°C
TDI	3.49 E -03 (I Stage) 1.98 E -03 (II Stage)	9.52 E -03	2.24 E -02	4.87 E -02
IPDI	2.20 E -04 (I Stage) 5.53 E -04 (II Stage)	7.43 E -04	2.36 E -03	7.92 E -03
MDCI	2.85 E -05	1.23 E -04	6.80 E -04	3.39 E -03
$k_{\text{TDI}}/k_{\text{IPDI}}$	16.1	12.8	9.5	6.1
$k_{\text{TDI}}/k_{\text{MDCI}}$	122.3	77.0	32.9	14.3
$k_{\text{IPDI}}/k_{\text{MDCI}}$	7.6	6.0	3.5	2.3

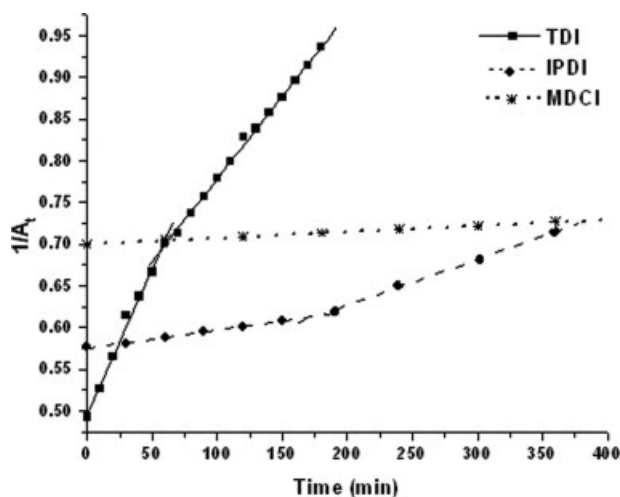


Figure 5 Second-order kinetic plots for the reaction between GAP and various diisocyanate compounds at 30°C.

and

$$[A]_t = \frac{\text{Absorbance of NCO (2273 cm}^{-1}\text{)} \text{ at any given time } t}{\text{Absorbance of CH}_3 \text{ (2930 cm}^{-1}\text{)} \text{ at any given time } t}$$

Thus, plotting $1/[A]_t$ against t yields straight lines and slopes of which are the 2nd order rate constants for the reaction between GAP and the isocyanate curative. Thus, 2nd order rate constants were obtained for various isocyanate compounds, namely: TDI, IPDI, and MDCI each at different temperatures viz: 30, 40, 50, and 60°C. Figures 2–4 depict the 2nd order plots for GAP-TDI, GAP-IPDI, and GAP-MDCI, respectively. For all the cases, linear plots with good correlation coefficients were obtained,

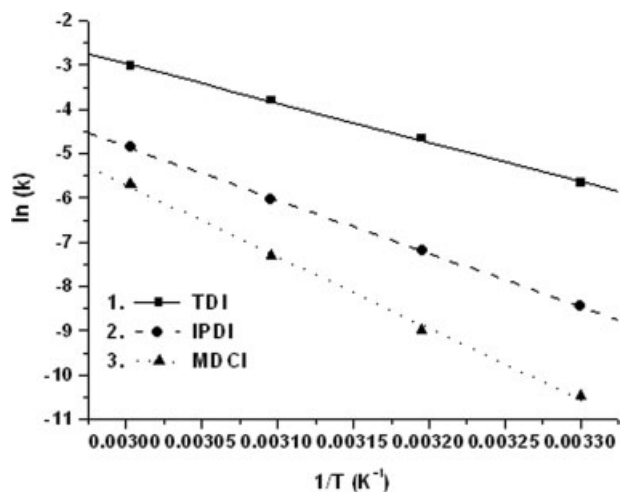


Figure 6 Arrhenius plots for GAP-TDI, IPDI, and MDCI.

indicating that the reactions between GAP and diisocyanate curatives follow second-order kinetics as reported by several authors for other similar systems.⁸ The slopes of the straight line plots are the rate constants for the reactions. The second-order rate constants thus obtained for the three diisocyanate compounds are listed in Table I.

Effect of isocyanate type on the rate constants

It can be seen that at any given temperature, the rate constants for the three diisocyanate compounds can be arranged in the order TDI > IPDI > MDCI. This is very much in accordance with reported trend obtained with conventional chemical kinetic approaches. Because of electron withdrawing mesomeric effect, which is very important for aromatic isocyanates,¹¹ TDI is more reactive than the aliphatic isocyanates used in the study. Between the two cycloaliphatic isocyanates used in the present study, IPDI is expected to be more reactive than MDCI as one of the two isocyanate groups in IPDI is primary in nature and the other is secondary. Both the isocyanate groups in MDCI are secondary and can be expected to be far more sluggish in its reaction with hydroxyl groups. A deviation from the general behavior was observed with TDI and IPDI at 30°C. Both exhibit a two-stage reaction pathway. With TDI, the second stage was slower than the first, while with IPDI the second stage was faster than the first; a typical example for autocatalysis. MDCI did not exhibit any stage separation. The two-stage kinetic behavior results from the difference in the reactivity of the two isocyanate groups. At higher temperatures, the difference in reactivity diminishes and the reaction tends to proceed in single stage. The comparison of second-order kinetics plots for the three curatives at 30°C is shown in Figure 5.

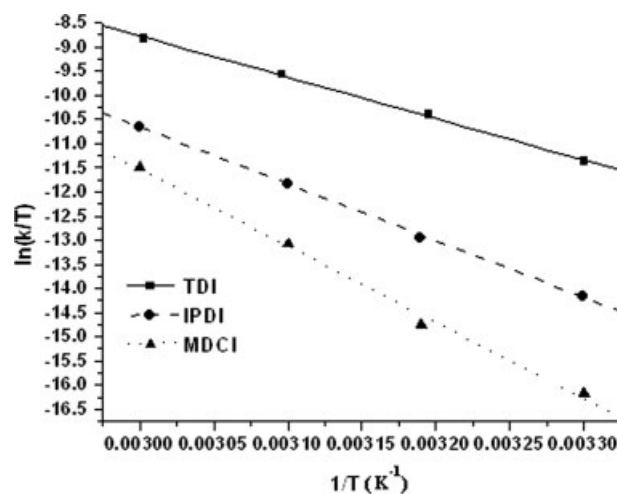


Figure 7 Eyring plots for GAP-TDI, IPDI, and MDCI.

TABLE II
Activation Parameters for the Reaction Between GAP and Various Isocyanate Compounds

Diisocyanate	Activation energy (kJ mol ⁻¹)	Activation enthalpy (kJ mol ⁻¹)	Activation entropy (J mol ⁻¹ K ⁻¹)
TDI	73.2	71.0	-57.6
IPDI	100.3	97.7	6.8
MDCI	134.5	131.7	101.8

It can be further noted that the ratio of the rate constants of higher reactive to a lower reactive isocyanate steadily reduces with temperature indicating that rise in temperature narrows down difference between the reactivities. Highest fall in the ratio occurs between TDI and MDCI. The ratio of the rate constants are shown in Table I.

Evaluation of activation energy and activation entropy

Activation energy for the reaction between GAP and the isocyanate curatives can be obtained using Arrhenius equation which is as given below

$$k = A e^{-E_a/RT} \quad (3)$$

where, k is the rate constant; E_a is the activation energy; T is the temperature in Kelvin scale; and R is the gas constant. A is known as pre-exponential factor or Arrhenius frequency factor. The logarithmic form of the above equation can be written as follows:

$$\ln k = \ln A - E_a/RT, \quad (4)$$

Thus, plotting $\ln k$ against $1/T$ should yield straight lines, the slope of which is $-E_a/R$

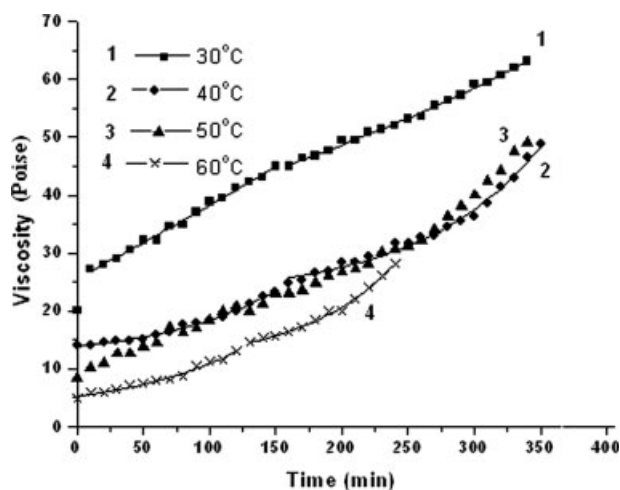


Figure 8 Viscosity build up during cure reaction between GAP and TDI at various temperatures.

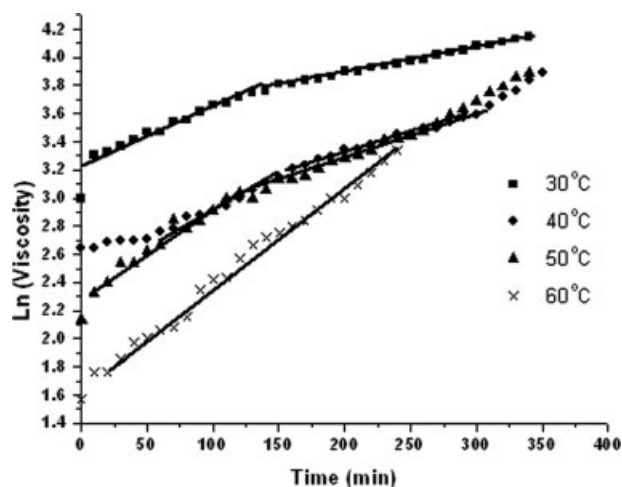


Figure 9 Plots of ln viscosity versus time at various temperatures: GAP-TDI system.

$$E_a = -\text{slope} \times R$$

Arrhenius plots for the reaction between GAP and the three isocyanates, viz.: TDI, IPDI, and MDCI are shown in Figure 6.

Entropy of activation can be calculated from Eyring equation, namely;

$$\ln(k/T) = -\Delta H^\ddagger/RT + \ln(k_N/h) + \Delta S^\ddagger/R, \quad (5)$$

where, ΔH^\ddagger is activation enthalpy, k_N is Boltzman constant, h is Plank's constant, and ΔS^\ddagger is activation entropy. From the slopes of the straight line plots between $\ln(k/T)$ and $1/T$, ΔH^\ddagger is obtained and the intercepts give activation entropy. Eyring plot is depicted in Figure 7. The corresponding activation parameters are listed in Table II.

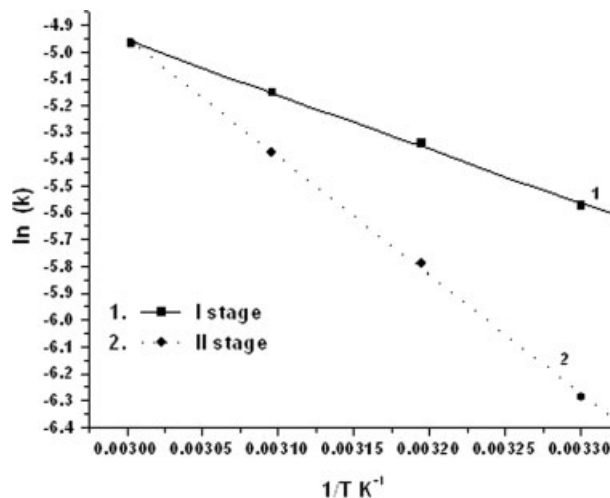


Figure 10 Arrhenius plots for viscosity build up: GAP-TDI system.

TABLE III
Rate Constants for Viscosity Build Up: GAP-TDI System

Temp (°C)	Rate constant (min ⁻¹)		k_1/k_2	Activation energy (kJ mol ⁻¹)	Activation entropy (J mol ⁻¹ K ⁻¹)
	Ist stage (k_1)	IIInd stage (k_2)			
30	3.80 E -03	1.86 E -03	2.04	16.8 (Ist stage)	-244.6 (Ist stage)
40	4.79 E -03	3.06 E -03	1.56		
50	5.79 E -03	4.63 E -03	1.25	36.7 (IIInd stage)	-184.9 (IIInd stage)
60	6.95 E -03	-	1		

The values obtained for activation energy (E_a) and activation enthalpy (ΔH^\ddagger) are in conformity with the trend in the reactivities of the isocyanate compounds with GAP. A negative value for activation entropy indicates that the transition state in the formation mechanism of polyurethane is more orderly than the ground state, while a positive value refers to a less-ordered transition state.

Kinetics of viscosity build up—Determination of rate constants for viscosity build up

The viscosity of the curing mixture increases with time as the curing reaction advances. The viscosity build up during the cure process can be attributed chiefly to two factors: (i) increase in molecular weight as a result of polymer chain growth; (ii) chain branching due to the presence of tri- or higher functional moieties present in the prepolymer or in the additives. In our previous publication,¹² it was shown that the viscosity (η_t) of the curing system (leading to polyurethane network formation) at any given time t , could be related to time in the form of an exponential function as given below:

$$\eta_t = \eta_0 e^{(k_v t)} \quad (6)$$

where, η_0 is the viscosity at $t = 0$ and k_v is the rate constant for viscosity build up. Taking logarithm

$$\ln \eta_t = \ln \eta_0 + k_v t \quad (7)$$

Thus, plotting $\ln \eta_t$ against t should yield a straight line, slope of which is the rate constant for viscosity build up. The rate of viscosity build up is a first-order process on viscosity of the curing mixture. The viscosity build up plots of GAP-TDI is shown in Figure 8. Corresponding semilog plot is depicted in Figure 9.

Figure 10 indicates that the viscosity build up occurs in two stages, the first stage being faster than the second. The stage separation may most probably be due to difference in the reactivities between the two isocyanate groups of TDI. It is well known that of the two isocyanate groups in TDI, NCO group in the ortho position is less reactive than the one in the

para position due to steric hindrance at the ortho position caused by the 1-methyl group.¹³ 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. However, the difference in the reactivities narrows down with increase in temperature as we see that the ratio of rate constants decreases with temperature and there is no stage separation at 60°C, in a way very similar to chemical kinetic parameters mentioned in the earlier sections. Activation energy and activation entropy for viscosity build up process were evaluated using Arrhenius and Eyring equations. The values of kinetic parameters are listed in Table III. Figures 11 and 12 show the Arrhenius and Eyring plots, respectively, for viscosity build up.

Relationship between viscosity build up and cure reaction kinetics

As mentioned earlier, it is always desirable to draw a relationship between chemical kinetic parameters and viscosity of the curing mixture. Such a correlation would help to predict the viscosity of the curing mixture at a given time during the pregel phase. Of

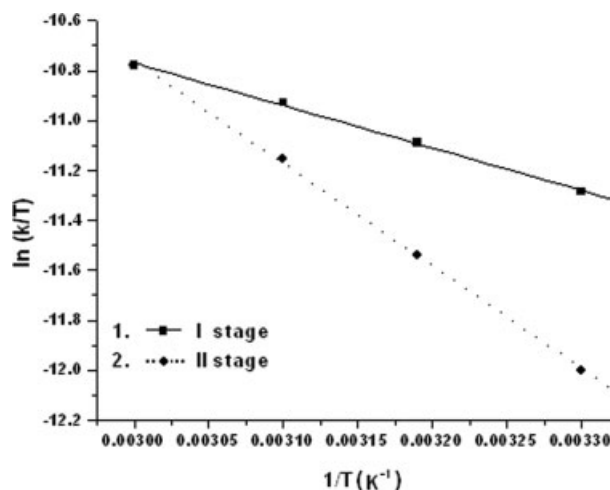


Figure 11 Eyring plots for viscosity build up: GAP-TDI system.

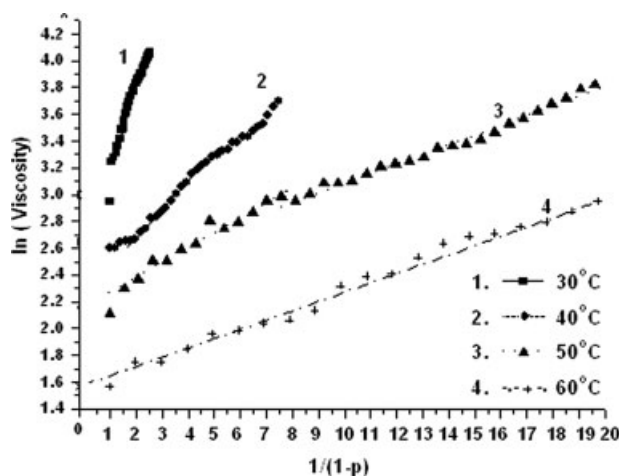


Figure 12 Dependence of viscosity of curing mixture on the extent of reaction.

the many attempts made, the parameters $1/(1-p)$ and $\ln \eta_t$ give rise to linear correlations with fairly good correlation coefficients, where p is extent of reaction between NCO and OH functionals obtainable from rate expressions. The linear plots for all temperatures except 60°C exhibit a well defined digression. The discontinuity in the linear plots is due to difference in the reactivities between the *o*- and *p*-NCO groups of TDI as explained in the previous sections. $1/(1-p)$ versus $\ln \eta_t$ plots for the relationship is depicted in Figure 12.

CONCLUSIONS

Based on the chemical and rheokinetic evaluation studies undertaken on the cure reaction of GAP diol with different diisocyanates namely, TDI, IPDI, and MDI, the following conclusions are arrived at:

The reactivities of the isocyanates used in this study could be arranged in the order: TDI > IPDI \gg MDI. The difference between the reactivities nar-

rowed down with temperature. Both TDI and IPDI exhibited a stage separation in the case of chemical kinetics at 30°C . Similar trend was observed with the viscosity build up for the reaction with TDI. Activation energy parameters also indicated the same trend for the isocyanates.

It has been shown that the chemical kinetic data obtained through FTIR spectroscopy was correlatable with viscosity build up data.

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