

# Basic Kinetic Model for the Reaction Yielding Linear Polyurethanes. II

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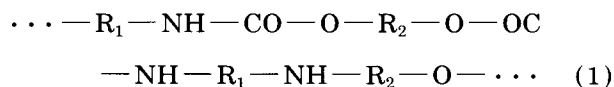
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## SYNOPSIS

On the basis of the gradual polyaddition kinetic model developed earlier, an attempt was made to provide a generalized mathematical model for the set of reactions yielding linear polyurethanes. The model is a system of first-order ordinary differential equations. It was assumed at the present stage of this model that the rate constants for the reaction considered do not change. The model developed was then solved numerically. Average molecular weight of the polymer and composition data for oligomers were calculated for a constant volume batch reactor and varied process parameters. The GPC method, which was tested for model urethane oligomers, was employed to verify the model developed. The reaction of 2,4-TDI with 1,4-butanediol proceeding in a solution was investigated. It was concluded that the model was applicable to a limited degree in describing the linear polyurethane manufacturing process which is more complex. However, it was suggested that the algorithms adopted could be utilized in developing further models which could assume changing rate constants for the polymer chain growth reactions. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

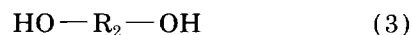
Linear polyurethanes of a general formula



are obtained in the process of gradual polyaddition of isocyanates



and polyols



where  $R_1$  is an aromatic, aliphatic, or cycloaliphatic radical, and  $R_2$  is usually an aliphatic group, derived from polyether or polyester. The reaction between diisocyanates (2) and diols (3), proceeding in the

presence of catalysts,<sup>1</sup> is a basic reaction used in syntheses of various polyurethanes.

Realizing the increasing importance of polyurethanes in various branches of technology, in common life, and in medical applications, much attention has been paid recently to synthesizing new types of these polymers with the use of newly developed monomers and processing methods.<sup>2</sup> For this purpose, it was found necessary to study kinetics of this apparently simple process wherein the physicochemical properties of polyurethanes resulted from the types and initial molecular ratios of the monomers utilized, from the process temperature, from a type and amount of a catalyst, as well as from a type of solvent which could possibly be employed.<sup>3</sup> The properly designed mathematical model could provide answers to many questions. So far, the investigations were limited to searching for models based on the assumption that this process could be described with sufficient precision after analyzing the reactions involving functional groups of parent substances. This approach made it possible to calculate conversion figures for monomers, and possibly to define chain branching as a result of side reactions yielding allophanates or other compounds. However, no poly-

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mer composition or molecular-weight distribution could be calculated versus process conditions.<sup>4-6</sup> Only two scientists mentioned this problem, but they could not gather satisfactory kinetic data to develop such a model.<sup>7</sup>

The basic purpose of this study is the attempt to develop a general mathematical model for the gradual polyaddition process involving diisocyanates and diols, and to develop algorithms applicable in calculations for some more complex models. This study adopted the assumption very popular in the available literature which says that the rate constant values for all the oligomerization reactions yielding linear polyurethanes are approximately equal to each other.<sup>6,8,9</sup> In other words, the kinetics of this process is dependent solely on functional groups present and their arrangement within monomer molecules, while the size of the oligomer molecule is a secondary factor. This is a considerable simplification. In his fundamental investigations of gradual chain growth polymerization, Flory revealed that interactions between oligomers lead to their reduced reactivity in the course of their chain growth.<sup>10</sup> When referred to the polymerization reaction of diisocyanates and diols, that issue was underestimated so far since in many cases obtaining high-molecular-weight oligomers is disadvantageous and adversely affects further processing because of the increased viscosity of those intermediates. Hence, there were no incentives to study the process that far. It was shown in the previous paper that the size of the urethane oligomer molecule affects oligomer reactivity. This effect, however, is appreciable only when other process parameters such as temperature, initial ratio of monomers, and type and amount of the catalyst employed, are set constant, i.e., when the reaction proceeds under ready-state conditions. The influence of molecule size on reactivity can then be described with the use of an equation based on the collision theory.<sup>11</sup>

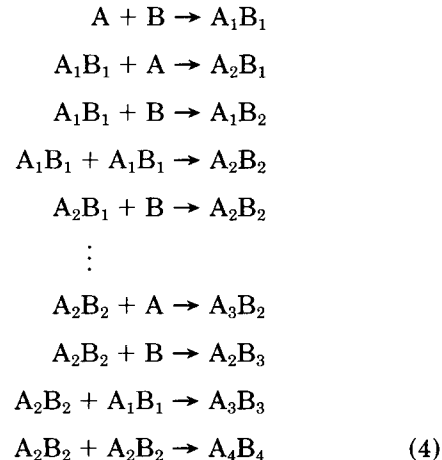
In order to develop a general mathematical model, it was necessary to adopt some simplifications and specific algorithms generating model equations in the course of numerical calculations. It was assumed at this stage that the reactivity of urethane oligomers is not dependent on their molecule size, although applicability of this thesis is limited.

A mathematical model was developed which was based on the general kinetic scheme of the diisocyanate and polyol polyaddition process. The model, comprising a complex system of differential equations, was subject to decomposition by introducing the concept of "polymer fraction." This "fraction" covered all oligourethanes with the same number of —NH—CO—O— groups in their molecules. The

rate constant values for unit reactions between isocyanates and compounds comprising hydroxyl group(s)—necessary for simulation calculations—were available from previous studies on model reactions.<sup>11</sup> Those values were then optimized with the use of a numerical method. Concentrations of polyurethane fractions were determined experimentally for a selected reaction with the use of the GPC method and then they were compared to those calculated from the model developed. The model was found to apply poorly to the simulations of the processes giving linear polyurethanes. Yet, the obtained procedural algorithms were found applicable in developing future and more complex models which would take into consideration the variability of rate constants for the reactions of the gradual polyaddition kinetic scheme.

## MATHEMATICAL MODEL FOR THE PROCESS

A process of gradual polyaddition of diisocyanates and polyols yielding linear polyurethanes (1) can be presented by means of the following scheme composed of subsequent and parallel reactions:



etc. for each component of the reaction mixture.

In the above scheme, A stands for difunctional polyol, B stands for diisocyanate, and  $A_iB_j$  is a urethane oligomer.

For  $i = j$ , this oligomer has one —NCO group at one end of its chain and one —OH group at the other end, hence is capable of reacting with any component of the system. For  $i = j + 1$ , the oligomer has —OH groups at both of its ends; it can then react with compounds comprising one —NCO group at least. For  $i = j - 1$ , the situation is the

opposite and the possible reaction can involve oligomers and/or compounds comprising one —OH group at least. In order to satisfy the condition resulting from the purpose of this study, it was assumed that the rate constant values for all the reactions in scheme (4) are the same. This refers for example to the reaction of 1,4-butanediol with toluene 2,6-diisocyanate (2,6-TDI). When employing the 2,4-TDI isomer, which has its (4)-placed isocyanate group about 1.5 times more active than its (2)-placed isocyanate group, we could be expected to further develop the kinetic model (4). The possibility of forming (at various rates) oligomers incorporating various structural elements derived from both the isomers should be considered. In the end, that would have given a much more complex kinetic model for the process studied. And that would be useful if the laboratory procedure employed to verify the model could identify and quantitatively analyze all the urethane oligomers resulting from the polyaddition process involving 2,4-TDI and 1,4-butanediol. The GPC method adopted in this study permits only  $A_iB_j$  oligomers with changing molecular weights to be determined. With the above factors in mind, we limited our investigation at this stage of our work only to the model resulting from the eqs. (4).

It was assumed that a noncatalyzed reaction between alcohol and isocyanate, yielding carbamate and further giving any urethane oligomer  $A_iB_j$ , is a simple second-order reaction, hence its rate can be expressed by the following equation<sup>6</sup>:

$$r = kC_A C_B \quad (5)$$

where  $C_A$  and  $C_B$  are instantaneous concentrations of polyol and isocyanate, respectively.

Taking advantage of the material balance for a batch reactor with constant volume and perfect mixing, and on the basis of scheme (4) and dependence (5), one can derive the system of ordinary differential equations describing changes in the concentration of every substrate present in the polymerization process:

$$\frac{dC_A}{dt} = -kC_A C_B - kC_A C_{A_1B_1} - kC_A C_{A_1B_2} - kC_{A_2B_2} - \dots \quad (6)$$

$$\frac{dC_B}{dt} = -kC_A C_B - kC_B C_{A_1B_1} - kC_B C_{A_2B_1} - kC_{A_2B_2} - \dots \quad (7)$$

$$\frac{dC_{A_1B_1}}{dt} = kC_A C_B - kC_A C_{A_1B_1} - kC_B C_{A_1B_1} - k(C_{A_1B_1})^2 - kC_{A_1B_2} C_{A_1B_1} - \dots \quad (8)$$

$$\frac{dC_{A_1B_2}}{dt} = kC_{A_1B_1} C_B - kC_A C_{A_1B_2} - kC_{A_1B_1} C_{A_1B_2} - kC_{A_2B_1} C_{A_1B_2} - \dots \quad (9)$$

etc. for each reactant within the system.

The model presented is composed of an infinite number, and in practice a very high number, of ordinary differential equations. Solving such a system is very difficult. It is necessary to find the algorithm for generating successive equations in this system in order to carry out numerical calculations.

It was found advantageous to decompose this model by introducing the concept of the "fraction of polymer of the  $n$ th order," which imposed no limitations to the general nature of the model. The reacting substances shown in scheme (4) were arranged into specific fractions. The  $F_n$  fraction comprises all the  $A_iB_j$  oligomers having the form

$$A_iB_{n-i} \quad (i = 1, 2, \dots, n) \quad (10)$$

wherein the A and B substrates make an  $F_1$  fraction, and its concentration is

$$C_{F_1} = C_A + C_B \quad (11)$$

The  $A_1B_1$  dimer is a single-element  $F_2$  fraction with the concentration

$$C_{F_2} = C_{A_1B_1} \quad (12)$$

The  $A_2B_1$  and  $A_1B_2$  trimers give an  $F_3$  fraction, and its concentration equals the sum of concentrations of both trimers:

$$C_{F_3} = C_{A_2B_1} + C_{A_1B_2} \quad (13)$$

etc. for each fraction considered.

Hence, the analyzed reaction system comprises single-component even fractions and two-component odd fractions. Theoretically, components of different fractions could react with each other. This depends on which of the —NCO and —OH groups terminate the oligomer chains at both sides, as mentioned earlier.

To make further analysis easier, it was assumed that the initial concentrations of monomers

$$C_A(0) = C_A^0 \quad C_B(0) = C_B^0 \quad (14)$$

are equal\*:

$$C_A^0 = C_B^0 \quad (15)$$

It results from condition (15) that instantaneous concentrations of both components of odd fractions are always equal:

$$\begin{aligned} C_A &= C_B = 0.5C_{F1} \\ C_{A_2B_1} &= C_{A_1B_2} = 0.5C_{F3} \\ C_{A_nB_n} &= C_{F_{2n}} \\ C_{A_{(n+1)B_n}} &= C_{A_nB_{(n+1)}} = 0.5C_{F_{(2n+1)}} \end{aligned} \quad (16)$$

etc. for each odd fraction.

Taking advantage of (16), eqs. (6)–(9) were converted for the condition of

$$V(t) = \text{const.} \quad (17)$$

and the following form was obtained:

$$\begin{aligned} \frac{dC_A}{dt} &= -kC_A(0.5C_{F1} + C_{F2} + 0.5C_{F3} \\ &+ C_{F4} + \dots + 0.5C_{F_{(n-1)}} + C_{F_{2n}}) \end{aligned} \quad (18)$$

which then gave

$$\begin{aligned} \frac{dC_A}{dt} &= kC_A[0.5C_{F1} + 0.5C_{F3} + \dots + 0.5C_{F_{(2n-1)}}] \\ &- kC_A[C_{F1} + C_{F2} + C_{F3} + \dots + C_{F_{(2n)}}] \end{aligned} \quad (19)$$

When the index of B is introduced instead of A, this equation refers to the isocyanate monomer:

$$\begin{aligned} \frac{dC_B}{dt} &= kC_B[0.5C_{F1} + 0.5C_{F3} + \dots + 0.5C_{F_{(2n-1)}}] \\ &- kC_B[C_{F1} + C_{F2} + C_{F3} + \dots + C_{F_{(2n)}}] \end{aligned} \quad (20)$$

When the denotation of  $C_S$  was adopted for the sum of concentrations for all the fractions within the re-

action solution, and  $C_{SNP}$  for the sum of concentrations for all the odd fractions

$$C_S = C_{F1} + C_{F2} + C_{F3} + \dots + C_{F_{(2k)}} \quad (21)$$

$$C_{SNP} = C_{F1} + C_{F3} + \dots + C_{F_{(2k-1)}} \quad (22)$$

and when the sides of eqs. (19) and (20) were added up, a differential equation was obtained which described changes in the concentration of the F1 fraction in the course of the process:

$$\begin{aligned} \frac{d(C_A + C_B)}{dt} &\equiv \frac{dC_{F1}}{dt} \\ &= 0.5kC_{F1} \cdot C_{SNP} - kC_{F1} \cdot C_S \end{aligned} \quad (23)$$

The numerical values of  $C_S$  and  $C_{SNP}$  are subject to changes in the course of the process and they have to be calculated at each step of the numerical integration.

After taking advantage of dependencies (16), (21) and (23), eq. (9) was transformed to the following form:

$$\frac{dC_{A_1B_1}}{dt} = \frac{dC_{F2}}{dt} = 0.25kC_{F1}^2 - kC_{F2} \cdot C_S \quad (24)$$

and analogous changes in the concentration of the sum of  $A_2B_1$  and  $A_1B_2$  trimers (fraction F3) were described by means of the following differential equation:

$$\begin{aligned} \frac{d(C_{A_2B_1} + C_{A_1B_2})}{dt} &\equiv \frac{dC_{F3}}{dt} \\ &= kC_{F1}C_{F2} + 0.5C_{F3}C_{SNP} - kC_{F3}C_S \end{aligned} \quad (25)$$

Identical reasoning gives differential equations for the next fractions:

$$\frac{dC_{F4}}{dt} = 0.5kC_{F1}C_{F3} + kC_{F2}^2 - kC_{F4}C_S \quad (26)$$

$$\begin{aligned} \frac{dC_{F5}}{dt} &= kC_{F1}C_{F4} + kC_{F2}C_{F4} + 0.5kC_{F5} \cdot C_{SNP} \\ &- kC_{F5} \cdot C_S \end{aligned} \quad (27)$$

$$\begin{aligned} \frac{dC_{F6}}{dt} &= 0.5kC_{F1}C_{F5} + kC_{F2}C_{F4} + 0.25kC_{F3}^2 \\ &- kC_{F6} \cdot C_S \end{aligned} \quad (28)$$

$$\begin{aligned} \frac{dC_{F7}}{dt} &= kC_{F1}C_{F6} + kC_{F2}C_{F5} + kC_{F3}C_{F4} \\ &+ 0.5kC_{F7} \cdot C_{SNP} - kC_{F7} \cdot C_S \end{aligned} \quad (29)$$

\* Also, the more general case of  $C_B^0 = \nu C_A^0$  may be analyzed. If  $\nu > 1$ , mainly urethane-isocyanate oligomers will be formed in the system. This specific case, interesting from the point of view of the isocyanate prepolymer manufacturing process, may also be studied on the basis of this model.

Taking advantage of the structural regularities of the polynomials on the right sides of differential equations (23), (25), and (29) as well as (24), (26), and (28), some generalization of the presented model was carried out.

Changes in the concentrations of odd fractions were described by means of a system of differential equations in the form of

$$\frac{dC_{F(2n-1)}}{dt} = 0.5kC_{F(2n-1)} \cdot C_{SNP} - kC_{F(2n-1)} \cdot C_S + \sum_{l=1}^{l < n-0.5} C_{Fi} C_{F(2n-l-1)} \quad (n = 1, 2 \dots k) \quad (30)$$

and even fractions were described by a system in the form of

$$\frac{dC_{F2n}}{dt} = -kC_{F2n} \cdot C_S + k \sum_{l=1}^{l \leq n} \alpha_1 C_{Fi} C_{F(2n-1)} \quad (n = 1, 2 \dots k) \quad (31)$$

where

$$\begin{aligned} \alpha_1 &= 1 \text{ when } l \text{ is an even number} \\ \alpha_1 &= 0.5 \text{ when } l \text{ is an odd number} \\ &\text{and } n \neq 1 \\ \alpha_1 &= 0.25 \text{ when } l \text{ is an odd number} \\ &\text{and } n = 1 \end{aligned} \quad (32)$$

Equations (30) and (31) describe changes in concentrations for all the fractions within the system, hence they are a general kinetic model for the linear polyurethane manufacturing process in a batch reactor. This model was called a basic model due to the constant value of "k" for successive reactions in scheme (4).

Initial conditions for eqs. (30) and (31) have the following form:

$$\begin{aligned} C_{Fi}(0) &= 2C_A^0 = 2C_B^0 \\ C_{Fn}(0) &= 0 \quad \text{for } n > 1 \end{aligned} \quad (33)$$

The mean molecular weight of the produced polyurethane changes in the course of the process. Employing the concept of fraction, the mean molecular weight was expressed as follows (numerically and by weight):

$$\bar{M}_n = \frac{\sum_{i=1}^n C_{Fi} M_{Fi}}{\sum_{i=1}^n C_{Fi}} = \frac{\sum_{i=1}^n C_{Fi} M_{Fi}}{C_S} \quad (34)$$

$$\bar{M}_w = \frac{\sum_{i=1}^n C_{Fi} M_{Fi}^2}{\sum_{i=1}^n C_{Fi} M_{Fi}} \quad (35)$$

where  $M_{Fi}$  stands for the molecular weight of a fraction.

In case of an even fraction, this certainly is the molecular weight of a specific polymer. In case of an odd fraction, mean molecular weight values for components of this fraction were employed. They were calculated from the basic model provided above.

The kinetic model presented in the form of eqs. (30) and (31) was derived from the commonly known reaction network (4). However, mathematical interpretation of the resulting differential equations, which describe changes in concentrations for successive urethane oligomer fractions, was not published earlier. The method adopted here for the decomposition of the complex system of differential equations (18), (24), and (25)–(29) is new. It provided the opportunity to create a mathematical algorithm for the generation of these equations in the course of the polymerization process. As a result, the developed system of model differential equations could be solved numerically with the use of a relatively simple procedure, and could be further utilized in simulating the process studied.

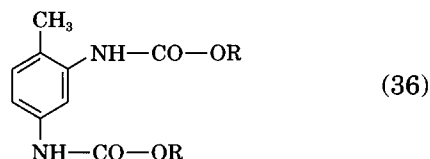
The system of equations provided (4) assumes that the reaction yielding linear urethane oligomers is the only reaction leading to the polyurethane chain propagation. Thus, the process must be carried out in such a way that the side reactions, e.g., those giving allophanates and di- or trimerization of aromatic isocyanates, could be considered negligible. It is possible if, as was assumed in this work, the process applies equimolar initial amounts of diol and diisocyanate, and additionally the reaction medium should be diluted considerably, with the latter rendering difficult any contact of isocyanates in case of no diffusion effects.

## EXPERIMENTAL

### Employed Reagents

The reagents used were toluene 2,4-diisocyanate (2,4-TDI) (Merck), 1,4-butanediol (1,4-BD) (Fluka),

chlorobenzene, analytically pure (POCh Gliwice), and tetrahydrofuran (THF) (POCh Gliwice) dried by distillation over metallic sodium. Standard carbamates with the following formula were employed in testing the GPC method<sup>12</sup>:



Specifications for these compounds are provided in Table I.

### Method for Experimental Verification of Developed Kinetic Model

The investigation covered the reaction between 2,4-TDI and 1,4-BD proceeding in a solution. This was run in a 500-cm<sup>3</sup> glass reactor, provided with a heating system, agitator, thermometer, and reflux condenser. Nitrogen was supplied through the latter. The reaction mixture was sampled by means of a syringe.

Two reaction temperatures were applied and they were controlled by boiling points of the employed solvent mixtures: C<sub>6</sub>H<sub>5</sub>Cl : THF = 1 : 1 and 3 : 1, by weight. The temperatures were 86 and 101°C, respectively.

2,4-TDI (30 g, 0.172 mol) was dissolved in 270 g of the above specified solvent mixture. Of the same solvent mixture 139.5 g was employed to dissolve 15.5 g (0.172 mol) of 1,4-BD and both obtained solutions were mixed together. Hence, the concentrations of both reactants amounted to 10% of the introduced solution. Density of the resulting solution was 0.951 and 0.903 g cm<sup>-3</sup>, at 86 and 101°C, re-

spectively. Depending on the temperature, the initial concentration of the F1 fraction amounted to 0.719 and 0.683 mol dm<sup>-3</sup>.

The reactions were run for as long as the solution stayed clear. The reaction time was different for different temperatures: at 86° and at 101°C this was 300 and 120 min, respectively. When those time limits were exceeded, some flocculent precipitate of obtained polymer was observed.

The reaction medium sample was diluted with THF to lower its concentration down to about 1.0%, and then it was immediately analyzed with the GPC method. A model 1090M Hewlett-Packard chromatograph was employed to take measurements. This was operated in the Chem Station system, and was equipped with a 300 × 7.5-mm column filled with PL-Gel having pore diameters of 50, 500, and 1000 Å. THF was the solvent used. The eluent flow rate amounted to 1 cm<sup>3</sup> min<sup>-1</sup>. An RI type HP 1047A detector was employed. The measurements were taken at 30°C, and the analyzed volume was 0.02 cm<sup>3</sup>. The obtained results were subject to computer analysis, which utilized the GPC-79999 A software provided by the same company. Exemplary chromatograms for the products studied are shown in Figure 1.

### Calibration of Chromatographic Columns of the GPC System

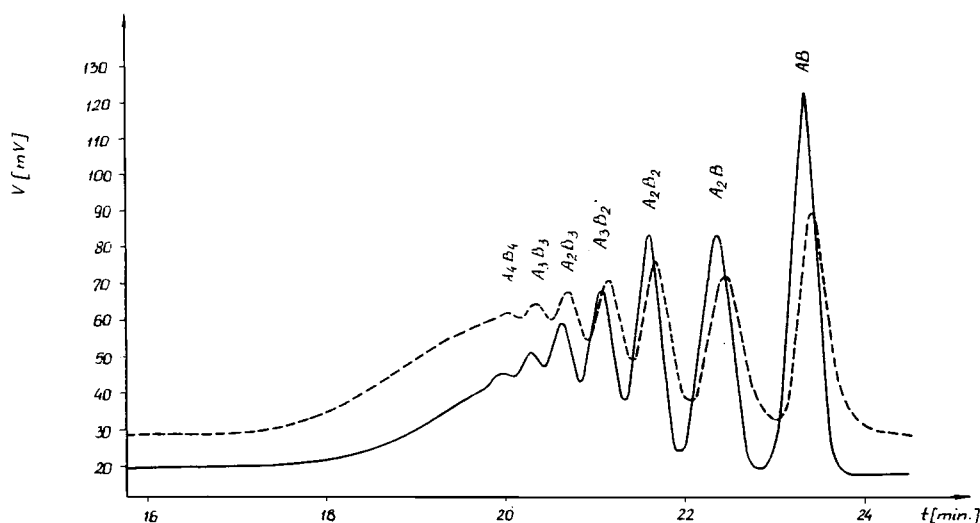
Calibration of the chromatographic columns was executed in the form of a logarithmic dependence of the polymer molecular weight versus retention volumes; the operation was based on the standard compounds shown in Table I and the following formula was obtained<sup>13</sup>:

$$\log M = 5.7994 - 0.00763 V_{\text{ret}} \quad (37)$$

**Table I** Specifications for Carbamate Standards Shown by the Structure (36)

Position	R in Structure (36)	Total Formula of Carbamate	Molecular Weight	Retention Time (min)	Peak Area Corresponding to Standard Conc. of 1 mg cm <sup>-1</sup> According to Figure 1 <sup>a</sup>
1	C <sub>2</sub> H <sub>5</sub>	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	266	34.142	792
2	C <sub>6</sub> H <sub>13</sub>	C <sub>21</sub> H <sub>34</sub> N <sub>2</sub> O <sub>4</sub>	378	33.308	558
3	C <sub>10</sub> H <sub>21</sub>	C <sub>29</sub> H <sub>50</sub> N <sub>2</sub> O <sub>4</sub>	490	32.717	529
4	C <sub>16</sub> H <sub>33</sub>	C <sub>41</sub> H <sub>74</sub> N <sub>2</sub> O <sub>4</sub>	658	32.017	569

<sup>a</sup> The units for peak areas are conventional; peak area is proportional to the integer of the detector signal.



**Figure 1** GPC chromatogram for the reaction solution of 2,4-TDI and 1,4-DB: (—) reaction time = 120 min, temp. = 86°C; (----) reaction time = 60 min, temp. = 101°C.

Mass fractions for  $A_iB_j$  oligomers in the reaction solution samples were determined by internal standardization of the GPC chromatograms obtained. The procedure covered numerical integration of elution curves and then peak areas for individual components were referred to the total area under the elution curve. The peak representing  $C_6H_5Cl$  was excluded from those considerations.

It was assumed for the quantitative interpretation of the elution curves that the RI detector signal is always proportional to the studied concentration in the eluat. With this type of detectors, this is true for polymers with molecular weights exceeding 10,000, i.e., outside the range specific for the oligomers investigated here.<sup>14,15</sup> Hence, applicability of the measuring system employed for the determination of oligourethanes had to be assessed. For this purpose, refractive indices  $n^{20}$  were found (Abbe method) for the solutions of standard carbamates in THF, at varied concentrations. The findings are provided in Table II. The values of  $n^{20}$  did not depend on the types of carbamate standards employed but—as was expected—they were apparently higher following the increasing solution concentrations. Similar results were obtained for a separated fraction of a linear polyurethane derived from 2,4-TDI and 1,4-butanediol.<sup>16</sup>

Moreover, quantitative calibrations of the RI detector with the use of selected carbamates were compared to those employing two hydrocarbon standards (Fig. 2). In Table I, column 6 specifies peak areas corresponding to the standard concentration of  $1 \text{ mg cm}^{-3}$ . As can be seen from the data, peak areas for carbamates are close to each other

and completely different from those for hydrocarbon standards. These findings allow—in our opinion—the use of the RI detector signals in the quantitative analysis of urethane oligomers. It is a prerequisite for correct findings that the carbamate standards utilized should have their structures close to those of the urethane oligomers studied, and of course the chromatographic separation of components should be satisfying. One can expect that from the initial oligomers of scheme (4), as can be seen from Figure 1.

It can be concluded from the comparison of molecular weights for eluated components and oligourethanes according to scheme (4), as expected, that no additional peaks were found which could suggest that some side reactions took place in the system, e.g., trimerization of 2,4-TDI, hence complicating the model adopted.

In our opinion, application of the GPC method and the refractometric detector in the analysis of urethane oligomers, and experimental confirmation of the applicability of this method, makes a contribution to the state of knowledge within the analysis of urethane oligomers. This method can now be utilized in experimental verification of the model developed.

### Procedure for Numerical Calculations

Changes in the concentrations of individual fractions and changes in the polyurethane mean molecular weight can be described by a system of ordinary linear differential equations. Owing to the concept of “fraction of polymer,” the model was decomposed

**Table II** Refractive Indices for Solutions of Carbamates in THF (at 20°C)

Position	Total Formula of Carbamate	Molecular Weight	$n_{20}$ Concentration (wt %)					
			0.5	1.0	1.5	2.0	2.5	3.0
1	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	266	1.4088	1.4090	1.4090	1.4112	1.4112	1.4113
2	C <sub>21</sub> H <sub>34</sub> N <sub>2</sub> O <sub>4</sub>	378	1.4081	1.4086	1.4095	1.4101	1.4114	1.4118
3	C <sub>29</sub> H <sub>50</sub> N <sub>2</sub> O <sub>4</sub>	490	1.4085	1.4094	1.4095	1.4103	1.4109	1.4120
4	C <sub>41</sub> H <sub>74</sub> N <sub>2</sub> O <sub>4</sub>	658	1.4087	1.4089	1.4095	1.4100	1.4106	1.4110

to a more condensed form of (30) and (31) wherein the number of equation corresponds to the number of fractions.

The obtained differential equations can thus be presented in a more general form:

$$\frac{dC_{F1}}{dt} = f_i(C_{F1}, C_{F2} \cdots C_{Fi} \cdots C_{Fn})$$

$$(i = 1, 2 \cdots n) \quad (38)$$

From a mathematical point of view, the above system of differential equations is provided in its normal form, and its solution is a typical initial-value problem since the concentrations of all the fractions are known for  $t = 0$ . The system of equations (36), to-

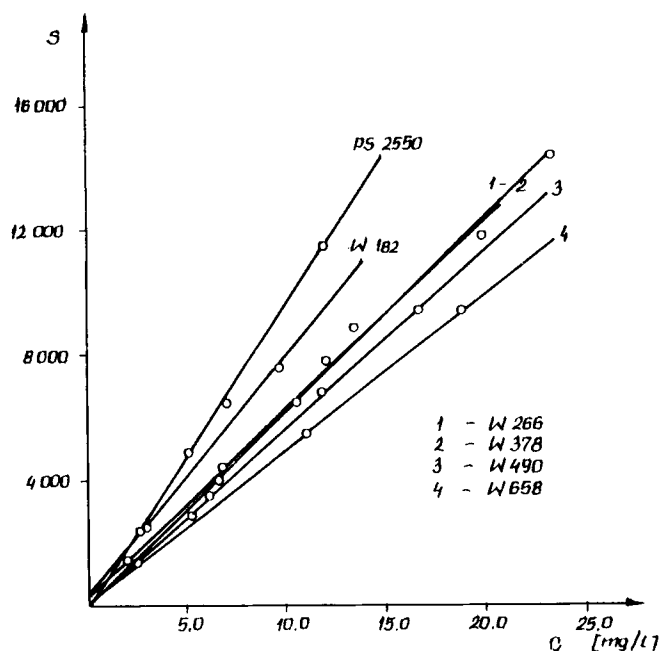
gether with its initial conditions (33), was subject to numerical integration which applied the Euler method with the following algorithm:

$$C_{Fi}^{(n+1)} = C_{Fi}^{(n)} + h \cdot f_i(C_{F1}^{(n)}, C_{F2}^{(n)} \cdots C_{Fi}^{(n)} \cdots C_{Fn}^{(n)}) \quad (39)$$

where  $h$  is a step of the integration operation. In our calculations, we assumed  $h = 5_s$ .

$C_S$ ,  $\bar{M}_n$ , and  $\bar{M}_w$  for polyurethane were calculated at the first step of numerical integration. It was assumed that

$$C_A^0 = C_B^0 = 0.5C_{F1} = 1.0 \text{ mol dm}^{-3} \quad (40)$$



**Figure 2** Dependencies of peak areas ( $s$ ) versus concentrations ( $c$ ) for carbamate standards 1-4 as per Table I, and for hydrocarbon standards, polystyrene (PS-2550) and diphenyl (W-182) (figures on the axis of ordinates have been given in units proportional to peak areas).



**Table III** Calculation Results for the Model Reaction of 2,4-TDI and 1,4-BD, at 86°C,  $k = 1.50 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 

Time (min)	$\bar{M}_n$	$P$	Concentration of Polyurethane Fraction (mol dm <sup>-3</sup> )										
			F1	F2	F3	F4	F5	F6	F7	F8	F9	F10-Fn	
0	132.14	—	2.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	138.35	1.048	1.828	0.076	0.006	—	—	—	—	—	—	—	—
3	152.21	1.153	1.532	0.163	0.040	0.006	0.001	—	—	—	—	—	—
5	167.53	1.255	1.295	0.199	0.077	0.016	0.005	0.001	—	—	—	—	—
10	209.53	1.454	0.887	0.198	0.134	0.042	0.024	0.006	0.004	0.001	—	—	—
20	300.24	1.675	0.486	0.133	0.146	0.058	0.053	0.018	0.018	0.007	0.006	0.007	0.007
40	489.00	1.857	0.212	0.059	0.098	0.042	0.056	0.022	0.030	0.014	0.017	0.038	0.038
60	682.69	1.933	0.120	0.031	0.065	0.026	0.044	0.017	0.028	0.013	0.019	0.063	0.063
90	974.39	1.989	0.065	0.015	0.039	0.015	0.029	0.011	0.021	0.010	0.016	0.080	0.080
120	1266.85	2.017	0.041	0.009	0.026	0.009	0.021	0.007	0.016	0.007	0.013	0.084	0.084
180	1841.65	2.015	0.022	0.004	0.014	0.004	0.012	0.004	0.010	0.004	0.008	0.078	0.078
240	2372.47	1.963	0.013	0.002	0.009	0.002	0.008	0.002	0.007	0.002	0.006	0.069	0.069
300	2834.58	1.896	0.010	0.001	0.006	0.002	0.006	0.002	0.005	0.002	0.004	0.007	0.007
360	3224.78	1.832	0.007	0.001	0.005	0.001	0.004	0.001	0.004	0.001	0.003	0.054	0.054

hence:

$$C_{F1} = 2.0 \text{ mol dm}^{-3} \quad \text{and} \quad C_S^{(1)} = 2.0 \text{ mol dm}^{-3}$$

Then, the right side of eq. (38) was calculated and the concentration values for the fractions  $C_{F1}$ ,  $C_{F2}$ ,  $\dots$ ,  $C_{Fn}$  were found after the time of  $\Delta t = h$  from eq. (39). Based on that, the numerical values of right sides of the system (38) were determined for the second step of numerical integration, etc.

For the temperature of 86°C, numerical integration was carried out for the reaction time changing within 0–21,600 s, and within 0–7,200 s for the temperature of 101°C.

The polyurethane chemical compositions at the successive process stages, which were found by means of the simulation method, were expressed with taking into consideration no solvents which in fact were present in the reaction system.<sup>†</sup>

The weight percentages obtained therefrom for oligomers were compared to their real values resulting from the experimental GPC method.

## DISCUSSION OF RESULTS

### Analysis of Findings for Simulation Calculations

The simulation of the reaction between 2,4-TDI and 1,4-BD was carried out for isothermal conditions.

<sup>†</sup> THF employed both as a process solvent and an eluent was not seen in chromatograms. The peak representing  $C_6H_5Cl$  was not taken into consideration during internal standardization of obtained chromatograms.<sup>13</sup>

It was assumed that the polymerization reaction proceeded in a batch reactor with constant volume and perfect mixing. Also, since the studied process was run in a solution, its rate was assumed not to depend on the rate of the reagents diffusion.

Numerical calculations adopted the initial numerical values for the rate constants as  $k_1 = 1.5 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_2 = 2.75 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , for process temperatures of 86 and 101°C, respectively.<sup>3,‡</sup> These values should be understood as mean rate constants for the reactions of both —NCO groups in 2,4-TDI with 1,4-butanediol or with oligourethanes  $A_iB_j$  or  $A_{i+1}B_i$ .

Those rate constant values were determined from the kinetic study of model reactions of phenyl isocyanate and 2,4-TDI with alcohols of the general formula of  $C_nH_{2n+1}OH$  (for  $2 \leq n \leq 18$ ), and with polyoxypropylene glycols of molecular weights below 2000. The obtained rate constant values were referred to reaction (5), and their temperature dependencies were described by the formula<sup>6</sup>

$$\ln k = 7.0 - \frac{40}{RT} \quad (41)$$

The findings from numerical calculations carried out for the oligomerization process are presented in Table III (for temperature of 86°C) and in Table IV (for 101°C). Numerical values for the polymer mean molecular weight and mean degree of molecular-

<sup>‡</sup> Further investigation of that reaction gave somewhat different estimated values of  $k$  for those temperatures.

**Table IV** Calculation Results for the Model Reaction of 2,4-TDI and 1,4-BD, at 101°C,  $k = 2.75 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 

Time (min)	$\bar{M}_n$	$P$	Concentration of Polyurethane Fraction (mol dm <sup>-3</sup> )										
			F1	F2	F3	F4	F5	F6	F7	F8	F9	F10-F $n$	
0	132.14	—	2.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	143.2	1.09	1.696	0.123	0.018	0.002	—	—	—	—	—	—	—
3	171.7	1.28	1.241	0.204	0.085	0.019	0.007	0.001	—	—	—	—	—
5	202.5	1.42	0.938	0.203	0.129	0.039	0.021	0.005	0.003	0.001	0.001	0.001	—
10	285.3	1.65	0.528	0.143	0.149	0.058	0.050	0.017	0.016	0.006	0.005	0.005	0.005
20	458.8	1.83	0.236	0.067	0.106	0.082	0.133	0.062	0.095	0.014	0.016	0.016	0.033
40	813.7	1.96	0.089	0.022	0.051	0.020	0.036	0.014	0.025	0.011	0.018	0.018	0.073
60	1171.4	2.01	0.047	0.010	0.030	0.010	0.023	0.008	0.017	0.008	0.014	0.014	0.083
90	1703.1	2.02	0.025	0.005	0.016	0.005	0.014	0.004	0.011	0.004	0.009	0.009	0.080
120	2205.3	1.98	0.019	0.003	0.010	0.003	0.009	0.003	0.007	0.003	0.006	0.006	0.072

weight distribution for successive reaction stages are also provided. The instantaneous concentrations are shown for fractions F1 to F9, while the concentrations for higher fractions (F10–F $n$ ) are summarized.

Changes in the concentrations of fractions F1, F2, F3, and F4 in the course of the reaction run at 86°C are presented graphically in Figure 3, limiting the reaction time to 120 min. Figure 4 provides integral model curves for the molecular-weight distribution of polyurethane synthesized at 86°C, after reaction times of 20, 100, and 300 min.

Analysis of the obtained results suggests that the basic model enables the chemical composition of linear polyurethane to be predicted depending on the reaction conditions, i.e., temperature and time.

The data provided in Tables III and IV suggest that the mean molecular weight of polyurethane precipitating from the solution in the form of flocculent precipitate<sup>§</sup> does not exceed 3300.

Our simulation confirms the results obtained by Johnson and Driscoll<sup>7</sup> who found that in general the linear polyurethane molecule comprises segments composed of not more than 10 urethane units. Hence, for 2,4-TDI and 1,4-BD monomers, the average molecular weight of polyurethane can be evaluated to reach about 2600.

The monomers present at the beginning of the process, isocyanate and polyol, react pretty quickly and yield a dimer molecule AB. So, its concentration increases quickly at early stages of the process. Those molecules react further and give higher fractions. As can be seen from Figure 3, concentrations of other fractions behave in the same way. Initially,

e.g., during the first 60 min of the process running at 101°C, a variety of oligomers can be observed in the system, hence its polymolecularity increases. Since a certain moment of the process, this feature no longer prevails and the system tends to polymer monomolecularity. Increased temperature favors this phenomenon.

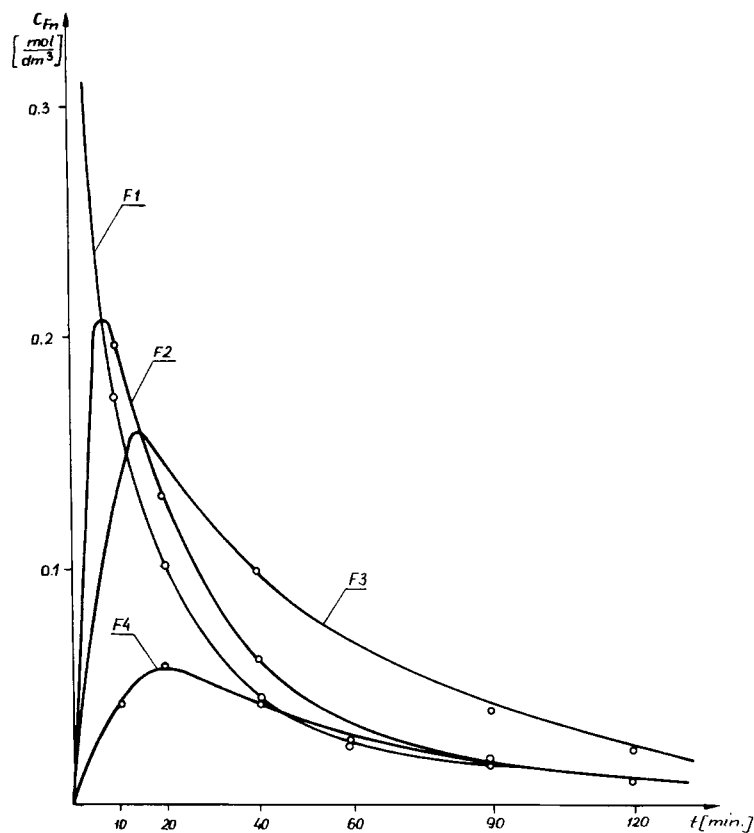
Additionally, higher concentrations of corresponding reactants can be observed for the same reaction time. In the course of the process, increasing polymer molecular weight gives a gradual decrease of molar concentrations for the sum of all fractions ( $C_S$ ) of the obtained polymer. Changes in the chemical composition of a fraction are illustrated by molecular-weight distribution curves, and their shape depends on the reaction conditions.

In practice, specially selected catalysts are employed in the diisocyanate and polyol polyaddition process. Their catalytic effects provide, for example, increased reaction rate constant. Thus, modifying the value of the rate constant (evaluated for example from studying model reactions) one can apply the developed basic model to analyze industrial polyurethane manufacturing processes, especially at their early stages, when low-molecular-weight oligomers are present in the system.

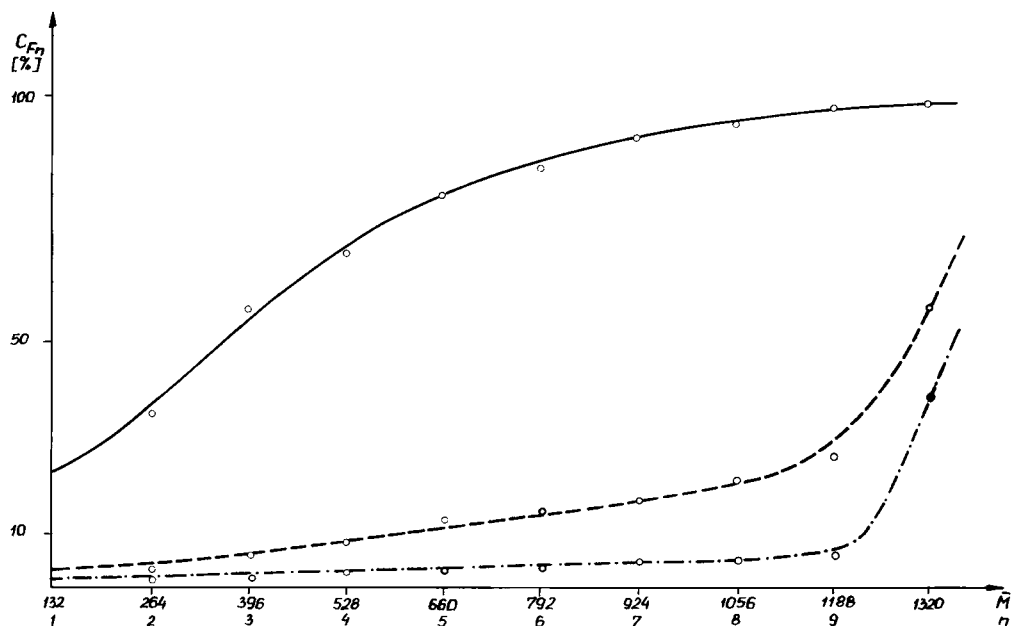
In Tables V and VI, weight percentages are provided for successive polyurethane fractions. They were found by means of the GPC method, for the polymer synthesized at 86 and 101°C, respectively. A method presented<sup>6</sup> was utilized to calculate the rate constant values for the reaction of 2,4-TDI and 1,4-BD at 86 and 101°C.

In Tables V and VI, results of our numerical calculations are also shown. They were obtained from our basic model for the evaluated rate constant val-

<sup>§</sup> When carrying out experiments, the precipitate was observed to be formed after 360 min and after 120 min for temperatures of 86 and 101°C, respectively.



**Figure 3** Model concentration profiles for fractions F1, F2, F3, and F4, for the reaction rate constant =  $1.5 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .



**Figure 4** Integral model curves for molecular-weight distribution of polyurethane synthesized in the reaction of  $k = 1.5 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ : (—)  $t = 20 \text{ min}$ ; (----)  $t = 100 \text{ min}$ ; (- · - · -)  $t = 300 \text{ min}$ .

**Table V Comparison of Experimental and Model Data for the Reaction of 2,4-TDI and 1,4-BD at 86°C**

Time (min)	Experimental Data ( $k = 5.00 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )				Results from Model calculations ( $k = 3.00 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )			
	$\bar{M}_n$	Mass Fraction (%)			$\bar{M}_n$	Mass Fraction (%)		
		F1 + F2	F3 + F4	F5 + F6		F1 + F2	F3 + F4	F5 + F6
20	309	73.0	25.2	1.6	159	88.1	11.0	0.8
40	332	57.4	35.2	7.4	193	69.4	24.1	5.3
60	356	46.0	38.4	15.5	230	53.1	30.6	11.3
90	412	32.0	35.4	22.5	294	35.3	31.1	17.8
120	456	25.1	31.4	26.7	370	17.6	26.6	19.9
180	537	16.4	23.4	26.9	570	11.1	16.1	16.2
240	667	8.7	15.7	21.8	861	5.1	8.9	10.4
300	801	6.7	11.2	16.6	1260	2.7	4.9	6.1

ues which minimize the deviations between the fraction concentrations found experimentally and those calculated numerically.

It was noticed that the decrease of concentrations for monomers in the reactions studied is overestimated in relation to other fractions. In order to reduce the effect of this error, which probably results from chromatographic analysis, changes in fraction sums of F1 + F2, F3 + F4, and F5 + F6 were subject to comparison, and the developed model was verified based just on them. The values of  $\bar{M}_n$  which were found experimentally with the use of a GPC method and were calculated numerically for various reaction conditions (Tables V and VI) were not utilized in the statistical verification of the model due to their different physical nature. Yet, the functions of  $\bar{M}_n$

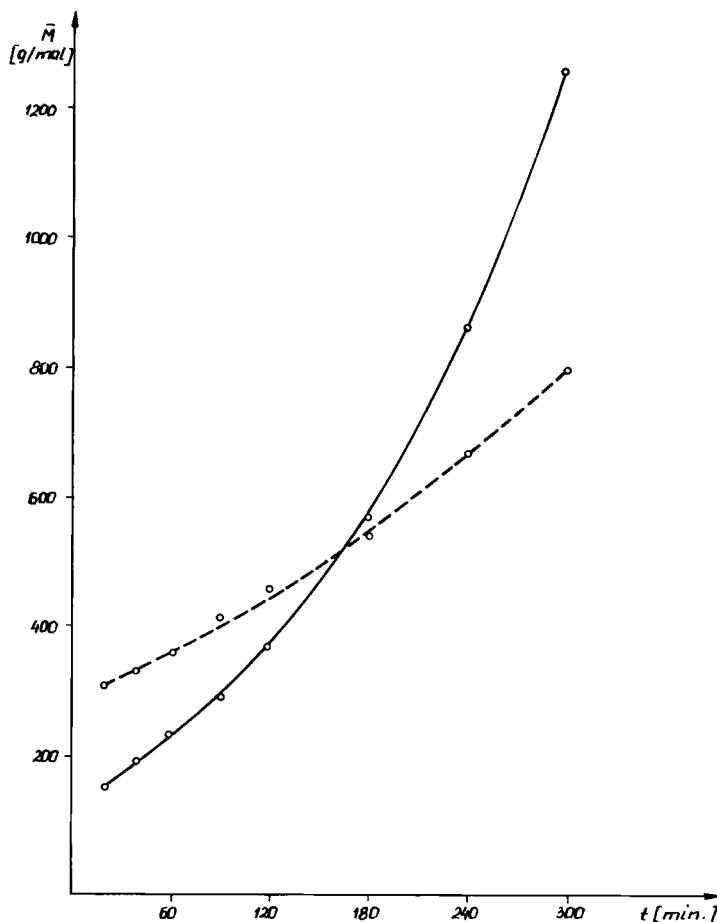
versus reaction time (for 86°C), obtained experimentally and calculated for  $k = 3.00 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , are compared in Figure 5.

It is noticeable that the estimated value of the rate constant at 86°C conforms to the value calculated from the changes of concentrations of —NCO groups. However, the estimated value of the rate constant at 101°C ( $8.00 \times 10^{-4}$ ) is much lower than the experimental value ( $23.2 \times 10^{-4}$ ) which conforms with the value calculated by means of the Arrhenius equation (41).

Those differences confirm the complex and multistage nature of the process. The reactions presented in scheme (4) manifest themselves with different intensities, which depend on the condition of the reaction system.

**Table VI Comparison of Experimental and Model Data for the Reaction of 2,4-TDI and 1,4-BD at 101°C**

Time (min)	Experimental Data ( $k = 23.20 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )				Results from Model Calculations ( $k = 8.00 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )			
	$\bar{M}_n$	Mass Fraction (%)			$\bar{M}_n$	Mass Fraction (%)		
		F1 + F2	F3 + F4	F5 + F6		F1 + F2	F3 + F4	F5 + F6
10	309	62.0	36.2	1.7	170	81.9	15.9	1.9
20	341	44.2	45.5	7.4	217	58.1	29.2	9.3
30	382	33.9	47.6	11.7	271	40.4	31.8	16.1
45	448	23.3	42.4	15.7	370	23.6	26.6	19.9
60	515	16.6	35.7	16.7	496	14.1	19.4	18.0
75	546	12.4	28.7	19.4	655	8.7	13.3	14.2
90	625	9.3	23.1	18.7	860	5.4	8.9	10.4
105	800	10.4	24.2	16.6	1115	3.5	6.0	7.4



**Figure 5** Graphic presentation of the dependence of polyurethane mean molecular weight versus reaction time, at 86°C: (—) profile calculated from the model ( $k = 3 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ); (----) experimental profile.

## CONCLUSIONS

Because of the “equal reactivity” concept for the urethane oligomers covered by scheme (4), the kinetic model suggested in this paper can be called a basic model for the reactions giving linear polyurethanes. This model offers a way to calculate conversion figures for monomers at the successive stages of the polyaddition reaction. Also, chemical composition data and polyurethane molecular weight distribution functions can be predicted on the basis of reaction conditions. For those calculations it is necessary to know rate constants and their dependence on the temperature profile. The latter can be found from independent kinetic investigation of some selected reactions between model isocyanates and hydroxyl compounds. The comparison of the rate constant values found experimentally and those estimated numerically for the reaction of 2,4-TDI with 1,4-BD proves the complex and multistage na-

ture of the studied process. This nature makes the successive reactions of scheme (4) prevail at the different process stages. The results obtained show that even for quasioptimum values of the reaction rate constants—which minimize the deviations between the data found experimentally and those calculated—the model based on the scheme provided cannot properly describe the studied process. It is hard to support the assumption of unchanged chemical reactivity for successively created urethane oligomers. This can make the simplest approximation for the process, at the outmost.

The recurrent formulas derived (30) and (31), which make it possible to gradually generate differential eqs. (6)–(9) in the process of numerical calculations, make a mathematical model of the process studied. The same values of rate constants were adopted to ease the numerical solution. However, this assumption is not necessary when the model is applied in the simulation of the polyaddition reac-

tion wherein reactivity characteristics of the oligomers change in time. In this case it is necessary to adopt some additional model describing variability of rate constants versus the type of oligomer considered. Such a model was developed in (11) and it was based on the assumptions for the collision theory. It provides rate constants as functions of molecular weights of the reactants employed:

$$M_A^{-1} + M_B^{-1} = \left( \frac{k_{AB}}{\beta} \right)^2 \quad (42)$$

where  $M_A$  is the molecular weight of polyol monomer or urethane oligomer which contains reacting —OH group(s),  $M_B$  is the molecular weight of isocyanate monomer or urethane oligomer which contains reacting —NCO group(s),  $k_{AB}$  is the reaction rate constant, and  $\beta$  is the experimentally found constant factor.

In further investigations, equation (42) can be utilized in developing a new model which takes advantage of the algorithm (30)–(32) for generating differential equations. This model will be verified experimentally, with the utilization of the data obtained during this study. Only then will it be possible to evaluate how far the reactivity of urethane oligomers changes in the course of the reaction between diisocyanate and diol.

The model developed allows us to employ computer simulation methods in studying the process of gradual polyaddition of isocyanates and polyols, and to predict fractional composition for oligomers at individual steps of the polymerization processes. After introducing some necessary modifications in initial assumptions, the model can also be utilized to control industrial polyaddition processes, e.g., the production of urethane prepolymers. The modifications required would have to involve the decreasing reactivity of urethane oligomers with the increasing molecule size (proved experimentally). In the future, quickly increasing viscosity of diisocyanate–polyol mixtures (if no diluent is present) should be considered, since this phenomenon is very important for commercial scale processes.

## NOMENCLATURE

A	polyol substrate
B	isocyanate substrate
$A_i B_j$	urethane oligomers
$i, j, l, m, n$	natural numbers

$M$	molecular weight of polymer, found experimentally from the calibration eq. (37)
$V_{\text{ret}}$	retention volume
$k$	reaction rate constant factors
$C_A$	concentration of polyol
$C_B$	concentration of isocyanate
$F_n$	oligomer fraction of $n$ order
$C_{F_n}$	concentration of oligomer fraction of $n$ order
$C_{A_i B_j}$	concentration of urethane oligomer
$C_A^0$	initial concentration of polyol
$C_B^0$	initial concentration of isocyanate
$r$	reaction rate according to eq. (5)
$V$	volume of reaction system
$t$	time
$T$	temperature
$C_S, C_{\text{SNP}}$	total concentrations of fractions, defined by eqs. (21) and (22)
$\alpha_1$	coefficient in the differential eq. (31)
$\bar{M}_n$	mean molecular weight of polymer (numerical)
$\bar{M}_w$	mean molecular weight of polymer (by weight)
$P$	molecular-weight distribution factor
$M_{F_i}$	molecular weight of $F_i$ oligomer fraction
$f_i$	function in eq. (37)
$R$	gas constant in eq. (39)
$h$	step length in numerical integration
$C_{F_i}^{(n)}$	concentration of $F_i$ fraction at $n$ th step of numerical calculations
$C_S^{(n)}$	concentration of sums of all oligomer fractions at $n$ th step of numerical calculations

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## REFERENCES

1. G. Woods, *The ICI Polyurethanes Book*, John Wiley, New York, 1987.
2. S. Cimmino, E. Martuscelli, C. Silvestre, R. Barbucci, A. Magnani, and F. Tempesti, *J. Appl. Polym. Sci.*, **47**, 631 (1993).
3. J. J. Tondeur, G. Vandendunghen, and M. Watelet, *Chim. Nouvelle*, **10**, 1148 (1992).
4. C. Chaffey and S. Orchanian, *J. Appl. Polym. Sci.*, **7**, 301 (1973).

5. S. C. Chorng-Shyan, *J. Appl. Polym. Sci.*, **40**, 2189 (1990).
6. P. Król, B. Atamańczuk, and J. Pielichowski, *J. Appl. Polym. Sci.*, **46**, 2139 (1992).
7. A. F. Johnson and K. F. Driscoll, *Eur. Polym. J.*, **20**, 979 (1984).
8. A. Ulińska and R. Mieczkowski, *Roczniki Chem.*, **49**, 1167 (1975).
9. K. J. Dorozhkin, K. J. Kimelblat, and J. A. Kirpikznikov, *Vysokomol. Soed. A.*, **23**, 2525 (1981).
10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
11. P. Król, *J. Appl. Polym. Sci.*, to appear (1995).
12. P. Król and Z. Wietrzyńska-Lalak, *Eur. Polym. Sci.*, **31**, 689 (1995).
13. P. Król and M. Dejnega, *Polimery Tworz. Wielkocz.*, **41**, 93 (1995).
14. Z. Tuzar and H. C. Beachell, *J. Polym. Sci. B.*, **9**, 37 (1971).
15. L. Simek, *Makromol. Chem. Rapid. Commun.*, **1**, 215 (1980).
16. P. Król and R. Chrzęszcz, *Polimery Tworz. Wielkocz.*, **39**, 677 (1994).