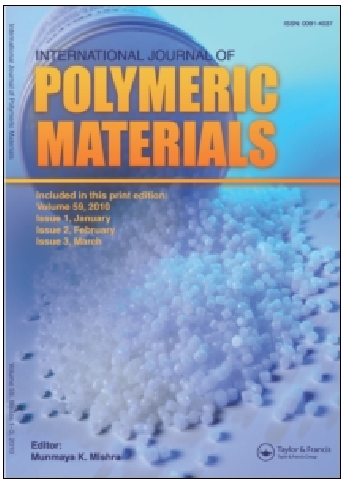

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Kinetic Study of Polyurethane Reaction between Castor Oil/TMP Polyol and Diphenyl Methane Diisocyanate in Bulk

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Kinetic Study of Polyurethane Reaction between Castor Oil/TMP Polyol and Diphenyl Methane Diisocyanate in Bulk

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Polyols as precursors of crosslinked polyurethanes were prepared by alcoholysis between castor oil (CO) and Trimethylol propane (TMP). The alcoholysis reaction produced an equilibrium mixture of monoglycerides, diglycerides, and triglycerides of TMP and some free TMP. The polyol thus prepared was characterized using FTIR, Atmospheric Pressure Chemical Ionization (APCI) under positive ion mode and various analytical techniques. A series of bulk polyurethane polymerization reactions were then carried out using the polyol and Diphenyl methane diisocyanate (MDI) at 25°C, and were investigated using Fourier transform Infrared (FTIR) spectroscopy with different NCO/OH ratios, that is, 0.75, 1.0, and 1.25. All the reactions obeyed second order kinetics. Second order rate constants were calculated and found to be 2.49×10^{-4} lit/eq. sec., 3.4×10^{-4} lit/eq. sec. and 2.38×10^{-4} lit/eq. sec. for NCO/OH ratio 1.25, 1.0, and 0.75, respectively.

Keywords: kinetics, polyurethane, castor oil, Trimethylol propane, FTIR spectroscopy

INTRODUCTION

Castor oil is a naturally occurring triglyceride of ricinoleic acid. Commercial castor oil consists of triglycerides that contain 90% ricinoleic acid residues and 10% non-functional acid residues, so that castor oil has effective hydroxyl functionality of 2.7 [1]. Once polymerized, the long pendant chains of the fatty acids impart flexibility and hydrolysis resistance to the network and the double bonds present

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Address correspondence to Anupama Kaushik, Department of Chemical Engineering & Technology, Panjab University, Chandigarh 160014, India. E-mail: anupama_chem.@yahoo.co.in in the castor oil may serve as grafting centers [2]. Urethane polymers prepared from castor oil exhibit excellent abrasion resistance. However, disadvantages with use of castor oil include low hydroxyl number leading to inherently low modulus materials, a sluggish rate of curing of secondary hydroxyl groups [3] and structural irregularity due to steric hindrances offered by the long pendant fatty acid chains during polyurethane formation, resulting in low tear strength [4].

To overcome these disadvantages, castor oil is transesterified with polyhydroxy alcohols, there-by introducing reactive hydroxyl groups [5–6]. This process involves heating an oil with poly-hydroxy alcohols such as glycerol, Trimethylol propane, pentaerythritol at elevated temperatures, usually in the presence of basic catalysts like litharge (PbO), calcium hydroxide, calcium soaps, and sodium carbonate [7]. This is a random reaction, which at equilibrium consists of different glycerides of varying functionality that can be used to react with diisocyanates for various applications. Large number of vegetable oils have been used for this purpose, including linseed oil, Rapeseed oil, soybean oil, rice bran oil, coffee meal oil, and castor oil [8–11].

In this study, a polyol was prepared using dehydrated castor oil and 1,1,1 Trimethylol propane. The prepared polyol was characterized using analytical techniques, instrumental techniques, FTIR, and Atmospheric Pressure Chemical Ionization (APCI) under positive ion mode. This polyol was then reacted with 4,4′-Di-phenylmethane diisocyanate (MDI) at different NCO/OH ratios. The basic aim was to establish kinetic data, which can be further used to model the system.

FTIR spectroscopy is a popularly used spectroscopic technique for polymer characterization and for monitoring the in-situ reaction kinetics of polyurethane polymerization [12–13]. Both urethane monomers and polymers have major and distinctive absorption peaks in the FTIR spectrum and hence, monitoring reaction kinetics with absolute accuracy is possible using FTIR. In this study, kinetic study using FTIR was done for some representative reactions, that is for NCO/OH ratios 0.75, 1.0, and 1.25, at temperature of 25°C.

EXPERIMENTAL

Materials Used

Castor oil was commercial grade and 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 has hydroxyl value of 1255.98. Pyridine (Qualigens), Dibutyl amine (E-Merck), Diphenyl methane diisocyanate (BASF, Korea) (isocyanate value 28.8%), Xylene (E-Merck), Toluene (Qualigens) were used as such.

Polyurethane Synthesis

Trans-esterification of castor oil. Polyol was synthesized from castor oil (CO) by reactions with Trimethylol propane (TMP) in CO/TMP equivalent ratio of 1:3, in nitrogen atmosphere with litharge (0.1%) catalyst. The reaction was carried out for approximately 3 h in a one-liter stainless steel–jacketed reactor under nitrogen atmosphere, connected to constant temperature bath/circulator through solenoid valve and electronic relay supplied by Julabo Instruments, Germany. The reaction temperature was 210 ± 0.5°C and the completion of the reaction was checked by dissolving the sample in ethanol. Hydroxyl value of the polyol prepared was 354.6 mg KOH/g (using acetylation method [14], Bianchini's method [15], and MALDI MS).

Characterization of polyol using FTIR and APCI. Polyols prepared from CO/TMP were analyzed using FTIR and APCI under positive ion mode. FTIR was carried out using a Perkin Elmer FTIR spectrometer at a spectral resolution of 4 cm^{-1} with 20 scans on a KBr pellet. LCMS was carried out in Thermo Quest, Fannigan MAT LCQ model mass spectrometer. Samples were dissolved in methanol (HPLC grade) followed by filtration through 0.45 μm Millipore filter and were analyzed using APCI (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 and 60–265 m/z ratio.

Kinetic study using FTIR spectroscopy. The progress of the reaction was followed by measuring percent transmittance of isocyanate group at 2265–2275 cm^{-1} using a Perkin Elmer FTIR spectrometer at a spectral resolution of 4 cm^{-1} resolution with 20 scans on a KBr pellet. The monomers in different NCO/OH ratios were thoroughly mixed together at room temperature (25°C) for two minutes and then the mixture was applied between two KBr pellets held together without any external force. The reaction mixture was in a very thin layer so that heat generated during the reaction was dissipated maintaining isothermal conditions. The reaction was followed by taking IR spectra of the sample at different time intervals depending on the curing time of the sample. The change in intensity of the transmittance peak for NCO stretching at 2265 cm^{-1} was calculated by taking the integral of band between 2097.8 and 2465.5 cm^{-1}. The integrated peak area calculated was normalized by using a reference peak at 915.7 cm^{-1}

(−CH=CH− stretch), which remained practically unaffected during the reaction. The conversion of the isocyanate group p_A is calculated as [13,16],

$$P_A = 1 - \frac{T_t}{T_o} \tag{1}$$

where T_o and T_t are normalized areas of the isocyanate transmittance bands at the beginning of the reaction and at time *t*, respectively.

RESULTS AND DISCUSSION

Characterization of Castor Oil/Trimethylol Propane Polyol

The polyol was characterized for hydroxyl value, acid value, and saponification value using analytical techniques [14] and for density, viscosity, and moisture content using instrumental techniques. The results have been summarized in Table 1. All the possible reaction products of transesterification of castor oil and trimethylol propane are given in Figure 1. The transesterification reaction between castor oil and TMP results in an equilibrium mixture of mono-, di-, and triglycerides of castor oil and TMP. All the components identified in Figure 1 contain three hydroxyl groups (because ricinoleic acid inherently contains hydroxyl group). The hydroxyl value of the polyol calculated using theoretical methods, that is, Bianchini's method [15] and Bailey's method [17] was the same as that calculated by analytical techniques (MALDI MS). The FTIR and APCI of polyol are given in Figures 2 and 3, respectively.

Infrared spectrum for CO/TMP polyol in the range 4000–400 cm^{-1} plotted on an absolute scale is shown in Figure 2. The broad peak at 3392 cm^{-1} represents the free hydroxyl groups [18–19]. The band at

TABLE 1 Different Properties of CO/TMP Polyol and MDI Determined Using Analytical and Instrumental Techniques

S. No.	Property	Values
1	Hydroxyl value (Acetylation method) [14]	354.6
2	Acid value [14]	2.1
3	Moisture content (using Karl Fischer)	0.81%
4	Viscosity (using Brookfield Viscometer)	1.6 cp
5	Specific gravity at 25°C	0.993 ± 0.001
6	Saponification value	311.67
7	Specific gravity of MDI determined experimentally	1.238 ± 0.001
8	NCO content of MDI [32]	28.8

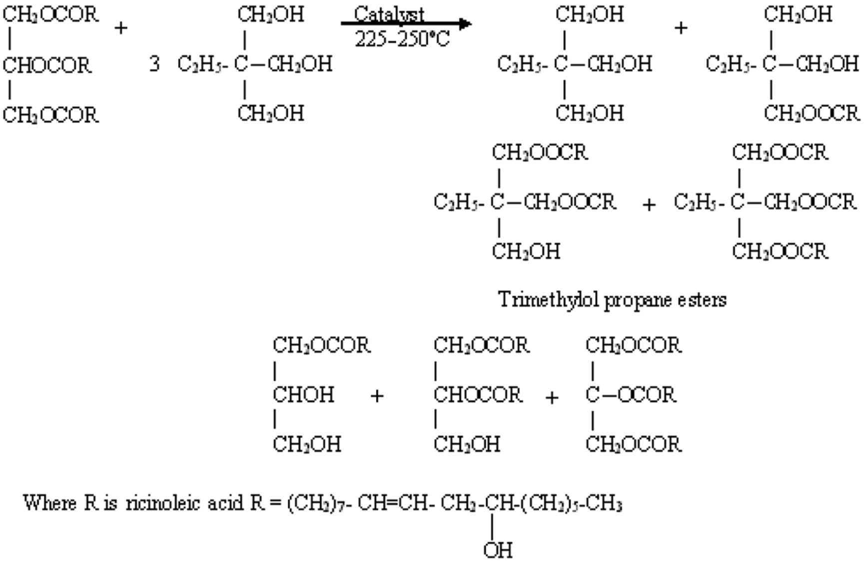

FIGURE 1 Reaction products of transesterification of castor oil and Trimethylol Propane.

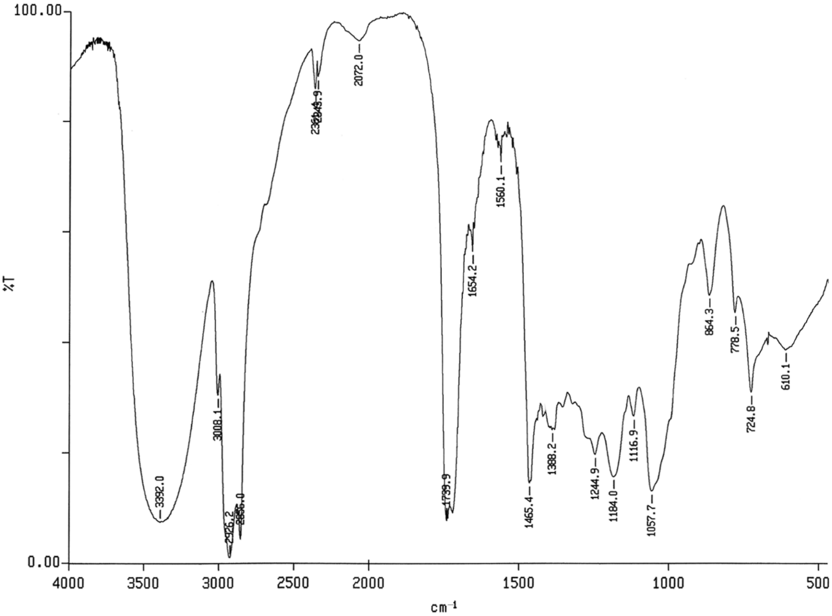

FIGURE 2 FTIR of polyol in the region 400–4000 cm^{-1}.

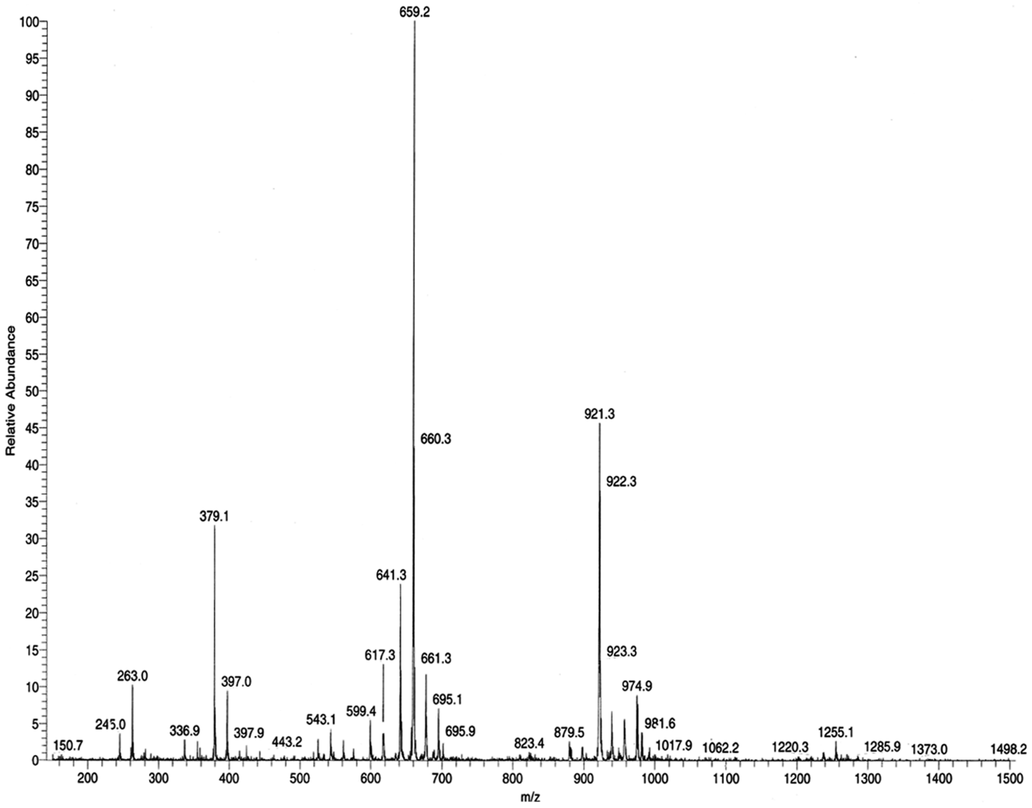

FIGURE 3 APCI Mass spectra of the CO/TMP polyol taken in methanol for the range 150–2000 m/z.

TABLE 2 Individual Components Identified in CO/TMP Polyol Based on APCI-Positive Ion Mode

LC fraction	$[M+H]^+$ observed	$[M+H]^+$ Calculated	Δm (%)	Glyceride structure
1	974.9	975.53	0.064	$[T+H]^+$
2	921.3	921.49	0.020	$[T-3H_2O]^+$
3	879.5	880.41	0.103	$[M+H-3H_2O]^+$
4	695.1	696.09	0.145	$[DT+H]^+$
5	659.2	660.06	0.130	$[DT+H-2H_2O]^+$
6	641.3	642.04	0.116	$[T+H-2H_2O-RCOOH]^+$
7	617.3	617.97	0.109	$[M+H-H_2O-RCOOH]^+$
8	599.4	599.94	0.091	$[M+H-2H_2O-RCOOH]^+$
9	397.0	397.62	0.156	$[MT+H-H_2O]^+$
10	379.1	379.60	0.134	$[T+H-2RCOOH]^+$
11	263.0	263.44	0.167	$[RCOOH+H-2H_2O]^+$
12	262.9	263.44	0.204	$[RCOOH+H-2H_2O]^+$
13	245.0	245.43	0.175	$[RCOOH+H-3H_2O]^+$

T refers to triricinoleate of TMP, DT refers to diricinoleate of TMP, MT refers to mono-ricinoleate of TMP, M refers to triricinoleate of glycerol.

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 in polyurethane formation, free hydroxyl groups in the polyol react with isocyanate groups in Diphenyl methane diisocyanate causing a decrease in intensity of −OH stretching peak whereas the intensity of −CH peak remains constant [12–13,20]. The FTIR of the Polyol also showed a peak at 1057 cm^{-1}, which is a characteristic of secondary hydroxyl group. The stretching peak for C−O is represented at frequency 1184 cm^{-1}.

In the APCI/MS spectrum for CO/TMP polyol, for the range 150–1500 m/z (Figure 2) all the peaks identified are listed in Table 2. From the peaks identified it is evident that the prepared polyol contains triglycerides, diglycerides, and monoglycerides of TMP as its major components and contains free hydroxyl groups, making it suitable for polyurethane preparation.

Results of Kinetic Study using FTIR

The variation of percent transmittance for reactions with NCO: OH ratio 0.75, 1.0, and 1.25 at different time intervals were plotted with the same y-axis scale, as shown in Figures 4–6, respectively. A closer look at the spectra (Figure 5) in the spectral region 1500 to 3000 cm^{-1}, reveals that the transmittance band for isocyanate double bond

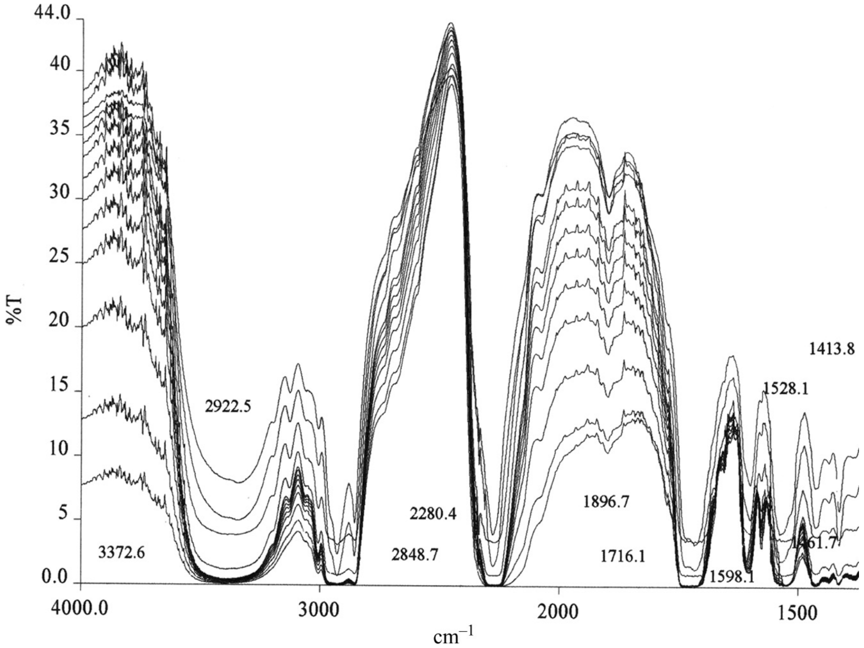

FIGURE 4 Variation of percent transmittance with time for CO/TMP Polyol MDI reaction with NCO/OH ratio of 0.75 for the range 1500–4000 cm^{-1}.

(N=C=O) is represented by the peak at 2265.6 cm^{-1}, which is consumed during the reaction [12–13,20–24]. The peak intensity decreased as a function of reaction time and after 20 min, it became constant, indicating the completion of reaction. During the reaction, a new peak grew at about 1723.5 cm^{-1}. The intensity of this peak increased as a function of time until the reaction was completed at about 20 min. This peak is attributed to the carbonyl band (C=O) in zthe reaction product, urethane [12,25]. In the region 3000–4000 cm^{-1}, the peaks at 3334.5 cm^{-1} and 1576.2 cm^{-1} increased as a function of reaction time, which are due to −NH stretching and bending vibrations [18,26]. Polyurethane formation is also confirmed by the absence of −OH absorbance band associated with polyol and presence of −NH band of polyurethane.

Polyurethane contains proton donor group (−NH) and proton acceptor group (CO). Therefore, hydrogen bonding between hard segment–hard segment or hard segment–soft segment can exist. Hydrogen bonding is reflected in the frequency change and change in shift intensity, as well as band width for −NH groups. Hydrogen bonded

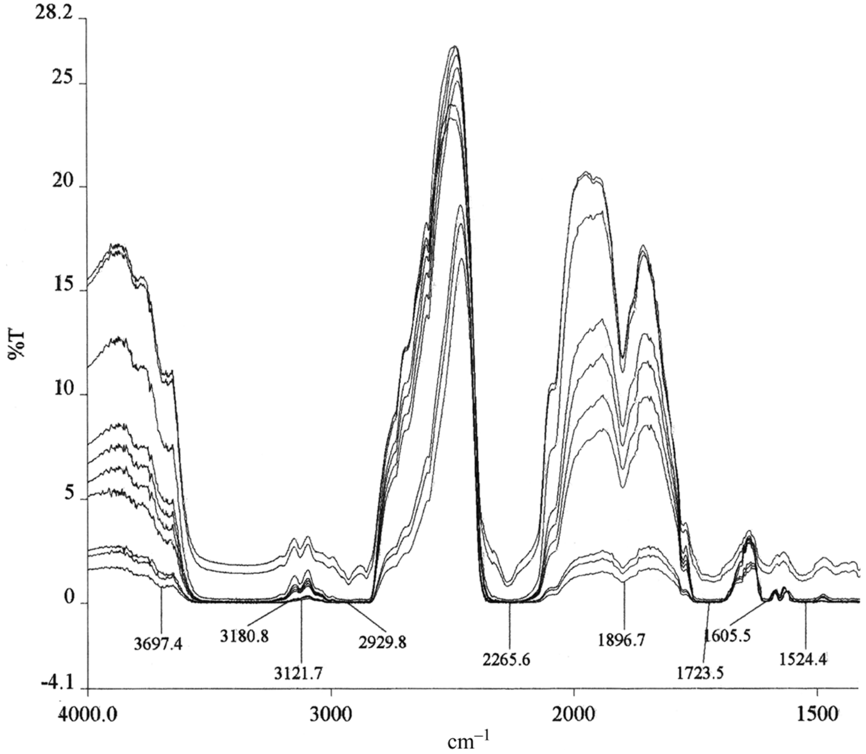

FIGURE 5 Variation of percent transmittance with time for CO/TMP Polyol MDI reaction with NCO/OH ratio of 1.0 for the range 1500–4000 cm^{-1}.

NH groups shift to lower frequencies (3375–3333 cm^{-1}) whereas nonhydrogen-bonded NH groups (3400–3460 cm^{-1}) do not show such shift [25].

In the spectra, very low intensity peak was observed at 1647 cm^{-1} whose intensity remained almost constant over a period of time. This peak is for urea molecule. The low intensity of this peak indicates that the moisture content in the system is meager and is not affecting the rate of polyurethane formation.

The transmittance band observed at 2929.8 cm^{-1} and low intensity neighboring peak at 2848.7 cm^{-1} is associated with asymmetric and symmetric $-CH_2$ groups [26]. Medium intensity peak at 1896.7 cm^{-1} indicates the presence of C−O−C ether linkage [18]. The peak at 1539 cm^{-1} indicates the presence of amide band (−NH−CO bond). No band was found at 2130 cm^{-1} in the spectra, which could represent carboimides.

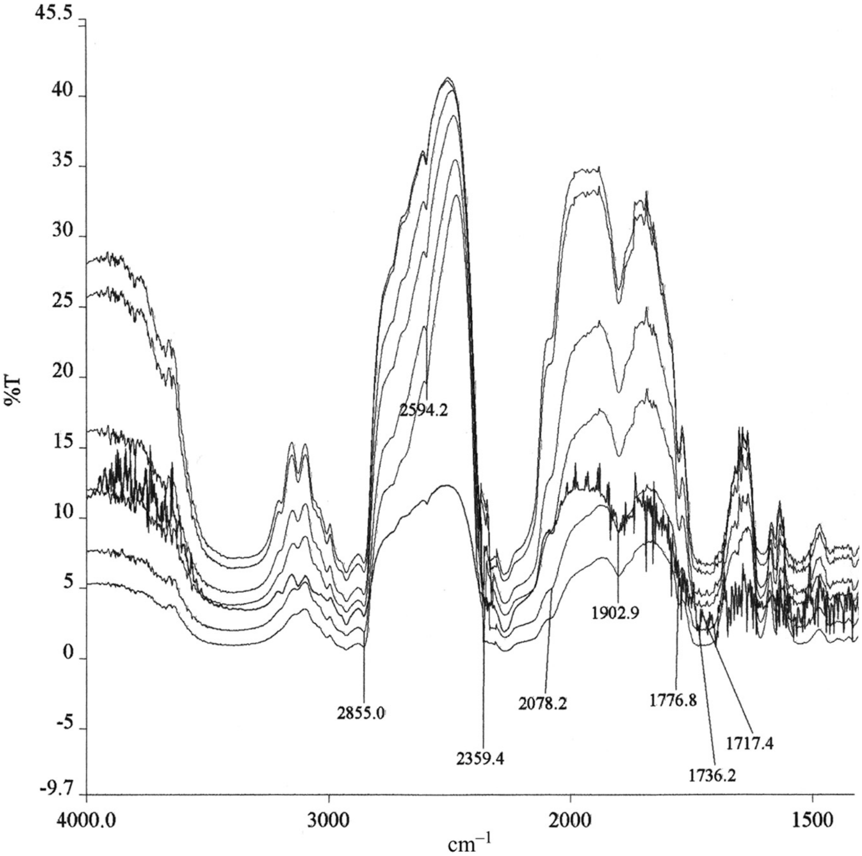

FIGURE 6 Variation of percent transmittance with time for CO/TMP Polyol MDI reaction with NCO/OH ratio of 1.25 for the range 1500–4000 cm^{-1}.

It is clear from the data that the peak area increases with time is indicating the increase in polyurethane group and decrease in isocyanate group.

Figure 7 shows conversion versus time for NCO/OH ratio 0.75, 1.0, 1.25 (without solvent) calculated using Eq. 1 from areas of the FTIR peak at 2265 cm^{-1} (–NH stretching band).

Assuming that all the curing reactions follow a second order kinetics [27–31], second order rate constants calculated for the three NCO/OH ratios have been summarized in Table 3. The rate of reaction was maximum for NCO/OH ratio 1.0 with rate constant 3.4×10^{-4} liters/Eq. sec., followed by NCO/OH ratio 1.25 with rate

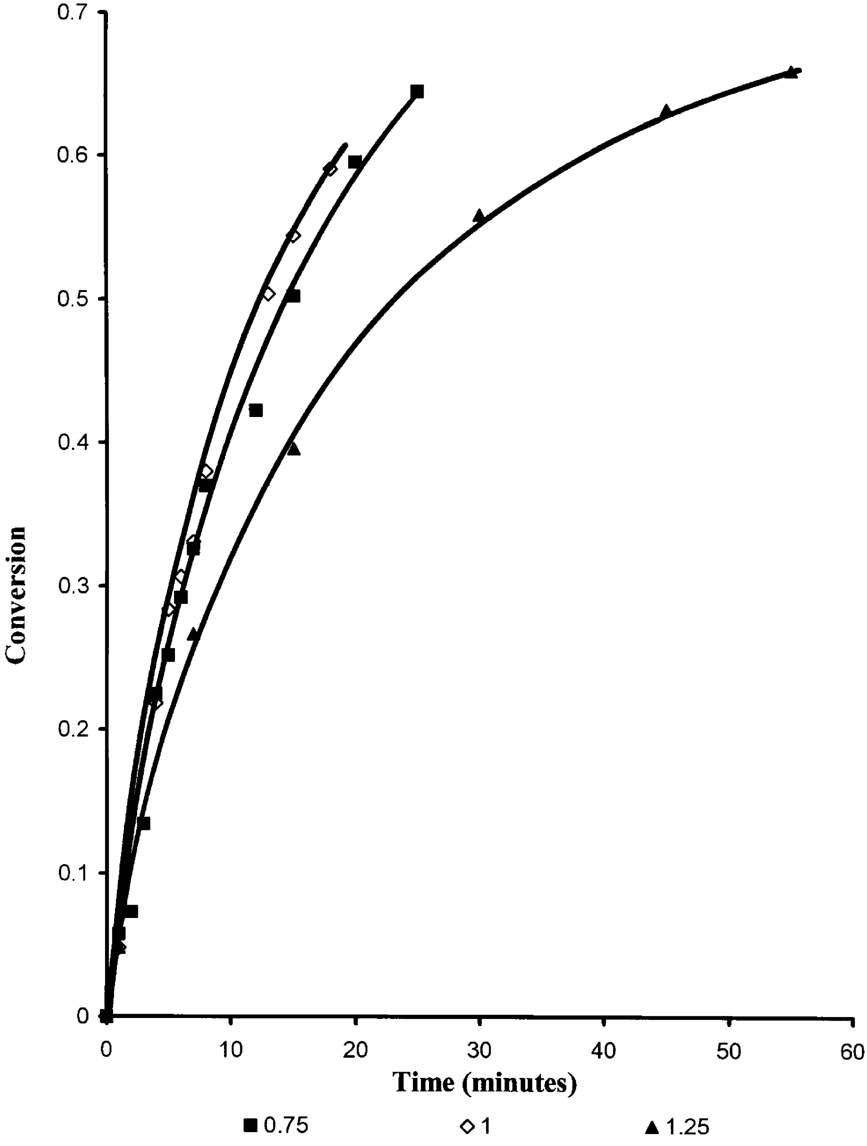

FIGURE 7 Time versus Conversion plot for NCO/OH ratio 0.75, 1.0, and 1.25, respectively using FTIR spectroscopy.

constant 2.49×10^{-4} liters/Eq. sec. The rate of reaction was minimum for NCO/OH ratio 0.75 with rate constant of 2.38×10^{-4} liters/Eq. sec.

TABLE 3 Kinetic Constants for Castor Oil/Trimethylol Propane Polyol and Diphenylmethane Diisocyanate Reactions Calculated Using FTIR Spectroscopy

	Kinetic constants (10^4 liters/Eq. seconds)
System specification	FTIR
NCO/OH ratio 0.75:1 (without solvent)	2.38
NCO/OH ratio 1:1 (without solvent)	3.4
NCO/OH ratio 1.25:1 (without solvent)	2.49

CONCLUSIONS

Transesterification reaction between castor oil and trimethylol propane results in an equilibrium mixture of triglycerides, diglycerides, and monoglycerides of castor oil and TMP. The kinetic study of the polyurethane formation between castor oil/trimethylol propane polyol and 4,4′-diphenyl methane diisocyanate by means of quantitative FTIR spectroscopy reveals the following points:

1. Uncatalyzed reactions of Castor Oil/TMP polyol with MDI at different NCO/OH ratios of 0.75, 1.0, and 1.25 follow a second order kinetics.
2. The polyurethane reaction can be followed by monitoring isocyanate double bond (N=C=O) peak at 2265.6 cm^{-1}, which was consumed during the reaction.
3. Rate of reactions were maximum for NCO/OH ratio 1:1 followed by NCO/OH ratio 1.25.

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