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M. Rochery[a]; I. Vroman[a]; T. M. Lam[a]
[a] Ecole Nationale Supérieure des Arts et Industries Textiles, Roubaix cedex, France

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KINETIC MODEL FOR THE REACTION OF IPDI AND MACRODIOLS: STUDY ON THE RELATIVE REACTIVITY OF ISOCYANATE GROUPS

M. Rochery, I. Vroman, and T. M. Lam*

Laboratoire de GEnie et Matériaux TEXtiles (GEMTEX)
Ecole Nationale Supérieure des Arts et Industries Textiles
59056 Roubaix cedex, France

Key Words: Isophorone Diisocyanate, Macrodiol, Kinetics, ^{13}C-NMR, Reactivity of Isocyanate Groups

ABSTRACT

The kinetics of the bulk polymerization reaction of 1-iso-cyanato-3-isocyanato methyl-3,5,5-trimethylcyclohexane or isophorone diisocyanate (IPDI) with poly(oxytetramethylene) glycol (POTM) was studied by ^{13}C nuclear magnetic resonance (^{13}C-NMR). The difference of reactivity of the NCO groups in this unsymmetrical diisocyanate was taken into account for the determination of the kinetics constants. A kinetic model using several chemical species is proposed. These are differentiated by their isocyanate or hydroxyl terminal functions. A second order reaction mechanism was used and modified to include catalysis by the urethane groups formed and the substitution effect. The kinetics constants were calculated by a numerical resolution, using the fourth order Runge-Kutta method.

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* Author to whom correspondence should be addressed.

INTRODUCTION

Polyurethanes have a broad range of applications which include flexible and rigid foams, elastomeric materials, adhesives, and very flexible or hard coatings. They are obtained by the reaction of a multi-functional isocyanate with a multi-functional material containing active hydrogens, usually a polyol. When working on the coating formulation, the coating chemist should consider a number of aspects such as polymer chemistry and polymer processing. It is, for instance, of great importance to be able to control the reaction time in order to obtain reliable industrial processes.

We have studied the polycondensation reaction between a diisocyanate and a diol. IPDI was chosen as isocyanate because of its easy handling (liquid at room temperature).

Many researchers have studied polyurethane reactions for many years. The original aspect of this study lies in the fact that it deals with the kinetics of condensation of IPDI with a polyol: this case is rarely found in the literature [1], although it better describes the real situation. The more common cases found in the literature concerned the condensation of toluene diisocyanate (TDI) or methylene diphenylene diisocyanate (MDI) with polyols or IPDI with monoalcohols. Only one paper [1] related the polycondensation of IPDI with a diol, which was in fact an alkylimino-diol. The reaction was performed in solution, the use of a solvent and the presence of nitrogen in the diol influencing the reactivity of the NCO groups.

The reactivity between the isocyanate and alcohol groups can depend on several factors. Among the most important ones, we can find the initial ratio of the NCO to OH concentrations, the nature of the reagents, the temperature, the type of solvent or its absence, the presence (or not) and the type of catalyst [2, 3, 4].

The reaction was carried out in bulk, without solvent. This is an industrially important process because of its good environmental impact and its lower energetically cost. We chose to study the influence of temperature and of the molecular weight of the macrodiol on the kinetics of the reaction. First, we will specify the conditions and the simplifying assumptions adopted for the development of the kinetic model. These assumptions were established in order to be able to describe the model in the form of differential equations. The numerical resolution is based on the fourth-order Runge-Kutta method and is carried out with the help of the X.Math software of MATRIX under UNIX. Secondly the follow-up of the synthesis and the analysis by nuclear magnetic resonance by ^{13}C provided the necessary information for the calculation of the rate constants.

Kinetic Scheme

IPDI is an asymmetric cycloaliphatic diisocyanate. The two isocyanate groups are different because one is bonded directly to the cycle (NCO_{sec}) whereas, the second one is bonded through a primary carbon (NCO_{prim}). Thus the molecule consists of a mixture of two isomers, *cis* and *trans*, relative to the position of NCO_{sec} and NCO_{prim} on the cyclohexane ring. Analyses by NMR or gas chromatography indicate a ratio of 72% of the *cis* isomer and 28% of the *trans* [3]. Hence, there are four types of isocyanate (Figure 1). In fact, the use of ^{13}C-NMR coupled with ^{1}H-NMR made it possible to establish clearly that the NCO_{sec} function is preferentially in an equatorial position in the two isomers [2, 5]. Subsequently, in this study we will consider only these two isomers. For each of these isomers, the reactivity of the two NCO groups is different and depends on a certain number of parameters like the temperature of the reaction, the use of catalysts, etc. We endeavored to determine the relative reactivity of these two functions. For the analytical follow-up, the most complete source of information is obtained by ^{13}C-NMR in quantitative mode. We not only determined the concentrations in NCO and IPDI, but also the concentrations in NCO_{sec} and NCO_{prim} functions of the diisocyanate which are essential data required to evaluate their reactivity.

We shall now specify the conditions and the simplifying assumptions used to work out a kinetic model. As a matter of fact, isocyanate chemistry is

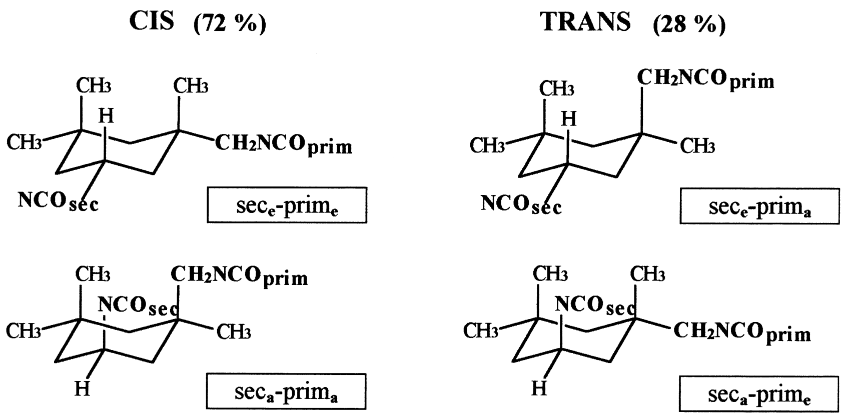


Figure 1. The four isomers of IPDI from *cis* and *trans* configurations [NCO_{sec} and NCO_{prim} in axial (a) or equatorial (e) positions].

quite complicated. There are often many potential side reactions in addition to the urethane formation. Most authors consider that the reaction is of second order with respect to the system [6], i. e., first-order relative to isocyanate and first-order relative to the alcohol function. This implies that the catalysis by the hydroxyl function is neglected. We have chosen to take into account the catalysis by the urethane function, which is more significant in the case of aliphatic isocyanates than for aromatic ones [3]. The operating conditions were selected in such a way that the secondary reactions could be neglected. This assumption was justified by the fact that all the peaks in NMR analysis were identified according to the conditions described above. The substitution effect is another important parameter: the reactivity of one NCO group depends on whether the other group has reacted or not, and namely whether it is in the form of isocyanate or urethane.

To translate this model in the form of equations, we considered 7 species represented as follows:

I : ${}_{prim}OCN\text{-}IPDI\text{-}NCO_{sec}$
II : HO~~~OH
III : $HO{\sim}{\sim}{\sim}NCO_{sec}$
IV : $HO{\sim}{\sim}{\sim}NCO_{prim}$
V : ${}_{prim}OCN{\sim}{\sim}{\sim}NCO_{sec}$
VI : ${}_{sec}OCN{\sim}{\sim}{\sim}NCO_{sec}$
VII : ${}_{prim}OCN{\sim}{\sim}{\sim}NCO_{prim}$

The choice of these species and the interpretations which follow do not take into account the possible influence of the molecular mass of the macrodiol reactant. This is a classical hypothesis in macromolecular kinetics. This can be justified by the results obtained with two macrodiols of different molecular weight. The curves representing the reaction rates of two mixtures at 80°C composed respectively of IPDI/POTM 1000 and IPDI/POTM 2000 were found to superpose perfectly, showing that the molecular weight of the diol has no effect on the reaction rate. Those curves are not reported in this paper.

We can then write the equations describing the rates of formation and of disappearance of these species, that is 7 differential equations. In Scheme 1, is developed one example for obtaining such a differential equation, namely by writing the rates of formation and of disappearance for species III. The value [3] is the ratio $[III]/[NCO]_0$, where $[NCO]_0$ is the initial concentration of NCO groups.

$$[3]=[III]/[NCO]_0=[HO\sim\sim\sim NCO_{sec}]/[NCO]_0$$

Reactions of formation		Corresponding terms
$HO\sim\sim\sim OH + {}_{prim}OCN\text{-}IPDI\text{-}NCO_{sec}$	[2] and [1]	$-2K_{prim}[1][2]$
$HO\sim\sim\sim OH + {}_{prim}OCN\sim\sim\sim NCO_{sec}$	[2] and [5]	$-2K_{sub}[2][5]$
$HO\sim\sim\sim OH + {}_{sec}OCN\sim\sim\sim NCO_{sec}$	[2] and [6]	$-4K_{sub}[2][6]$
Reactions of disappearance with :		
${}_{prim}OCN\text{-}IPDI\text{-}NCO_{sec}$	[1]	$(K_{sec}+K_{prim})[1][3]$
$HO\sim\sim\sim OH$	[2]	$+2K_{sub}[2][3]$
$HO\sim\sim\sim NCO_{prim}$	[4]	$+K_{sub}[3][4]$
${}_{prim}OCN\sim\sim\sim NCO_{sec}$	[5]	$+K_{sub}[3][5]$
${}_{sec}OCN\sim\sim\sim NCO_{sec}$	[6]	$+2K_{sub}[3][6]$
${}_{prim}OCN\sim\sim\sim NCO_{prim}$	[7]	$+2K_{sub}[3][7]$
2 disappearances for 1 creation		
$HO\sim\sim\sim NCO_{sec} + HO\sim\sim\sim NCO_{sec} \longrightarrow HO\sim\sim\sim NCO_{sec}$		$+2K_{sub}[3]^2$

$$-d[3]/dt=\{-2K_{prim}[1][2]-2K_{sub}[2][5]-4K_{sub}[2][6]+(K_{sec}+K_{prim})[1][3]+2K_{sub}[2][3]$$
$$+K_{sub}[3][4]+K_{sub}[3][5]+2K_{sub}[3][6]+2K_{sub}[3][7]+2K_{sub}[3]^2\}.\{1+K_u[8]\}$$

Scheme 1. Method to obtain the differential equations relating to the species III.

To the 7 equations thus obtained, we added those concerning the disappearance of the total NCO function, that is comprising both NCO_{prim} and NCO_{sec} functions. We thus have a system of 10 differential equations shown on Scheme 2. The notations employed are as follows :

$[i]=/[NCO]_0$ (i = 1 to 7 and S = I to VII)
$[8]= [NCO]/[NCO]_0$
$[9]=([NCO_{sec}]_0- [NCO_{sec}])/[NCO]_0$
$[10]=([NCO_{prim}]_0- [NCO_{prim}])/[NCO]_0$

$K_{sec}=k_{sec}.[NCO]_0$ $\quad$ $K_u.K_{sec}=k_{u(sec)}.[NCO]_0^2$

$K_{prim}=k_{prim}.[NCO]_0$ $\quad$ $K_u.K_{prim}=k_{u(prim)}.[NCO]_0^2$

$K_{sub}=k_{sub}.[NCO]_0$ $\quad$ $K_u.K_{sub}=k_{u(sub)}.[NCO]_0^2$

The constants k_{sec} and k_{prim} represent the reaction rate constants of the NCO_{sec} and NCO_{prim} functions respectively, and k_{sub} the constant relating to NCO functions when the diisocyanate is monosubstituted. For convenience the concentrations of the various entities are divided by the initial concentration of the isocyanate function. The $k_{u(sec)}$, $k_{u(prim)}$ and $k_{u(sub)}$ constants correspond to the rate constants of con-

$$\mathbf{[1]=[I]/[NCO]_0=[{}_{prim}OCN\text{-}IPDI\text{-}NCO_{sec}]/[NCO]_0}$$

$$-d[1]/dt=\{2(K_{sec}+K_{prim})[1][2]+(K_{sec}+K_{prim})[1][3]+(K_{sec}+K_{prim})[1][4]\}.\{1+K_u[8]\}$$

$$\mathbf{[2]=[II]/[NCO]_0=[HO{\sim\sim\sim}OH]/[NCO]_0}$$

$$-d[2]/dt=\{2(K_{sec}+K_{prim})[1][2]+4K_{sub}[2][5]+4K_{sub}[2][6]+4K_{sub}[2][7]\}.\{1+K_u[8]\}$$

$$\mathbf{[3]=[III]/[NCO]_0=[HO{\sim\sim\sim}NCO_{sec}]/[NCO]_0}$$

$$-d[3]/dt=\{-2K_{prim}[1][2]-2K_{sub}[2][5]-4K_{sub}[2][6]+(K_{sec}+K_{prim})[1][3]+2K_{sub}[2][3]$$
$$+K_{sub}[3][4]+K_{sub}[3][5]+2K_{sub}[3][6]+2K_{sub}[3][7]+2K_{sub}[3]^2\}.\{1+K_u[8]\}$$

$$\mathbf{[4]=[IV]/[NCO]_0=[HO{\sim\sim\sim}NCO_{prim}]/[NCO]_0}$$

$$-d[4]/dt=\{-2K_{sec}[1][2]-2K_{sub}[2][5]-4K_{sub}[2][7]+(K_{sec}+K_{prim})[1][4]+2K_{sub}[2][4]$$
$$+K_{sub}[3][4]+K_{sub}[4][5]+2K_{sub}[4][6]+2K_{sub}[4][7]+2K_{sub}[4]^2\}.\{1+K_u[8]\}$$

$$\mathbf{[5]=[V]/[NCO]_0=[{}_{prim}OCN{\sim\sim\sim}NCO_{sec}]/[NCO]_0}$$

$$-d[5]/dt=\{-K_{sec}[1][3]-K_{prim}[1][4]-2K_{sub}[3][7]-2K_{sub}[4][6]+4K_{sub}[2][5]+K_{sub}[3][5]+$$
$$K_{sub}[4][5]\}.\{1+K_u[8]\}$$

$$\mathbf{[6]=[VI]/[NCO]_0=[{}_{sec}OCN{\sim\sim\sim}NCO_{sec}]/[NCO]_0}$$

$$-d[6]/dt=\{-K_{prim}[1][3]-K_{sub}[3][5]+4K_{sub}[2][6]+2K_{sub}[4][6]\}.\{1+K_u[8]\}$$

$$\mathbf{[7]=[VII]/[NCO]_0=[{}_{prim}OCN{\sim\sim\sim}NCO_{prim}]/[NCO]_0}$$

$$-d[7]/dt=\{-K_{sec}[1][4]-K_{sub}[4][5]+4K_{sub}[2][7]+2K_{sub}[4][7]\}.\{1+K_u[8]\}$$

$$\mathbf{\frac{d[8]}{dt}=-\frac{d[NCO]/[NCO]_0}{dt}=-\frac{d([NCO_{sec}]+[NCO_{prim}])/[NCO]_0}{dt}}$$

$$\frac{d[8]}{dt}=\frac{d[9]}{dt}+\frac{d[10]}{dt}$$

$$\mathbf{\frac{d[9]}{dt}=-\frac{d[NCO_{sec}]/[NCO]_0}{dt}}$$

$$d[9]/dt=\{(K_{sec}[1]+K_{sub}[3]+K_{sub}[5]+2K_{sub}[6]).\ (2[2]+[3]+[4])+K_{sub}[3]^2\}.\{1+K_u[8]\}$$

$$\mathbf{\frac{d[10]}{dt}=-\frac{d[NCO_{prim}]/[NCO]_0}{dt}}$$

$$d[10]/dt=\{(K_{prim}[1]+K_{sub}[4]+K_{sub}[5]+2K_{sub}[7]).\ (2[2]+[3]+[4])+K_{sub}[4]^2\}.\{1+K_u[8]\}$$

Scheme 2. Differential equations relating to the kinetic model.

densation catalyzed by urethane acting in parallel with k_{sec}, k_{prim} and k_{sub}. The boundary conditions are then:

$$[1]_0=[2]_0=0{,}5$$

$$[3]_0=[4]_0=[5]_0=[6]_0=[7]_0=[8]_0=[9]_0=[10]_0=0$$

With these conditions and the experimental data obtained, it is possible to solve the differential equations and obtain the various constants of reaction. Numerical calculation is based on the fourth-order Runge-Kutta method and is carried out using the X.Math software of MATRIX.

First of all, it was necessary to schematise all the differential equations in accordance with the software language. The program then plots the curves of the various entities calculated from the pre-defined constants. It is then advisable to readjust these values to reduce to the maximum the difference between calculation and the experimental data.

EXPERIMENTAL

Materials

All the reagents were provided by Aldrich. IPDI was used as such without further purification. The POTM of average molecular weight in number: $\overline{M_n}$ 1000 and 2000 g.mol^{-1} was dried under primary vacuum at 70°C for 24 hours before use.

Bulk Reaction

We carried out the bulk synthesis in a three-necked flask equipped with a high torque stirrer, a nitrogen inlet and an outlet (to take out a sample). The temperature of the reaction was controlled by immersion in to an oil bath. Two syntheses were performed, the first starting from POTM 2000 at 80°C and the second from POTM 1000 at 110°C, and lasted for at least 24 hours. The mixtures were prepared in stoichiometric proportions of diisocyanate and diol. We worked in this case without catalyst with an initial total mixture of approximately 50 g.

Kinetic Follow-up by NMR

During the course of the synthesis, we took a sample from the mixture every hour. The samples were put in solution in $CDCl_3$ in 5 mm diameter tubes.

Dissolution was almost immediate and did not require any stirring. We assumed that the reaction did not go on during the accumulation time for three reasons. By putting samples in solution, we induced an effect of dilution. Moreover, the NMR analysis is done at room temperature and the reaction is performed without catalyst. In these conditions we considered that the condensation is stopped during the accumulation.

The spectra were analyzed with the software Win NMR.

NMR Measurements

The spectra were taken with a Brücker ASX spectrometer working at 100 MHz according to a routine program used in a ^{13}C quantitative analysis. In order to obtain reliable data, the relaxation times of the NCO and the urethane carbons were estimated to 6 seconds. The ^{13}C NMR measurements were carried out with 90° pulse, an impulsion time of 90 μseconds and the number of accumulations was then equal to 480, corresponding to a time of acquisition of about 50 minutes.

RESULTS AND DISCUSSION

Study of ^{13}C-NMR Spectra

^{13}C-NMR spectra of the starting reagents and the assignments of the peaks are given in Figures 2 and 3. For the diol, the data were attributed by comparison with the values calculated from the Tables [7] found in the literature. For the IPDI, the assignments of the peaks are made by comparison with those carried out by Hatada [5]. At any time during the synthesis, urethane functions are present. Figure 4 shows the chemical shifts of the carbon in the NCO_{prim} and NCO_{sec} groups before and after condensation with benzyl alcohol. It can be noted that the carbon of the NCO_{sec} group is observed at a larger frequency compared to the NCO_{prim} group. This higher chemical shift indicates a less important electronic density, and consequently its preferred reaction with nucleophilic species such as alcohol. The examination of Figure 4 also reveals that the carbon of the NCO_{prim} group is observed at a smaller chemical shift (122.2 ppm) when the complementary group (NCO_{sec}) has reacted, compared to IPDI (122.42 ppm). This is the same case with the NCO_{sec} group. This implies that their reactivity decreases under the substitution effect. To simplify, we can thus assume that once the IPDI is monosubstituted, the NCO group reacts with the same constant. Moreover, the chemical shifts of the carbons of the primary and secondary urethane groups are reversed compared to those of the corresponding NCO groups.

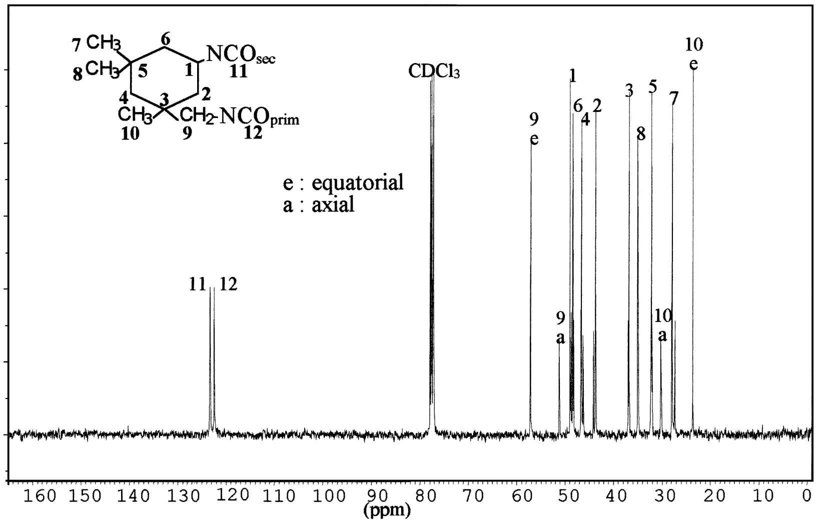


Figure 2. ^{13}C NMR spectrum and assignments for IPDI (Solvent $CDCl_3$; analysis temperature: 20°C; NS =160).

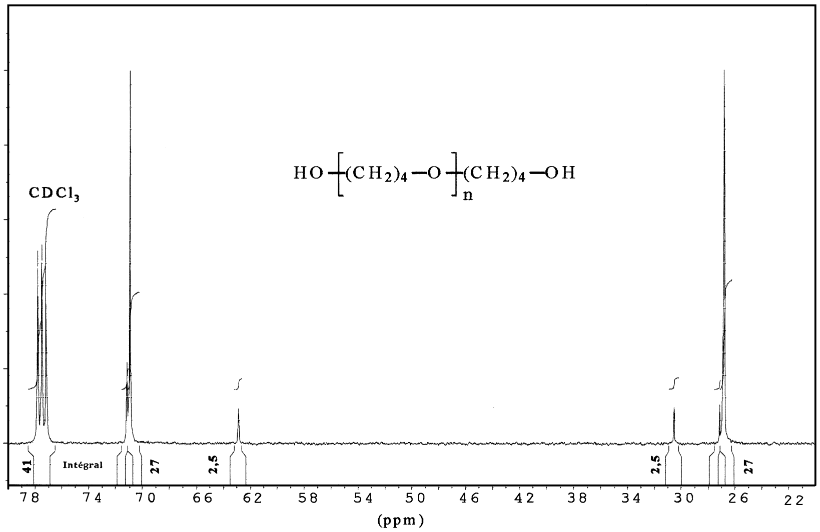


Figure 3. ^{13}C-NMR and assignments for POTM 1000 (Solvent $CDCl_3$; analysis temperature: 20°C; NS =160).

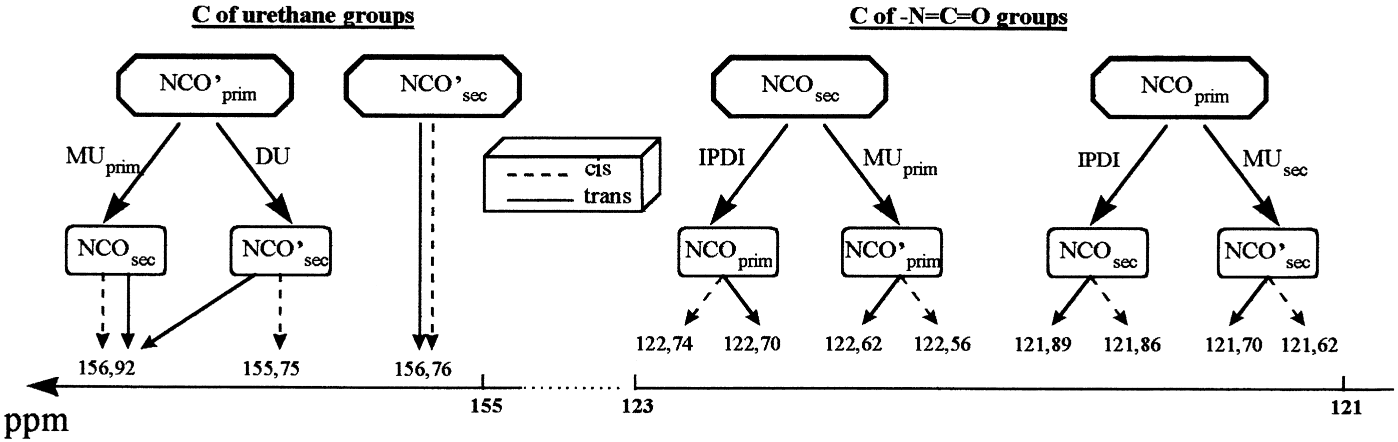


Figure 4. Chemical shift in ^{13}C-RMN of the *cis* and *trans* isomers before and after the carbamate formation with benzyl alcohol [5] Notation: $MU_{prim\ or\ sec}$ (monourethane obtained from $NCO_{prim\ or\ sec}$), DU (diurethane), $NCO'_{prim\ or\ sec}$ ($NCO_{prim\ or\ sec}$ incorporated in an urethane group).

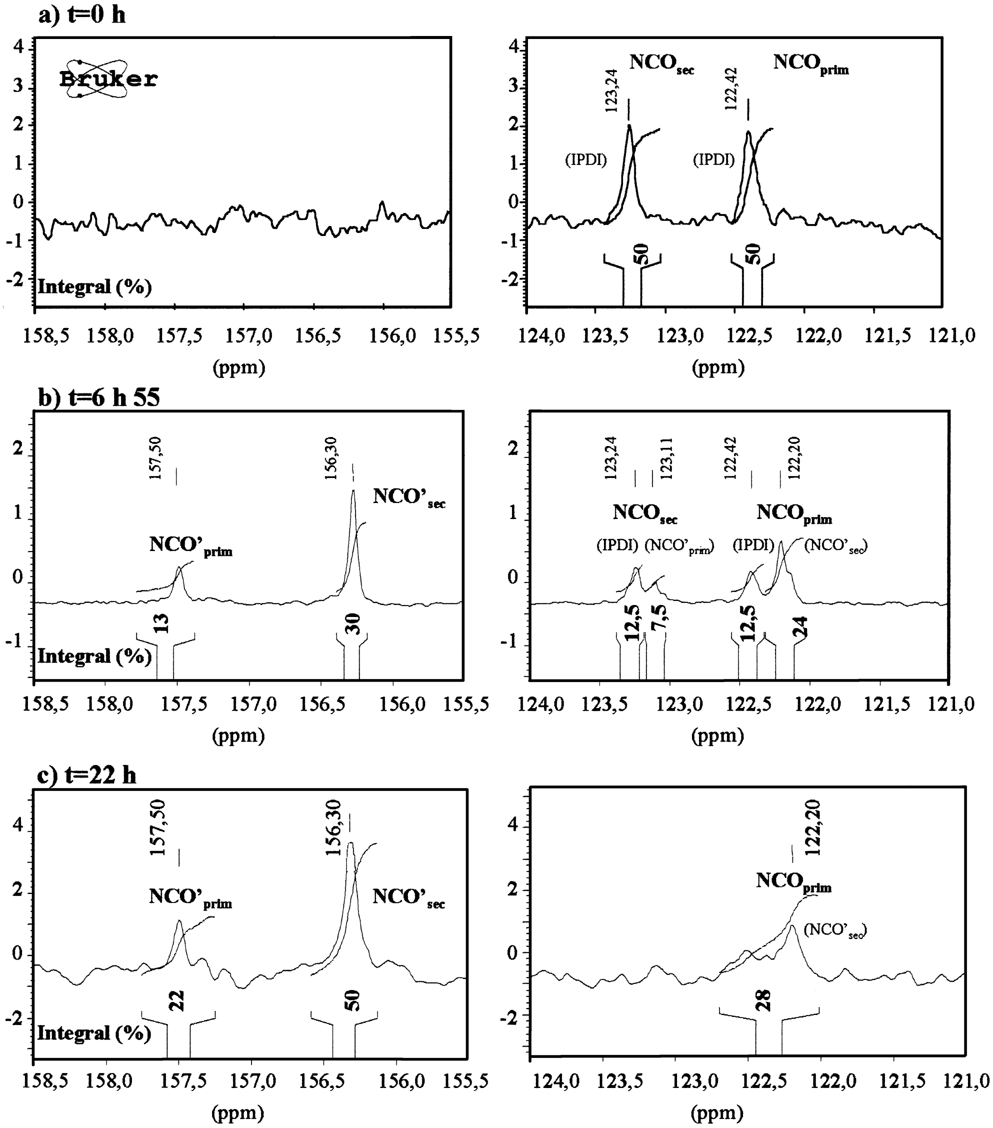


Figure 5. ^{13}C-NMR spectra of a mixture of IPDI/POTM 2000 at 80°C at different steps of the reaction (NCO' represents the NCO group after the condensation with the alcohol).

In our case, we were mainly interested in the resonance range between 121 and 124 ppm (NCO$_{prim}$ and NCO$_{sec}$ before condensation) and 155.5 and 158.5 ppm (NCO$_{prim}$ and NCO$_{sec}$ in urethanes). An example of the kinetic follow-up is given in Figure 5. The components resulting from the cis and trans configurations

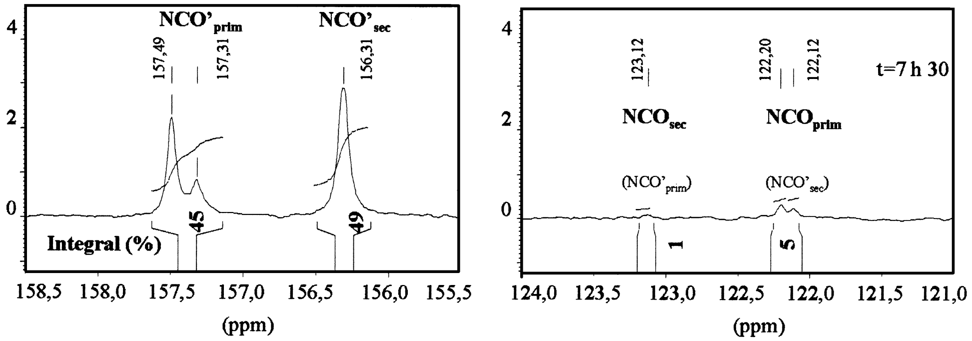


Figure 6. ^{13}C-NMR spectra of a mixture of IPDI/POTM 1000 at 110°C at the end of the reaction.

are not identifiable. As described above, we note a shift towards the low frequencies of the carbon peaks relating to two NCO functions of the IPDI, as soon as the molecule is monosubstituted. The carbons of the urethane groups reveal two peaks, according to whether they are formed with NCO_{sec} or NCO_{prim}. On the other hand, their resonance is the same at the end and in the middle of the chain, and is not influenced by the fact whether the second function has condensed or not. In the case of the synthesis with POTM 1000, we noticed at the end of the reaction a splitting in two of the peak of the NCO'_{prim} (Figure 6). Hatada attributes the signal located at larger chemical shift to the monourethane (*cis* and *trans*) and to the *trans* diurethane (Figure 4) [5]. We prefer, by comparing the relative intensity of the integrals of the signals, to attribute the signal at the highest δ value to the *cis* compound and the signal located at the lowest (value to the trans compound, these assignments being also supported by Ono [4] although he deals with ^{1}H NMR spectra.

Calculation of the Rate Constants

For the calculation of the constants of the reaction, we evaluate, in the course of time, the extent of the reaction of the two NCO of the IPDI which is based on the conservation of the carbon number in the isocyanate functions. The integrated surface areas of the peaks noted NCO'_{prim} and NCO'_{sec} are related to the total surface area, which comprises up to six principal peaks. The rate of disappearance of IPDI can be estimated by evaluating the relative intensities of the peaks marked by $NCO_{prim(ipdi)}$ and $NCO_{sec(ipdi)}$. At any time of the reaction, both

TABLE 1. Determination of Optimal Rate Constants of Condensation for the Kinetic Follow-up by ^{13}C-NMR

IPDI/POTM 2000 at 80 °C		IPDI/POTM 1000 at 110 °C	
in min^{-1}	in $kg.mol^{-1}.s^{-1}$ or $kg^2.mol^{-2}.s^{-1}$ ▲	in min^{-1}	in $kg.mol^{-1}.s^{-1}$ or $kg^2.mol^{-2}.s^{-1}$ ▲
$K_{sec} = 26x10^{-4}$	$k_{sec} = 48x10^{-6}$	$K_{sec} = 12x10^{-3}$	$k_{sec} = 12x10^{-5}$
	$k_{u(sec)} = 18 \text{ x } 10^{-7}$ ▲		$k_{u(sec)} = 5.6x10^{-6}$ ▲
$K_{prim} = 3.6x10^{-4}$	$k_{prim} = 6.7x10^{-6}$	$K_{prim} = 5x10^{-3}$	$k_{prim} = 5x10^{-5}$
	$k_{u(prim)} = 2.5x10^{-7}$ ▲		$k_{u(prim)} = 2.3x10^{-6}$ ▲
$K_{sub} = 5.0x10^{-4}$	$k_{sub} = 9.3x10^{-6}$	$K_{sub} = 11x10^{-3}$	$k_{sub} = 11x10^{-5}$
$K_u = 2$ *	$k_{u(sub)} = 3.4x10^{-7}$	$K_u = 4.5$ *	$k_{u(sub)} = 5.1x10^{-6}$

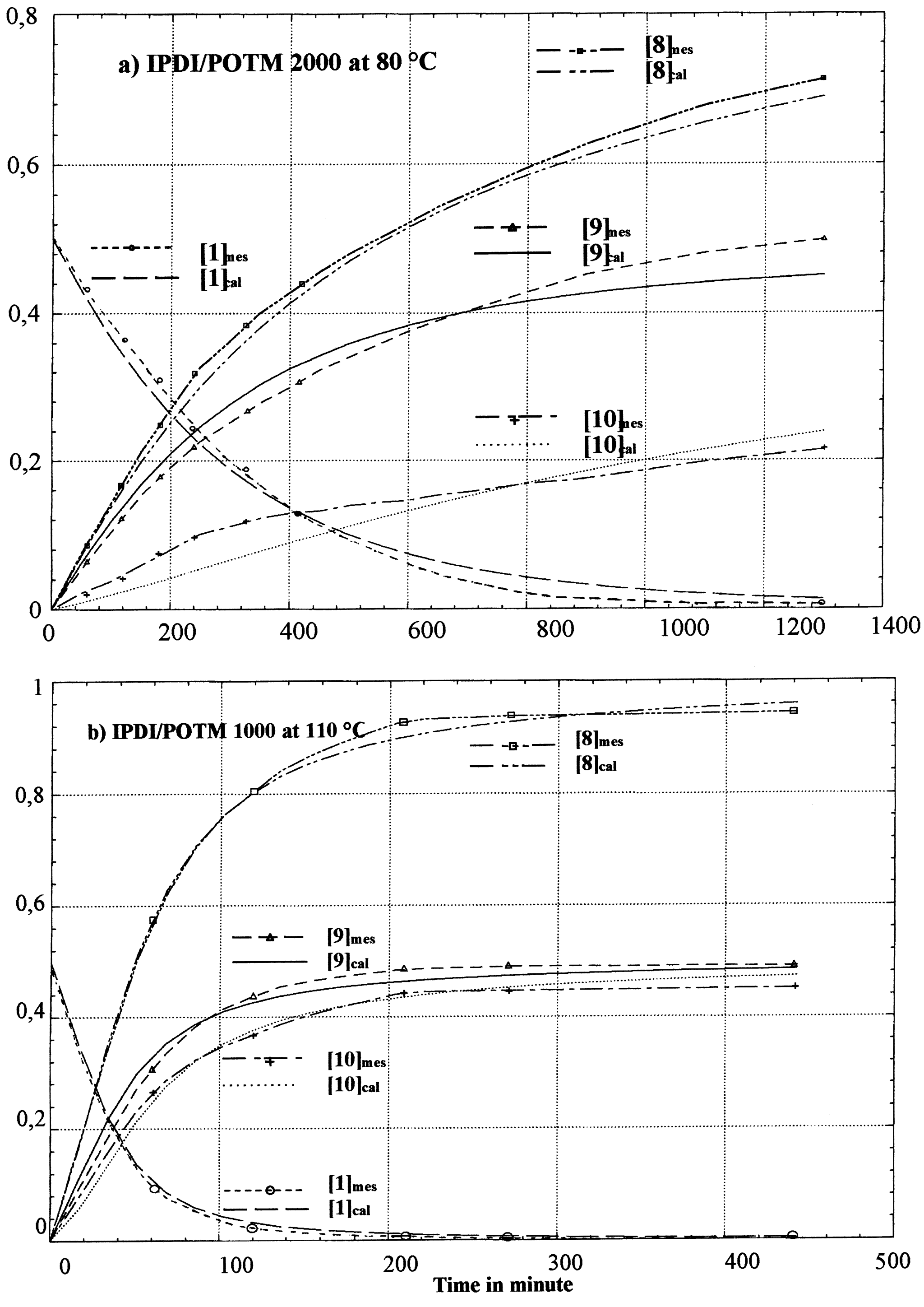
* without unit

terms are equal. The attribution assignment of the chemical shifts can thus be validated. These values are entered in the X.Math program.

We thus determined the optimal values of the constants K_{prim}, K_{sec}, K_{sub} and K_u as well as the associated values k_{prim}, k_{sec}, k_{sub}, $k_{u(sec)}$, $k_{u(prim)}$, $k_{u(sub)}$ according to the method detailed previously. The results are given in Table 1. The plot layout of the experimental and theoretical curves can also be obtained with the software (Figure 7). We notice a good agreement between the experimental and calculated curves, which validates the kinetic scheme used as well as the values of the reaction constants.

In the two cases studied, K_{sub} is greater than K_{prim}, which means that the NCO_{prim} of the monosubstituted IPDI has a greater reactivity compared to that of the starting molecule. This surprising result can be explained by considering the inhibiting role of the NCO_{sec} on the reactivity of NCO_{prim}. However, this tendency disappears as soon as NCO_{sec} condenses with the alcohol.

The reactivity ratios are listed in Table 2. The difference in reactivity between NCO_{sec} and NCO_{prim} decreases with the increase in temperature since the k_{sec}/k_{prim} ratio decreases from 7.2 to 2.4 from 80°C to 110°C. This tendency is confirmed in the literature [3, 8]. It is difficult however, to compare our values with those mentioned in the bibliography, the reaction conditions being different. Moreover, the k_{sec}/k_{prim} ratio is calculated in different ways: it can be obtained from the ratio of the rate constants, either at a precise time of the reaction (i. e., at a certain percentage of conversion) or at the end of the reaction. Another method consists of calculating the reactivity difference from the ratio of the monourethane concentrations. Cunliffe *et al.* [3] mentioned a ratio of 2.5 in the case of the reac-



$$[1] = \frac{[IPDI]}{[NCO]_0} \quad [9] = 1 - \frac{[NCO_{sec}]}{[NCO]_0} \quad [10] = 1 - \frac{[NCO_{prim}]}{[NCO]_0} \quad [8] = [NCO]/[NCO]_0$$

Figure 7. Calculated ($[i]_{cal}$) and measured ([i])$_{mes}$) curves for two mixtures (a and b).

TABLE 2. Reactivity Ratio

IPDI			
/POTM 2000 at 80 °C		/POTM 1000 at 110 °C	
k_{sec}/k_{prim}	= 7.2	k_{sec}/k_{prim}	= 2.4
k_{sec}/k_{sub}	= 5.2	k_{sec}/k_{sub}	= 1.1
K_u	= 2	K_u	= 4.5

tion of IPDI with isopropanol (NCO/OH=1) in heptane at 60°C, as well as Surivet *et al.* [9] in the case of IPDI and benzyl alcohol at 80°C (NCO/OH=1). With an excess of IPDI and n-butanol at 110°C, Lorenz et al. [10] obtained a ratio of 4-5. In brief, the reactivity ratio given in literature varies between 2.5 and 10 in the case of the condensation of IPDI with a monoalcohol. As mentioned in the introduction, only one article [1] deals with the condensation of IPDI with a diol. But we cannot compare the reactivity ratio because the diol contained an amine group that influences the condensation by catalyzing the reaction.

When we look at the values of the constants, we note that the substitution effect falls with the rise in temperature. Indeed, at 110°C the remaining function of the monosubstituted IPDI reacts with a constant rate similar to that of the NCO_{sec} of the molecule. The k_{sec}/k_{sub} ratio increases from 1.1 at 110°C to 5.2 at 80°C.

The temperature also influences the catalysis by urethane. It is possible to evaluate the importance of the catalysis by considering the value of K_u: it doubles when the temperature is raised from 80°C to 110°C.

We can suppose that the increase in temperature favors the mobility between chains and facilitates the creation of hydrogen bonds between the urethane groups and the isocyanate functions, which will condense with alcohol functions.

The influence of the temperature on the reaction is also visible on these curves. The curves representing [9] and [10], characteristic of the respective disappearance of NCO_{sec} and NCO_{prim}, are almost superposed at 110°C, but distant at 80°C. This confirms that a rise in temperature reduces the difference in reactivity.

CONCLUSION

The bulk reaction of the diisocyanate, IPDI, with a macrodiol, POTM, was studied by ^{13}C-NMR. We considered that the reaction is of second order and involves catalysis by the urethane functions. A kinetic scheme is used to describe quantitatively the system. The primary and secondary isocyanates functions are differentiated. Seven chemical species have been considered, each having two reactive functions. In this model, we assume that the reactivity of NCO groups do not depend on the macromolecular mass, which is a classical hypothesis in macromolecular kinetics. The substitution effect was also taken into account. The kinetic model was translated in ten differential equations and a numerical resolution of the system was achieved using the X.Math software of MATRIX. The use of NMR allowed us to determine the concentrations of the primary and secondary NCO groups separately. The rate constants and the reactivity ratio of the two isocyanate functions have thus been calculated. The difference in reactivity decreases as the temperature increases and is in the range given in literature. The substitution effect was confirmed. As soon as the IPDI has reacted, the second function is less reactive, this difference being smaller with the increase in temperature. The opposite tendency is obtained for the urethane catalysis. The increase in the degree of mobility of the molecules facilitates the formation of hydrogen bonds between urethane and NCO groups, and indirectly the nucleophilic attack of OH. Our kinetic model was validated by the good agreement between the experimental and theoretical curves.

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