Modeling and Simulation of Urethane Acrylates Synthesis. I. Kinetics of Uncatalyzed Reaction of Toluene Diisocyanate with a Monoalcohol

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ABSTRACT: Toluene diisocyanate (TDI) reacts with 2-hydroxyethyl acrylate (HEA) during the synthesis of some urethane acrylate oligomers. The present work deals with kinetic studies of the uncatalyzed bulk reaction of TDI with this monoalcohol. Back-titration and ^{1}H -NMR in combination with HPLC are used to follow the reaction and allow a complete description of the system. The global reaction rate as well as those of each individual isocyanate group are well described by a second-order equation. Kinetic constants were calculated using the software SIMULBATCH®. The rates of the different isocyanate groups, which characterize their selectivity, are compared and the model developed in the present study allows for a good prediction of the product structure and a better control of the polymerization process and the end-use properties as well. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 705–712, 2000

Key words: kinetics; toluene diisocyanate; ^{1}H-NMR; modeling; simulation

INTRODUCTION

Polyurethane acrylates are a family of UV-crosslinkable resins which, according to the nature of isocyanates and alcohols involved in their synthesis, can be used as adhesives, coating materials, or optical fibers. They are typically made of a polyester or polyether diol of low molecular weight, an hydroxy-terminated acrylate or methacrylate, and a diisocyanate.[1]

Toluene diisocyanate (TDI) is one of the most currently used diisocyanates in urethane technology for flexible foams and glues.[2] Commercial TDI is a mixture of 2,4- and 2,6-isomers (Fig. 1) which have different reactivities and structures. 2,6-TDI is symmetrical and so the two isocyanate groups are initially indistinguishable, whereas the asymmetrical 2,4-isomer possesses different NCO group reactivities in the *para* and *ortho* positions in relation to the —CH$_3$— group. Many authors have suggested that these different reactivities depend on the reaction temperature.[3,4]

The substantially different reactivity of the NCO groups influences the kinetics of polyurethane formation and, thus, the structure of the reaction products. To predict the polyurethane structure, and for a better control of the polymerization process, it is necessary to have a better understanding of the process kinetics. The purpose of the present work was, therefore, to study the reaction of TDI with hydroxyethyl acrylate (HEA) with regard to the kinetic equations which describe the reaction of each individual isocyanate group and their relative reactivities as a function of temperature, without varying the reactants' concentrations.
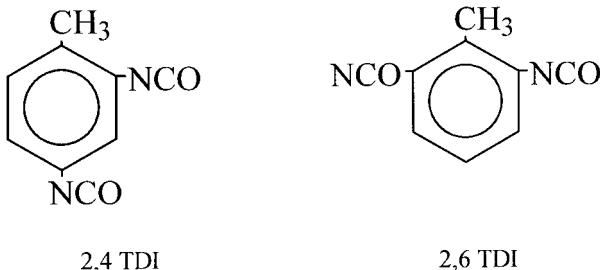
2,4 TDI   2,6 TDI

Figure 1   Structure of TDI.

KINETIC EQUATIONS

A number of equations have been 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[5]:

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

(1)

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

However, deviations from second-order kinetics to higher kinetic order can appear for the following reasons:

- Side reactions such as formation of allophanates from urethanes or of biurets from traces of water[6–8];
- catalysis of urethane products[9]; and
- difference in reactivity of the isocyanate groups in a bifunctional molecule.

To take into account the catalysis of urethane products, Cunliffe et al.[10] proposed, for a constant initial alcohol concentration, the following second-order rate equation modified to include a term of autocatalysis:

$$\frac{d[\text{U}]}{dt} = k[\text{NCO}][\text{OH}] + k_{\text{auto}}[\text{U}][\text{NCO}][\text{OH}]$$ (2)

In recent years, several articles related to the reaction kinetics of pure 2,4-TDI with alcohols have been published. Some authors[4,11,12] did not consider the substitution effect and established a kinetic model with only two rate constants, for the

para-isocyanate group and for the *ortho*-isocyanate group, respectively. Other authors[6,13–15] took into account the substitution effect with some simplifying assumptions about the reactivity ratios. However, data concerning the mixture of both isomers have not been published yet. In this study, a kinetic model was established by considering the two isomers without any simplification.

The successive reactions of a monoalcohol 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 due to a substitution effect.[16] The reaction kinetics of TDI are complex if the initial difference in reactivities of the three individual isocyanate groups and the substitution effects are taken into account. The corresponding scheme is given as a series of six parallel and consecutive reactions (Fig. 2).

According to second-order kinetics, the evolution of the different components are then defined by the following reaction rates:

$$\frac{d[\text{MU2,4}o]}{dt} = k_{24o}[\text{2,4-TDI}][\text{ROH}]$$
$$- k'_{24p}[\text{MU2,4}o][\text{ROH}]$$

$$\frac{d[\text{MU2,4}p]}{dt} = k_{24p}[\text{2,4-TDI}][\text{ROH}]$$
$$- k'_{24o}[\text{MU2,4}p][\text{ROH}]$$

$$\frac{d[\text{MU2,6}o]}{dt} = k_{26o}[\text{2,6-TDI}][\text{ROH}]$$
$$- k'_{26o}[\text{MU2,6}o][\text{ROH}]$$ (3)

$$\frac{d[\text{DU2,4}]}{dt} = k'_{24p}[\text{MU2,4}o][\text{ROH}]$$
$$+ k'_{24o}[\text{MU2,4}p][\text{ROH}]$$

$$\frac{d[\text{DU2,6}]}{dt} = k'_{26o}[\text{MU2,6}o][\text{ROH}]$$

The molar instantaneous balance is

$$(n_{\text{2,4-TDI}})_0 = (n_{\text{2,4-TDI}})_{\text{free}} + n_{\text{MU2,4}p} + n_{\text{MU2,4}o} + n_{\text{DU2,4}}$$

$$(n_{\text{2,6-TDI}})_0 = (n_{\text{2,6-TDI}})_{\text{free}} + n_{\text{MU2,6}o} + n_{\text{DU2,6}}$$ (4)

$$(n_{\text{TDI}})_{\text{free}} = (n_{\text{2,4-TDI}})_{\text{free}} + (n_{\text{2,6-TDI}})_{\text{free}}$$

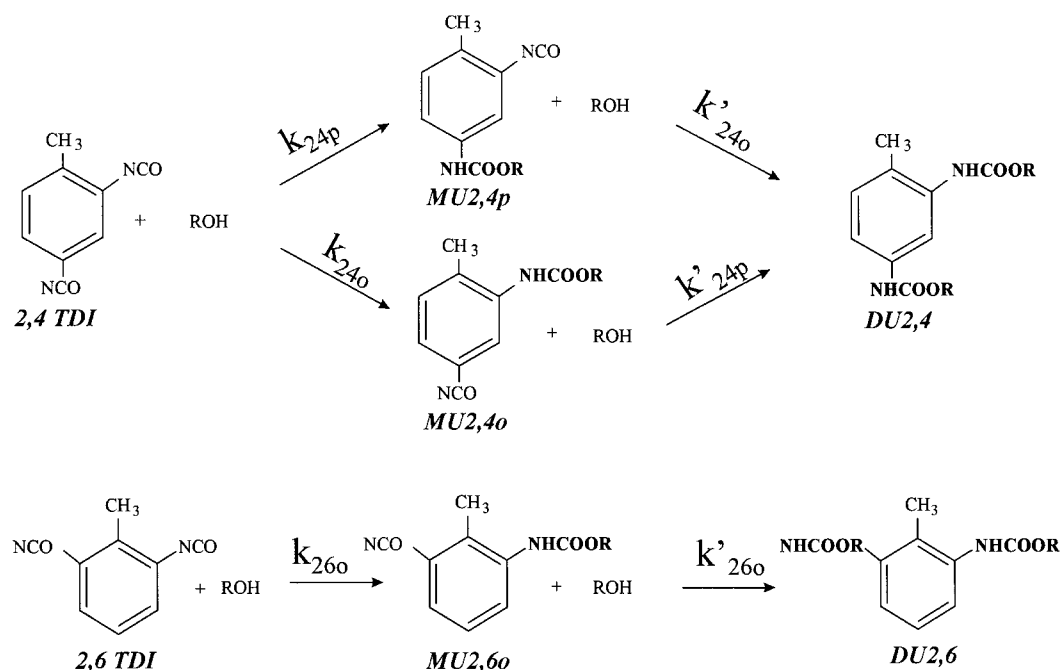$$n_{\text{MU ortho}} = n_{\text{MU2,4}o} + n_{\text{MU2,6}o}$$

Figure 2 Kinetic scheme.

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 HEA, were calculated using the software SIMULBATCH®,[17] which integrates the algebro-differential equations system (3) using a GEAR numerical method based on the DASSL code. The Rosenbrock method is used for the estimation of kinetic parameters on the basis of experimental data.

In the present study, it was assumed and then confirmed that the catalysis of urethanes and the side reactions could be neglected. The absence of secondary products was, indeed, checked by a titration method.[18]

EXPERIMENTAL

Reactions

Prepolymers were prepared from HEA and TDI (80:20) at different temperatures (30, 40, 50, and 60°C) with a constant initial $[NCO]_0$:$[OH]_0$ ratio equal to 2. Prior to reaction, the moisture content of the alcohol was checked by the Karl Fisher method.[19] It was less than 0.1%, 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

The global reaction was followed by determining the unreacted isocyanate concentration as a function of reaction time, using the standard dibutylamine back-titration.[18] The isocyanate values allow one to follow the global rate of isocyanate 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.

To determine the reactivity of the different isocyanate groups, it is necessary to know the concentrations of each individual group. ^{1}H-NMR in combination with HPLC allows a complete description of the system at any time. ^{1}H-NMR spectra were acquired in deuterated chloroform ($CDCl_3$) using a 360-MHz Bruker spectrometer at 40°C. The corresponding analysis was performed on samples directly dissolved in $CDCl_3$ without any previous treatment. The chemical shifts were determined according to the literature[20] and model compounds were prepared with pure 2,4-TDI or 2,6-TDI. They are presented in Table I. Urethane groups were well identified in the —CH_3— region of the toluene ring. For HEA, the

Table I ^{1}H-NMR Chemical Shifts Urethane Groups (360 MHz, CDCl$_3$)

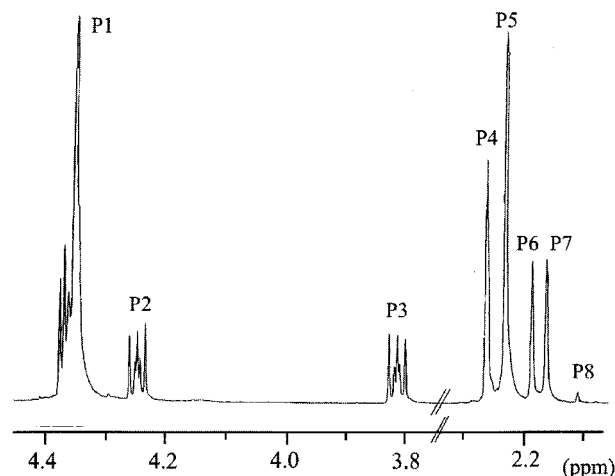| Compound	Chemical Shift δ (ppm)
Reacted HEA	$P_1 = 4.40$
Free HEA (ester part)	$P_2 = 4.30$
Free HEA (alcohol part)	$P_3 = 3.85$
Free TDI	$P_4 = 2.26$
MU 2,4p	$P_5 = 2.23$
MU ortho	$P_6 = 2.19$
DU 2,4	$P_7 = 2.16$
DU 2,6	$P_8 = 2.11$

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

T (°C)	Global Kinetic Constant k (kg mol^{-1} s^{-1})	Activation Energy (kJ/mol)
30	2.41×10^{-5}	56.3
40	4.76×10^{-5}	
50	9.73×10^{-5}	
60	1.78×10^{-4}	

region between 3.8 and 4.4 ppm was used (Fig. 3). Concentrations of the species were calculated from the integrals of the corresponding signals.

With this method, both free TDI and MUs substituted in the *ortho* position cannot be distinguished. To solve the molar balance and to obtain a more detailed kinetic scheme, the concentrations of each isomer should be then determined. The HPLC method allows one to separate both isomers after derivatization with dibutylamine in toluene.[21] The diluted samples were analyzed by HPLC using a Waters 600E apparatus with an ultraviolet absorbance detector (254 nm). The dibutylamine derivatives of isocyanates were determined using gradient elution with a mobile phase of acetonitrile–water (60%/40%).

RESULTS AND DISCUSSION

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

Global Estimation from Isocyanate Concentrations and Validation of the Kinetic Model

In the first approach and according to the isocyanate concentrations as determined by back-titration, a global reaction scheme was then considered: NCO + OH→NHCOO (U).

Second-Order Kinetic Scheme

The rate constant corresponding to eq. (1) was calculated at each temperature. The results are given in Table II. Using an Arrhenius relation of $k = A \exp(-E_a/RT)$, the activation energy for the OH/NCO reaction was determined, as shown in Figure 4, and is similar to values found in the literature.[1,12,13] These data were then used to

Figure 3 ^{1}H-NMR spectrum of reaction products of TDI and HEA.
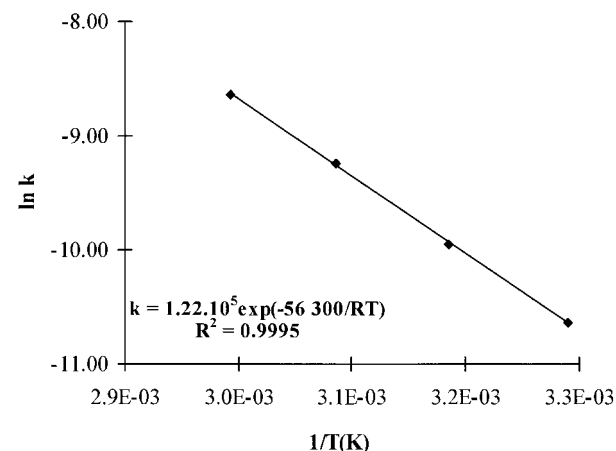
Figure 4 Arrhenius plot for a second-order OH/NCO reaction.

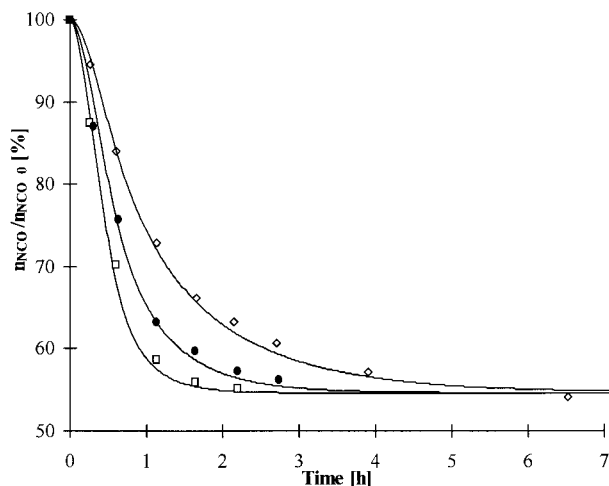$$k = 1.22 \cdot 10^5 \exp(-56\,300/RT)$$
$$R^2 = 0.9995$$

Figure 5   HEA/TDI reaction at ($\diamond$) 40°C, ($\bullet$) 50°C, and ($\square$) 60°C.

simulate the evolution of the ratio of residual to initial isocyanate. Figure 5 shows a good fit between the measured and calculated values. The temperature effect on the reaction kinetics of TDI/HEA is important. For example, an increase of 20°C allows a synthesis time reduction of 60%.

Autocatalytic Scheme

Using the same numerical method as for the uncatalyzed scheme, the kinetic constants of eq. (2) (k and k_{auto}) were calculated at different temperatures. The results, given in Table III, show that the constant related to the uncatalyzed reaction, k, is unchanged when compared to the previous calculations, while that related to the autocatalyzed reaction is negligible. Moreover, the evolution of the autocatalytic rate constant is irregular with the temperature and the value of the activation energy ($E_a = 237$ kJ/mol) is unusual for such reactions. These results confirm the validity of the second-order kinetic scheme which will be used for the following kinetic study.

Detailed Kinetic Study

^{1}H-NMR in combination with HPLC gives precise information on all the species 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 species according to the kinetic model at different temperatures. As an example, the kinetic constants for the reaction at 40°C are given in Table IV. Figures 6 and 7 show the results of the simulations at 40 and 60°C and the corresponding values of the standard deviations. A rather good agreement was obtained between experimental and calculated values, confirming the validity of the second-order kinetic model for each isocyanate group.

DISCUSSION

This system is characterized by (i) the different reactivities of isocyanate groups and (ii) the substitution effect.

Different Reactivities of Isocyanate Groups

The specific rate constants for the MU formation show that the difference in reactivity between the isocyanate groups cannot be neglected. The ratios between the rate constants of the *para*-isocyanate group of 2,4-TDI and the *ortho*-isocyanate groups of both isomers are shown in Figure 8 as a function of temperature. As could be expected, the *para*-isocyanate group is more active than is the *ortho* one in the asymmetric isomer 2,4-TDI and the reactivity ratio is equal to 5.8 ± 0.3. The *ortho*-isocyanate group is obviously less reactive due to steric hindrance and the electronic effect

Table III   Kinetic Constants of OH/NCO Reaction Calculated Using an Autocatalytic Scheme

T (°C)	k (kg mol^{-1} s^{-1})	E (kJ/mol)	k_{auto} (kg^2 mol^{-2} s^{-1})	E_{auto} (kJ/mol)
30	2.41×10^{-5}	56.3	5.79×10^{-20}	237
40	4.76×10^{-5}		7.67×10^{-21}	
50	9.73×10^{-5}		1.54×10^{-20}	
60	1.78×10^{-4}		7.65×10^{-16}	

Table IV   Rate Constants Calculated for the Reaction Carried Out at 40°C

$k24o$ (kg mol^{-1} s^{-1})	$k24p$ (kg mol^{-1} s^{-1})	$k26o$ (kg mol^{-1} s^{-1})	$k'24o$ (kg mol^{-1} s^{-1})	$k'24p$ (kg mol^{-1} s^{-1})	$k'26o$ (kg mol^{-1} s^{-1})
2.32×10^{-5}	1.39×10^{-4}	3.06×10^{-5}	1.75×10^{-6}	9.45×10^{-5}	8.31×10^{-6}

involved by the methyl group. Some ratios of these rate constants found in the literature and given in Table V are in relative concordance with the data obtained in the present study.

The ratio between the rates constants of the 2,4-TDI *para*-isocyanate group and the 2,6-TDI *ortho*-isocyanate group is relevant to the isomer reactivity in a commercial mixture. The *ortho*-isocyanate groups of 2,6-TDI have an intermediate reactivity when compared with both isocyanate groups of 2,4-TDI; however, 2,4-TDI is about four times more reactive than is 2,6-TDI when reacting with HEA. Over the investigated temperature range, the ratios are fairly constant, which indicates that the MU formation does not depend on the process temperature, contrary to Aranguren and Williams[3] (first comparison in Table V), for the reaction between TDI and a polyol of functionality of 4. For comparison, the other studies presented in Table V show that, for the reactions with an oligobutadiene diol or an oligodiene diol, the ratio between the *para*- and *ortho*-isocyanate groups of 2,4-TDI is not much influenced by the process temperature. The evolution

of this ratio with temperature depends mainly on the activation energies which are, in the case of the reaction of HEA with 2,4-TDI, very close.

Substitution Effect

The substitution effect is usually defined by the ratio k'/k. The substitution constants k' allow one to characterize the formation of diadducts. They are necessary to well describe the system in the case of the reaction of TDI with HEA, while 10% of the diadducts are clearly identified by ^{1}H-NMR and cannot be neglected, even with an experimental error of 5% on the species concentrations. As shown in Figure 9, this effect is higher for the *ortho*-isocyanate groups, indicating that DUs are mainly formed from MUs substituted in the *ortho* position. When the process temperature is increased, the amount of diadduct DU 2,4 is increased, whereas the proportion of DU 2,6 decreases.

The substitution effect is different for each isocyanate group which reacts with HEA, especially for MUs produced from 2,4-TDI. These results are
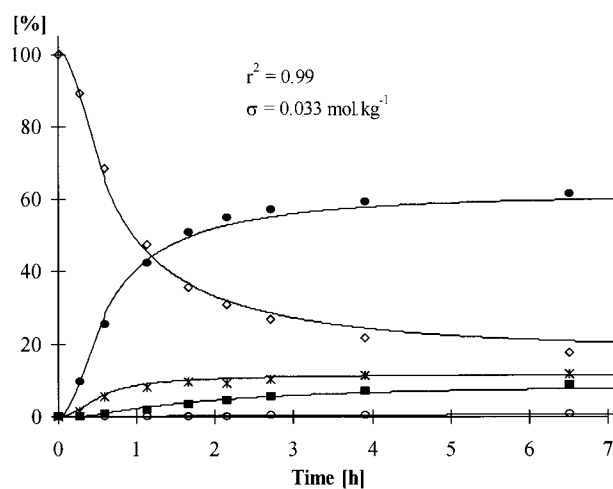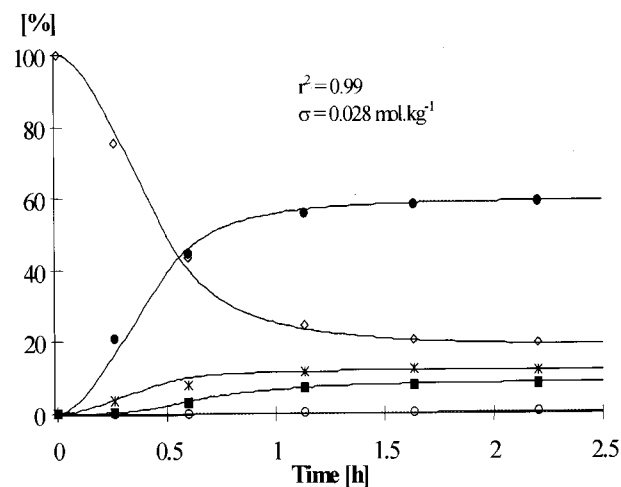

Figure 6   Comparison between experimental and calculated values (full curves): (○) (DU2,6)/(TDI)$_0$; (●) (MU 2,4p)/(TDI)$_0$; (■) (DU 2,4)/(TDI)$_0$; (◇) (TDI)/(TDI)$_0$; (*) (MU *ortho*)/(TDI)$_0$ at 40°C.

Figure 7   Comparison between experimental and calculated values (full curves) of (○) (DU2,6)/(TDI)$_0$, (●) (MU 2,4p)/(TDI)$_0$, (■) (DU 2,4)/(TDI)$_0$, (◇) (TDI)/(TDI)$_0$, and (*) (MU *ortho*)/(TDI)$_0$ at 60°C.

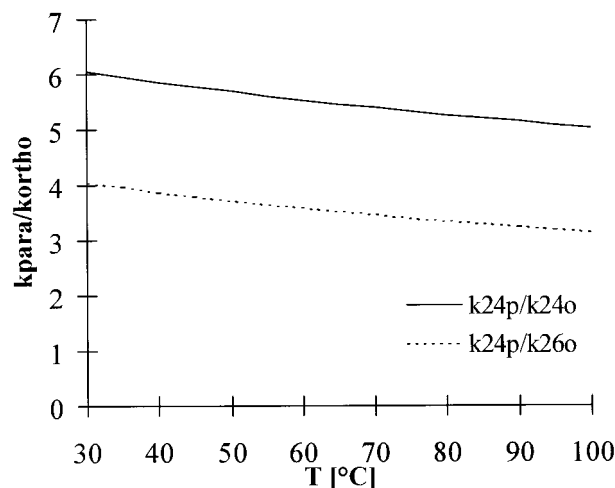**Figure 8**   Reactivity ratios as a function of temperature.

Figure 9   Substitution ratios as a function of temperature.

not in concordance with Lodygina et al.,[6] who made the assumption of equal reactivity of both MUs (MU 2,4*p* and MU 2,4*o*) when reacting with oligobutadiene diol. The amount of DU 2,4 formed from MUs substituted in the *para* position is small and the corresponding constant could be neglected for low temperatures in the case of HEA. Nevertheless, the purpose of this study was to elaborate the most detailed model structure which can be used to describe the reactions of TDI with different kind of alcohols and to allow a comparison of the kinetic parameters.
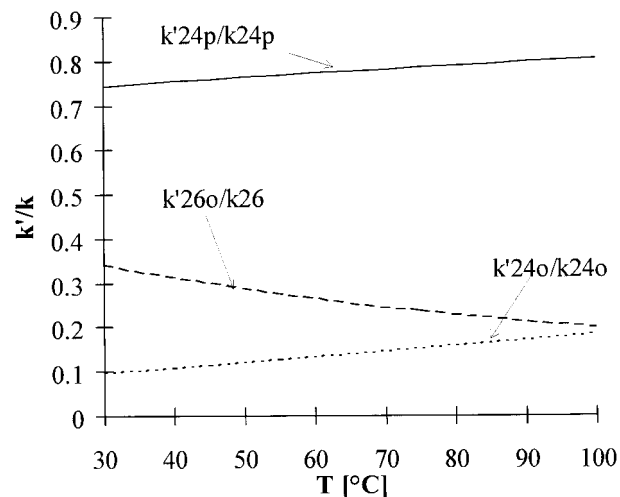
CONCLUSIONS

The reaction of TDI with HEA was studied. The evolution of the reactions was analyzed by back-titration, ^{1}H-NMR, and HPLC and the kinetic models were established for the uncatalyzed bulk system, considering both TDI isomers. The method developed in the present work allows one to determine, without any simplification, the six individual rate constants and to study the influence of temperature on the reactivity and substitution ratios.

Table V   Ratios of the Rate Constants of the Noncatalytic Reactions of TDI with Hydroxy-containing Reagents

Reagent	Solvent	Temperature (°C)	k_{24p}/k_{24o}
Polyether polyol (functionality: 4)[3]	In bulk	30	100
		125	1
Oligobutadiene diol[6]	In bulk	40	7.2
		50	6.2
		64	6
Oligodienediol[22]	In bulk	30	8.5
		50	6.6
		70	4
Methanol or butanol[15]	Benzene	30	4
Butanol[22]	Toluene	50	6.7
	Benzene	20	11
HEA	In bulk	40	5.8
		60	5.5

The kinetics of each isocyanate group are properly described by a second-order rate equation and the data necessary for a predictive study of the medium composition can then be calculated. It was shown that 2,4-TDI is four times more reactive than is 2,6-TDI and that, in 2,4-TDI, the reactivity ratio between the *para-* and *ortho-*isocyanate groups is equal to 6. The substitution effect, which is different according to the isocyanate groups, is confirmed by the amount of diadducts of 10%. In our further work, a similar approach will be proposed in order to study the reaction of the same diisocyanate with a polyether diol.

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