

# Modeling and Simulation of Urethane Acrylates Synthesis. II. Kinetics of Uncatalyzed Reaction of Toluene Diisocyanate with a Polyether Diol

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**ABSTRACT:** Toluene diisocyanate reacts with poly(propylene glycol) during the synthesis of some urethane acrylate oligomers. The present work deals with kinetic studies and molecular characterization of the uncatalyzed bulk reaction of these two difunctional monomers. Back titration and H<sup>1</sup>-NMR are used to follow the reaction of the different isocyanate groups with an alcohol group belonging to poly(propylene glycol) and to allow a good description of the urethane groups evolution. The global reaction rate as well as that of each individual isocyanate group are well described by a second-order equation. Kinetic constants were calculated by using the software SIMUL-BATCH<sup>®</sup>. The reaction of two difunctional monomers leads to the formation of oligomers of different polymerization degrees, opposite to the reaction of TDI with a monoalcohol. Thus, another approach was developed to characterize the oligomers by size exclusion chromatography and to calculate the molecular weight distribution by using a combination of kinetic and probabilistic arguments. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3149–3160, 2001

**Key words:** kinetics; toluene diisocyanate; diol; urethane acrylate; H<sup>1</sup>-NMR; SEC; modeling; simulation

## INTRODUCTION

Polyurethane acrylates are a family of UV crosslinkable resins made of a polyester or a polyether diol of low molecular weight, a hydroxy-terminated acrylate, or methacrylate and a diisocyanate.<sup>1</sup> These oligomers are commonly prepared via a prepolymer route. The optimum prepolymer species would be a single diol molecule capped with two diisocyanate molecules.

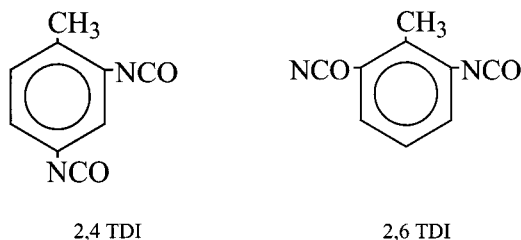
In a previous study, the reaction of toluene diisocyanate (TDI) with an acrylated monoalcohol (2-hydroxyethyl acrylate, HEA) was studied.<sup>2</sup> Commercial TDI is indeed interesting to study because it is a mixture of 2,4 and 2,6 isomers (Fig. 1), which have different reactivities and structures. 2,6-TDI is symmetrical and therefore the two isocyanate groups are initially identical, whereas the asymmetrical 2,4 isomer possesses NCO groups in the *para* and *ortho* positions in relation to the —CH<sub>3</sub>— group, with different reactivities.

The substantially different reactivity of the NCO groups influences the kinetics of polyurethane formation and, thus, the structure of the reaction products, particularly molecular weight

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**Figure 1** Structure of toluene diisocyanate.

distribution. To predict the polyurethane structure and to control the polymerization process, it is necessary to have a better understanding of the process kinetics and molecular composition in relation to the end-use properties.

Therefore, the purpose of the present work is to study the prepolymer formation [i.e., the reaction of TDI with poly(propylene glycol) with regard to the kinetic equations], which describe the reaction of each individual isocyanate group and to the probabilistic approach, used to determine the molecular distribution of the produced oligomers.

### MODEL AND KINETICS OF THE REACTION OF THE ISOCYANATE WITH THE ALCOHOL GROUPS

A number of equations were suggested to describe the reaction kinetics of an isocyanate with an alcohol. It is commonly accepted that the uncatalyzed reaction is a second-order one, especially for aromatic isocyanates<sup>3</sup>:

$$\frac{-d[\text{OH}]}{dt} = \frac{-d[\text{NCO}]}{dt} = \frac{d[\text{U}]}{dt} = k[\text{NCO}][\text{OH}] \quad (1)$$

where [OH], [NCO], and [U] are, respectively, the concentrations of alcohol, isocyanate, and produced urethane, and  $k$  represents the rate constant.

In this study, a kinetic model was established by considering the two isomers without any simplification on both the initial asymmetry and the substitution effect.

The successive reactions of an alcohol function with a diisocyanate first led to a monourethane (MU) and then to a diurethane (DU). It is usually considered that once the first isocyanate group has reacted to form an urethane, the reactivity of the second one is decreased because of a substitution effect.<sup>4</sup> The reaction kinetics of TDI diiso-

cyanate is complex if the initial difference in reactivities of the three individual isocyanate groups and the substitution effects are taken into account. It was assumed that the diol has neither asymmetry nor induced asymmetry. This was confirmed for the poly(propylene glycol) 1010, which is made of 17 repeated units and contains more than 95% of secondary alcohol groups. The corresponding scheme already used, for the description of the reaction of TDI with a monoalcohol,<sup>2</sup> is given in Figure 2 as a series of six parallel and consecutive reactions. According to second-order kinetics, the evolution of the different components are then defined by the following reaction rates:

$$\begin{aligned} \frac{d[\text{MU2,4o}]}{dt} &= k_{24o}[2,4\text{TDI}][\text{ROH}] \\ &\quad - k'_{24p}[\text{MU2,4o}][\text{ROH}] \\ \frac{d[\text{MU2,4p}]}{dt} &= k_{24p}[2,4\text{TDI}][\text{ROH}] \\ &\quad - k'_{24o}[\text{MU2,4p}][\text{ROH}] \\ \frac{d[\text{MU2,6o}]}{dt} &= k_{26o}[2,6\text{TDI}][\text{ROH}] \\ &\quad - k'_{26o}[\text{MU2,6o}][\text{ROH}] \\ \frac{d[\text{DU2,4}]}{dt} &= k'_{24p}[\text{MU2,4o}][\text{ROH}] \\ &\quad + k'_{24o}[\text{MU2,4p}][\text{ROH}] \\ \frac{d[\text{DU2,6}]}{dt} &= k'_{26o}[\text{MU2,6o}][\text{ROH}] \end{aligned} \quad (2)$$

The molar instantaneous balance is

$$\begin{aligned} (n_{2,4\text{TDI}})_0 &= (n_{2,4\text{TDI}})_{\text{free}} + n_{\text{MU2,4p}} + n_{\text{MU2,4o}} + n_{\text{DU2,4}} \\ (n_{2,6\text{TDI}})_0 &= (n_{2,6\text{TDI}})_{\text{free}} + n_{\text{MU2,6o}} + n_{\text{DU2,6}} \\ (n_{\text{TDI}})_{\text{free}} &= (n_{2,4\text{TDI}})_{\text{free}} + (n_{2,6\text{TDI}})_{\text{free}} \\ n_{\text{MU ortho}} &= n_{\text{MU2,4o}} + n_{\text{MU2,6o}} \end{aligned} \quad (3)$$

The individual rate constants  $k_{24o}$ ,  $k_{24p}$ ,  $k_{26o}$ ,  $k'_{24o}$ ,  $k'_{24p}$ , and  $k'_{26o}$ , which describe the interaction of the free and urethane substituted isocyanate with the —OH group of poly(propylene glycol), were calculated by the use of the software SIMUL-BATCH<sup>®</sup>,<sup>5</sup> which integrates the differential equations system (2) using a GEAR numerical method based on DASSL code. Rosenbrock's method is

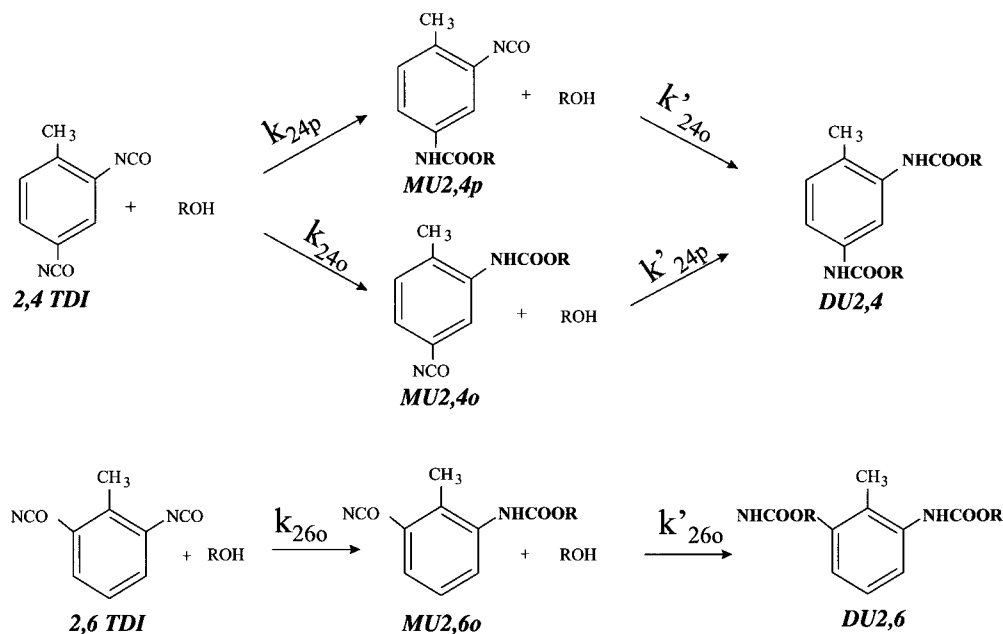


Figure 2 Kinetic scheme.

used for the estimation of the kinetic parameters on the basis of experimental data.

In the present study, it was assumed and then confirmed that the catalysis of urethanes and side reactions could be neglected. The absence of secondary products was, indeed, checked by a titration method.<sup>6</sup>

## MODELING OF MOLECULAR WEIGHT DISTRIBUTION BASED ON KINETIC AND PROBABILISTIC ARGUMENTS

Step polymers such as polyurethanes can be considered as products of reaction between two difunctional monomers. Although it is usually assumed that the two groups of the monomer are equally reactive, many exceptions remain:

Asymmetric monomers such as a diol, which contain a primary and a secondary hydroxyl group. The two groups may be expected to react with different rates.

Monomers, such as 2,6-TDI, with induced asymmetry, also called the substitution effect. Indeed, reaction of one group may induce asymmetry and alter the reactivity of the other group.

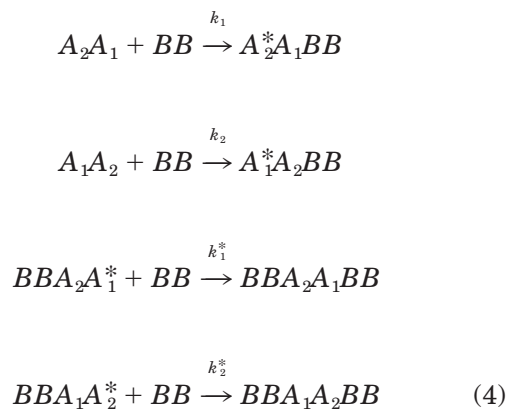
Monomers, such as 2,4-TDI, for which the reactive functional groups have unequal reac-

tivities and exhibit simultaneous, induced asymmetry.

### Asymmetric Monomer with Induced Asymmetry

#### Model

Let  $A_1A_2$  be a functional monomer that simultaneously exhibits asymmetry and induced asymmetry. Let it react with a monomer  $BB$ , which has neither asymmetry nor induced asymmetry; the reactions can be represented as in the kinetic model for 2,4-TDI:



$A_1$  and  $A_2$  groups belong to the monomer and  $A_1^*$  and  $A_2^*$  are located at the ends of the chains.

The various types of species present at any time during the polymerization process are

$A_1A_2$	of amount $A$
$(A_1^*A_2BB)_n$	of amount $r_n^1$
$(A_2^*A_1BB)_n$	of amount $r_n^2$
$(A_1^*A_2BB)_nA_1A_2^*$	of amount $p_n^{12}$
$(A_1^*A_2BB)_nA_2A_1^*$	of amount $p_n^{11}$
$(A_2^*A_1BB)_nA_1A_2^*$	of amount $p_n^{22}$
$(BBA_1A_2)_{n-1}BB$	of amount $q_n$

### Definitions of Probabilities of Reaction

The instantaneous probability of reaction of a particular group is defined as the fraction of the groups that have reacted at that time.

*Probability of Reaction of Alcohol Groups.* The probability of reaction of  $B$  groups,  $\beta$ , is equal to the fraction of the initial  $B$  groups that have reacted:

$$\beta = 1 - \frac{[B]}{2B_0}$$

with  $B_0$  the initial concentration of diol.

*Probability of Reaction of Monomeric A Groups.*

The concentration of  $A_1$  groups can decrease by direct and indirect reactions, when an  $A_2$  group of the monomer reacts. However, the probability of reaction of monomeric  $A_1$  groups is only related to the direct reaction. Let  $A_1^r$  denote the total monomeric  $A_1$  groups that were consumed since the beginning of the reaction by direct reaction with  $B$  groups. The probability of reaction of monomeric  $A_1$  groups,  $\alpha_1$ , can be defined as

$$\alpha_1 = \frac{A_1^r}{A + A_1^r}$$

Similarly, the probability of reaction of monomeric  $A_2$  groups,  $\alpha_2$ , can be defined as

$$\alpha_2 = \frac{A_2^r}{A + A_2^r}$$

*Probability of Reaction of Polymeric A Groups.*

The probability of polymeric  $A_1$  groups (i.e.,  $A_1^*$  groups) will be defined as the fraction of available  $A_1^*$  groups that have reacted with  $B$  groups. Because initially  $[A_1^*] = 0$ , the total number of  $A_1^*$  that were available for reaction is equal to the

total number of  $A_1^*$  groups that were created. Hence,  $(A_1^*)_0 = A_2^r$  and the probability of reaction of  $A_1^*$  is

$$\alpha_1^* = \frac{(A_2^r - A_1^*)}{A_2^r}$$

Similarly, the probability of reaction of polymeric  $A_1^*$  is defined as

$$\alpha_2^* = \frac{(A_1^r - A_2^*)}{A_1^r}$$

### Oligomer Distribution

According to the detailed procedure described by Gandhi and Babu,<sup>7</sup> the molar concentrations relative to the molecular weight distribution are given by:

$$\begin{aligned} A &= \frac{B_0R(1 - \alpha_1)}{K\alpha_1 + 1} \\ r_n^1 &= \frac{B_0RK\alpha_1(1 - \beta)(1 - \alpha_1^*)(R\delta)^{n-1}}{K\alpha_1 + 1} \\ r_n^2 &= \frac{B_0R\alpha_1(1 - \beta)(1 - \alpha_2^*)(R\delta)^{n-1}}{K\alpha_1 + 1} \\ p_n^{11} &= \frac{B_0R^2K^2\alpha_1^2(1 - \alpha_1^*)^2(R\delta)^{n-1}}{\{2(K\alpha_1 + 1)\}^2} \\ p_n^{22} &= \frac{B_0R^2\alpha_1^2(1 - \alpha_2^*)^2(R\delta)^{n-1}}{\{2(K\alpha_1 + 1)\}^2} \\ p_n^{12} &= \frac{B_0R^2K\alpha_1^2(1 - \alpha_2^*)(1 - \alpha_1^*)(R\delta)^{n-1}}{2(K\alpha_1 + 1)^2} \\ q_n &= B_0(1 - \beta)^2(R\delta)^{n-1} \end{aligned} \quad (5)$$

with

$$R = \frac{A_0}{B_0} = \frac{(A_1A_2)_0}{(BB)_0}$$

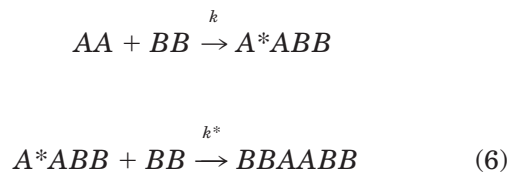
$$K = \frac{k_2}{k_1}$$

$$R\delta = 2\beta \frac{A_2^r\alpha_1^* + A_1^r\alpha_2^*}{A_2^r(1 + \alpha_1^*) + A_1^r(1 + \alpha_2^*)}$$

### Symmetric Monomer with Induced Asymmetry

Let us consider the polymerization of  $AA$  and  $BB$ , with an induced asymmetry in  $AA$ . Thus, once one

of the  $A$  groups of the monomer has reacted, the other  $A$  group reacts at a rate different from the first one. For this system, the reactions are then



where  $A$  belongs to the monomer and  $A^*$  to the polymer.  $\beta$  and  $\alpha$  are, respectively, the fraction of initial  $B$  groups and moles of  $AA$  that have reacted.  $\alpha^*$  is the ratio of the number of  $A$  groups attached to a chain ( $A^*$ ) that have reacted to the initial number of  $AA$  molecules. The species that are present at any time during the polymerization process are

$AA$	of amount $A$
$(AABB)_n AA^*$	of amount $p_n$
$(AABB)_n$	of amount $r_n$
$(BBAA)_{n-1} BB$	of amount $q_n$

The molecular weight distribution is characterized by the following concentrations<sup>8</sup>:

$$A = A_0(1 - \alpha)$$

$$r_n = 2B_0(1 - \beta)(\beta - R\alpha^*)(R\alpha^*)^{n-1}$$

$$p_n = B_0(\beta - R\alpha^*)^2(R\alpha^*)^{n-1}$$

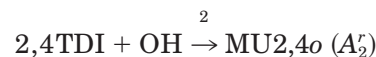
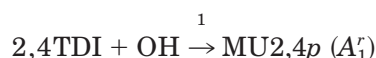
$$q_n = B_0(1 - \beta)^2(R\alpha^*)^{n-1} \quad (7)$$

with

$$R = \frac{A_0}{B_0} = \frac{(AA)_0}{(BB)_0}$$

#### Application of the Model to the Studied Process

The probabilities of reaction can be written differently, using the concentrations obtained by  $H^1$ -NMR during the reaction of TDI with poly(propylene glycol):



Consumed 2,4-TDI can be expressed as:

$$(2,4TDI)_0 - 2,4TDI(t) = A_1^r + A_2^r$$

For a semibatch process,

$$R = (n_{TDI})_0 / (n_{PPG})_{introduced}$$

Considering the above expressions, the concentrations may be written as follows:

$$p_n^{11} = \frac{B_0 R^2 \times MU2,4o^2}{4(2,4TDI)_0^2} (R\delta)^{(n-1)}$$

$$p_n^{22} = \frac{B_0 R^2 \times MU2,4p^2}{4(2,4TDI)_0^2} (R\delta)^{(n-1)}$$

$$p_n^{12} = \frac{B_0 R^2 \times MU2,4p \times MU2,4o}{2(2,4TDI)_0^2} (R\delta)^{(n-1)}$$

$$r_n^1 = \frac{B_0 R \times MU2,4o \times (1 - \beta)}{(2,4TDI)_0} (R\delta)^{(n-1)}$$

$$r_n^2 = \frac{B_0 R \times MU2,4p \times (1 - \beta)}{(2,4TDI)_0} (R\delta)^{(n-1)}$$

$$A = \frac{B_0 R \times 2,4TDI(t)}{(2,4TDI)_0} \quad (8)$$

with

$$R\delta = 2\beta \frac{[(2,4TDI)_0 - 2,4TDI(t)] - [MU2,4o + MU2,4p]}{2[(2,4TDI)_0 - 2,4TDI(t)] - [MU2,4o + MU2,4p]}$$

For 2,6-TDI:

$$\alpha^* = \frac{DU2,6}{(2,6TDI)_0} \quad (9)$$

Once the concentrations of the different functional groups are determined by  $H^1$ -NMR or by the kinetic model described in the first part, the previous equations can be used to determine molar fractions of the oligomers with different polymerization degrees. Then, the theoretical data can be compared to the data obtained from size exclusion chromatography (SEC).

**Table I**  $H^1$ -NMR Chemical Shifts (360 MHz,  $CDCl_3$ )

Compound	Chemical Shift $\delta$ (ppm)
—OH reacted	$P_1 = 5$
Free TDI	$P_2 = 2.28$
MU2,4 <i>p</i>	$P_3 = 2.24$
MU2,6 <i>o</i>	$P_4 = 2.21$
MU2,4 <i>o</i>	$P_5 = 2.19$
DU2,4	$P_6 = 2.16$
DU2,6	$P_7 = 2.11$

## EXPERIMENTAL

### Reactions

Prepolymers were prepared from poly(propylene glycol) (PPG 1010 from Arco), the average molecular weight of which is 1000 g/mol, and TDI (80 : 20%) from Arco. The monomers were used as received from the supplier. The uncatalyzed reactions were performed at different temperatures (60, 70, 80, and 90°C) with a constant  $[NCO]_0 : [OH]_{added}$  ratio equal to 2. Prior to the reaction, the moisture content of the alcohol was checked by Karl Fisher method.<sup>9</sup> It was <0.05%, which avoids side reactions with residual water. The reactions were performed in bulk by a semibatch

process using a calorimeter kettle Mettler RC1 under isothermal conditions. The samples for kinetics study were withdrawn at fixed time intervals.

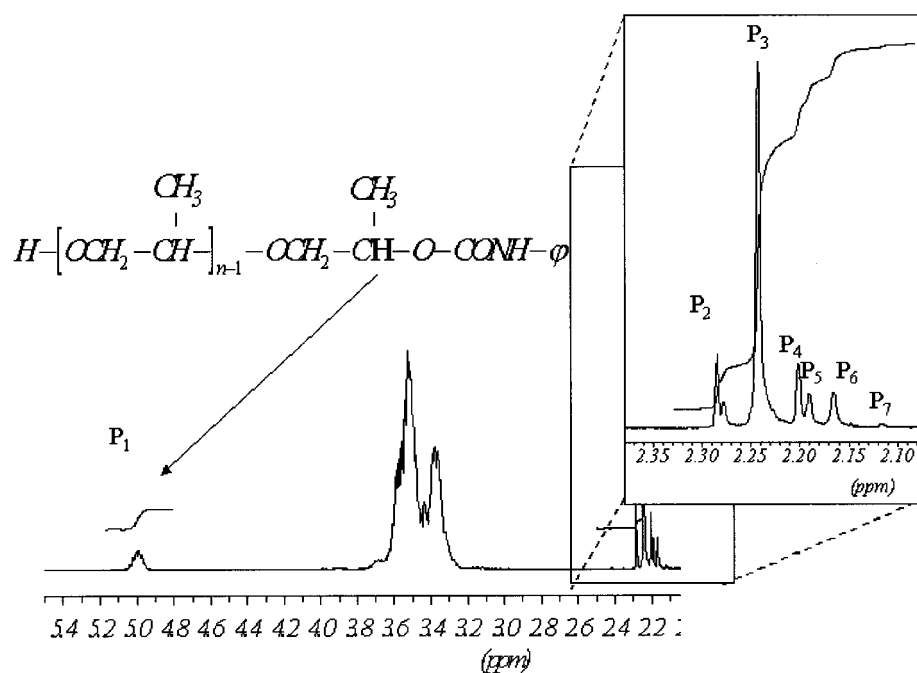
### Characterization

#### Back Titration

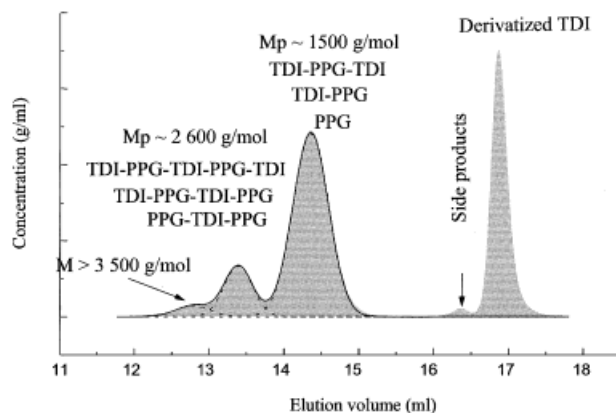
Global reaction was followed by determining the unreacted isocyanate concentration as a function of reaction time, using the standard dibutylamine back titration.<sup>6</sup> The isocyanate values allow one to follow the global rate of isocyanates disappearance without any mechanism distinction. The back titration method can also be used to check the amount of secondary products when the obtained values are lower than the theoretical ones, as calculated from the main reaction.

#### $H^1$ -NMR

To determine the reactivity of the different isocyanate groups, it is necessary to know the concentrations of each individual groups.  $H^1$ -NMR allows a complete description of the system at any time and the determination of the concentrations of the different isocyanate and urethane groups, without considering the polymerization degree of the oligomers they belong to.



**Figure 3**  $H^1$ -NMR spectrum of reaction products of TDI and PPG 1010.



**Figure 4** SEC of reaction products of TDI/PPG 1010.

$^1\text{H}$ -NMR spectra were acquired in deuterated chloroform ( $\text{CDCl}_3$ ) by using a 360 MHz Bruker spectrometer at a temperature  $> 40^\circ\text{C}$ , to separate monourethanes substituted in *ortho* position. The corresponding analysis was performed on samples directly dissolved in  $\text{CDCl}_3$  without any previous treatment.

The chemical shifts, presented in Table I, were determined according to the literature<sup>10</sup> and model compounds were prepared with pure 2,4-TDI or 2,6-TDI. Urethane groups were well identified in the  $-\text{CH}_3-$  region of the toluene ring. For poly(propylene glycol), the region around 5 ppm was used to characterize the extent of alcohol reaction (Fig. 3). Concentrations of the functional groups were calculated from the integrals of the corresponding signals.

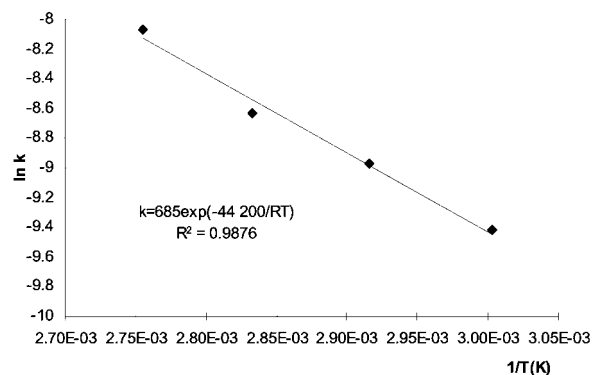
### Size Exclusion Chromatography

The potential of SEC as an analytical tool to be applied to oligomers was recognized in literature.<sup>11–13</sup>

The samples, after derivatization with dibutylamine in toluene, were analyzed by SEC, which was performed with a Waters 510 device

**Table II** Global Kinetic Constant of OH/NCO Reaction at Different Temperatures

$T$ ( $^\circ\text{C}$ )	Global Kinetic Constant, $k$ ( $\text{kg/mol s}$ )	Activation Energy ( $\text{kJ/mol}$ )
60	$8.1 \times 10^{-5}$	44.2
70	$1.3 \times 10^{-4}$	
80	$1.8 \times 10^{-4}$	
90	$3.1 \times 10^{-4}$	



**Figure 5** Arrhenius plot for second-order OH/NCO reaction.

equipped with a differential refractometer. Tetrahydrofuran (THF) was the mobile phase used at a 1 mL/min flow rate. The oligomers are separated by two columns Plgel 3  $\mu\text{m}$  MIXED-E from Polymer Laboratories. Identification of the different oligomers was possible after the calibration of the system with poly(propylene glycol) standards from American Polymer Standards Corp. and with prepolymers prepared from TDI and the poly(propylene glycol) standards.

The peak areas in the chromatograms are proportional to the molar concentration of the species. The peaks are not well separated by the columns because the molecular weight of the different molecules formed during the reaction are very close. To get the peaks areas, the signal was treated by mathematical deconvolution. The validity of this method was confirmed by deconvolution on mixtures of poly(propylene glycol) standards with known composition.

Figure 4 presents an SEC chromatogram of the reaction products of TDI with PPG 1010.

From the peak areas and the concentration of TDI given by  $^1\text{H}$ -NMR or HPLC, the molar concentrations of the oligomers of different molecular weights can be calculated.

## RESULTS AND DISCUSSION

The extent of the reaction is characterized by the changes in the concentration of both reactants and reaction products. The kinetic analysis was developed on the basis of the reaction scheme and equations proposed in the first part of this article. The corresponding rate constants were calculated using SIMULBATCH<sup>®</sup> software.

**Table III** Rate Constants Calculated for the Reaction Carried Out at 60°C

$k_{24o}$ (kg/mol s)	$k_{24p}$ (kg/mol s)	$k_{26o}$ (kg/mol s)	$k'_{24o}$ (kg/mol s)	$k'_{24p}$ (kg/mol s)	$k'_{26o}$ (kg/mol s)
$3.37 \times 10^{-5}$	$2.06 \times 10^{-4}$	$6.92 \times 10^{-5}$	$1.3 \times 10^{-5}$	$2.75 \times 10^{-5}$	$1.2 \times 10^{-5}$

### Global Estimation from Experimental Isocyanate Concentrations and Validation of the Kinetic Model for Uncatalyzed Reaction

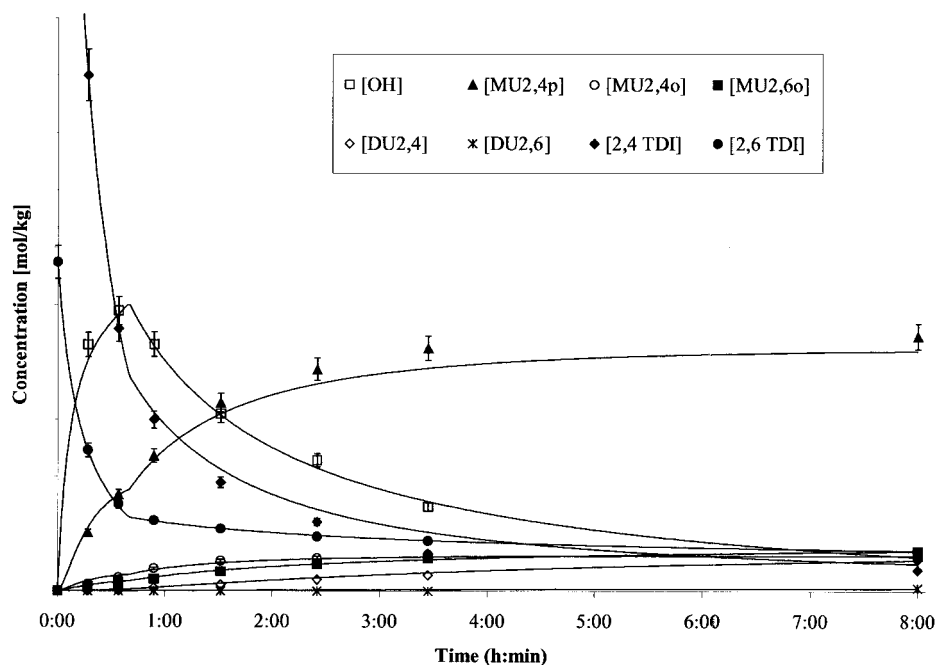
In a first approach and according to the isocyanate concentrations as determined by back titration, a global reaction scheme was considered:  $\text{NCO} + \text{OH} \rightarrow \text{NHCOO}$  (U).

The rate constant corresponding to eq. (1) was calculated at each temperature. Results are given in Table II. Using an Arrhenius relation  $k = A \exp(-E_a/RT)$ , the activation energy for the OH/NCO reaction was determined, as shown in Figure 5, and corresponds to the values found in the literature.<sup>1,14,15</sup> Temperature effect on the reaction kinetics of TDI/PPG 1010 is important. For example, an increase of 20°C allows a synthesis time reduction of 60%, as in the reaction with HEA.

These results confirm the validity of the second-order kinetic scheme, which will be used for the following kinetic study.

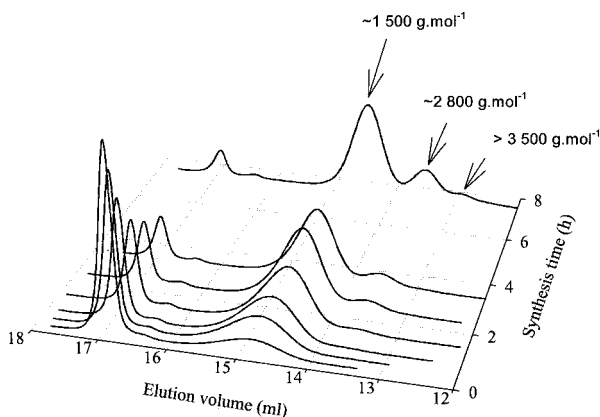
### Detailed Kinetic Study

$^1\text{H-NMR}$  gives precise information on the functional groups present in the reaction medium, which allows one to determine the kinetic constants of the detailed kinetic scheme established herein. Kinetic constants were determined for each temperature and according to an Arrhenius relation, the activation parameters were calculated. The data were then used to simulate the evolution of the concentration of each functional group according to the kinetic model at different temperatures. As an example, the kinetic constants for the reaction at 60°C are given in Table III. Figure 6 shows the results of the simulations at 60°C. Rather good agreement was obtained between experimental and calculated values, which confirm the validity of the second-order kinetic model for each isocyanate group.



**Figure 6** Comparison between experimental and calculated values (full curves) at 60°C.





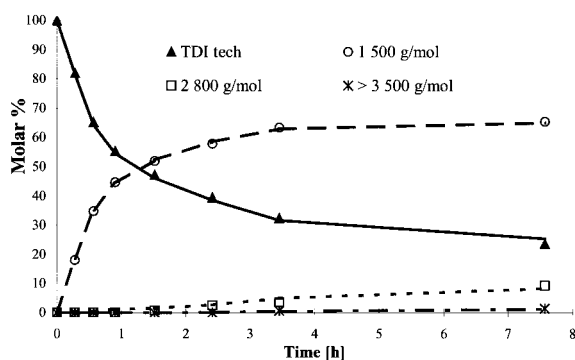
**Figure 7** SEC spectra along the reaction of TDI with PPG 1010.

### Oligomers Molecular Distribution

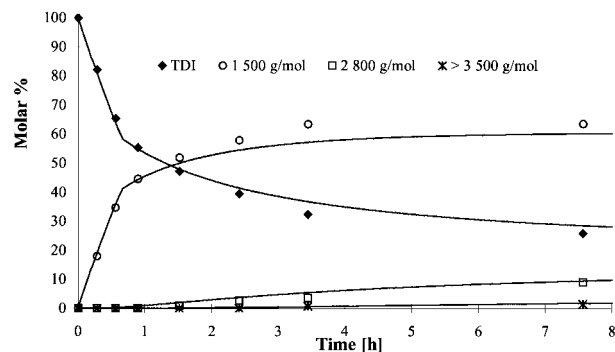
Once the concentrations of each functional group are determined as a function of time at different temperatures, these data can be introduced in the statistical model to determine the molecular distribution as described by eqs. 5 and 7. Then they can be compared to the data obtained from SEC spectra, of which an example is given Figure 7 for the reaction between TDI and PPG 1010 at 60°C.

From SEC spectra, the molar concentrations are experimentally determined along a whole synthesis and are compared to the theoretical values calculated from the probabilistic equations and by using the data determined by H<sup>1</sup>-NMR. Figure 8 shows clearly rather good agreement between experimental and calculated values.

The theoretical oligomer molecular distribution can be calculated directly either from the experimental urethane groups concentrations or from the simulated values calculated by the detailed kinetic model. Figure 9 shows the compar-



**Figure 8** Comparison of the simulated (full curves) and the experimental data TDI/PPG 1010 at 60°C.



**Figure 9** Validation of the statistical model with the simulated value.

ison between the experimental distribution and the statistical model based on simulated urethane concentrations. The agreement between the theoretical statistical model based on the data issued from the detailed kinetic model and the experimental data is quite good. The modeling errors are responsible for the small differences between experimental and simulated values of TDI and oligomers of molecular weight equal to 1 500 g/mol, but it still allows a correct description of the molecular composition of the medium.

The global procedure for the modeling part of this work consisted of calculating, from the experimental data obtained from H<sup>1</sup>-NMR, the kinetic parameters, this to simulate concentrations of the functional groups as a function of time and temperature. The simulated data determined in the previous step allow one to calculate the molecular distribution of the oligomers at different polymerization degrees, by using a statistical model based on kinetic and probabilistic considerations.

### Kinetic Parameters Sensitivity

The parameters sensitivity was tested to determine the relevance of the constants of the detailed kinetic model for the description of the system. The global criterion used for the optimization procedure is equal to

$$J = \sum_i w_i j_i$$

with

$$j_i = \sum_j w_j \sum_k (y_{\text{calc}}^{i,j,k} - y_{\text{exp}}^{i,j,k})^2,$$

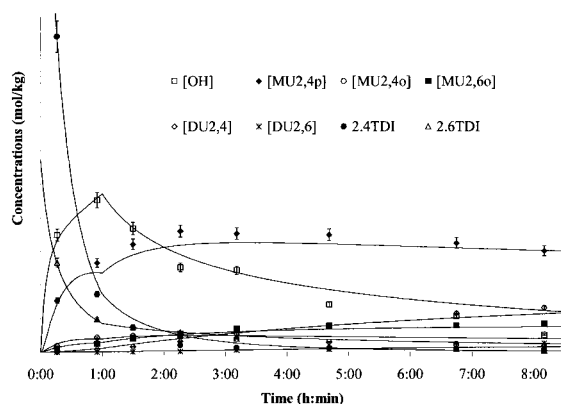
the individual criteria of experiment  $i$  (10)

**Table IV Kinetic Parameters Sensitivity**

Constant and Temperature	$\Delta J$ (-20%)	$\Delta J$ (+20%)
$k_{2,4o}$ 60°C	20.1%	17.9%
$k_{2,4o}$ 90°C	20.1%	15.8%
$k_{2,4p}$ 60°C	25.4%	17.4%
$k_{2,4p}$ 90°C	26.5%	19.3%
$k_{2,6o}$ 60°C	18.9%	15.1%
$k_{2,6o}$ 90°C	19.5%	16.3%
$k'_{24p}$ 60°C	2.9%	1.9%
$k'_{24p}$ 90°C	3.7%	1.6%
$k'_{24o}$ 60°C	18.7%	13.9%
$k'_{24o}$ 90°C	16.1%	13.1%
$k'_{26o}$ 60°C	3.2%	2.9%
$k'_{26o}$ 90°C	6.7%	6.1%

where  $w_i$  is the weight factor for experiments,  $w_j$  is the weight factor for a category of experimental data, and  $k$  is a point of  $j$ . A variation of  $\pm 20\%$  from its optimal value was applied to each kinetic constant and the induced variation percentage of the global criterion was calculated. The results are described in Table IV. The sensitivity calculations show that less precision is required on  $k'_{24p}$  and  $k'_{26o}$  kinetic parameter calculation to describe the evolution of the species concentrations. However, this does not mean that these constants are not significant for the whole characterization of the system. Table V presents the composition variation at 60°C, when each kinetic constant is increased by 20%.

The  $H^1$ -NMR experimental error on the urethane groups concentrations is 5% and, except for  $k'_{24p}$ , a variation of 20% on the constants involves an inaccuracy larger than the experimental error. A simulation was made without  $k'_{24p}$  and shows that this constant is required in the kinetic scheme even if it is not notable as far as variations are concerned.

**Figure 10** Use of the kinetic model with another stoichiometric ratio at 70°C.

### Validity of the Kinetic Parameters for Another Stoichiometric Ratio

To check the validity of the kinetic constants, a synthesis was made with a different stoichiometric ratio between the isocyanate and alcohol functions. With a ratio equal to 1.5, a greater amount of diadducts is formed, which allows one to confirm the values of the substitution constants. A comparison of the simulation made with the kinetic parameters calculated from the detailed study of the reaction between TDI and PPG 1010, and the experimental data (Fig. 10) shows again rather good agreement between the model and the experiment.

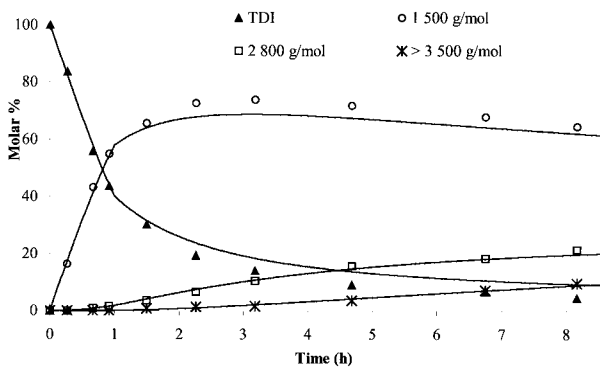
The statistical model is also valid for a different experimental procedure as shown in Figure 11. Oligomers of higher polymerization degrees are formed as compared to a lower stoichiometric ratio and this evolution is well simulated by the statistical model based on the calculated data.

### Influence of the Temperature

Similar to the monoalcohol, the final composition of the medium is characterized by the initial dif-

**Table V Influence of Kinetic Parameters Variation on the Structure for 90% of Alcohol Conversion**

	2,6TDI (%)	2,4TDI (%)	MU(2,4o) (%)	MU(2,4p) (%)	DU(2,4) (%)	MU(2,6o) (%)	DU(2,6) (%)
$k_{24o} + 20\%$	1.3	1.8	17.4	2.4	0.4	1.2	3.4
$k_{24p} + 20\%$	5.9	14.9	12.2	4.7	7.1	5.6	14.7
$k_{26o} + 20\%$	9.9	8.8	0.3	0.6	5.3	10.6	8.2
$k'_{24p} + 20\%$	0.5	1.9	3.5	0.1	3.1	0.4	1.3
Without $k'_{24p}$	3.4	11.2	20.8	0.7	19.3	3.2	9.3
$k'_{24o} + 20\%$	1.6	6.0	0.2	2.0	10.1	1.6	4.3
$k'_{26o} + 20\%$	0.1	0.7	0.1	0.0	0.5	1.4	18.6

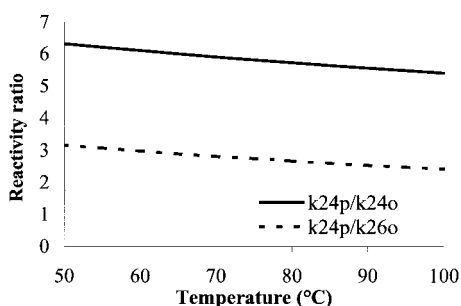


**Figure 11** Modeling of oligomers molecular distribution for a ratio equal to 1.5 at 70°C.

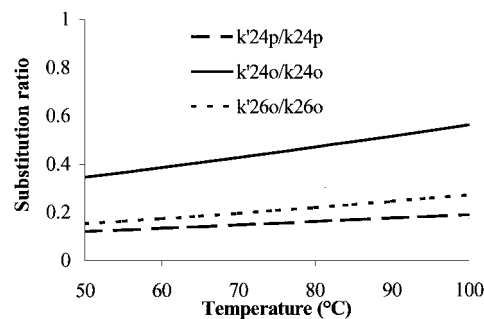
ferent reactivities of the isocyanate groups and the substitution effect.

As shown in Figure 12, the reactivity of the *para*-isocyanate group of 2,4-TDI is more important than that of the *ortho*-isocyanate groups for both isomers because of steric hindrance and the electronic effect involved by the methyl group. The reactivity ratio between both isocyanate groups of 2,4-TDI is equal to  $5.8 \pm 0.5$ . Moreover, the *ortho*-isocyanate group of 2,6-TDI has an intermediate reactivity when compared with both isocyanate groups of 2,4-TDI. The reactivity ratio between the two isomers, when reacting with the alcohol groups of poly(propylene glycol), is equal to  $2.8 \pm 0.4$ . The ratios are fairly constant over the investigated temperature range, which indicates that the amount of monourethanes does not depend on the process temperature.

The substitution effect, usually defined as the ratio  $k'/k$ , characterizes the formation of the diadducts DU-2,4 and DU-2,6. As shown in Figure 13, it is confirmed that the reactivity of the second isocyanate group is decreased by the presence of a urethane group on the molecule. Urethane groups are indeed constituents that are less electron



**Figure 12** Reactivity ratios versus temperature.



**Figure 13** Substitution ratios versus temperature.

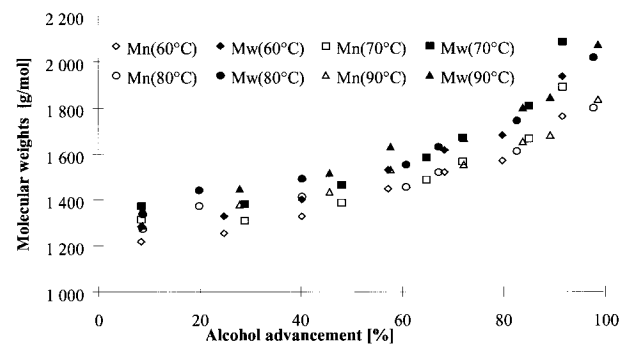
withdrawing than isocyanate groups. Thus, they reduce the positive partial charge on the free isocyanate carbon atom. This makes the attack by an electron donor on the carbon more difficult, hence reducing the reaction rate. This effect is observed for each isocyanate group. When the process temperature is increased, the amount of diadducts is also increased, without altering the properties such as viscosity, because the substitution ratios are not influenced much by temperature.

Moreover, as observed for the urethane groups, the molecular weights of the oligomers are not influenced significantly by temperature, as shown in Figure 14.

The process temperature can be thus increased to accelerate the reaction without modifying the structure of the product and then the end-use properties.

## CONCLUSION

The reaction of TDI diisocyanate with poly(propylene glycol) 1010 was studied. Back titration,



**Figure 14** Average molecular weights evolution during synthesis as a function of temperature.

$H^1$ -NMR, and SEC analyzed the evolution of the reactions. Kinetic models, characterizing the evolution of the different urethane and isocyanate groups, were established for uncatalyzed bulk system, considering both TDI isomers. The method developed in the present work allows one to determine, without any simplification, six individual rate constants and to study the influence of the temperature on the reactivity and substitution ratios. Moreover, to describe the medium composition from a molecular point of view, a statistical model based on probabilistic considerations was developed. This allows one to simulate the evolution of the oligomers distribution with only the knowledge of the urethane groups and TDI concentrations, directly obtained by  $H^1$ -NMR or by the detailed kinetic model.

The kinetics of each isocyanate group are properly described by a second-order rate equation, and then the data necessary for a predictive study of the medium composition can be calculated. It was shown that 2,4-TDI is three times more reactive than 2,6-TDI and that, in 2,4-TDI, the reactivity ratio between *para*- and *ortho*-isocyanate groups is equal to six. For a stoichiometric ratio of two, only a small amount of diadducts (10%) is formed. This confirms the substitution effect, which is different according to the isocyanate groups. The validity of the detailed kinetic and statistical models was checked for synthesis by using a lower stoichiometric ratio.

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