Kinetics of Copolyurethane Network Formation

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ABSTRACT: Cure kinetics for the formation of copolyurethane networks of various compositions based on hydroxy-terminated polybutadiene (HTPB), poly(12-hydroxy stearic acid-*co*-TMP) ester polyol (PEP), and different isocyanates has been studied through viscosity build up during the cure reaction. The viscosity (N)−time (t) plots conform to the equation $N = ae^{bt}$, where a and b are empirical constants, dependent on the composition and the nature of the polyols and the isocyanates. The rate constants (k) for viscosity build up, evaluated from the slopes of dN/dt versus N plots at different temperatures, were found to vary significantly from 0.0073 to 0.25 min^{-1}; and the activation energies for gelation were found to be in the range 20 to 40 kJ mol^{-1}. The results have been interpreted in terms of the dependence of the rate constants on structural characteristics of the prepolymers. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1795−1801, 1997

Key words: polyurethanes; HTPB; solid propellants; binders; cure kinetics; pot life

INTRODUCTION

Hydroxy-terminated polybutadiene (HTPB) is a workhorse propellant binder system used in composite propellants and missiles in most of the advanced launch vehicle missions.[1] The urethane network obtained by curing HTPB with a suitable diisocyanate curative provides a matrix for inorganic oxidizer and metallic fuel which are dispersed in the propellant grain. Thorough mixing of the propellant slurry is a necessary process condition to ensure defect-free casting and homogeneity of the mechanical and ballistic properties in the cast propellant grains. During the propellant mixing, the viscosity of the curing slurry increases as a result of the formation of a urethane network. The propellant slurry should have sufficiently long pot life, particularly when large size motors are cast.

Pot life extensions are often accomplished by many methods, which include (1) chemical modification of HTPB, such as transformation of more reactive primary hydroxyl groups to less reactive secondary hydroxyls by reacting HTPB with propylene oxide; (2) reduction of the average functionality by partial acetylation of OH groups in HTPB[2]; (3) use of secondary or tertiary hydroxyls containing diols and triols as chain extenders and crosslinkers; and (4) use of blocked isocyanate compounds as curatives.[3] An alternative approach could be the use of copolyurethanes based on HTPB and a polyol having less reactive hydroxyl groups.

In the present work, copolyurethanes prepared using mixtures of HTPB and poly(12-hydroxy stearic acid-*co*-TMP) ester polyol (PEP) have been studied for their potential to extend the pot life. PEP contains less reactive secondary OH groups in addition to the primary OH groups. Also, the functionality of PEP is lower than that of HTPB. It is therefore expected that copolyurethanes based on HTPB and PEP will have longer pot life than HTPB-based urethane curing systems. However, an understanding of the role of
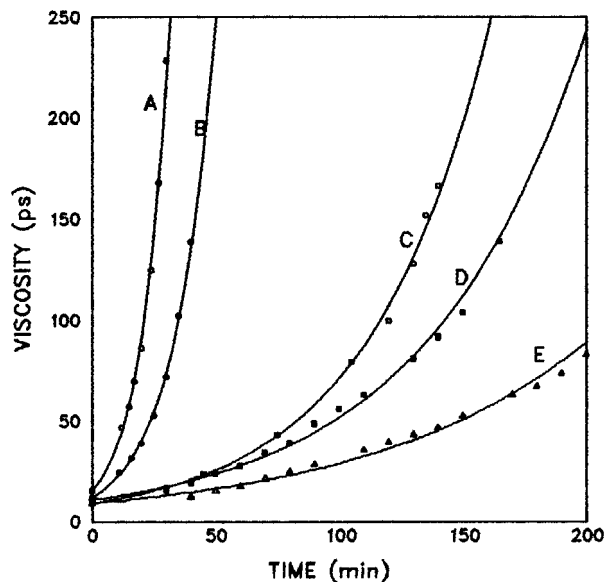
Figure 1 Viscosity build up in the HTPB–PEP–TDI system. Ratios of HTPB to PEP: (A) 80 : 20; (B) 60 : 40; (C) 40 : 60; (D) 20 : 80; (E) 0 : 100.

Figure 3 Viscosity build up in the HTPB–PEP–IPDI system. Ratios of HTPB to PEP: (A) 100 : 0; (B) 80 : 20; (C) 60 : 40; (D) 0 : 100.

the structural factors in quantitative terms that influence the viscosity build up (gelation process) is not only crucial in controlling the pot life but also enables one to predict its value conveniently. A study of the viscosity build up characteristics of copolyurethanes involving HTPB and PEP at various compositions is reported in this article. The rate co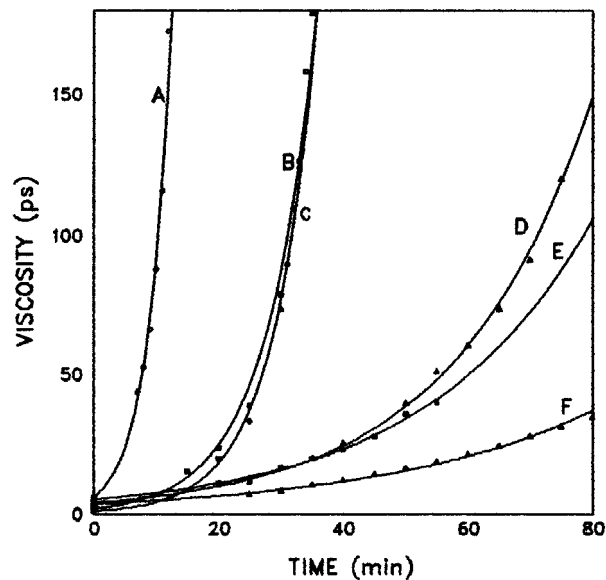nstants for the viscosity build up for various copolyurethane compositions with different isocyanates have been evaluated and correlated with the structural parameters of the prepolymers. The activation energies for gelation have also been calculated for HTPB systems cured with different isocyanates.

Figure 2 Viscosity build up in the HTPB–PEP– HMDI system. Ratios of HTPB to PEP: (A) 100 : 0; (B) 80 : 20; (C) 60 : 40; (D) 40 : 60; (E) 20 : 80; (F) 0 : 100.
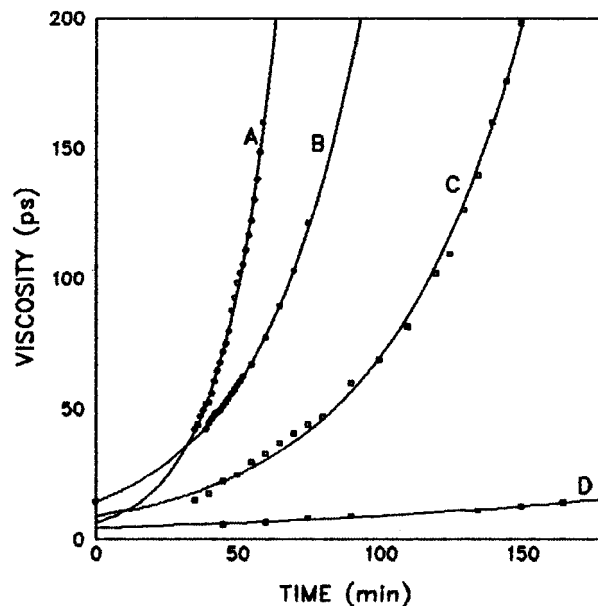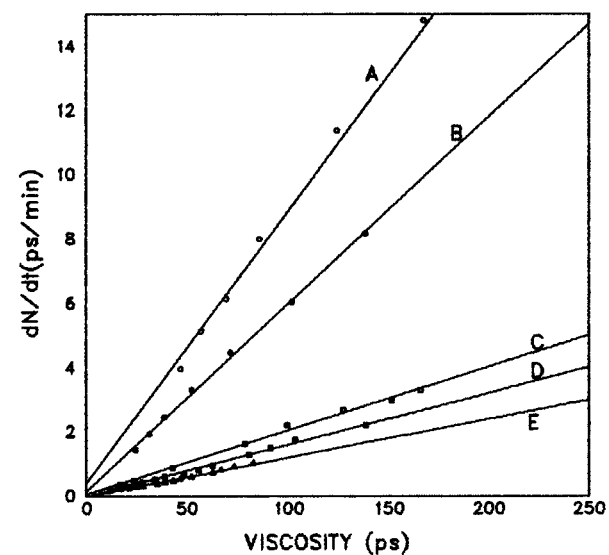

Figure 4 Viscosity versus dN/dt in the HTPB–PEP– TDI system. Ratios of HTPB to PEP: (A) 80 : 20; (B) 60 : 40; (C) 40 : 60; (D) 20 : 80; (E) 0 : 100.
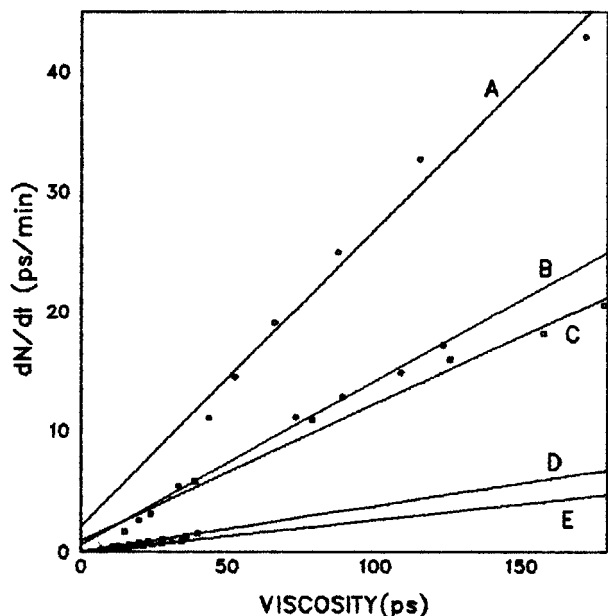
Figure 5 Viscosity versus dN/dt in the HTPB–PEP–HMDI system. Ratios of HTPB to PEP: (A) 100 : 0; (B) 80 : 20; (C) 60 : 40; (D) 40 : 60; (E) 20 : 80; (F) 0 : 100.

EXPERIMENTAL

Materials

Hydroxy-Terminated Polybutadiene

The HTPB prepolymer, HO—(CH$_2$—CH=CH—CH$_2$)$_n$—OH, was prepared in Vikram Sarabhai
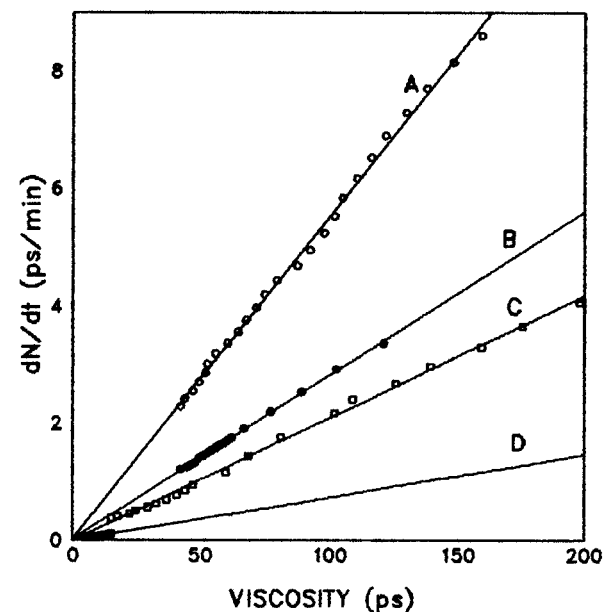

Figure 6 Viscosity versus dN/dt in the HTPB–PEP–IPDI system. Ratios of HTPB to PEP: (A) 100 : 0; (B) 80 : 20; (C) 60 : 40; (D) 0 : 100.

Table I Rate Constants for Viscosity Build Up

Composition HTPB : PEP (Eq. Ratio)	Rate Constants (min^{-1})		
	TDI	HMDI	IPDI
100 : 0	—	0.25	0.055
80 : 20	0.084	0.14	0.028
60 : 40	0.058	0.11	0.021
40 : 60	0.034	0.038	—
20 : 80	0.016	—	—
0 : 100	0.012	0.030	0.0073

Catalyst = DBTDL; r = 1.0; Temp = 70°C.

Space Centre (VSSC) by H$_2$O$_2$-initiated free radical polymerization of butadiene in 2-propanol–H$_2$O solvent system.[4]

Poly(12-hydroxy stearic acid-co-TMP) Ester Polyol

PEP, HO[{CHR—(CH$_2$)$_{10}$—COO}$_x$—{CH$_2$—CR'-(CH$_2$OH)—CH$_2$}]$_n$OH where, R = —(CH$_2$)$_5$CH$_3$ and R' = —CH$_2$CH$_3$, was prepared in two stages. In the first stage, self-condensation of 12-hydroxy stearic acid (THSA) was conducted in the presence of an acid catalyst, followed by copolyesterification with TMP in the second stage, according to the details given elsewhere.[5]

The diisocyanate compounds used in the present study were toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI), and isophorone diisocyanate (IPDI), which were supplied by M/s. A. G. Bayer, Germany and Fluka Co., Switzerland.

Viscosity Measurement

A HBT model Brookfield viscometer was used to measure the viscosity during the cure reaction of the copolyurethanes with various isocyanates. HTPB and PEP taken in various equivalent ratios

Table II Prepolymer Structural Characteristics

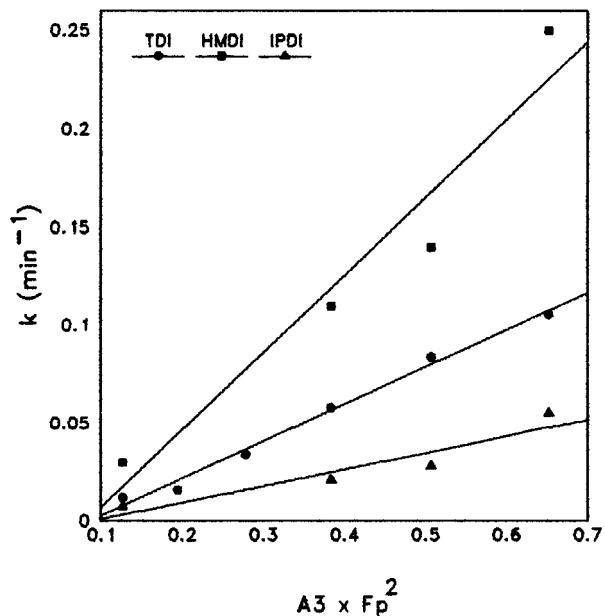| Composition HTPB : PEP (Eq. ratio)	A_3	f_p
100 : 0	0.6529	1.0000
80 : 20	0.6165	0.9078
60 : 40	0.5776	0.8157
40 : 60	0.5355	0.7235
20 : 80	0.4900	0.6314
0 : 100	0.4406	0.5392

Figure 7   Plot of $A_3 \times F_p^2$ versus rate constant for viscosity build up (k).

were thoroughly mixed with calculated amounts of the isocyanate compound, required for a stoichiometric ratio of $r = $ NCO to OH $= 1.0$, and placed in a thermostatically controlled constant temperature bath, maintained at the desired temperature. The reaction was catalyzed by dibutyltindilaurate (DBTDL). The viscosity of the curing mixture was measured at regular intervals of time using Spindle No. 6 in the shear rates range of 29.41 to 1.47 per min.
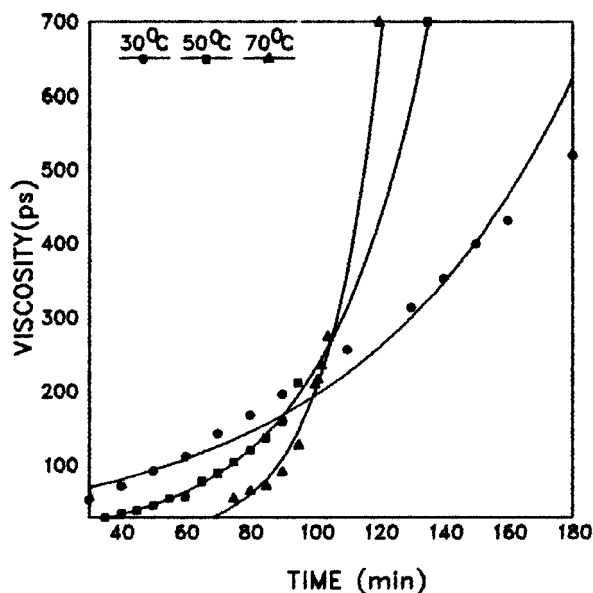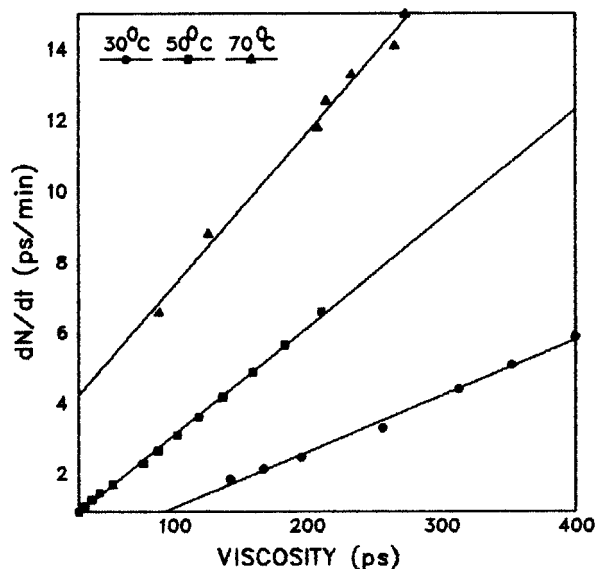

Figure 9   Viscosity versus dN/dt in the HTPB–TDI uncatalyzed system.

RESULTS AND DISCUSSION

Determination of Rate Constants for Viscosity Build Up

The viscosity of the curing copolyurethanes increases as the extent of urethane formation advances with time. This is evident from the viscosity (N)–time (t) plots, shown in Figures 1–3, at 70°C. A mathematical relationship between viscosity and time was obtained by fitting the data, conforming
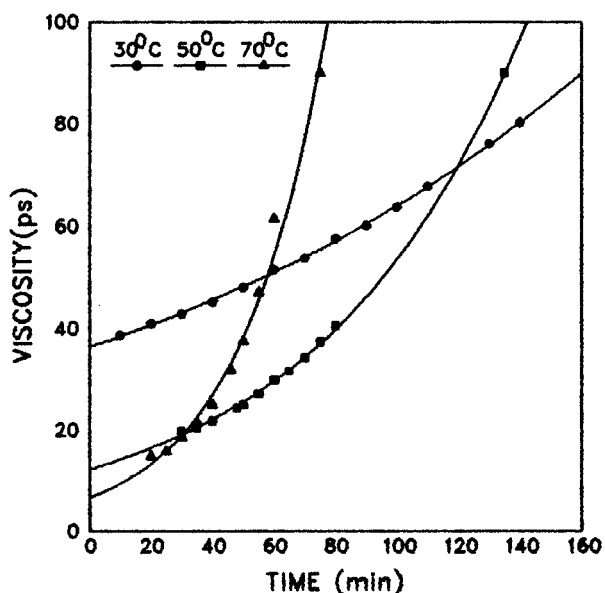

Figure 8   Viscosity build up in the HTPB–TDI uncatalyzed system.

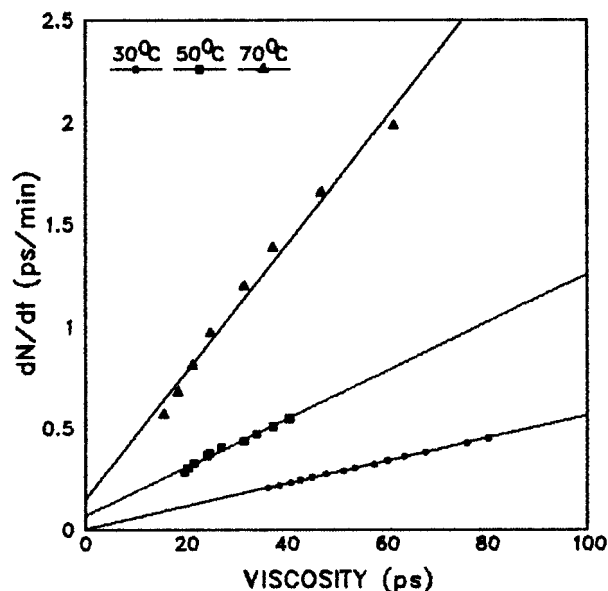**Figure 10**   Viscosity build up in the HTPB–HMDI uncatalyzed system.

Figure 11 Viscosity versus dN/dt in the HTPB–HMDI uncatalyzed system.

to an exponential function. The general form of the relationship is given as $N = ae^{bt}$, where a and b are empirical constants. From the exponential fit equation, the rates of viscosity build up (dN/dt) were computed at various time intervals and are plotted against the corresponding viscosity values, as shown in Figures 4–6. Good linearity of these plots indicate that the viscosity build up is a first-order process, and the slopes of dN/dt versus n plots could be a measure of the rate constants (k) of viscosity build up. A similar procedure has been adopted by Varghese et al.[6] to calculate the rate constants of viscosity build up of HTPB systems. The calculated rate constants for various systems are listed in Table I.

Effect of Copolyurethane Composition on Viscosity Build Up

It is seen from Table I that rate constants for viscosity build up decrease with increase of PEP

content in the copolyurethane compositions. The viscosity build up during the cure should be visualized as a composite effect of functionality distribution and reactivity of the functional groups. The average functionality of PEP ($f_n \approx 1.9$) is significantly lower than that of HTPB ($f_n \approx 2.4$). In addition to this, PEP contains secondary OH groups apart from primary OH groups. The ratio of the primary to secondary hydroxyls were estimated to be 1.17, using ^{29}Si–NMR spectrum of trimethyl silylated PEP and chemical analysis data.[7] The secondary OH groups due to their lower reactivity[8] can cause a significant decrease in the reaction rate. These two effects will jointly result in retardation in the viscosity build up, thereby giving a longer pot life for the formulations containing PEP.

The differential rates of viscosity build up among the various compositions of copolyurethanes can be explained, perhaps quantitatively, on the basis of functionality type distributions and relative content of primary and secondary OH groups. The methods by which the functionality distribution of HTPB and PEP are determined are explained elsewhere.[7,9] The relative amounts of various functionalities present in the prepolymers are as follows. HTPB: di- (d) = 0.4437; tri- (t) = 0.5563. PEP: mono- (m) = 0.2018; di- (d) = 0.4886; tri- (t) = 0.3096. From the functionality distribution data of the prepolymers, the mole fraction of the hydroxyl groups present in the trifunctional components are calculated using the following expression:

$$A_3 = 3t/(m + 2d + 3t)$$

where, m, d, and t denote the relative contents of mono-, di-, and trifunctional moieties present in the various formulations. The fraction of primary hydroxyls (f_p) and A_3 calculated for various copolyurethane compositions are listed in Table II.

Attempts to plot the rate constants against A_3

Table III   Activation Energy for Gelation

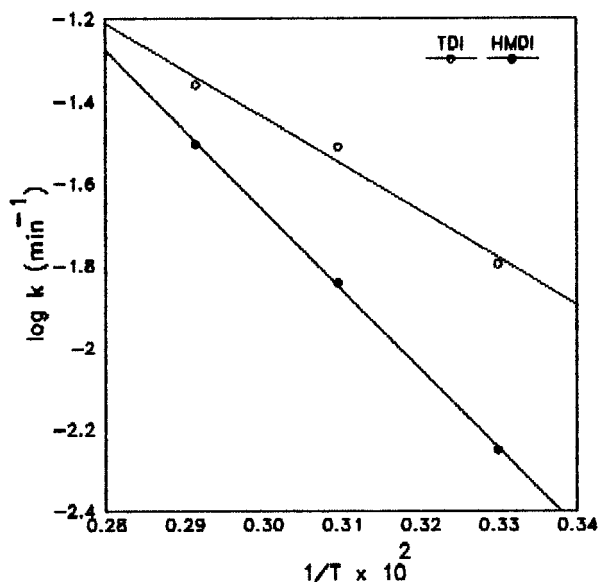| Curative	Temperature (°C)	k (min⁻¹)	Activation Energy (kJ mol⁻¹)
TDI	70	0.044	—
TDI	50	0.031	21.8
TDI	30	0.016	—
HMDI	70	0.031	—
HMDI	50	0.014	37.1
HMDI	30	0.0056	—

HTPB; No catalyst; $r = 1.0$.

Figure 12 Arrhenius plots; $1/T$ versus log k.

and f_p separately did not yield good linear fits, indicating that the rate constants do not depend on either A_3 or f_p alone. It was visualized that since the urethane formation is a second-order reaction (first order each on OH and NCO), the rate constant for viscosity build up (k) may be related to the product $A_3 \times f_p^2$. It was indeed found that the rate constants show good linear correlations with the product $A_3 \times f_p^2$ for various isocyanate curators. (Fig. 7). This confirms that the rate constant for viscosity build up can be correlated to the basic structural parameters of the prepolymers. Furthermore, from the knowledge of functionality distribution and primary hydroxyl content in the prepolymers, one can predict the viscosity of the curing system at any given time and, hence, the pot life.

Effect of Nature of Isocyanate Compound on Viscosity Build Up

Based on the rate constants for viscosity build up (Table I), the reactivity of isocyanates, when catalyzed by DBTDL, can be arranged in the following order: HMDI > TDI > IPDI. This order is rather unexpected since HMDI, being an aliphatic isocyanate, is expected to be less reactive than TDI.[10] However, it was suggested[11] that the hydroxyl compound first forms a complex with the organometallic catalyst (DBTDL), followed by the attack of the isocyanate at the reaction site. According to this mechanism, aliphatic isocyanates, such as HMDI, can react faster since the isocya-

nate groups in HMDI are not sterically hindered; whereas two and six positions in TDI are considerably hindered. On the other hand, in the case of IPDI, because of the bulkiness of IPDI molecule and the secondary nature of one of the isocyanate groups, similar catalytic assistance is not available. Hence, IPDI is found to be less reactive, even in the presence of DBTDL catalyst.

Activation Energy for Gelation of HTPB

In order to evaluate the effect of catalyst in the curing process, viscosity–time measurements were made for curing uncatalyzed HTPB system, with TDI and HMDI as the isocyanate curatives, at 30, 50, and 70°C. (Figs. 8–11). It is evident from the data presented in Table III that the rate constants of uncatalyzed systems are much lower than those obtained when DBTDL is used. It is also to be noticed that in the absence of DBTDL, a reversal of reactivity is seen; TDI is found to be more reactive than HMDI. This confirms the fact that the aliphatic isocyanates are less reactive than TDI. From the Arrhenius plots shown in Figure 12, the activation energies for gelation for the reaction of HTPB with TDI and HMDI are found to be 21.8 and 37.1 kJ mol^{-1}, respectively (Table III). These values compare favorably with the value of 14 to 40 kJ mol^{-1} for the HTPB system reported by Descheres and Pham.[12]

CONCLUSIONS

The following conclusions can be drawn from the above studies.

1. Pot life of HTPB-based polyurethanes can be extended by introduction of PEP, a prepolymer with less reactive secondary hydroxyl groups.
2. The rate constants of viscosity build up can be determined from viscosity–time plots.
3. The order of the reactivity of the isocyanates, used in the present study is HMDI > TDI > IPDI, when catalyzed by DBTDL. However, the reactivity of HMDI is lower than that of TDI, in the absence of a catalyst.

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