

# Castor Oil/Trimethylol Propane-Based Polyurethane Reactions: Modeling in a Batch Reactor

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**ABSTRACT:** Polyol as precursor of crosslinked polyurethanes was prepared through alcoholysis from castor oil having triglycerides of saturated and unsaturated fatty acids. Alcoholysis between castor oil (CO) and Trimethylol propane (TMP) at elevated temperature results in an equilibrium mixture consisting mainly of monoglycerides, diglycerides and triglycerides of castor oil and trimethylol propane as well as some free trimethylol propane. Polyol thus prepared was characterized using FTIR, Liquid Chromatography Mass Spectroscopy (LCMS) and Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectroscopy (MALDI TOF MS). Series of bulk polyurethane polymerization reactions were carried out in a batch reactor in presence of solvent, xylene, using CO/TMP polyol and diphenyl methane diisocyanate (MDI) at different temperatures and different Stoichiometric Imbalance Ratio (NCO/OH) ratio i.e., 0.75, 1.0, and 1.25. All the reactions obeyed second order

kinetics. Second order rate constants were calculated and were used to model the system using kinetic approach given by Gupta and Kumar. The kinetic model allows for the calculation of concentrations of all the species in the system. Different reactivities for isocyanate functional groups located in different positions of the monomer and polymer molecules, as well as the hydroxyl functional groups of different molecules, were allowed. Allophanate and biuret ramification reactions, as well as gel formation due to crosslinking, were considered in the model. Agreement between the model predictions and experimental data on isocyanate conversion and weight-average molecular weight was satisfactory for the entire conversion range. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** modeling; kinetics; polyurethane reactions; MALDI

## INTRODUCTION

Polyurethanes are an interesting family of polymers which have been used in many different applications such as biomedical, coatings, adhesives and composites. However, one of the problems facing polyurethanes nowadays is their dependence on petroleum derivative products. Due to oil crisis and global warming effects, PU based on renewable resources has generated worldwide interest, especially development of vegetable oil based polyurethanes.<sup>1–6</sup>

Castor oil is a low-cost, abundantly available, renewable raw material that has been attracting research effort due to its use in coatings, adhesives, paints, sealants, encapsulating compounds.<sup>1,7–12</sup> The unique feature of castor oil is that it contains considerable amount of hydroxylated triacylglycerols, which are important ingredients for polyurethane polymer. Long pendant chains of the fatty acids impart flexibility and hydrolytic resistance to the network and the double bond

present in the castor oil serves as a grafting center.<sup>13</sup> PU obtained from castor oil have certain disadvantages, including: low hydroxyl number leading to low modulus materials; a slower rate of curing of secondary hydroxyl groups<sup>14</sup> and structural irregularity due to steric hindrances offered by the long pendant fatty acid chains during polyurethane formation, resulting in low tear strength.<sup>15</sup> To offset these disadvantages, castor oil is transesterified or alcoholized with polyhydroxy alcohols, most commonly by glycerol, pentaerythritol and trimethylol propane.<sup>16–19</sup> Transesterification leads to increase in hydroxyl value of the system thereby rendering hardness to the product, while long chain fatty acids induce flexibility. Thus resulting polyurethane polymer is relatively tough. Transesterified product of castor oil and polyhydroxy alcohol is mixture of monoester, diester and triester and unreacted polyhydroxy alcohol, all having functionality 3.<sup>20</sup>

Several mathematical techniques are available for kinetics and molecular weight development modeling in step-growth and chain-growth polymerizations.<sup>21,22</sup> They usually work well for linear polymers, but their direct application to the production of nonlinear polymers is at best an approximation of actual behavior of these systems. Predictive power of these models decreases when crosslinking reactions are considered.

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Main statistical theories used to model gelation in step-growth polymerization include Flory-Stockmayer classical theory,<sup>23</sup> Macosko-Miller conditional probability model,<sup>24</sup> and Gordon's cascade theory.<sup>25</sup> Most publications with a quantitative view of production of polyurethanes and other step-growth resins have used simplified kinetic expressions to calculate concentrations of all species involved in polymerization. Reaction rate is usually given by the product of a single kinetic constant with concentration of one reactant (e.g., isocyanate functional group) raised to a reaction order and concentration of the other reactant (e.g., hydroxyl functional group) raised to its respective reaction order,<sup>26,27</sup> with the assumption of equal reactivities for each functional group, regardless of position or size of the monomer or polymer molecules.

This study was undertaken with the objective to develop an effective mathematical model for industrial applications for nonlinear polyurethane production from castor oil/trimethylol propane polyol and MDI. In this study, polyol has been prepared using moisture free castor oil and trimethylol propane via alcoholysis at elevated temperature. Polyol prepared was reacted with 4,4' diphenylmethane diisocyanate (MDI) at different temperatures i.e., 15, 20, 25, and 30°C and 15, 20, 25, and 30% solvent concentration as well as Stoichiometric Imbalance Ratio (SIR) (NCO/OH) ratio of 0.75, 1.0, and 1.25. For this study, kinetic approach pioneered by Gupta and Kumar<sup>21</sup> has been used to develop kinetic equations for the system. For molecular weight determination, recursive probability approach given by Macosko and Miller<sup>24</sup> has been followed.

## EXPERIMENTAL

### Materials used

Commercial grade castor oil was purchased from the local market and was dehydrated by heating at 105°C in inert atmosphere. Dehydrated castor oil was characterized for hydroxyl value (148 mg of KOH/g of sample) and acid value.<sup>2</sup> Trimethylol propane (Aldrich, Germany) was used as such and has hydroxyl value of 1255.98 g of KOH/g of sample, pyridine (Qualigens), dibutyl amine (E-Merck), diphenyl methane diisocyanate (BASF, Korea) of isocyanate value 28.8%, xylene (E-Merck), toluene (Qualigens) were used as such. Litharge catalyst was supplied by National Chemicals, India.

### Modification of castor oil by transesterification with trimethylol propane and its characterization

Polyol was synthesized from castor oil through reaction with trimethylol propane in ratio of 1 : 3 in nitrogen atmosphere with catalyst litharge (0.1%). The reaction was carried out for ~ 3 h in 1 L 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. Reaction temperature was  $210 \pm 0.1^\circ\text{C}$  and completion of the reaction was checked by dissolving the sample in ethanol. The reaction product was dried under vacuum at 75°C and kept in dark bottle with molecular sieves.

Hydroxyl value of polyol was 376.4 mg KOH/g, weight average molecular weight was 521.05/mol and moisture content using Karl Fisher titration was 0.0081%. Polyol prepared from CO/TMP was analyzed using LCMS carried out in Thermo Quest, Fannigan MAT LCQ model mass spectrometer. Samples were dissolved in methanol (HPLC grade) followed by filtration through 0.45  $\mu\text{m}$  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.

MALDI TOF measurements were performed with Bruker Daltonics Ultraflex TOF/TOF MALDI Tandem TOF mass spectrometer. 25-kV acceleration voltage was used with pulsed ion extraction (PIE). Positive ions were detected with reflectron mode (20 kV). Nitrogen laser (337 nm, 1-ns pulse width) operating at 4 Hz was used to produce laser desorption, and 125–225 single shot mass spectra were summed to give a complete spectrum. The sample was dissolved in dimethyl formamide (DMF) with a concentration of 10 mg/mL and matrix material 2,5-dihydroxybenzoic acid (DHB,  $M = 153$  g/mol) was also dissolved in DMF.

### Synthesis of trimethylol propane modified castor oil polyurethane

The reaction was carried out in a five-necked, 500-mL, round-bottom flask fitted with an agitator, a temperature indicator and nitrogen inlet-out tubes. Flask was kept in a water bath maintained at desired temperature. Polyol was mixed with xylene for 2 h. After mixing, a calculated amount of MDI was introduced into the flask so as to maintain a particular SIR. Progress of all the reactions was followed by measuring the amount of free isocyanate left behind in the system using Stagg method.<sup>28</sup> Identical experiments were conducted at varying temperatures of 15, 20, 25, and 30°C with 15, 20, 25, and 30% solvent concentration at SIR of 0.75, 1.0, and 1.25. Three sets of reactions were carried out at each condition. Table I gives the summary of all the polyurethane reactions.

### Modeling of the polyurethane reactions using kinetic probabilistic approach and parameter estimation model

#### Kinetic description of the system

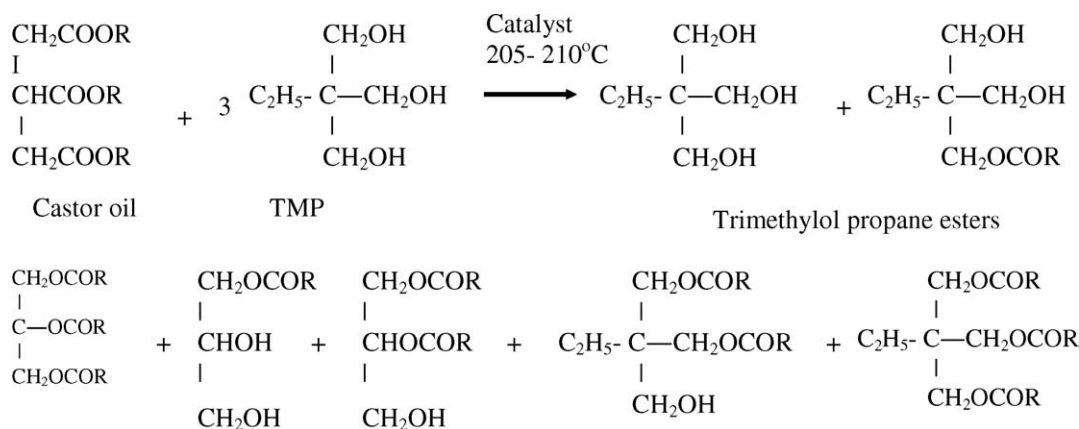
The system consists of diisocyanate  $A_2$  (MDI) and polyol of functionality  $f$  (formed from transesterification

**TABLE I**  
**Second Order Rate Constants for Different Temperatures and Different NCO/OH Ratios**

S. No.	System description	Solvent concentration (percent of total mixture)	Second order rate constants (10 <sup>4</sup> liters/ Eq. s) Temperatures (°C)				
			10	15	20	25	30
1.	NCO/OH ratio 0.75	15	1.240	1.279	1.705	2.074	2.384
		20	0.958	1.041	1.417	1.708	1.875
		25	0.844	0.889	1.178	1.333	1.711
		30	0.773	0.797	1.015	1.184	1.618
2.	NCO/OH ratio 1.0	15	1.968	2.215	2.505	2.796	3.898
		20	1.631	2.097	2.409	2.703	3.515
		25	1.476	1.908	2.036	2.443	3.282
		30	1.260	1.708	1.846	2.362	3.023
3.	NCO/OH ratio 1.25	15	1.393	1.816	1.965	2.040	2.687
		20	1.156	1.640	1.774	2.016	2.419
		25	1.063	1.494	1.667	1.925	2.040
		30	0.943	1.226	1.572	1.824	1.855

of castor oil and TMP). Polyol is treated as a mixture of esters of trimethylol propane (Anupama, 2005). In kinetic analysis, equal reactivity of functional groups has been assumed which seems reasonable as all hydroxyl

groups in predominantly existing components, ricinoleic acid esters and TMP esters, are attached at primary positions. Following reaction schematic shows the reaction products of castor oil and trimethylol propane.



Where R is ricinoleic acid  $\text{R} = (\text{CH}_2)_7\text{-CH=CH-CH}_2\text{-CH(OH)-(CH}_2)_5\text{-CH}_3$

#### Modeling of reactions using Macosko Miller Approach

The reaction scheme used is similar to that used by Gupta and Kumar.<sup>21</sup> Model consists of a set of kinetic equations that describes the rates of consumption of reactants or formation of polyurethane and side products. In the system, a set of algebraic equations have been developed using recursive probabilistic approach of Macosko and Miller,<sup>24</sup> which allows calculation of molecular weight averages and the gelation point.

#### Abbreviations used are given below

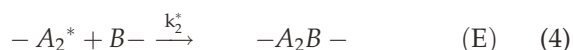
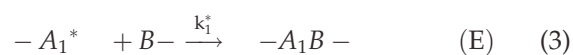
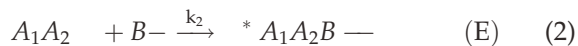
- B hydroxy functional group or polyol  
 $[ ]_0$ ,  $[ ]_t$  concentration, where subscript 0 indicates value at initial conditions, mol L<sup>-1</sup>  
A<sub>2</sub>A<sub>1</sub> diisocyanate with two isocyanate end groups. In case of MDI, both the groups have same reactivity hence A<sub>2</sub>A<sub>1</sub> is same as A<sub>1</sub>A<sub>2</sub>  
E Urethane molecule  
D Amine molecule

M	Allophanate molecule
F	Urea molecule
F	functionality of polyol
$-A_1^*$ , $-A_2^*$	Isocyanate group attached to a polymer chain
$k_i$	kinetic rate constants, L/eq. s
$k_i^*$	kinetic rate constants, where superscript indicates reactivity of a functional group bound to a polymer molecule, L/eq. s. It is assumed that the value of rate constant for the reaction of functional groups bound to a polymer molecule is less than those bound to monomer molecule <sup>29</sup>
$R_3$	It is a constant that indicates that the rate of allophanates formation and is proportional to the rate of urethane formation <sup>21</sup>
$p_i$	Conversion of various functional groups present in the system

Generalized equations for the reaction of diisocyanate and polyol (of functionality  $f$ ) system are:

Primary reaction is between MDI and the modified castor oil polyol to yield polyurethane. The reaction can proceed in two ways, one when monomeric isocyanate reacts with polyol and the other when isocyanate group attached to the chain reacts with polyol. It is assumed that the value of rate constant for the reaction of functional groups bound to a polymer molecule is less than those bound to monomer molecule.

#### Polyurethane formation



As the reactivity of both the isocyanate groups in MDI is same  $k_1$  is equal to  $k_2$  and also  $k_1^*$  and  $k_2^*$ .

If some moisture is present in the system it will react to form amine which further reacts with isocyanate to form urea.

#### Reactions for urea formation



As the reactivity of both the isocyanate groups in MDI is same,  $k_3$  is equal to  $k_4$  as well as  $k_3^*$  and  $k_4^*$

Some of the urethane present in the system reacts with unreacted isocyanate resulting in Allophanate formation



#### Kinetic Equations of the system

From the reaction scheme represented by eqs. (1–12), the following kinetic equations can be derived

$$\frac{d[A_1]}{dt} = -k_1[A_1][B] - k_3[A_1][D] - k_1R_3[E] \quad (2.1)$$

$$\frac{d[A_1]}{dt} = -k_1[A_2][B] - k_3[A_2][D] - k_2R_3[E] \quad (2.2)$$

$$\begin{aligned} \frac{d[A_1]}{dt} = & k_2[A_2][B] + k_4[A_2][D] - k_1^*[A_1^*][B] - k_3^*[A_1^*][D] \\ & + k_2R_3[A_2][E] - k_1^*R_3[A_1^*][E] \end{aligned} \quad (2.3)$$

$$\begin{aligned} \frac{d[A_2]}{dt} = & k_1[A_1][B] + k_3[A_1][D] - k_2^*[A_2^*][B] - k_4^*[A_2^*][D] \\ & + k_1R_3[A_1][E] - k_2^*R_3[A_2^*][E] \end{aligned} \quad (2.4)$$

$$\frac{d[B]}{dt} = -k_1[A_1][B] - k_2[A_2][B] - k_1^*[A_1^*][B] - k_2^*[A_2^*][B] \quad (2.5)$$

$$\begin{aligned} \frac{d[E]}{dt} = & k_1[A_1][B] + k_2[A_2][B] + k_1^*[A_1^*][B] + k_2^*[A_2^*][B] \\ & - R_3[E](k_1[A_1] + k_2[A_2]) \end{aligned} \quad (2.6)$$

$$\begin{aligned} \frac{d[D]}{dt} = & -k_3[A_1][D] - k_4[A_2][D] - k_3^*[A_1^*][D] \\ & - k_4^*[A_2^*][D] \end{aligned} \quad (2.7)$$

$$\frac{d[F]}{dt} = k_3[A_1][D] + k_4[A_2][D] + k_3^*[A_1^*][D] + k_4^*[A_2^*][D] \quad (2.8)$$

$$\frac{d[M]}{dt} = R_3[E](k_1[A_1] + k_2[A_2]) + k_1^*[A_1^*] + k_2^*[A_2^*] \quad (2.9)$$

Concentration of different species can be expressed in terms of conversion or fractional conversion;

$$p_A = 1 - \frac{[A]}{[A]_0} \quad (2.10)$$



$$p_{A_1} = 1 - \frac{[A_1]}{2[A]_0} \quad (2.11)$$

$$p_{A_2} = 1 - \frac{[A_2]}{2[A]_0} \quad (2.12)$$

$$p_{A_1}^* = 1 - \frac{[A_1^*]}{2[A]_0} \quad (2.13)$$

$$p_{A_2}^* = 1 - \frac{[A_2^*]}{2[A]_0} \quad (2.14)$$

$$p_B = 1 - \frac{[B]}{f[B]_0} \quad (2.15)$$

$$p_D = 1 - \frac{[D]}{2[D]_0} \quad (2.16)$$

$$p_E = 1 - \frac{[E]}{[B]_0} \quad (2.17)$$

$$p_F = 1 - \frac{[F]}{2[D]_0} \quad (2.18)$$

where,  $p_A$  is the conversion of total isocyanate groups in the system, which was determined experimentally. Similarly,  $p_B$ ,  $p_E$ ,  $p_D$ ,  $p_F$  are the conversions of hydroxyl, urethane, moisture, and urea end groups, respectively. In the developed model, only conversion of total isocyanate end groups has been compared.

Macosko Miller approach for molecular weight determination

Macosko Miller approach<sup>24</sup> was used to determine molecular weight of the polymer formed at various conversions.

*Mole fractions of various components*

$$a_{B_i} = \frac{f_j[B(j)]}{\sum f_j[B(j)]} \quad \text{where, } B(j) = [B], [D] \text{ and } [F] \quad (2.19)$$

$$a_{A_i} = \frac{[A_i]}{\sum [A_i]} \quad \text{where, } A_i = [A_1], [A_2], [A_1^*], [A_2^*] \quad (2.20)$$

*Weight average molecular weight*

$$M_w = \sum W_{X_i} E(X_i) \quad (2.21)$$

where  $X_i = A_1, A_2, A_1^*, A_2^*, B, D$  and  $F$

$$W_{X_i} = \frac{M_{X_i} X_i}{\sum M_{X_i} X_i} \quad (2.22)$$

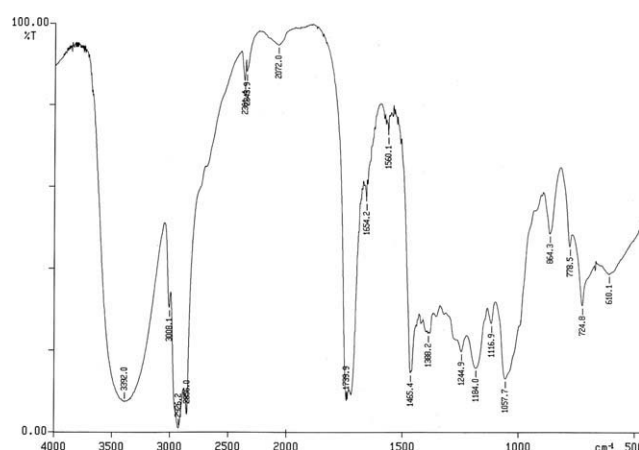
Concentrations of various species in the system were derived from eqs. (2.10–2.18) and were used for molecular weight predictions. Molecular weights as predicted by the model were compared with those calculated experimentally as well as those obtained using MALDI MS for few representative samples.

## RESULTS AND DISCUSSION

### Results for FTIR, LCMS, and Maldi MS for polyol characterization

Figure 1 shows Infrared spectrum for CO/TMP polyol in the range 4000–400  $\text{cm}^{-1}$  plotted on an absolute scale. Broad peak appearing at 3392  $\text{cm}^{-1}$  represents free hydroxyl groups.<sup>30,31</sup> Band observed at 2926.2  $\text{cm}^{-1}$  is due to  $-\text{CH}$  stretching and the peak for the carbonyl group ( $\text{C}=\text{O}$ ) appears at 1739.9  $\text{cm}^{-1}$ . During the reaction of polyol for polyurethane formation, free hydroxyl groups in the polyol react with isocyanate groups in MDI, and hence there is a decrease in intensity of  $-\text{OH}$  stretching peak while the intensity of  $-\text{CH}$  peak remains constant.<sup>32–34</sup> FTIR of the polyol also showed a peak at 1057  $\text{cm}^{-1}$ , which is characteristic of secondary hydroxyl group. Stretching peak for  $\text{C}-\text{O}$  is represented at frequency 1184  $\text{cm}^{-1}$ .

Figure 2 shows 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 water molecules; at 659.2  $m/z$  representing diricinoleate of TMP after removal of two water molecules and at 921.3  $m/z$  representing tricinoleate of TMP after removal of three water molecules. Medium intensity peaks at 695.1  $m/z$  and 974.9  $m/z$  represent intact molecules of diricinoleate and tricinoleate of trimethylol propane, respectively. Very low intensity peak



**Figure 1** FTIR spectrum for pure (without solvent) modified castor oil polyol at 25°C in the range 4000–400  $\text{cm}^{-1}$ .

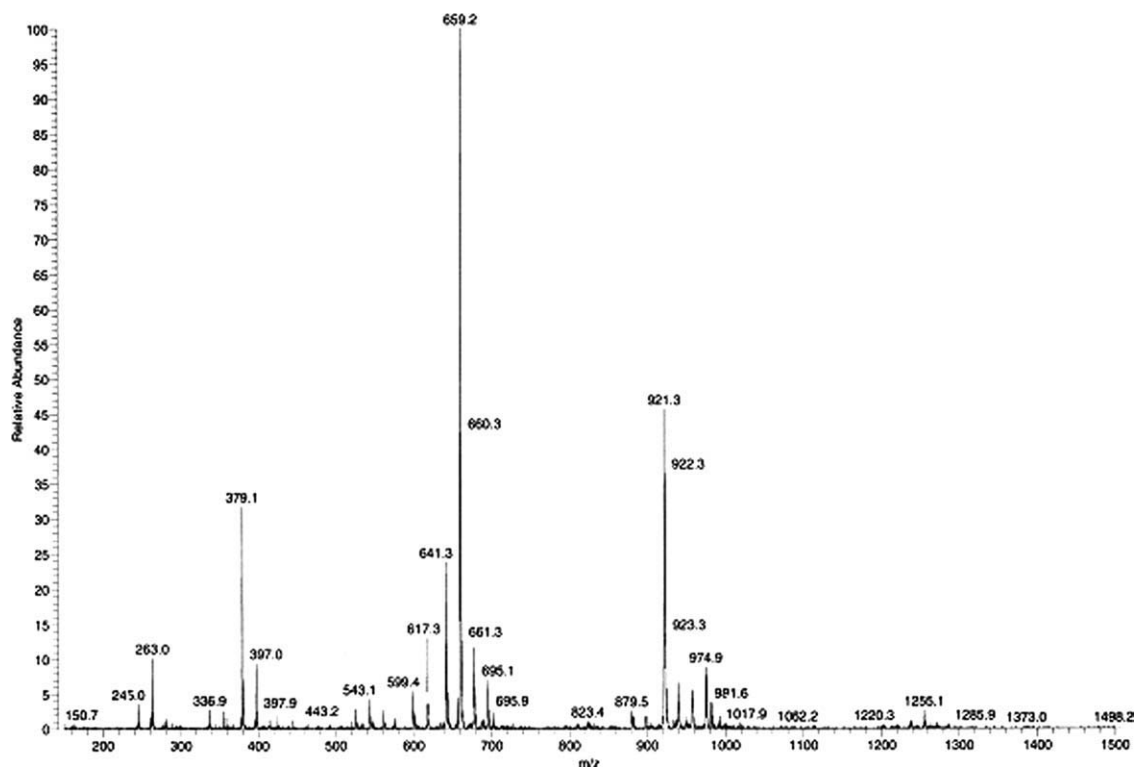


Figure 2 APCI mass spectra of modified castor oil polyol (without solvent) at 25°C for the range 150–1500  $m/z$ .

at  $m/z$  981.6 may be due to removal of one water molecule from tricinoleate of TMP and association of one  $\text{Na}^+$  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 monoricinoleate of

TMP after removal of one water molecule. The actual molecular weight is one less than the peak value of di- and tricinoleate of TMP. This may be due to addition of  $\text{H}^+$  during ionization of the sample. Medium intensity peak at  $m/z$  617.3 refers to

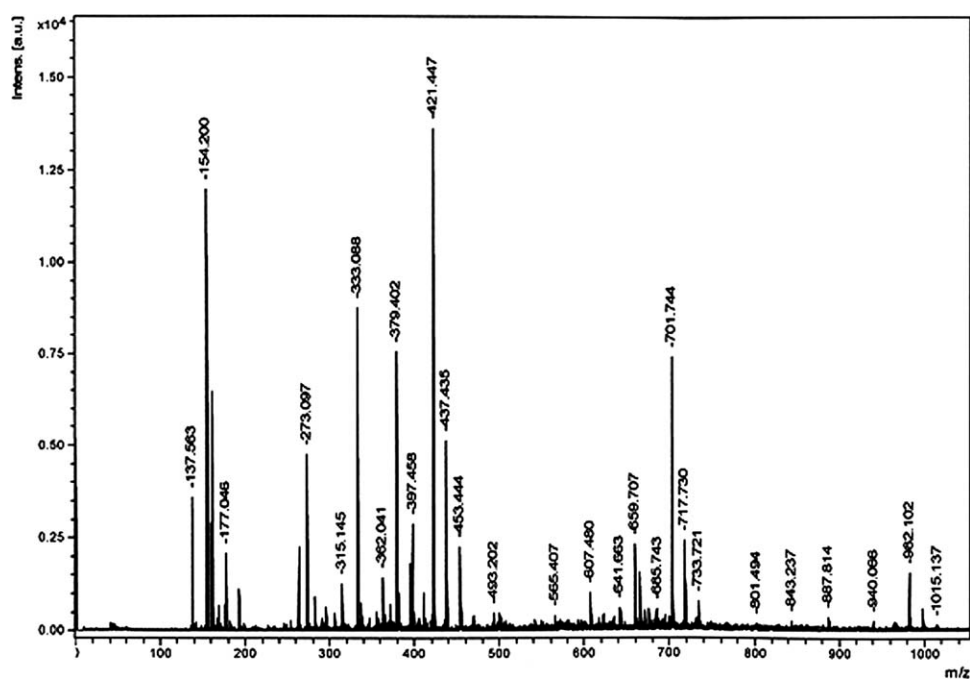


Figure 3 MALDI TOF mass spectrum for modified castor oil polyol (without solvent) at 25°C for the range 0–1000  $m/z$ .

**TABLE II**  
Theoretical Values of Different Properties of CO/TMP Polyol

S. No.	Property	Values
1	Hydroxyl value (Acetylation method)	354.6
2	Acid value	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

diricinoleate of castor oil after removal of one water molecule, and low intensity peak at  $m/z$  879.5<sup>35</sup> refers to triricinoleate of glycerol after removal of three water molecules. The details can be seen elsewhere.<sup>20</sup>

In the MALDI TOF Mass spectrum for CO/TMP polyol, for the range 0–1000  $m/z$  (Fig. 3), there are three high intensity peaks at  $m/z$  379.402,  $m/z$  421.447,  $m/z$  701.744. Peaks at  $m/z$  379.402 and  $m/z$  421.447 are for monoricinoleoyl trimethylol propane. Peak at  $m/z$  379.402 is after removal of two water molecules, and peak at  $m/z$  421.447 is due to sodiation and removal of one water molecule. The loss of water molecule could be due to the presence of the hydroxyl group and an adjacent hydrogen atom from the C-11 or C-13 position of the ricinoleic acid portion of the molecule is removed as water. This yields a mixture of two acids, each containing two double bonds but in one case, they are conjugated. Medium intensity peak at  $m/z$  437.435 is due to sodiated monoricinoleoyl trimethylol propane. High intensity peak at  $m/z$  701.744 is due to sodiated diricinoleoyl trimethylol propane after removal of one water molecule and medium intensity peak at  $m/z$  717.730 refers to sodiated diricinoleoyl trimethylol. Low intensity peak at  $m/z$  998.064 and 982.10 refers to sodiated tri ricinoleoyltrimethylol propane as such and after removal of one water molecule, respectively, and at  $m/z$  940.066 refers to triricinoleoyltrimethylol propane after removal of two water molecules.

Peak at  $m/z$  333.088 may be due to sodiated methyl ricinoleate, commonly found in fatty acid methyl esters (FAMES) from castor oil. Peak at  $m/z$

**TABLE III**  
Values of Polymerization Rate Constant ( $k_1^*$  and  $k_2^*$ ) Calculated Using Parameter Estimation Model

S. No.	NCO/OH ratio	Polymerization rate constant ( $k_1^*$ and $k_2^*$ ) $10^4$ Lit/eq. s.
1	0.75	0.0167
2	1.0	0.0833
3	1.25	0.0835

263.295, is due to sodiated ricinoleic acid after removal of one water molecule.

### Results of bulk polyurethane polymerization reactions under isothermal conditions in the reactor

All the bulk polymerization reactions were carried out at five different temperatures (10, 15, 20, 25, and 30°C), four different solvent concentrations (15, 20, 25, and 30%) and three different SIR i.e., 0.75, 1.0, and 1.25. All the bulk polymerization reactions follow a second order kinetics.<sup>36–39</sup> The conversion data and calculation of kinetic parameters for all the reactions has been reported elsewhere.<sup>40</sup> Rate constants for reference of modeling for different NCO/OH ratios are given below in Table II. These reactions are conducted at varying solvent concentration and varying NCO/OH ratio. That leads to different values of rate constant. From the second order rate constant data, it is evident that rate constants increase with increase in temperature and decrease with increase in solvent concentration. These values of rate constants were used to model reactions of modified castor oil polyol and MDI.

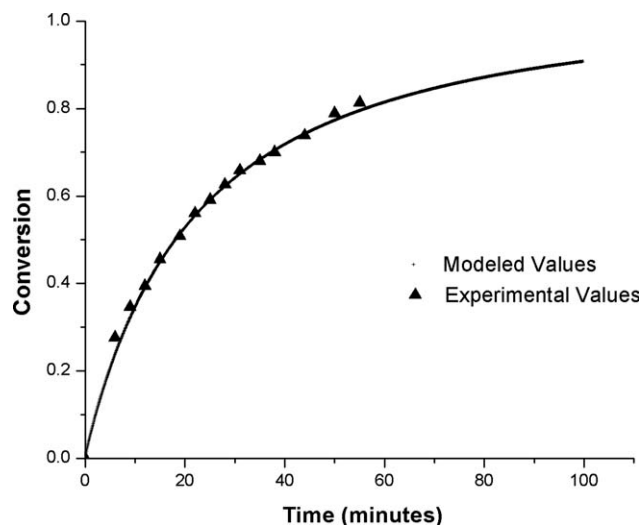
### Modeling of reactions using Kinetic Probabilistic Approach and Macosko Miller Approach

All the differential eqs. i.e., 2.1–2.18 were solved simultaneously using Euler's method in Bordland C. Final values for the unknown or uncertain model parameters were estimated using the method of "error in variables," a weighted multivariable nonlinear regression procedure, using experimental data from Kaushik and Singh.<sup>40</sup> Error in variable method aims at minimizing the Root Mean Square Error (RMSE) and Mean Relative Quadratic Error (MRQE) between the simulated and experimental data for the system.<sup>41–43</sup> The root mean square error and mean relative quadratic error are given by the following equations:

$$\text{RMSE} = \left( \frac{1}{N} \left( \sum_{i=1}^N (\text{observed} - \text{Modeled})^2 \right) \right)^{1/2}$$

**TABLE IV**  
Molecular Weights and Functionality of Different Species

S. No.	Property	Values
1	$M_A$	250 g/mol
2	$M_B$	524.62 g/mol
3	$f$	3
4	$M_E$	59 g/mol
5	$M_F$	58 g/mol
6	$M_{Aloph}$	101 g/mol

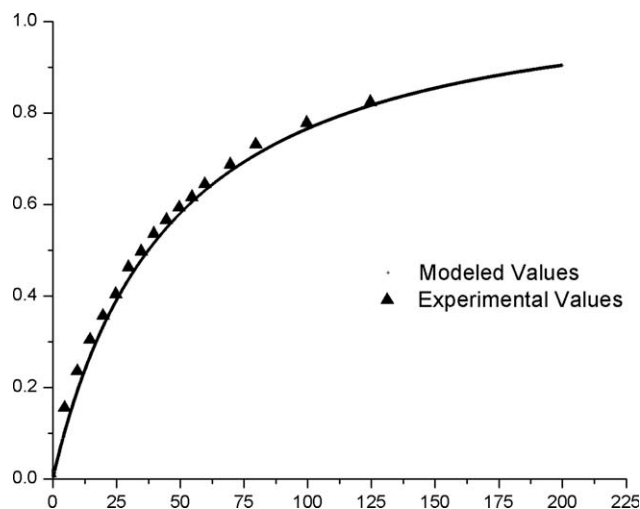


**Figure 4** Modeled and experimental values for reaction with NCO:OH ratio 0.75, temperature 30°C, and 15% solvent concentration.

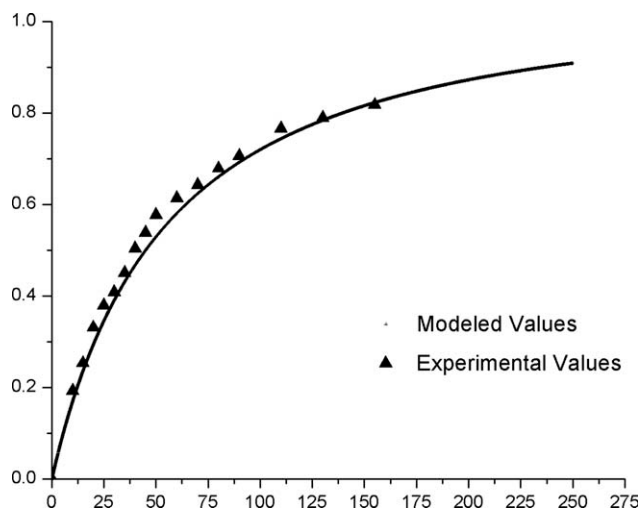
One more approach to minimize MRQE is given by equation

$$\text{MRQE} = \left[ \frac{1}{N-1} \sum_{i=1}^N \left( \frac{\text{Observed} - \text{Modeled}}{\text{Observed}} \right)^2 \right]^{1/2}$$

The simulations and parameter estimation calculations were carried out with Borland C implementation of the model equations. All of the unknown parameters were estimated simultaneously using the experimental data available (hydroxyl conversion). Initial value of  $k_1^*$  and  $k_2^*$  were varied from zero to 0.02 L/eq. s with an increment of 0.000001 and value of  $k_1^*$  and  $k_2^*$  which gave minimum value of RMSE and MRQE were



**Figure 5** Modeled and experimental values for reaction with NCO:OH ratio 0.75, temperature 25°C, and 25% solvent concentration.



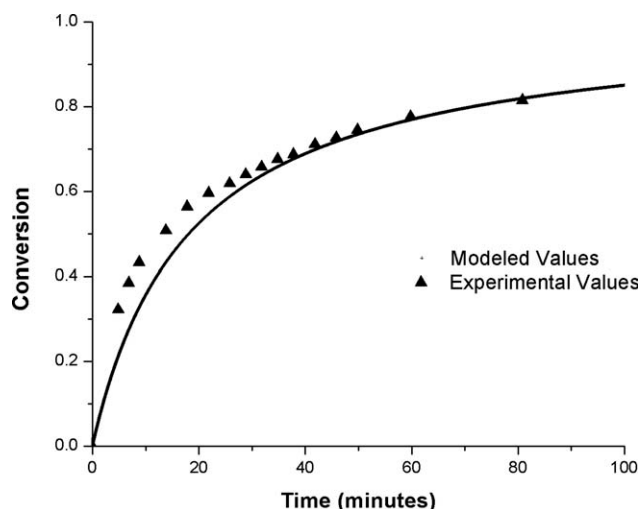
**Figure 6** Modeled and experimental values for reaction with NCO:OH ratio 0.75, temperature 15°C, and 20% solvent concentration.

taken. In all the cases the values match for the two approaches.

Rate constants  $k_3^*$  and  $k_4^*$ , polymerization rate constant for urea reactions, have been taken as zero because the concentration of water in the system is very low (0.008%). The rate constant for allophanate formation, from MDI and urethane formed i.e.,  $R_3$  has been taken as 0.00263.<sup>21</sup>

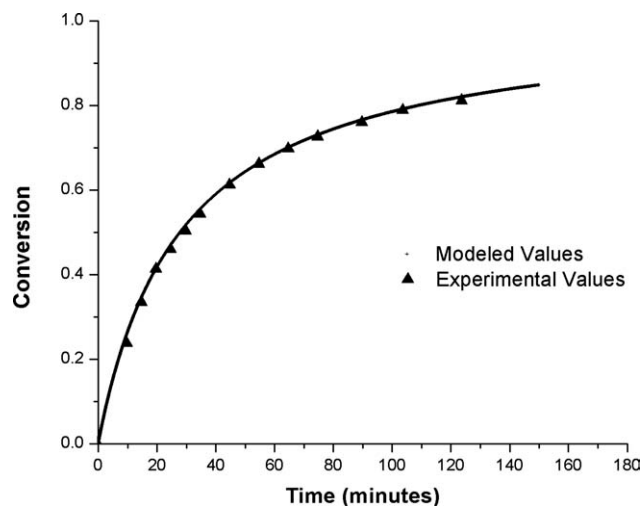
Polymerization conditions, molecular weights of different reactive species, and estimated kinetic constants are summarized in Tables I-IV.

Conversion versus time data obtained from the model was compared with the experimental data. The agreement was very good for all conversions for NCO/OH ratio 0.75 for all the solvent



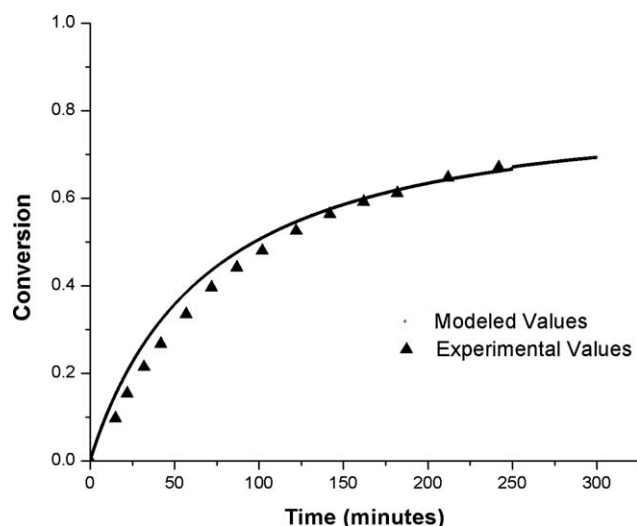
**Figure 7** Modeled and experimental values for reaction with NCO:OH ratio 1, temperature 30°C, and 25% solvent concentration.



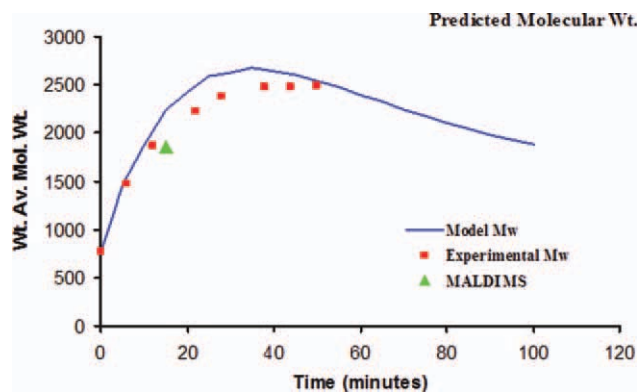


**Figure 8** Modeled and experimental values for reaction with NCO:OH ratio 1, temperature 15°C, and 20% solvent concentration.

concentrations. For NCO/OH ratio 1.0 and temperatures 10, 15, and 20°C, modeled and experimental data were in coherence for all the solvent concentrations. But for NCO/OH ratio 1.0, at 30°C and 25°C, at all solvent concentrations, model values were less than the experimental values. The reason could be very high rates of these reactions at prevailing temperature conditions. For NCO/OH ratio 1.25, modeled values were slightly higher than the experimental values, especially at low temperatures and high solvent concentrations i.e., 10–20°C and solvent concentrations of 25 and 30%. This indicated that the model developed for the system is a reasonable representation of the system.



**Figure 9** Modeled and experimental values for reaction with NCO:OH ratio 1.25, temperature 10°C, and 30% solvent concentration.



**Figure 10** Modeled and experimental values of molecular weight for reaction 21, NCO:OH ratio 1, temperature 30°C, and 15% solvent concentration. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

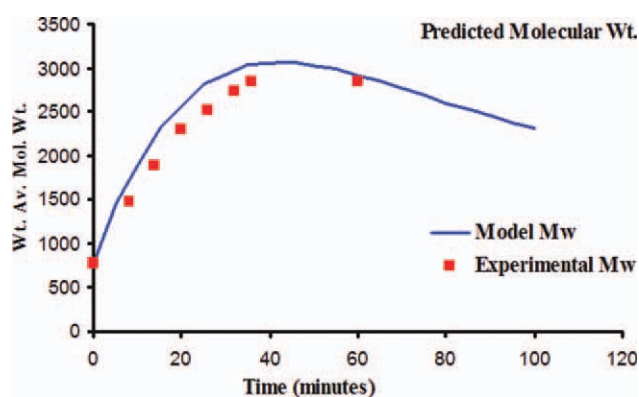
The results for three representative reactions are given in Figure 4–9.

Values of weight and number average molecular weights following Macosko Miller recursive approach for certain representative reactions have been shown in Figures 10 and 11. The figures show that experimental values are slightly less than the predicted values of molecular weights.

## CONCLUSIONS

It can be concluded that:

- i. Transesterification reaction between castor oil and trimethylol propane results in an equilibrium mixture of triglycerides, diglycerides, and monoglycerides of castor oil and TMP. In the two analyses, i.e., LCMS and MALDI MS, most of the peaks are common indicating the



**Figure 11** Modeled and experimental values of molecular weight for reaction 41, NCO:OH ratio 1.25, temperature 30°C, and 15% solvent concentration. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

presence of esters of trimethylol propane and glycerol. Intensity of the peaks varies because of the inherent difference in sample preparation.

- ii. Kinetic study of the polyurethane formation between castor oil/trimethylol propane polyol and 4,4'-diphenyl methane diisocyanate confirms that the 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 and second order rate constant increases with the temperature and decreases with the increase in solvent concentration.
- iii. Polyurethane reactions between MDI and CO/TMP polyol were modeled using Kinetic Probabilistic approach and Macosko Miller approach. The conversion versus time data obtained from the model was compared with the experimental data. The agreement was fairly good for all range of conversions for NCO/OH ratio 0.75 and 1.25. For NCO/OH ratio 1 at higher temperatures i.e., 25 and 20°C, modeled values were less than the experimental values.

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