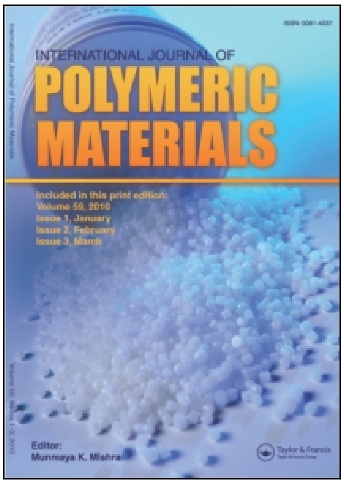

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Kinetics of Reaction of Castor Oil Trimethylol Propane Polyol and 4,4' Diphenyl Methane Diisocyanate

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Kinetics of Reaction of Castor Oil Trimethylol Propane Polyol and 4,4′ Diphenyl Methane Diisocyanate

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The kinetics of the uncatalyzed reaction of diphenyl methane diisocyanate and castor oil (CO)/trimethylol propane (TMP) polyol, with xylene as solvent at different temperatures, solvent concentration and NCO/OH ratios were investigated. The polyol was synthesized from castor oil and trimethylol propane (2-ethyl-2-(hydroxymethyl)-1,3-propanediol) with equivalent ratio of 1:3 via transesterification mechanism. Polyol was then characterized using FTIR spectroscopy and liquid chromatography mass spectroscopy (LCMS) under atmospheric pressure chemical ionization mode. All the reactions obeyed second order kinetics. Enthalpy changes, activation energies and entropies of activation were also calculated. Kinetic data from these reactions will facilitate modeling of these reactions in a batch reactor.

Keywords: castor oil, kinetics, MALDI MS, polyol, polyurethane, propane, trimethylol

INTRODUCTION

Polyurethanes are a class of very useful and versatile materials, widely used due to their good flexibility and elasticity. There is a growing worldwide interest in the development of vegetable oil-based polyurethanes. This interest is economical since vegetable oils are relatively inexpensive and are renewable resources [1–4]. In addition, due to the hydrophobic nature of triglycerides, vegetable oils produce polyurethanes, which have excellent chemical and physical properties such as enhanced hydrolytic and thermal stability.

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Among all these oils, castor oil is the most popular because of its three reactive hydroxyl groups, ester groups and double bonds [1,5–15]. The unique feature of castor oil is that it contains a considerable amount of hydroxylated triacylglycerols, which are important starting materials in oil and polymer chemistry. The hydroxyl groups are important from the polyurethane viewpoint, where esterification can play an important role in establishing the structure-property relationship [16]. The disadvantages of castor oil include: low hydroxyl number leading to low modulus material sluggish rate of curing of secondary hydroxyl groups [9], and structural irregularity due to steric hindrances offered by the long pendant fatty acid chains during polyurethane formation, resulting in low tear strength [17]. To offset these disadvantages, castor oil is either mixed with other polymers to form interpenetrating networks [18–21] or transesterified or alcoholyzed with polyhydroxy alcohols, most commonly by glycerol and trimethylol propane [22–24]. Although a lot of work has been done on castor oil-based polyurethane, little work has been reported on castor oil/trimethylol propane transesterified products and their use for polyurethane production. Transesterification leads to increased hydroxyl value of the system, thereby leading towards hardness of the product, while long-chain fatty acids induce flexibility in the product. Thus the polymer formed is relatively tough.

In this study, polyol has been prepared using dehydrated castor oil and trimethylol propane via alcoholysis at elevated temperature. The polyol prepared was reacted with 4,4′ di-phenylmethane diisocyanate (MDI) at different temperatures, i.e., 30, 25, 20, and 15°C, and for three solvent concentrations, with NCO/OH ratios of 0.75, 1.0 and 1.25. The basic aim was to establish kinetic data and Arrhenius constants which can be further used to model the system.

These oil-based polyols find applications in potting compounds, encapsulation, varnishes, polyurethane foams and IPN-based crosslinked polymers. Castor oil and its polyols have been used in polyurethane coatings, foams, and adhesives for a long time.

EXPERIMENTAL

Materials

Castor oil of commercial grade was purchased from Qualikems, India. It was dehydrated at 105°C in nitrogen atmosphere and was characterized for hydroxyl value (148), acid value (2) and moisture content (0.379%). Trimethylol propane (Aldrich, Germany) was used as such and had a hydroxyl value of 1255.98. Pyridine (Qualigens), dibutyl amine (E-Merck), diphenyl methane diisocyanate (BASF, Korea) isocyanate value 28.8% xylene (E-Merck), and toluene (Qualigens) were used as such.

Polyurethane Synthesis

Transesterification of Castor Oil

Polyol was synthesized from castor oil by reaction with trimethylol propane in ratio of 1:3 in nitrogen atmosphere with the catalyst litharge (0.1%). The reaction was carried out for approximately 3 h in a 1-liter stainless steel jacketed reactor connected to constant temperature bath/circulator (model-F-20VC/3, VC-5 and SC-12HT/10) through solenoid valve and electronic relay supplied by Julabo Instruments, Germany. The reaction temperature was 210 ± 0.1°C and the completion of the reaction was checked by dissolving samples in ethanol.

Characterization of Polyol Using FTIR

FTIR was carried out with a Perkin Elmer FTIR spectrometer at a spectral resolution of 4 cm^{-1} with 20 scans using KBr pellets. A thin layer was applied on each KBr pellet and spectrum was taken.

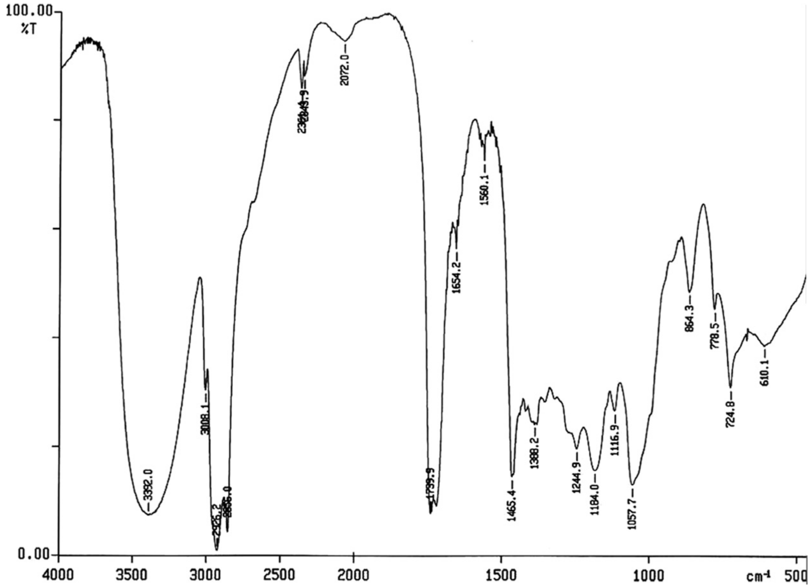

FIGURE 1 FTIR of castor oil/trimethylol propane polyol.

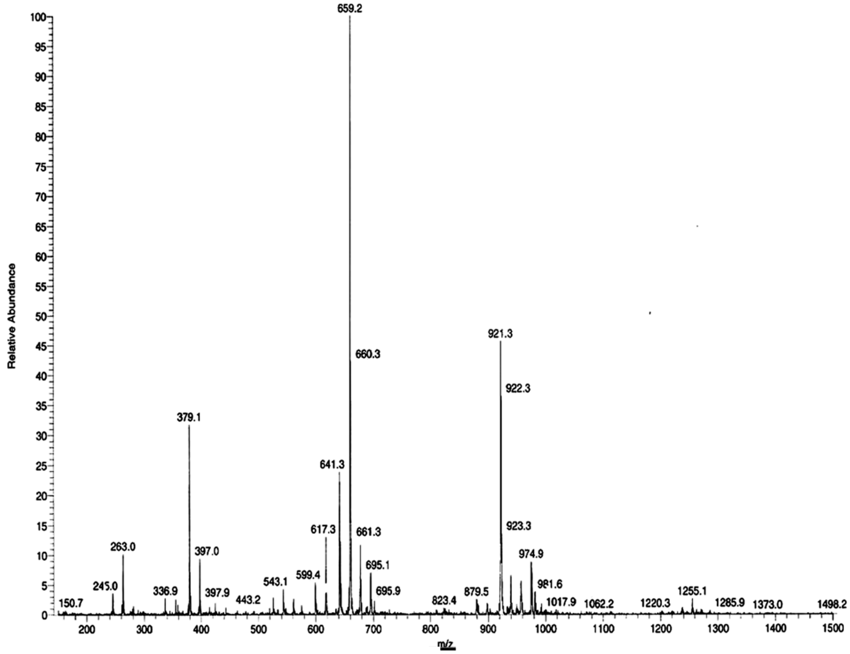

FIGURE 2 Liquid chromatographic mass spectrograph of the castor oil/TMP polyol for the range 150–1500 m/z.

Characterization of Polyol Using LCMS

Polyol prepared from CO/TMP was analyzed using LCMS. LCMS was carried out in a Thermo Quest, Fannigan MAT LCQ model mass spectrometer. Samples were dissolved in methanol (HPLC grade) followed by filtration through a 0.45 μm Millipore filter and were analyzed using APCI mode (atmospheric pressure chemical ionization) in positive mode by direct infusion without column. X-Caliber software was used and spectrum was taken in the range of 150–2000 m/z ratio.

Kinetic Study of Polymerization Reactions

The polyol prepared was reacted with MDI in a three-necked round-bottom flask having the provision for nitrogen flushing. Polyol and xylene were taken in the flask and kept in a constant temperature bath with continuous stirring. After proper mixing has taken place, a calculated quantity of MDI was introduced into the flask so as to maintain a particular NCO/OH ratio. The progress of all the reactions was followed by measuring the amount of free isocyanate left

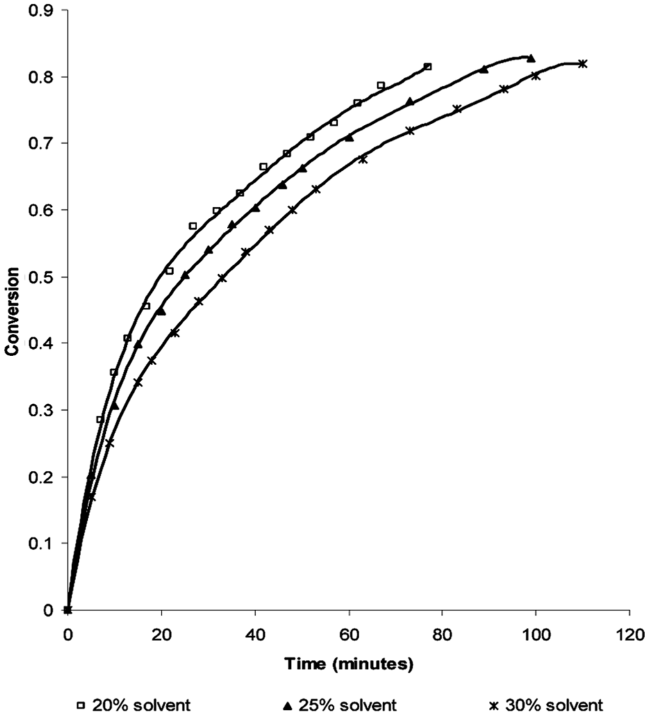

FIGURE 3 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 0.75 and temperature 30°C.

behind in the system using the Stagg method [25]. Identical experiments were conducted at varying temperatures of 30, 25, and 20°C with 20, 25 and 30% solvent concentration at NCO/OH ratios of 0.75, 1.0 and 1.25.

RESULTS AND DISCUSSION

Results of FTIR and LCMS for Polyol Characterization

Figure 1 shows the infrared spectrum of CO/TMP polyol in the range 4000–400 cm^{-1} plotted on an absolute scale. The broad peak appearing at 3392 cm^{-1} represents the free hydroxyl groups [17,26]. The band observed at 2926.2 cm^{-1} is due to the –CH stretching and the peak for the carbonyl group (C=O) appears at 1739.9 cm^{-1}. During the reaction of polyol for polyurethane formation, free hydroxyl groups in the polyol react with isocyanate groups in diphenyl methane diisocyanate,

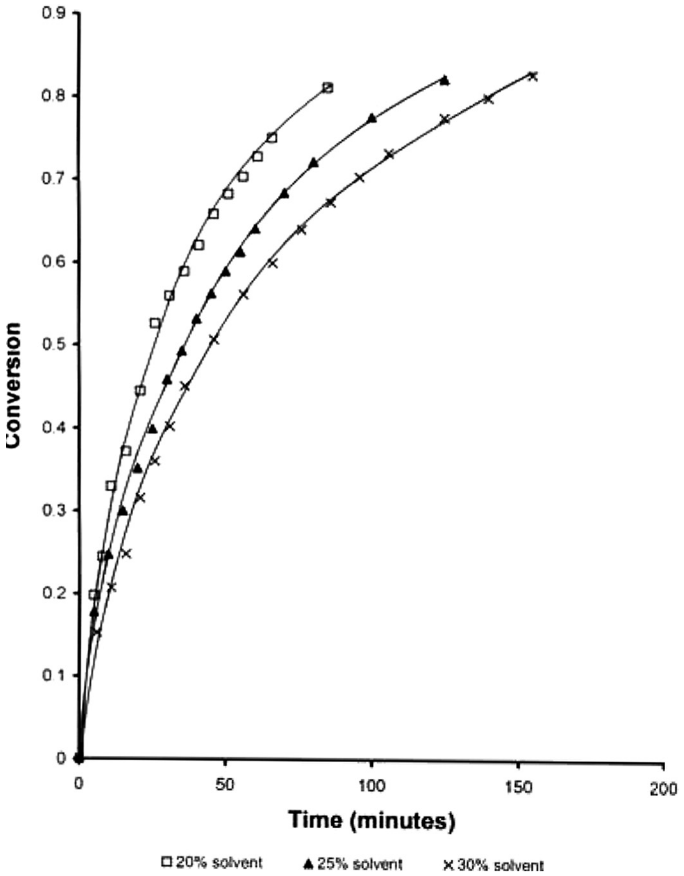

FIGURE 4 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 0.75 and temperature 25°C.

and hence there is a decrease in intensity of the −OH stretching peak, while the intensity of −CH peak remains constant [27–30]. The FTIR of the polyol also showed a peak at 1057 cm^{-1}, which is characteristic of secondary hydroxyl group. The stretching peak for C−O appears at 1184cm^{-1}.

Figure 2 shows the APCI mass spectra of CO/TMP polyol for the range 150–1500 m/z. There are three high intensity peaks, at m/z 379.1 corresponding to monoricinoleate of TMP after removal of two molecules; at m/z 659.2 referring to diricinoleate of TMP after removal of two water molecules; and m/z 921.3 representing

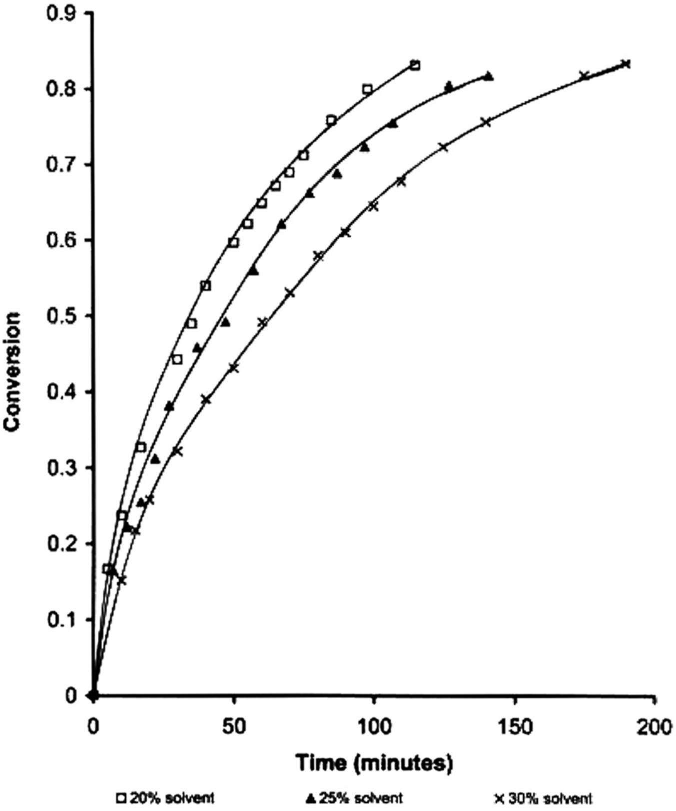

FIGURE 5 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 0.75 and temperature 20°C.

triricinoleate of TMP after removal of three water molecules. Medium intensity peaks at m/z 695.1 and m/z 974.9 represent intact molecules of diricinoleate and triricinoleate of TMP, respectively. Very low intensity peak at m/z 981.6 may be due to the removal of one water molecule from triricinoleate of TMP and association of one Na^+ ion. Medium intensity peak at m/z 641.3 refers to diricinoleate of TMP after removal of three water molecules and m/z 397.0 belong to monoricinoleate of TMP after removal of one water molecule. The actual molecular weight is one less than the peak value of di- and triricinoleate of TMP; this may be due to the addition of H^+ during ionization of the sample. Medium intensity peak at m/z 617.3 refers to diricinoleate of glycerol after removal of one

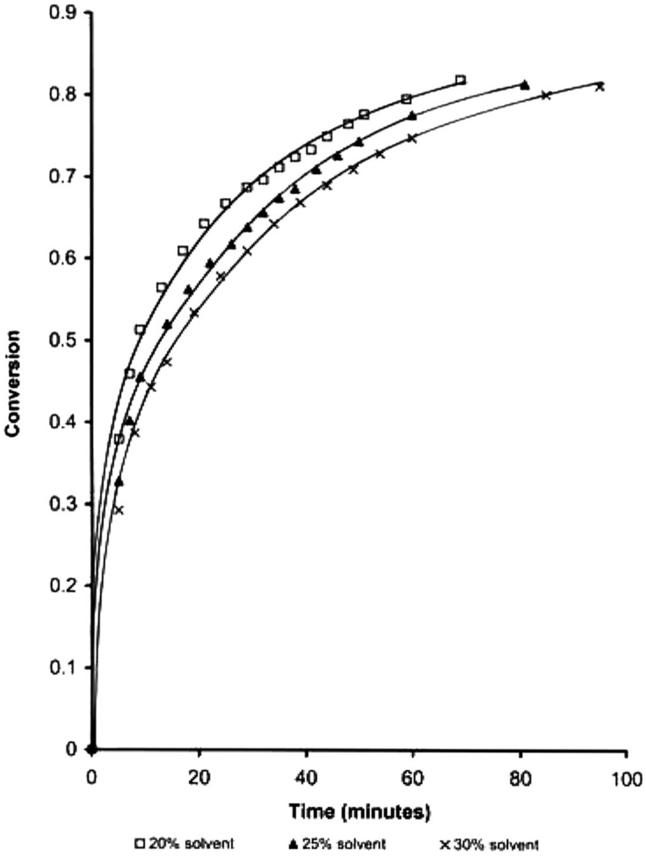

FIGURE 6 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 1.0 and temperature 30°C.

water molecule, and low intensity peak at m/z 879.5 [31] refers to triricinoleate of glycerol after removal of three water molecules.

Results of Bulk Polyurethane Polymerization Reactions Under Isothermal Conditions in the Reactor

All the bulk polymerization reactions carried out in the reactor were carried out at three different temperatures (20, 25 and 30°C). Assuming that all the bulk polymerization reactions follow a second order kinetics [32–36], rate equation for different NCO/OH ratios are given below in Eqs. (1–3).

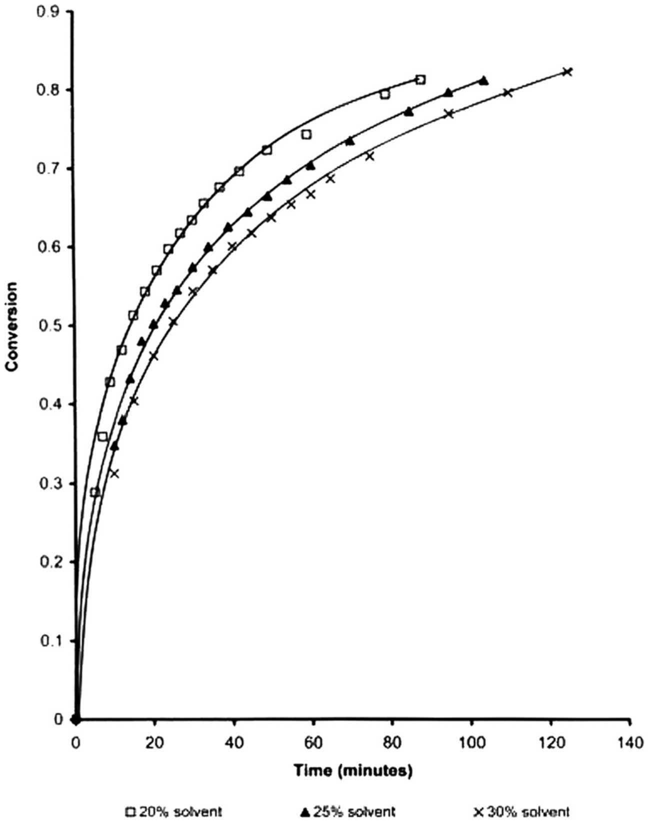

FIGURE 7 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 1.0 and temperature 25°C.

Second Order Rate Constants have been Calculated Using the Expressions:

Case I, where NCO/OH ratio is 0.75, $M = C_{Bo}/C_{Ao} = 1.25$

$$\ln\frac{(M - p_A)}{M(1 - p_A)} = (C_{B_o} - C_{A_o})kt \qquad \text{For } M \neq 1 \quad \text{and} \quad M > 1 \tag{1}$$

A plot of L.H.S. vs t has a slope $(C_{Bo} - C_{Ao})$ k.

Case II, where NCO/OH ratio is 1, $M = C_{Bo}/\ C_{Ao} = 1$

$$\frac{1}{1 - p_A} = C_{A_o}k\ t \qquad \text{For} \quad M = 1 \tag{2}$$

A plot of L.H.S. vs t has a slope C_{Ao} k.

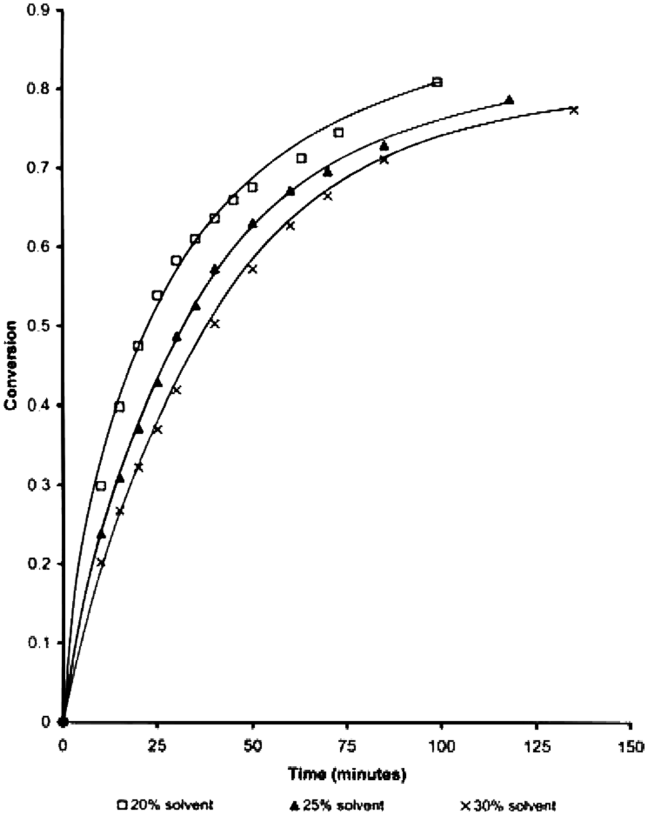

FIGURE 8 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 1.0 and temperature 20°C.

Case III, where NCO/OH ratio is 1.25, $M = C_{Ao}/C_{Bo} = 1.25$

$$\ln\frac{(1-p_A)}{(1-Mp_A)} = (C_{A_o} - C_{B_o})k\ t \qquad \text{For} \quad M = 1.25 \tag{3}$$

A plot of L.H.S. vs t has a slope $(C_{Ao} - C_{Bo})$ k.

where,
C_{Ao} = Initial concentration of isocyanate functional groups
C_{Bo} = Initial concentration of hydroxyl functional groups
p_A = conversion of isocyanate groups at time t
p_B = conversion of hydroxyl functional groups at time t
M = Ratio of initial concentration of reactants

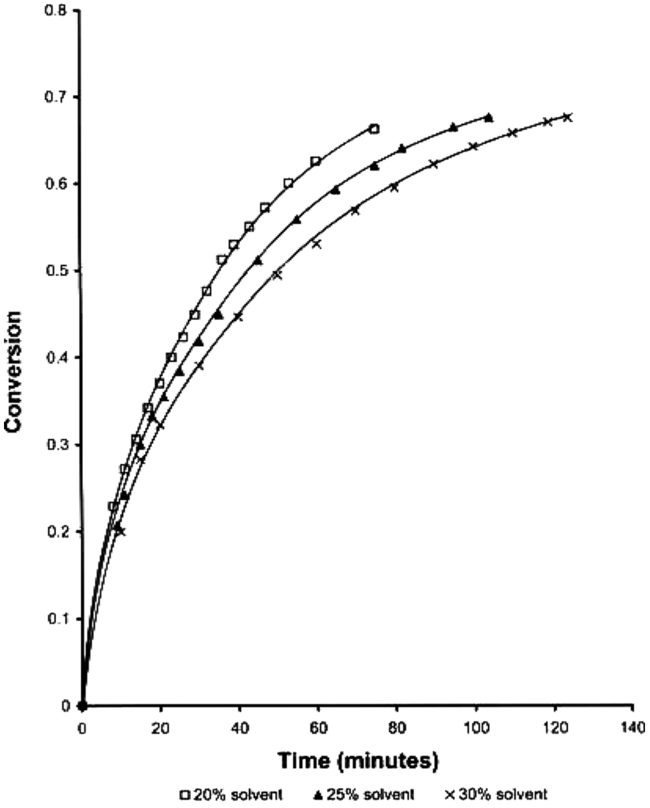

FIGURE 9 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 1.25 and temperature 30°C.

The conversion vs. time plots for uncatalyzed reactions of castor oil/TMP polyol with MDI for different NCO/OH ratio and solvent concentrations are showed in Figures 3 to 11. Arrhenius plots for these reactions are shown in Figures 12–14. The values of kinetic constants, activation energies and entropies of activation are shown in Table 1. The values of the kinetic constants clearly indicate that the rate of reaction is highest for NCO:OH ratio 1.0, and it also increases with an increase in temperature and decreases with an increase in solvent (xylene) concentration, which acts as a diluent [37]. Second order rate constants are higher than those for castor oil MDI reactions [38]. Although, the rate of reaction in solvents like toluene and benzene increases with the decrease in NCO/OH ratio, but it purely depends

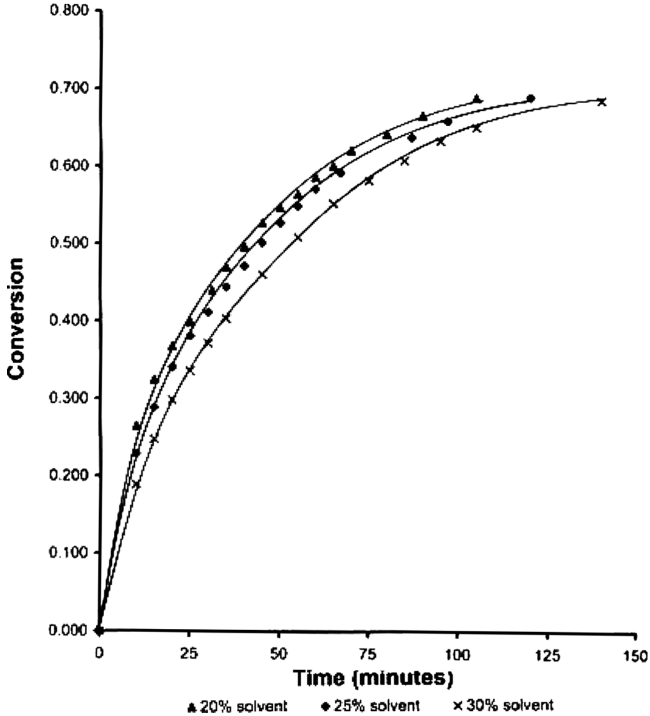

FIGURE 10 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 1.25 and temperature 25°C.

upon the nature of the hydroxyl component employed for the reaction [39]. Activation energies are minimum for NCO/OH ratio 1.25, and the value increases with increase in solvent concentration for NCO/OH ratio 0.75 and 1.0. Activation energies decrease for increase in solvent concentration for NCO/OH ratio 1.25.

The entropy of activation, $\Delta S^{\#}$ was calculated for these reactions using the following equation [40]

$$\Delta S^{\#} = \left[\log\frac{k'}{T} - \log\frac{k}{h} + \frac{\Delta H^{\#}}{2.303RT}\right]2.303R$$

where $\Delta H^{\#} = Ea - RT, k' =$ rate constant, $k =$ Boltzmann constant, and $h =$ Planks constant.

The apparent entropies of activation and enthalpy values are listed in Table 1. The entropies of activation show high negative values in all cases, which is due to shift towards a more ordered transition state of

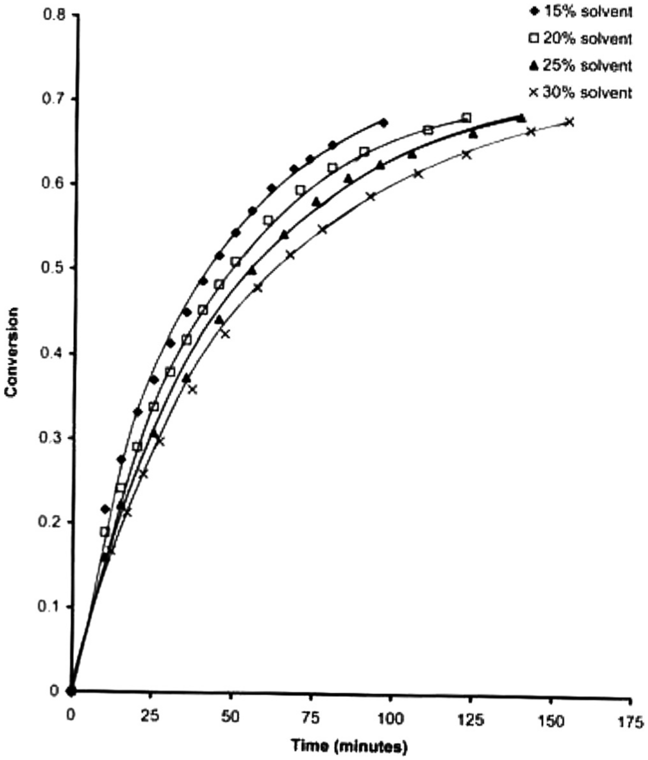

FIGURE 11 Conversion vs. time plots for uncatalyzed reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 1.25 and temperature 20°C.

the reactants in the system. The values of activation energies and entropies of activation are in agreement with the published literature on castor oil [38].

CONCLUSIONS

The basic aim for carrying out uncatalyzed reactions of castor oil/TMP polyol with MDI for different NCO/OH ratio and solvent concentrations was to establish kinetic data and Arrhenius constants which can be further used to model the system. The following conclusions were made:

1. The values of the kinetic constants clearly indicate that the rate of reaction is highest for NCO:OH ratio 1.0 and it also increases with

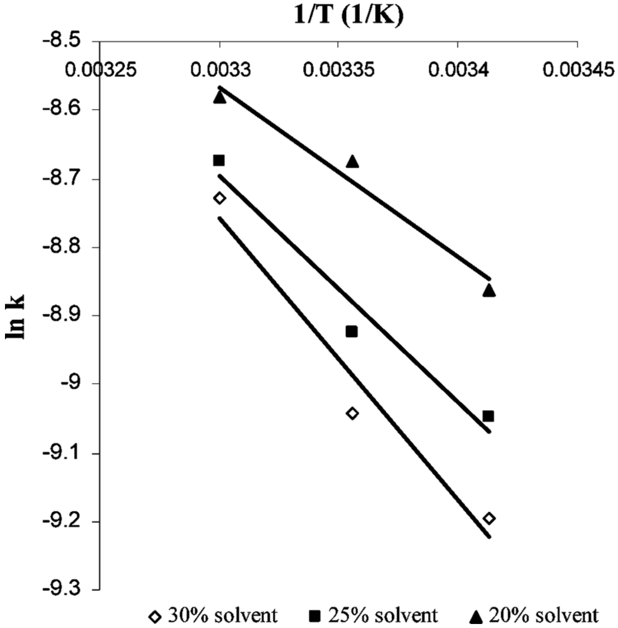

FIGURE 12 Arrhenius plot for second order reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 0.75.

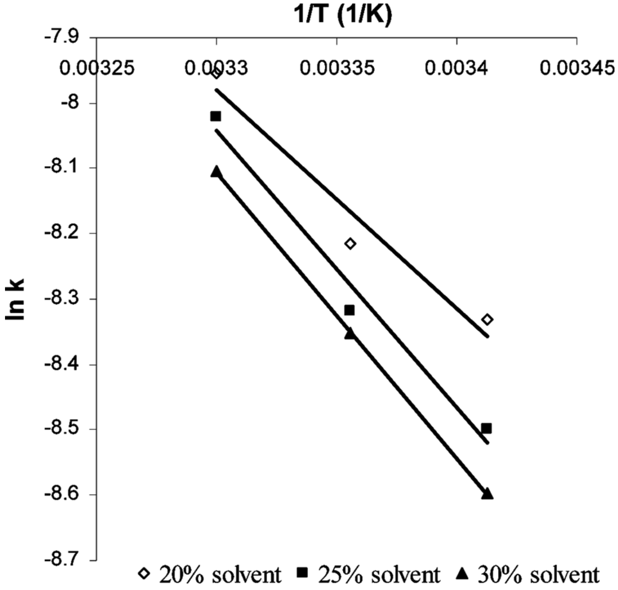

FIGURE 13 Arrhenius plot for second order reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 1.0.

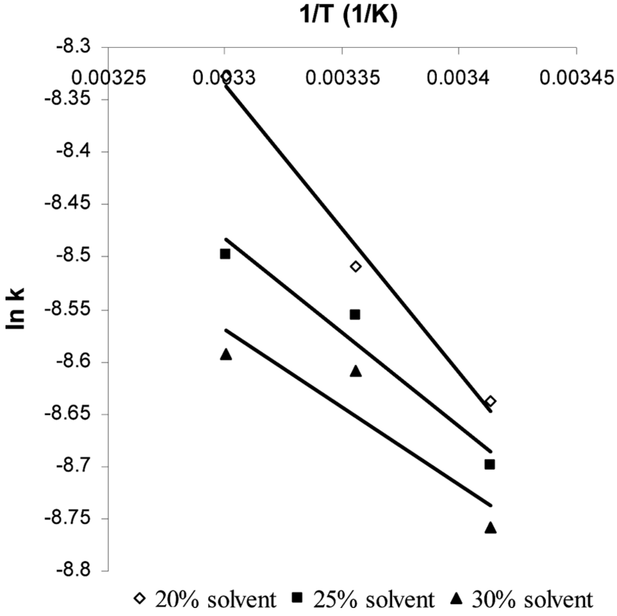

FIGURE 14 Arrhenius plot for second order reactions between castor oil/TMP polyol and diphenyl methane diisocyanate for NCO/OH ratio 1.25.

TABLE 1 Second Order Kinetic Constants, Activation Energies and Entropy of Activation for the Uncatalyzed Reaction Between Castor Oil/TMP Polyol and MDI

S. No.	System description	Solvent concentration (percent of total mixture)	Second order rate constants (10^4 liters/Eq. seconds) Temperatures°C			Activation energy (KJ/moles)	Entropies of activation (ΔS) $J \cdot K^{-1} \cdot mol^{-1}$
			20	25	30		
1.	NCO/OH ratio 0.75 (M = 1.33)	20	1.417	1.708	1.875	−20.709	−314.68
		25	1.178	1.333	1.711	−27.496	−339.20
		30	1.015	1.184	1.618	−34.349	−363.47
2.	NCO/OH ratio 1.0 (M = 1)	20	2.409	2.703	3.515	−27.824	−334.24
		25	2.036	2.443	3.282	−35.192	−360.28
		30	1.846	2.362	3.023	−36.402	−365.22
3.	NCO/OH ratio 1.25 (M = 1.25)	20	1.774	2.016	2.232	−22.865	−319.90
		25	1.667	1.925	2.040	−14.939	−293.59
		30	1.572	1.824	1.855	−12.271	−285.35

an increase in temperature and decreases with an increase in solvent concentration which acts as a diluent

2. The entropies of activation show high negative values in all cases, which is due to shift towards a more ordered transition state of the reactants in the system and in accordance with the published literature on castor oil.

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