

Bulk Polymerization of Hydroxyl Terminated Polybutadiene (HTPB) with Toluene Diisocyanate (TDI): A Kinetics Study Using ^{13}C -NMR Spectroscopy

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SYNOPSIS

The bulk polymerization of hydroxyl-terminated polybutadiene with toluene diisocyanate has been studied in uncatalyzed isothermal reactions. The conversion in urethane was monitored by ^{13}C -NMR spectroscopy of the $\text{C}=\text{O}$ function at level up to 70%. Effects of reagents ratio and temperature were investigated. The experimental data were modeled by a set of two competitive second-order reactions to account for the difference in reactivity of *o*-NCO and *p*-NCO groups of toluene 2,4 diisocyanate. The apparent kinetic constants calculated appeared to be statistically higher than previous results found in literature from work in aromatic solvents. Deviations from second-order law were observed during the last stage of polymerization. Activation energies were estimated at $12.3 \text{ kJ} \cdot \text{mol}^{-1}$ and $42.8 \text{ kJ} \cdot \text{mol}^{-1}$ for the *p*-NCO and *o*-NCO groups, respectively. The difference in their reactivity tended to decrease as temperature of reaction was increased. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The polymerization kinetics of polyfunctional polyols is of interest for a large class of polyurethane formation processes.¹ This was recognized by the early work of Macosko² in reactive injection molding (RIM) applications. Lately, the increased use and diversification of liquid polyether and polyester glycols resins have created a need for the development of more reliable kinetic models. These models could later be included in process numerical simulation and control strategy in order to improve end-products quality.

The rate of urethane formation from the reaction of a hydroxylated polymer with a difunctional isocyanate has been extensively studied in solvent media.^{1,3-6} However, the extremely high viscosity observed when conversion in urethane reaches a significant level brings analytical problems that have

limited the number of systems studied in bulk polymerization state.^{8,9}

Kinetics of urethane formation have already been measured by chemical titration,^{1-3,5,6} adiabatic reaction curves,^{7,8} infrared,⁸ and NMR spectroscopy.⁴ The fast conversion of hydroxyl function to urethane is easier to monitor when an inhibitor is used to stop the reaction. This allows more time to precisely determine the concentration of chemical species in the sample. Because of the polymer viscosity, titration techniques of the unreacted inhibitor are often inapplicable. Instead, NMR spectroscopy should be considered as a technique of choice to directly measure the conversion.

Hydroxyl-terminated polybutadiene (HTPB) is the workhorse of numerous formulations of solid rockets propellants and castable explosives.¹⁰ After polymerization with a suitable curing agent, it gives an elastomer characterized by very good mechanical properties in terms of strength, elongation, and glass transition temperature.^{10,11} Reactivity of HTPB with toluene diisocyanate (TDI) in solvent has been reported by numerous authors under different conditions of temperature, concentration, and catalyst.^{3,5,6} However, kinetics aspects of HTPB-TDI

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Table I Experimental Plan

NCO/O H	Temperatures (°C)		
	30	50	70
0.8	—	—	S
1.0	S	R	S
1.2	—	S	—

S: single run; R: one replicate.

bulk polymerization has been studied only from a viscometric point of view.¹² It is thought that reaction rates may be significantly different in solution than in direct polymerization.

The aim of this article is to present an experimental study of HTPB-TDI bulk polymerization over the usual working range of temperature and reagents ratio. The direct determination of conversion by ¹³C-NMR spectroscopy of the C=O urethane band at 153.8 ppm is also reported as an original technique for this kind of application.

EXPERIMENTAL

Materials

The liquid prepolymer HTPB bought from Arco Chemicals has a nominal molecular weight of 2800

and a hydroxyl equivalent weight evaluated at 40.2 mg KOH/g as determined by FTIR spectroscopy. Humidity content of HTPB was checked before use and was found to be below 300 ppm by mean of a Karl-Fisher titration. An amount of 0.5% w/w of di-terbutyl hydroxy quinone (DTBHQ) was dissolved in the polymer to prevent early oxidation. The tolylene diisocyanate obtained from Kodak Ltd. was a mixture of 97% and 3% of 2,4 and 2,6 isomers, respectively. Diethylamine, from Baker Co., was used as an isocyanate inhibitor. Deuterated chloroform, bought from Aldrich Co. was used to dissolve urethane samples required for ¹³C-NMR spectroscopy.

Polymerization

Bulk polymerizations were carried out in small cylindrical mold (6 cm in dia.) placed into a temperature-controlled oven. Effect of reagents concentration was studied at three levels of NCO/OH ratio (0.8, 1.0, and 1.2). Reaction rate measurements were taken at three temperatures according to the experimental plan detailed in Table I.

Conversion Determination by NMR Spectroscopy

The ¹³C-NMR spectra were acquired at 50.3 MHz in CDCl₃ on a Bruker WP-200 spectrometer

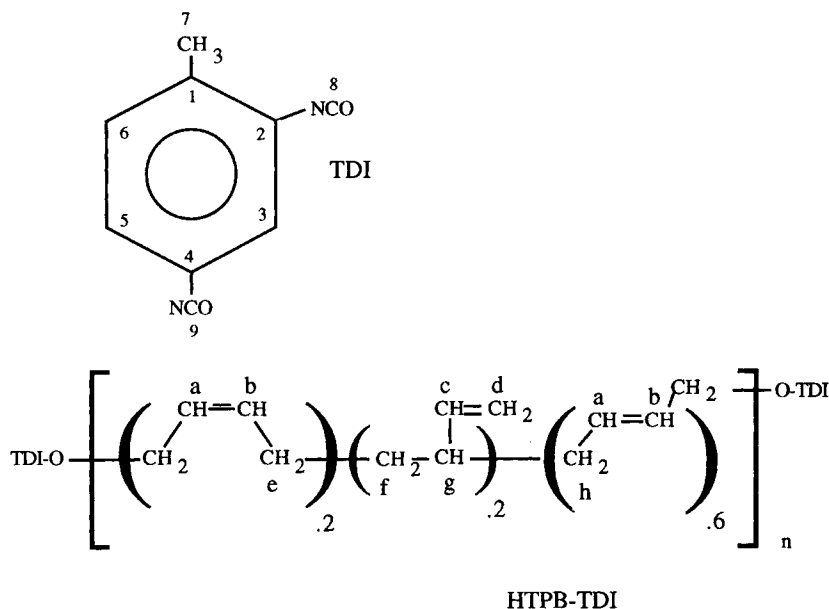


Figure 1 HTPB-TDI and TDI structures TDI: δ (ppm): 133.4 (C-2); 132.3 (C-4); 131.6 (C-6); 130.8 (C-1); 125.2 (C-8,9-NCO); 122.4 (C-5); 121.1 (C-3), 17.8 (C-7, CH₃) HTPB-TDI: δ (ppm): 153.8 (C=O; urethane), 143.0 (c; 1,2-butadiene), 132.2–127.8 (a,b; 1,4-butadiene); 114.7 (d; 1,2-butadiene), 43.9–25.3 (e,f,g,h; butadiene CH₂ and CH), 137.2–122.4, 17.9 (C1–C7; TDI).

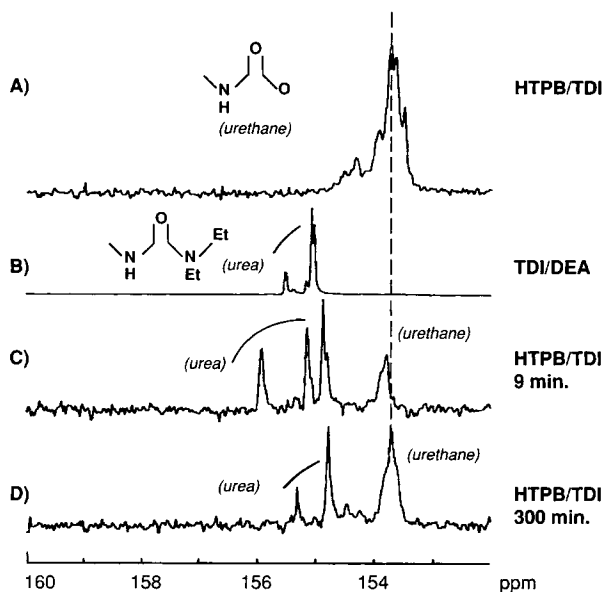


Figure 2 ^{13}C -NMR spectra of $\text{C}=\text{O}$ region in HTPB/TDI polymerization.

equipped with a 10 mm probe. An amount of 2 g of polymer was dissolved in 3 g of CDCl_3 solvent to give a homogeneous solution. The reliable ^{13}C integrations of the urethane conversions were made possible by using the inverse gate decoupling technique¹³ with a 40° pulse and a 10 s delay (de-

coupler off). Longer relaxing delays from 10–90 s were also tried but they gave insignificant changes on the conversion values. For each sample, a good signal to noise ratio was obtained after 2500–5000 scans over a period of 7–14 h. A simple Fourier transform was applied without any resolution or signal to noise enhancement methods.

^{13}C assignment of TDI was made possible from the empirical substituent chemical shift effects on tolylene.¹⁴ In addition, the attribution of the peaks was reinforced by using the ^{13}C coupled NMR spectra. Hence, various J_{CH} ($^1J_{\text{CH}}$, $^2J_{\text{ortho}}$, $^3J_{\text{meta}}$, $^2J_{\text{C-methyl}}$, $^3J_{\text{C-methyl}}$) gave typical multiplicity in agreement with documented coupling parameters.¹⁴ Assignment of HTPB–TDI signals was based on published results for HTPB–MDI polymerization.¹⁵ Chemical shifts of pure TDI and cure HTPB are detailed in Figure 1.

RESULTS AND DISCUSSION

As a first approach, the bulk polymerization kinetics was carried out on HTPB/TDI reaction ($\text{NCO}/\text{OH} = 1$) at 50°C for a hydroxyl conversion of about 50%. A sample was then analyzed by ^{13}C -NMR spectroscopy. The resulting $\text{C}=\text{O}$ urethane region is shown in Figure 2(a). The multiplicity and broad-

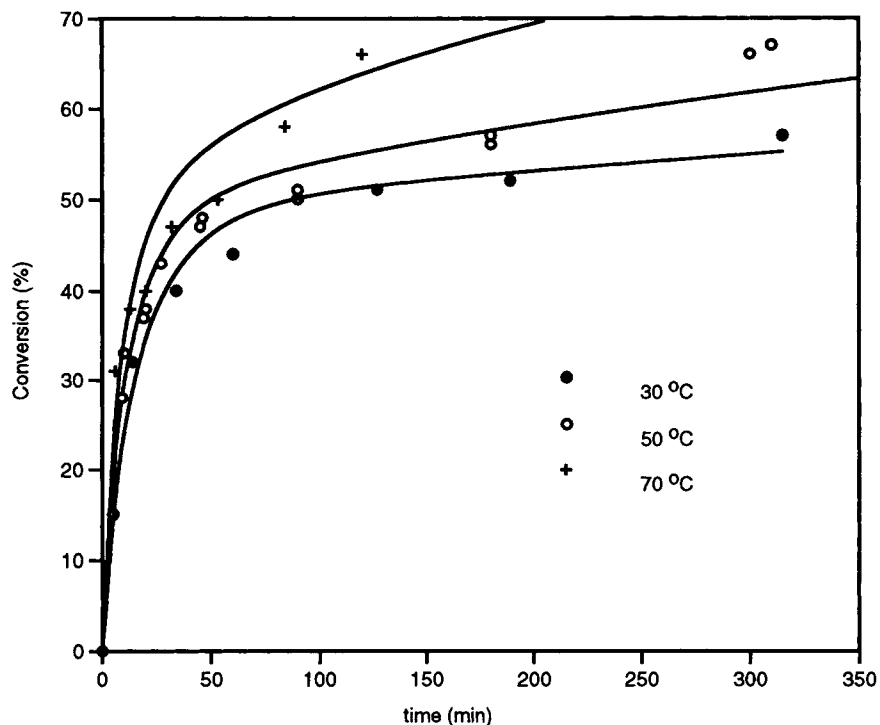


Figure 3 Conversion vs. time curves for $\text{NCO}/\text{OH} = 1.0$.

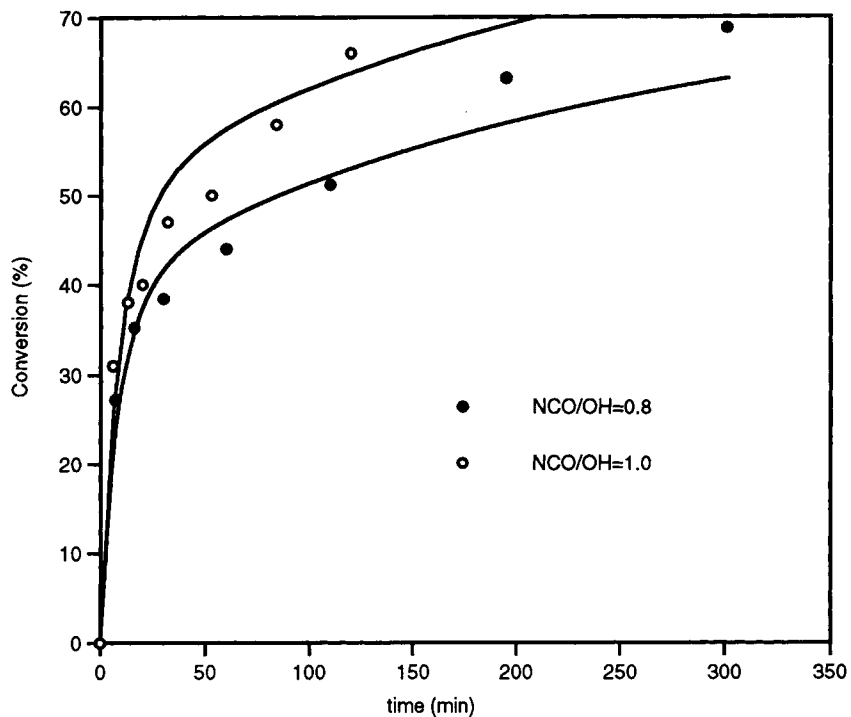


Figure 4 Conversion vs. time curves at 50°C for two reagents ratio.

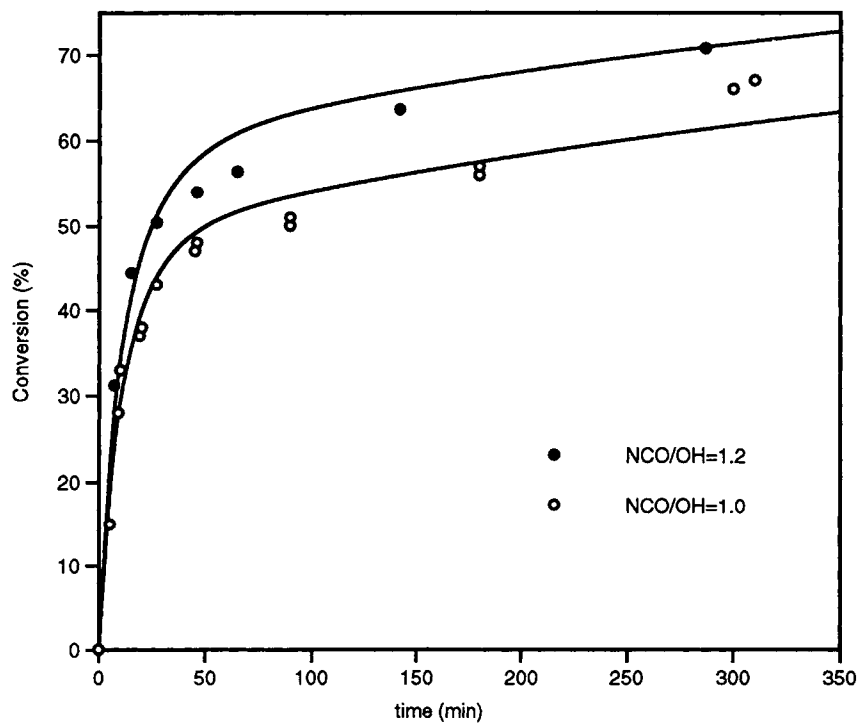


Figure 5 Conversion vs. time curves at 70°C for two reagents ratio.

Table II Second-Order Rates Constants

T (K)	k_o (L mol ⁻¹ min ⁻¹)	k_p (L mol ⁻¹ min ⁻¹)	k_p/k_o
303.15	0.0014	0.124	88
323.15	0.0035	0.142	50
343.15	0.0102	0.221	22

ening of the signal centered at 153.8 ppm is a result of the reduced mobility of various urethane fractions in the polymer chain. Other experiments at lower conversions indicated that the reaction progress at room temperature during spectrum acquisition could not be neglected. Consequently, diethyl amine (DEA) was used as an isocyanate inhibitor. ¹³C spectrum of TDI inhibited with DEA is plotted in Figure 2(b) and shows narrow signals from various urea functions (2,4 and 2,6 *cis*- and *trans*-isomers). The efficiency of this inhibitor toward isocyanate has been verified from an experiment consisting of the addition of TDI to a mixture of DEA inhibitor and HTPB at 50°C. Resulting ¹³C-NMR spectra confirmed that DEA-TDI reaction was fast enough to avoid urethane formation. As typical examples, Figures 2(c) and (d) show the ¹³C of HTPB/TDI reaction stopped by DEA inhibitor after 9 min and 300 min, respectively. The conversion was then eas-

ily determined from the relative intensity of urethane (153.8–154.5 ppm) and urea inhibitor (154.6–156.2 ppm).

Polymerization data measured by NMR were gathered as conversion vs. time curves where total conversion (X) is defined as:

$$X = 100 \times \left(1 - \frac{[OH]}{[OH]^0} \right) \quad (1)$$

in which $[OH]^0$ and $[OH]$ are the initial and transient hydroxyl concentrations.

The effect of temperature on conversion is presented in Figure 3, while the effect of $[NCO]/[OH]$ ratio is studied in Figures 4 and 5. Each curve is characterized by an initial fast increase of the conversion followed by a considerably slower region of reaction rate. This accounts for the fact that *p*-NCO group is significantly more reactive than *o*-NCO.

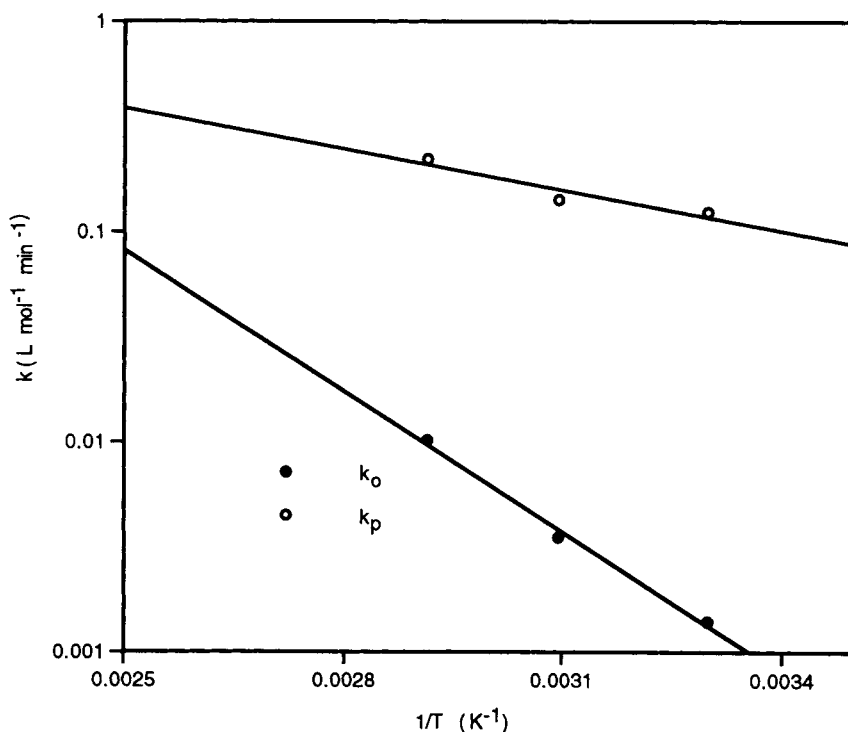
**Figure 6** Temperature dependence of second-order rate constants.

Table III Reaction Rates Constants as Reported in Literature and Recalculated for Competitive Second-Order Reactions

Solvent	T (K)	Consecutive Model			Competitive Model			Ref #
		k_o (L mol ⁻¹ min ⁻¹)	k_p (L mol ⁻¹ min ⁻¹)	k_p/k_o	k_o (L mol ⁻¹ min ⁻¹)	k_p (L mol ⁻¹ min ⁻¹)	k_p/k_o	
Tolylene	303.15	0.0033	0.014	4.1	—	—	—	3
	313.15	0.0100	0.018	1.8	0.0018	0.0545	30	
	323.15	0.0170	0.026	1.6	0.0045	0.0800	18	
	328.15	0.0230	0.033	1.4	0.0093	0.0853	9	
Tolylene	303.15	0.0042	0.012	3.0	0.0021	0.0463	22	6
	313.15	0.0072	0.017	2.4	0.0042	0.0498	12	
	323.15	0.0120	0.026	2.2	0.0076	0.0780	10	
	333.15	0.0230	0.038	1.7	0.0098	0.1320	13	
Nitrobenzene	303.15	0.0032	0.008	2.4	0.0009	0.0239	27	5
	313.15	0.0045	0.011	2.3	0.0022	0.0313	14	
	323.15	0.0075	0.015	1.9	0.0043	0.0429	10	
	333.15	0.0110	0.019	1.8	0.0058	0.0576	10	

This difference in reactivity has already been observed in TDI-based urethane bulk polymerization studies⁸ and for HTPB-TDI reaction in aromatic solvent.⁴⁻⁷

The particular reactivity of each isocyanate group in TDI makes the apparent kinetics modeling more complicated. A common strategy found in recent literature consists of considering the reactive system as a set of two consecutive reactions.^{3,5,6} Each of them is assumed to comply, with specific rate constants (k), to the same second-order kinetics law where conversion with time (t) is expressed as:

$$\frac{X}{(1-X)} = [\text{OH}]^0 kt \quad (2)$$

Unfortunately, with this procedure, it is assumed that while the conversion of *p*-NCO group proceeds, no reaction occurs at the *ortho* site. Moreover, the discontinuity in the second-order plot must be estimated graphically in order to evaluate the rate constants.

A more rigorous approach to the problem is to consider a set of two simultaneous, competitive reactions. This has already been recognized by the work of Williams⁸ on polymerization of Voranol[®] with TDI. Using this strategy, the total rate of conversion is function of *o*-NCO conversion (X_o) and *p*-NCO conversion (X_p) as showed by eq. (3).

$$\frac{dX}{dt} = \frac{[o\text{NCO}]^0}{[\text{OH}]^0} \frac{dX_o}{dt} + \frac{[p\text{NCO}]^0}{[\text{OH}]^0} \frac{dX_p}{dt} \quad (3)$$

The rate of conversion for each reactive group is then expressed by a second-order reaction of hydroxyl and the corresponding NCO concentrations. When conversions replace the respective concentration functions, eqs. (4) and (5) are obtained.

$$\frac{dX_o}{dt} = [\text{OH}]^0 k_o (1 - X_o)(1 - X) \quad (4)$$

$$\frac{dX_p}{dt} = [\text{OH}]^0 k_p (1 - X_p)(1 - X) \quad (5)$$

Table IV Apparent Activation Energies as Reported in Literature and Recalculated for Competitive Second-Order Reactions

Solvent	Consecutive Model		Competitive Model		Ref #
	Ea_{ortho} (kJ/mol)	Ea_{para} (kJ/mol)	Ea_{ortho} (kJ/mol)	Ea_{para} (kJ/mol)	
Tolylene	62.8	28.1	91.0	26.6	3
Tolylene	47.0	32.6	44.0	29.9	6
Nitrobenzene	35.3	24.4	109.1	24.8	5
Bulk	—	—	42.8	12.3	—

The latter model has been retained to plot curves in Figures 3, 4, and 5. The set of differential equations was integrated using a fourth-order Runge-Kutta algorithm where the step in time was proportionally scaled to the inverse of the conversion function first derivative. This produced a smoother integration for the steep part of the curve while limiting the computational effort required. Minimization of the sum of squared errors was the criteria to best estimate the respective second-rate constants by a surface response methodology.¹⁶ The apparent reaction rate constants for *o*-NCO and *p*-NCO groups (k_o , k_p) are reported in Table II.

Statistical analysis of the regression model shows a F_o significance at the 95% level for each isothermal set of data in bulk polymerization experiments. The lack of fit to the second order model is greater above 50% in conversion. Indeed, when statistical weight of data points collected during the initial stage of polymerization is doubled, the overall variance is decreased. Pham⁴ has already suggested that third-order models would be more appropriate to urethane chemistry. However, a limited data analysis for a third-order fit showed an increase in the model contribution to the sum of squared errors because of the additional rate constant that must be estimated. Physically, the observed deviations could also be attributed to tremendous changes in molecular mobility as the reactions progressed toward a higher level of conversion.

Figure 6 shows the temperature dependence of kinetics constants. A possible lack of agreement with the Arrhenius law may be suggested by the slight curvature in the points for each reactive groups. This may indicate a temperature compensation effect in the frequency factor [$A(T)$] that could be expressed in the form of:

$$k = A(T)e^{(E_a / RT)} \quad (6)$$

Unfortunately, the limited number of temperatures available did not allow a statistically significant estimation of the temperature dependence of the frequency factor. Hence, the data were simply fitted to Arrhenius law and the activation energies (E_a) were estimated at respectively 12.3 kJ·mol⁻¹ and 42.8 kJ mol⁻¹ for the *p*-NCO and *o*-NCO groups. Thus, the difference in their reactivity tends to diminish as temperature of reaction is increased. This indicates that the hindrance effect of the methyl group on the *o*-NCO site becomes less important at higher temperature. The reactivity ratio for bulk polymerization are in agreement with data found in literature.⁸

Literature data of polymerizations carried out in aromatic solvents^{3,5,6} were recalculated with the competitive kinetics model. Estimated kinetics constants are summarized in Table III, while activation energies are presented in Table IV. When compared with the consecutive set of reactions approach previously reported,^{3,5,6} lower values of k_o and higher values of k_p were found. This was expected, considering that in the consecutive model, k_p is estimated from the cumulative effect of the reaction of the ortho and para groups.

Effects of polymerization on the rate of urethane formation medium were observed. By using a Student's statistical comparison test, we found a relative reactivity summarized by bulk > tolylene > nitrobenzene at a minimum confidence level of 90%. The increased reactivity is mostly attributed to the *p*-NCO reaction. Rate constants for the *o*-NCO reactive site appear to be similar to those reported for polymerization in solvent, probably because the conversion of this group occurs at a stage where the molecular weight and the viscosity of the polymer have already grown. The important variability in activation energies calculated refrains from establishing a reliable correlation with the reaction medium. However, the ratio $E_{a_{ortho}}/E_{a_{para}}$ remains about the same for each set of data.

CONCLUSIONS

Kinetics study of polyurethane elastomer formation requires either an in-site analytical method or an external technique with a proper mean to stop the polymerization after sample removal. Even though direct nonperturbing measurement methods should be favored, their application are often limited in bulk reactions. ¹³C-NMR spectroscopy proved to be a highly practical way to monitor polymerization progress even with high molecular weight prepolymer.

Although apparent kinetics do not give any insights on molecular reaction mechanisms, they are useful for modeling purposes. Because the diisocyanate reactivity is affected by the medium of polymerization, kinetics studies for accurate process simulation should always be carried out in bulk to ensure reliable data.

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