

Experimental Verification of the Kinetic Model for the Reaction Yielding Linear Polyurethanes, Claiming Dependence of Oligomer Reactivities on Molecular Weights. III

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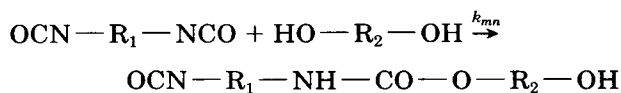
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SYNOPSIS

Taking advantage of the algorithm developed earlier which makes it possible to calculate rate constants for the parallel-subsequent reactions of the kinetic model for the diisocyanate and diol polyaddition process, a mathematical model was developed for this process which then was subjected to mathematical decomposition. The procedure adopted allowed me to numerically resolve the obtained system of differential equations and to perform the numerical simulation of the polymerization process studied. For the reactions of 2,4-TDI and 1,4-butanediol, the results obtained were compared to experimental concentrations of urethane oligomer fractions found by means of GPC. It was found that the model suggested provides a better fit than does the model claiming dependence of chemical activity of oligomers solely on reactivity specifications for their functional groups. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Initial steps of a linear polyurethane synthesis process can be presented by a network of parallel-subsequent reactions yielding urethane oligomers. Each reaction has its own specific rate constant, e.g.:



A mathematical model for the linear polyurethane producing process was given in Ref. 1, wherein rate constants k_{mn} depend on the molecular weights of oligourethanes. The study concluded that the algorithm obtained gives a chance to develop a new and generalized model for the process studied.

Following the Flory's postulate, it was so far assumed that the reactivity of oligomers remains the same at the subsequent stages of the polyaddition process and that it depends solely on the chemical nature of the functional groups within reacting sub-

stances.² A further simplification is represented by the assumption that the reactivity of each oligomer is the same and dependent on functional groups, in this case on isocyanate and hydroxyl groups. The mathematical model which was based on this assumption was composed of a system of ordinary differential equations which involved only one rate constant. This model was verified experimentally in the reaction of 2,4-TDI and 1,4-butanediol, under conditions making it possible to neglect diffusion effects, and produced a considerable error.³ When side reactions were taken into consideration, e.g., those yielding allophanate groups, and the model was slightly modified, the branching of linear polyurethane chains could be evaluated.⁴

The purpose of this study was to provide a mathematical model for the polyaddition process involving diisocyanates and polyols. The investigations assumed that chemical reactivity of urethane oligomers depended on their molecular weights, which was based on an equation derived from the collision theory and on the findings from kinetic studies on model reactions of isocyanates and hydroxyl compounds.¹ Then, the simulation calculation results

were verified on the basis of experimental reactions of 2,4-TDI with 1,4-butanediol described in Ref. 3.

A MATHEMATICAL MODEL FOR THE REACTION YIELDING LINEAR POLYURETHANES

The kinetic model for the process studied was based on the kinetic network of parallel-subsequent reactions. As in Ref. 3, the following denotation was applied: A , difunctional polyol-type substrate, e.g., 1,4-butanediol; B , diisocyanate, e.g., 2,4-TDI; and $A_i B_j$, where $i = j$ or $i = j \pm 1$, a linear urethane oligomer.

When $i = j$, the oligomer has one $-\text{NCO}$ group at one chain of its end and one $-\text{OH}$ group at the other end; hence, it is capable of reacting with both monomers and/or with any product. When $i = j + 1$ or $i = j - 1$, the oligomer chain ends with $-\text{OH}$ or $-\text{NCO}$ groups, respectively, at its both ends, so in the first case, it can react with the B monomer and with $A_i B_i$ and $A_i B_{i+1}$ oligomers, and in the latter case, it can react with the A monomer and with $A_i B_i$ and $A_{i+1} B_i$ oligomers.

F_n is the oligomer fraction of "n" order, composed of $A_i B_j$ oligomers which meet the following equation:

$$i + j = n \quad (1)$$

In accordance with this definition, A and B reacting substances make an F_1 fraction with the following concentration of

$$C_{F_1} = C_A + C_B \quad (2)$$

The $A_1 B_1$ dimer makes a single-component fraction F_2 with the concentration of

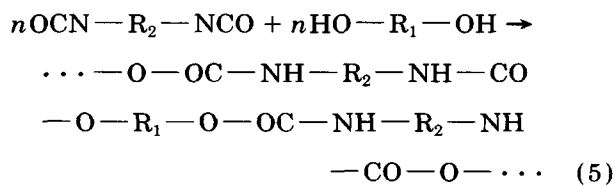
$$C_{F_2} = C_{A_1 B_1} \quad (3)$$

The $A_1 B_1$ and $A_1 B_2$ trimers form an F_3 fraction:

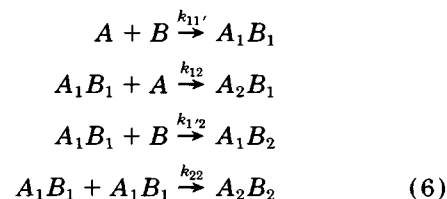
$$C_{F_3} = C_{A_2 B_1} + C_{A_1 B_2} \quad (4)$$

etc. So, there can be oligomers present in the reaction system considered, which form even fractions, composed always of a single component, and oligomers which form odd fractions, always two-component fractions.

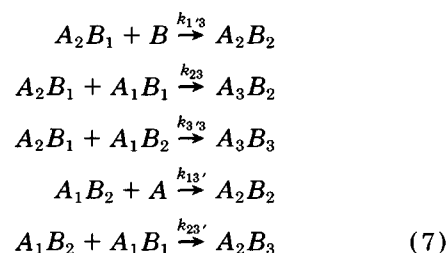
The above assumption makes it possible to present the general polyaddition reaction with the chain gradual growth like



by means of the following kinetic scheme:

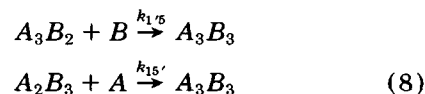


The $A_2 B_1$, $A_1 B_2$, and $A_2 B_2$ oligourethanes formed at the first process stage can further react with initial materials and/or with each other increasing gradually the polyurethane molecule:



It is important in this case to determine precisely and univocally the rate constants for the subsequent individual reactions within this system.

In the rules adopted here, the "mn" subscript for a k_{mn} constant means that this constant refers to the reaction involving components of the F_m and F_n fractions. To distinguish the components of odd fractions, an oligomer with $-\text{NCO}$ end groups on both its sides was additionally marked with the primed superscript. Following the above, e.g., the adopted notation for the rate constants of the reactions involving two different oligomers of the F_5 fraction is



When it is assumed that all the reactions (6) and (7) are irreversible second-order reactions, which is postulated in most references,^{5,6} the rate of each reaction can be expressed by the following equation:

$$r = k_{mn} C_A C_B \quad (9)$$

where C_A is a concentration of any polyol-type reacting substance, and C_B , a concentration of an isocyanate-type reacting substance. When assuming, for the need of simplicity, that the volume of the reacting mixture is constant over time,

$$V(t) = \text{const} \quad (10)$$

and taking advantage of the design equation for a batch reactor with perfect mixing, one can derive the following differential equations describing changes in concentrations of monomers and of created and disappearing oligomers:

$$\begin{aligned} \frac{dC_A}{dt} = & -k_{11}C_A C_B - k_{12}C_A C_{A_1 B_1} \\ & - k_{13}C_A C_{A_2 B_1} - k_{14}C_A C_{A_2 B_2} - \dots \quad (11) \end{aligned}$$

$$\begin{aligned} \frac{dC_B}{dt} = & -k_{11}C_A C_B - k_{1'2}C_B C_{A_1 B_1} \\ & - k_{1'3}C_B C_{A_2 B_1} - k_{1'4}C_B C_{A_2 B_2} - \dots \quad (12) \end{aligned}$$

$$\begin{aligned} \frac{dC_{A_1 B_1}}{dt} = & k_{11}C_A C_B - k_{12}C_A C_{A_1 B_1} - k_{1'2}C_B C_{A_1 B_1} \\ & - k_{22}C_{A_1 B_1}^2 - k_{23}C_{A_1 B_1} C_{A_2 B_1} - \dots \quad (13) \end{aligned}$$

$$\begin{aligned} \frac{dC_{A_2 B_1}}{dt} = & k_{12}C_A C_{A_1 B_1} - k_{1'3}C_{A_2 B_1} C_B \\ & - k_{23}C_{A_2 B_1} C_{A_1 B_1} - k_{3'3}C_{A_2 B_1} C_{A_1 B_2} - \dots \quad (14) \end{aligned}$$

$$\begin{aligned} \frac{dC_{A_1 B_2}}{dt} = & k_{1'2}C_B C_{A_1 B_1} - k_{13}C_{A_1 B_2} C_A \\ & - k_{23}C_{A_1 B_2} C_{A_2 B_1} - k_{3'3}C_{A_2 B_1} C_{A_1 B_2} - \dots \quad (15) \end{aligned}$$

$$\begin{aligned} \frac{dC_{A_2 B_2}}{dt} = & k_{22}C_{A_1 B_1}^2 + k_{13}C_A C_{A_1 B_2} \\ & + k_{1'3}C_B C_{A_2 B_1} - k_{14}C_A C_{A_2 B_2} \\ & - k_{1'4}C_B C_{A_2 B_2} - k_{24}C_{A_1 B_1} C_{A_2 B_2} - \dots \quad (16) \end{aligned}$$

etc., for each oligomer present in the system.

The system contains only monomers, i.e., diisocyanate and polyol, at the beginning. Hence, eqs. (11)–(16) should meet the following initial conditions:

$$C_A(0) = C_A^0$$

$$C_B(0) = C_B^0$$

$$C_{A_i B_j}(0) = 0$$

$$\text{for any } i = 1, 2, \dots \quad j = 1, 2, \dots \quad (17)$$

The following equations can be derived from the dependence (7):

$$C_A = C_B = 0.5C_{F1}$$

$$C_{A_2 B_1} = C_{A_1 B_2} = 0.5C_{F3} \quad (18)$$

It was assumed in this model that rate constants k_{mn} in (6) can change with the increase of molecular size of the reacting oligomers despite no diffusion effects present in the reaction medium. It was also assumed that any rate constant can be expressed as a product of

$$k_{mn} = k_m \cdot k_n \quad (19)$$

The factors of this product were called “partial rate constants.” They are dependent solely on the components of an individual reaction within the kinetic model adopted, and they do not change in the course of the process.

This way for separating rate constants k_{mn} is a mathematical method which makes it possible, as will be shown further, to decompose the system of differential eqs. (11)–(16). “Partial rate constants k_m and k_n ” have been assigned to the components of the fractions F_m and F_n , while rate constants k_{mn} have been assigned to chemical reactions between these components. For the need of simplicity, it was assumed that the components of the odd fractions, i.e., components with slightly different molecular weights only, have the same “partial rate constants.”

These “partial rate constants” were calculated on the basis of the model developed from collision theory and from kinetic studies on model reactions between isocyanates and hydroxyl compounds¹:

$$k_{mn} = \frac{\gamma^2}{(M_X + M_Y)^{0.5}} \quad (20)$$

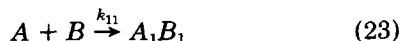
wherein (on the analogy of the collision theory

$$k_{mn} = \frac{\beta'(M_X + M_Y)^{0.5}}{(M_X \cdot M_Y)^{0.5}} \quad (21)$$

the numerical value for γ is assumed to be the same for all reactions:

$$\gamma^2 = \beta'(M_X + M_Y)^{0.5} \approx \text{const.} \quad (22)$$

This is dependent on temperature only and can be calculated from the rate constant k_{11} of the reaction involving monomers:



Rate constant k_{11} is known and it was assumed to correspond to all the reactions (6) in the previous model which adopted constant values for rate constants.³

From eqs. (19) and (21), it directly results that

$$k_{11} = k_1 \cdot k_1 = \frac{\gamma^2}{\sqrt{M_A M_B}} \quad (24)$$

$$\gamma = \sqrt{k_{11} \sqrt{M_A M_B}} \quad (25)$$

where M_A is the molecular weight for monomer A , and M_B , the molecular weight of monomer B .

When the value of γ and molecular weights of the urethane oligomers (6) and (7) are known, any partial rate constant k_m can be calculated from eqs. (19) and (21):

$$k_1 = \sqrt{k_{11}} = \frac{\gamma}{\sqrt[4]{M_A M_B}} \quad (26)$$

$$k_2 = \sqrt{k_{22}} = \frac{\gamma}{\sqrt[4]{M_{A_1B_1} M_{A_1B_1}}} = \frac{\gamma}{\sqrt{M_{A_1B_1}}} \quad (27)$$

$$k_3 = \sqrt{k_{33}} = \frac{\gamma}{\sqrt[4]{M_{A_2B_1} M_{A_1B_2}}} \quad (28)$$

In general,

$$k_m = \sqrt{k_{mm}} = \frac{\gamma}{\sqrt{M_{F_m}}} \quad (29)$$

where M_{F_m} is the molecular weight of the oligomer "m" fraction.

In the case of an odd fraction ($m = 2n - 1$), this is the geometric mean of molecular weights of both its components:

$$M_{F_{2n-1}} = \sqrt{M_{A_n B_{(n-1)}} \cdot M_{A_{(n-1)} B_n}} \quad (30)$$

Introducing a notion of "partial rate constant" [in accordance with eq. (19)] and assuming that the values of these constants for both compounds within the odd fraction are the same makes it possible to more simply set forth the equations of the kinetic

model (11)–(16). In particular, it removes "primed" subscripts for rate constants in reactions (6) and (7):

$$\begin{aligned} \frac{dC_A}{dt} = & -k_1^2 C_A C_B - k_1 k_2 C_A C_{A_1 B_1} \\ & - k_1 k_3 C_A C_{A_1 B_2} - k_1 k_4 C_A C_{A_2 B_2} - \dots \quad (31) \end{aligned}$$

$$\begin{aligned} \frac{dC_B}{dt} = & -k_2^2 C_A C_B - k_1 k_2 C_B C_{A_1 B_1} \\ & - k_1 k_3 C_B C_{A_2 B_1} - k_1 k_4 C_A C_{A_2 B_2} - \dots \quad (32) \end{aligned}$$

$$\begin{aligned} \frac{dC_{A_1 B_1}}{dt} = & k_1^2 C_A C_B - k_1 k_2 C_A C_{A_1 B_1} - k_1 k_2 C_B C_{A_1 B_1} \\ & - k_2^2 C_{A_1 B_1}^2 - k_2 k_3 C_{A_1 B_1} C_{A_2 B_1} - \dots \quad (33) \end{aligned}$$

$$\begin{aligned} \frac{dC_{A_2 B_1}}{dt} = & k_1 k_2 C_A C_{A_1 B_1} - k_1 k_3 C_{A_2 B_1} C_B \\ & - k_2 k_3 C_{A_2 B_1} C_{A_1 B_1} - k_3^2 C_{A_2 B_1} C_{A_1 B_2} - \dots \quad (34) \end{aligned}$$

$$\begin{aligned} \frac{dC_{A_1 B_2}}{dt} = & k_1 k_2 C_B C_{A_1 B_1} - k_1 k_3 C_{A_1 B_2} C_A \\ & - k_2 k_3 C_{A_1 B_2} C_{A_1 B_1} - k_3^2 C_{A_1 B_2} C_{A_2 B_1} - \dots \quad (35) \end{aligned}$$

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etc., for each oligourethane present in the system. Hence, "partial rate constants" and concentrations for all components of the system are present in the above equations.

Taking advantage of dependence (18), further simplifications can be introduced:

$$\begin{aligned} \frac{dC_A}{dt} = & -k_1 C_A (k_1 C_B + k_2 C_{A_1 B_1} \\ & + k_3 C_{A_1 B_2} + k_4 C_{A_2 B_2} + \dots) \quad (36) \end{aligned}$$

$$\begin{aligned} \frac{dC_B}{dt} = & -k_1 C_B (k_1 C_A + k_2 C_{A_1 B_1} \\ & + k_3 C_{A_2 B_1} + k_4 C_{A_2 B_2} + \dots) \quad (37) \end{aligned}$$

After having added the sides of the above equations, and having in mind dependence (18), it was derived that

$$\frac{d(C_A + C_B)}{dt} = -k_1 C_A [k_1(C_A + C_B) + 2k_2 C_{A_1 B_1} + k_3(C_{A_1 B_2} + C_{A_2 B_1}) + 2k_4 C_{A_2 B_2} + \dots] \quad (38)$$

This is equivalent to

$$\frac{dC_{F_1}}{dt} = -\frac{1}{2} k_1 C_{F_1} (k_1 C_{F_1} + 2k_2 C_{F_2} + k_3 C_{F_3} + 2k_4 C_{F_4} + \dots) \quad (39)$$

In analogy, and on the basis of eqs. (18) and (33), one can draw up the equation for the F_2 fraction, and then for the F_3 fraction on the basis of eqs. (18), (34), and (35):

$$\frac{dC_{F_2}}{dt} = (\frac{1}{2} k_1 C_{F_1})^2 - k_2 C_{A_1 B_1} [k_1(C_A + C_B) + k_2 C_{A_1 B_1} + k_3(C_{A_2 B_1} + C_{A_1 B_2}) + k_4 C_{A_2 B_2} + \dots] \quad (40)$$

$$\frac{d(C_{A_2 B_1} + C_{A_1 B_2})}{dt} = \frac{dC_{F_3}}{dt} = k_1 k_2 C_{A_1 B_1} (C_A + C_B) - k_3 C_{A_2 B_1} \cdot [k_1(C_A + C_B) + 2k_2 C_{A_1 B_1} + k_3(C_{A_1 B_2} + C_{A_2 B_1}) + \dots] \quad (41)$$

Some substitutions were adopted to make the expressions easier:

$$W_S = k_1 C_{F_1} + k_2 C_{F_2} + \dots = \sum_{i=1}^{2n} k_i C_{F_i} \quad (42)$$

The summation involves all $2n$ fractions:

$$W_{SP} = k_2 C_{F_2} + k_4 C_{F_4} + \dots = \sum_{i=1}^n k_{2i} C_{F_{2i}} \quad (43)$$

The summation in this case is carried out over even n fractions.

Equations (42) and (43) make it possible to convert the dependencies (39), (40), and (41) to the following forms:

$$\frac{dC_{F_1}}{dT} = -\frac{1}{2} k_1 C_{F_1} (W_S + W_{SP}) \quad (44)$$

$$\frac{dC_{F_2}}{dt} = \left(\frac{1}{2} k_1 C_{F_1}\right)^2 - k_2 C_{F_2} W_S \quad (45)$$

$$\frac{dC_{F_3}}{dt} = k_1 C_{F_1} k_2 C_{F_2} - \frac{1}{2} k_3 C_{F_3} (W_S + W_{SP}) \quad (46)$$

Equations (44)–(46) can be generalized to cover any odd or even fractions. In this case, the expression describing changes in concentrations of odd fractions takes on the following form:

$$\frac{dC_{F(2n-1)}}{dt} = -0.5 k_{(2n-1)} C_{F(2n-1)} (W_S + W_{SP}) + \sum_{l=1}^{l < n - 0.5} k_l C_{F_l} k_{(2n-l-1)} C_{F(2n-l-1)} \quad (47)$$

For even fractions, this dependence reads

$$\frac{dC_{F(2n)}}{dt} = -k_{(2n)} C_{F(2n)} W_S + \sum_{l=1}^{l \leq n} \alpha_l k_l C_{F_l} k_{(2n-l)} C_{F(2n-l)} \quad (48)$$

where

$$\begin{aligned} \alpha_l &= 1 && \text{when } l \text{ is an even number} \\ \alpha_l &= 0.5 && \text{when } l \text{ is an odd number and } n \neq l \\ \alpha_l &= 0.25 && \text{when } l \text{ is an odd number and } n = l \end{aligned} \quad (49)$$

Formulas (47)–(49) are much similar to dependencies (30)–(32) of the previous model.³ This similarity will be even much closer when the substitution below is applied:

$$S_i = k_i C_{F_i} \quad (50)$$

In such a case, and in accordance with (42) and (43), the dependencies provided below are also true:

$$W_S = \sum_{i=1}^{2n} S_i \quad (51)$$

$$W_{SP} = \sum_{i=1}^n S_{2i} \quad (52)$$

The changes in concentrations of odd fractions can then be described by the equation

$$\frac{1}{k_{(2n-1)}} \frac{dS_{(2n-1)}}{dt} = -0.5 S_{(2n-1)} (W_S + W_{SP}) + \sum_{l=1}^{l < n - 0.5} S_l S_{(2n-l-1)} \quad (53)$$

which for even fractions looks like this:

Table I Results from Model Calculations for Polymerization of 2,4-TDI and 1,4-Butanediol at 86°C
($\gamma = 0.4333$; $k_{11} = 1.50 \cdot 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)

Time (Min)	\bar{M}_n	\bar{P}	Concentrations of Oligomer Fractions (mol dm ⁻³)										
			F1	F2	F3	F4	F5	F6	F7	F8	F9	F10-Fn	
0	132.14	—	2.0	0	0	0	0	0	0	0	0	0	0
1	138.20	1.045	1.829	0.0785	0.0044	0.001	—	—	—	—	—	—	—
3	150.81	1.129	1.544	0.1780	0.0300	0.0028	0.0003	$2 \cdot 10^{-5}$	—	—	—	—	—
5	163.82	1.200	1.319	0.2297	0.0624	0.0089	0.0016	0.0002	$3 \cdot 10^{-5}$	—	—	—	—
10	196.69	1.317	0.9320	0.2639	0.1305	0.0307	0.0098	0.0016	0.0006	0.0001	$3.1 \cdot 10^{-6}$	—	—
20	258.72	1.403	0.5403	0.2241	0.1900	0.0650	0.0341	0.0085	0.0048	0.0014	0.0006	$2.6 \cdot 10^{-4}$	—
40	363.38	1.424	0.2526	0.1374	0.1898	0.0833	0.0661	0.0221	0.0181	0.0073	0.0046	0.0035	—
60	449.13	1.416	0.1473	0.0895	0.1631	0.0780	0.0768	0.0289	0.0284	0.0129	0.0099	0.0102	—
90	555.92	1.405	0.0805	0.0529	0.1278	0.0640	0.0771	0.0315	0.0367	0.0182	0.0163	0.0230	—
120	645.98	1.397	0.0504	0.0344	0.1026	0.0515	0.0719	0.0305	0.0397	0.0205	0.0204	0.0357	—
180	759.96	1.390	0.0246	0.0173	0.0711	0.0350	0.0598	0.0259	0.0394	0.0211	0.0240	0.0566	—
240	921.16	1.387	0.0141	0.0100	0.0529	0.0250	0.0498	0.0215	0.0365	0.0197	0.0247	0.0715	—
300	1030.71	1.387	0.0090	0.0063	0.0412	0.0186	0.0421	0.0179	0.0332	0.0178	0.0341	0.0818	—
360	1129.29	1.387	0.0061	0.0042	0.0332	0.0143	0.362	0.0151	0.0301	0.0160	0.0230	0.0890	—

$$\frac{1}{k_{(2n)}} \frac{dS_{(2n)}}{dt} = -S_{(2n)} W_S + \sum_{l=1}^{l=2n} \alpha_l S_l S_{(2n-l)} \quad (54)$$

where α_l is defined by (49).

Formulas (53) and (54) are very similar to dependencies (30) and (31) in the model which assumes that reaction rate constants do not change.³ The difference between them is that the rate constants used are "partial rate constants" which are different for successive reactions, i.e., $k_1 \neq k_2 \neq \dots \neq k_{2n}$. These constants are defined by eq. (19).

The initial conditions attributed to the system of $2n$ differential equations in the form of (52) and (54) have the form of

$$\begin{aligned} S_1(0) &= k_1[C_A(0) + C_B(0)] = \sqrt{k_{11}}[C_A(0) + C_B(0)] \\ S_2(0) &= 0 \\ &\cdot \\ &\cdot \\ S_{2n}(0) &= 0 \end{aligned} \quad (55)$$

where k_{11} is a simulated value of the rate constant for the first reaction.

EXPERIMENTAL

The model developed was verified experimentally on the basis of the results from the polyaddition

process of 2,4-TDI and 1,4-butanediol. The polymerization reaction was carried out in a mixture of chlorobenzene and tetrahydrofuran, at weight ratios 3 : 1 and 1 : 1, which allowed the process temperature to be maintained constant at 86 and 101°C, respectively.

Chemical compositions for polyurethanes obtained at successive polymerization stages and their numerically mean molecular weights were determined with GPC. The components present in schemes (6) and (7) were identified with the use of a calibration curve prepared earlier on the basis of carbamates synthesized from 2,4-TDI and alcohols with various chain lengths. Details on the GPC analysis adopted herein were provided in Ref. 7. A procedure for numerical calculations simulating chemical compositions and molecular weight distributions for linear polyurethanes followed the principle presented in Ref. 3. Gravimetric and numerical polyurethane mean molecular weights were found from dependencies analogous to eqs. (34) and (35).³

RESULTS AND DISCUSSION

Table I provides results from numerical calculations of mean molecular weight M_n , degree of polydispersion $P = M_w/M_n$, and chemical composition for linear polyurethanes obtained at 86°C ($k_{11} = 1.50 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\gamma = 0.4333$). It was assumed in the calculations that initial concentrations of isocyanate and hydroxyl monomers were 1 mol dm⁻³. The concentrations calculated for fractions F1–F9

are tabulated separately while those for F_{10} – F_n have been totaled.

Comparison of experimental and model data for the 2,4-TDI and 1,4-butanediol polymerization process carried out in 86 and 101°C is provided in Tables II and III. With the use of a numerical estimation method, the values of rate constant k_{11} were found for which calculated results approach experimental ones for the process temperatures of 86 and 101°C.

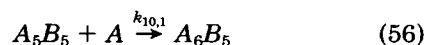
It was found that the decrease in monomer concentrations was too high in every case compared to the changes in concentrations of other fractions. This can result from a systematic error of the GPC analysis. To minimize this influence, changes were observed for fractions put together: $F_1 + F_2$, $F_3 + F_4$, and $F_5 + F_6$, and the verification of the model obtained was based just on them.

Figure 1 shows profiles for model functions illustrating the changes in concentrations of F_1 , F_2 , F_3 , and F_4 fractions, for the process wherein $k_{11} = 1.50 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $\gamma = 0.4333$. Figure 2 presents model curves for integral molecular weight distributions of polyurethanes, after 20, 100, and 300 min, from the reaction carried out at 86°C. Figure 3 compares the diagrams for changes of numerical mean molecular weight determined experimentally by means of GPC and calculated from the model developed.

The results provided in Tables I–III and the diagrams in Figures 1–3 are presented following the same convention as in Ref. 3. Hence, it is possible both to compare compliance of an earlier developed constant rate model to the presented model assum-

ing the dependence of reactivity of urethane oligomers on their molecular weights and to compare dynamics of the linear polyurethane processes described by these models.

Figure 4 shows the plots which illustrate changing values of rate constants k_{mn} at various stages of the polyaddition process. These rate constants were calculated from (20) and then (19) was utilized to calculate k_{mn} values for the reactions between the components of various fractions. The chart obtained visualizes that, e.g., the rate constant $k_{10,1}$ in the reaction



decreases to $5.5 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the value of $k_{11} = 18 \times 10^{-4}$ merely because of the increased molecular weight of the isocyanate component.

When corresponding concentrations of the polyurethane fractions provided in Tables I and II and in Figures 1 and 2 of this study are compared to data from Ref. 3, it can be seen that the model claiming dependence of the component reactivity on the molecular weight yields a process with, in general, lower dynamics. This can be observed clearly in Figure 2, which shows the chemical composition of the polymer at successive process stages. Also, the profiles in Figure 3 reveal that the rate constants estimated from the model developed herein are much closer to the experimental values than are those obtainable from the earlier model.³ However, the obtained rate constant values k_{11} are below those calculated from the Arrhenius eq. (16) provided in Ref. 1. Despite having searched through a relatively wide range of

Table II Comparison of Experimental and Calculated Values for 2,4-TDI and 1,4-Butanediol Polyaddition at 86°C

Time (Min)	Experimental Data: $k = 5.00 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				Data Calculated from Model: $k_{11} = 8.00 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			
	\bar{M}_n	Concentration of Polymer Fraction (wt %)			\bar{M}_n	Concentration of Polymer Fraction (wt %)		
		$F_1 + F_2$	$F_3 + F_4$	$F_5 + F_6$		$F_1 + F_2$	$F_3 + F_4$	$F_5 + F_6$
20	309	73.0	25.2	1.6	201	69.9	26.7	3.3
40	332	57.4	35.2	7.4	266	45.0	40.4	11.5
60	356	46.0	38.4	15.5	324	31.1	42.8	18.2
90	412	32.0	35.4	22.5	399	19.8	41.9	23.6
120	456	25.1	31.4	26.7	464	13.6	35.4	25.7
180	537	16.4	23.4	26.9				
240	667	8.7	15.7	21.8				
300	801	6.7	11.2	16.6				

variability for k_{11} , no value was found which could offer an acceptably low estimation error. This was concluded to be just a feature of the model considered, which is believed to much better describe the 2,4-TDI and 1,4-butanediol polyaddition than did the previous model which assumed constant reactivities of oligourethanes.

Resulting from the above, an auxiliary empirical model was developed which was based on the model provided herein. In this modified model, "partial rate constants" were calculated from the following equation:

$$k_m = \frac{\sqrt{k_{11} \sqrt{M_A M_B}}}{\sqrt{M_{Fm}}} \quad (57)$$

where M_A , M_B are the molecular weights for monomers A and B ; M_{Fm} , the molecular weight for polyurethane Fm fraction; and k_{11} , the rate constant for the first reaction in scheme (6).

The "partial rate constants k_1 and k_2 " are presented here in the form corrected in accordance with the equations

$$k_1 = a_1 \cdot k_{1m} \quad (58)$$

$$k_2 = a_2 \cdot k_{1m} \quad (59)$$

where k_{1m} are the "partial rate constants" for the reactions involving components of fraction 1 (monomers) calculated from (57) on the basis of assumed and verified experimentally rate constant k_{11} , and a_1 , a_2 , the correction factors minimizing deviations of model values from experimental ones. This

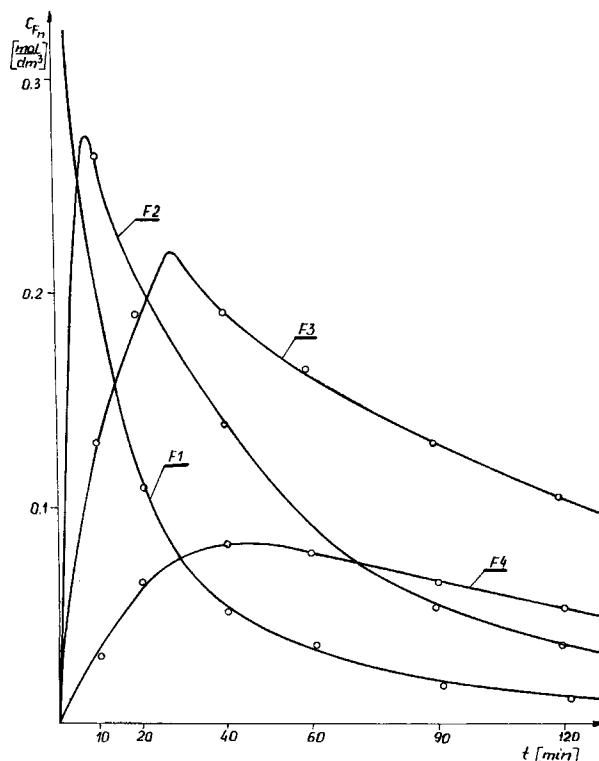


Figure 1 Model concentration profiles for fractions $F1$, $F2$, $F3$, and $F4$, for the reaction of $k_{11} = 1.50 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $\gamma = 0.433$.

model, compared to the basic one, not only calculates "partial constants k_1 and k_2 " in a different manner but also introduces—on the basis of the eq. (19)—considerable changes in values of numerous rate constants marked in Figure 4 with k_{1n} and k_{2n} . The k_{11} constant is no longer the calculated rate constant

Table III Comparison of Experimental and Calculated Values for 2,4-TDI and 1,4-Butanediol Polyaddition at 101°C

Time (Min)	Experimental Data: $k = 23.2 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				Data Calculated from Model: $k_{11} = 18.00 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			
	\bar{M}_n	Concentration of Polymer Fraction (wt %)			\bar{M}_n	Concentration of Polymer Fraction (wt %)		
		$F1 + F2$	$F3 + F4$	$F5 + F6$		$F1 + F2$	$F3 + F4$	$F5 + F6$
10	309	62.0	36.2	1.7	210	65.5	29.6	4.2
20	341	44.2	45.3	7.4	282	40.7	41.8	13.5
30	382	33.9	47.6	11.7	344	27.5	42.5	20.0
45	448	23.3	42.4	15.7	425	17.0	38.2	24.7
60	515	16.6	35.7	16.7	495	11.6	33.2	26.0
75	546	12.4	28.7	19.4	556	8.4	29.8	25.9
90	625	9.3	23.1	18.4	612	6.3	25.1	25.0
105	—	10.4	24.2	16.6	663	5.0	20.1	23.9

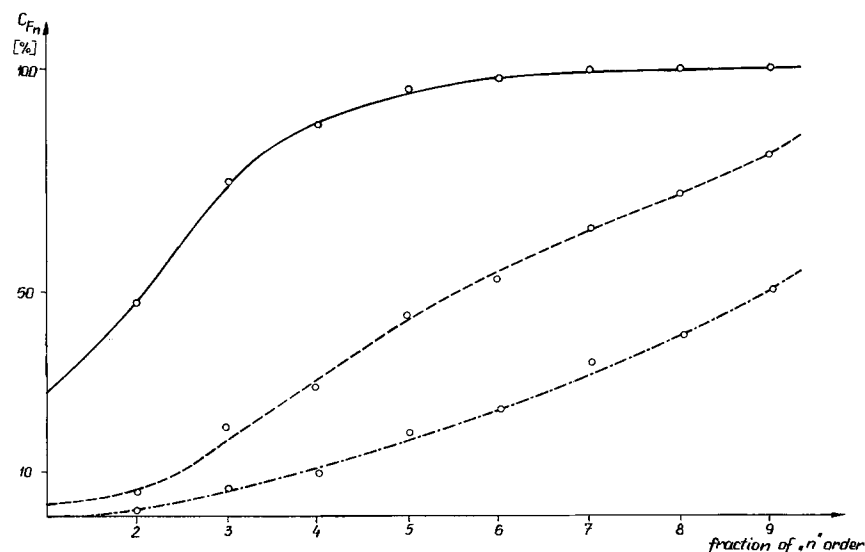


Figure 2 Integral models, curves for molecular weight distribution of polyurethane in the reaction of $k_{11} = 1.50 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $\gamma = 0.433$: (—) $t = 20$ min; (----) $t = 100$ min; (- · -) $t = 300$ min.

for the reaction between monomers, but for $a_1 > 1$, the reaction is characterized by a much higher constant $k_{11}^* = (a_1 k_{1m})^2$. By analogy, when $a_2 < 1$, the rate constant for the reaction $A_1 B_1 + A_1 B_1 \rightarrow A_2 B_2$ which equals $k_{22}^* = (a_2 k_{1m})^2$ is relatively lower.

The results from calculations of numerically mean molecular weight, molecular weight distribution, and chemical composition of the polyurethane product carried out following this model for reactions at 86 and 101°C are shown in Table IV. The values of the a_1 and a_2 factors are specified there for which the error of the model is minimized. The values obtained can be easily compared to the experimental values provided in Tables I and II. The plots of numerically mean molecular weights obtained from the new model are compared in Figures 5 and 6 to experimental values obtained from GPC analysis of polyurethanes synthesized at 86 and 101°C. The results suggest that this new model offers the best description of the process studied; hence, at this stage, it can be considered a "quasi-optimum" model for the process producing linear polyurethanes.

The model developed assumes that the chemical reactivity of —NCO groups in 2,4-TDI is the same, while it is widely known that the reactivity of this group at position 4 is on average 1.15–1.63 times higher than is the reactivity of this group at position 2, depending on temperature.⁸ This fact is negligible in a general model covering reactions of various diisocyanates. One has to remember, however, that including the above would make the model fit better

to the experimental data. On the other hand, additional parallel reactions in the kinetic schemes (6) and (7) would have to be considered. The analogical approximation was adopted for the statistical modeling of the diisocyanate and diol polyaddition processes.⁹

A key issue requiring explanation is the fact that the use of a kinetic model assuming that the oligomer reactivity is dependent on molecular weight is inconsistent with the generally accepted Flory's postulate wherein—for stepwise polymerization processes—it is only the chemical environment around the functional groups that contributes to the polymer activity and not the polymer molecule size. The presented study confronts the calculated results with the experimental data to shake this latter theory.

Hence, it should be decided what additional assumptions can be introduced to the initial model to give better conformity of model-derived and experimental data. These assumptions should bind reactivity specifications of isocyanate oligomers to the chemical neighborhood of their functional groups.

The assumption of independent reactivity specifications for —NCO groups in diisocyanates, apart from aliphatic diisocyanate 1,6-hexamethylene diisocyanate (HDI), seems true for such aromatic compounds like methylenediphenylene diisocyanate (MDI) and 1,5-naphthyl diisocyanate (NDI) where coupling over aromatic rings is small.¹⁰ The model developed for progressive polyaddition of diisocyanate and diol appears suitable in such cases. It is ob-

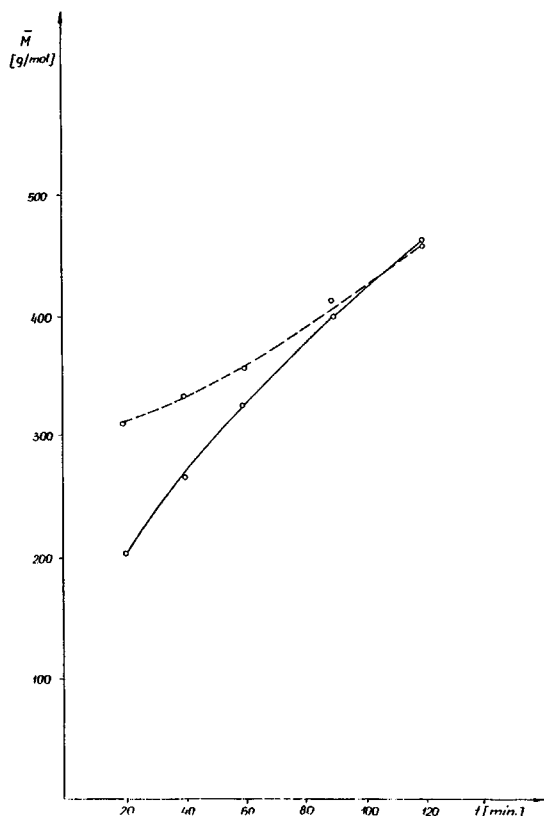


Figure 3 Graphical presentation of dependence: polyurethane mean molecular weight vs. reaction time, at 86°C: (—) profile calculated from model ($k_{11} = 1.50 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $\gamma = 0.433$); (-----) experimental profile.

vious that any experimental verification should pass a critical judgment now when the accuracy of calculation methods far exceeds that for instrumental analysis, all the more so as the model dependencies of rate constants on molecular weights presented in Figures 1–4 of Ref. 1 underwent indirect verification only by way of comparing the model presented in this study with experiments.

However, it seems advisable to develop an additional model. This should consider not only different reactivities of —NCO groups in 2,4-TDI but also kinetic effects of substitution(s), i.e., the impact of one group present at the ring on the chemical reactivity of other group. The chemical reactivity of the —NCO group is to a considerable extent influenced by other substituents present. An electron-acceptor substituent, e.g., the —NO₂ group, adds its mesomeric effect to the system and acts across the ring to increase the positive charge at the carbon atom of the —NCO group. Hence, any attack from some nucleophilic group is easier at this carbon atom. As a result, the rate for the

reaction between phenylene 1,4-nitroisocyanate and alcohol can be as much as 35 times higher than the rate for just isocyanate. Found from investigating the activity of phenyl isocyanate in its reaction with alcohols was that the electron-acceptor —NCO group in 2,4-TDI or 2,6-TDI significantly boosts the reactivity of the isocyanate group, which is the first to react with the —OH group. The urethane group exerts a smaller effect on the reactivity of the —NCO group which reacts in the background. The presence of —CH₃ weakens the said effects.^{11,12}

Having in mind the above, I developed an additional model conforming to the Flory's postulate,

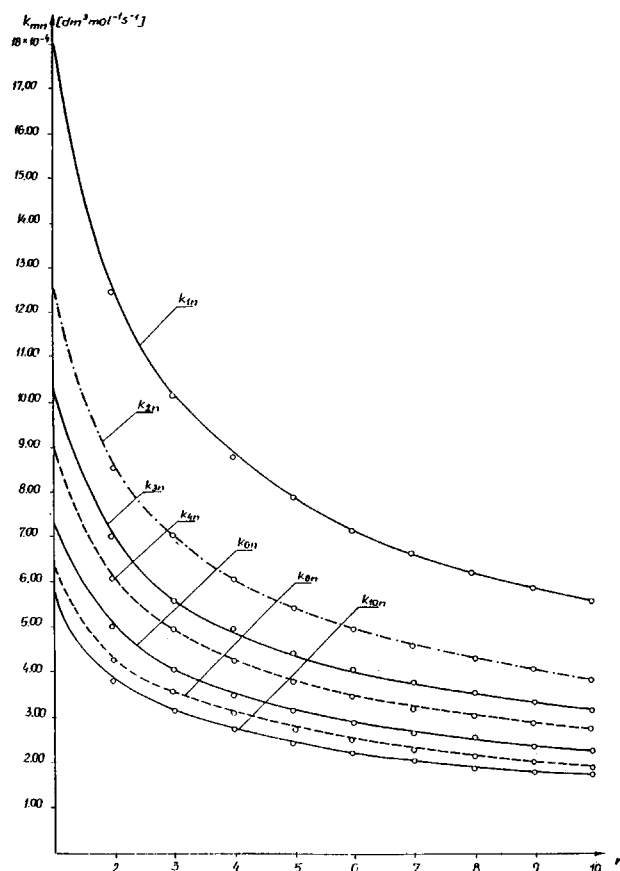


Figure 4 Plots for model dependencies of rate constants for fractions m and n , obtained for the linear polyurethane process at 100°C [$k_{m,n}$ values for reactions (6) and (7) were calculated from model (20) after having assumed the following kinetic parameters: $\beta' = 29.23 \cdot 10^{-3}$; $\gamma = 0.475$; $k_{11} = 29.23 \cdot 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$]. k_{1n} is the rate constant for the reaction of monomers with oligomers; k_{2n} , the rate constant for the reaction of A_1B_1 dimer with oligomers; and k_{3n} , the rate constant for the reaction of A_1B_2 and A_2B_1 trimers with oligomers, etc.

Table IV Characteristics of 2,4-TDI and 1,4-Butanediol Polyaddition Obtained from "Quasi-optimum" Model

$T = 86^{\circ}\text{C}; a_1 = 2.0; a_2 = 0.5;$ $k = 8.00 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$					$T = 101^{\circ}\text{C}; a_1 = 2.0; a_2 = 0.5;$ $k = 18.00 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				
Time (Min)	\bar{M}_n	Concentration of Polymer Fraction (wt %)			Time (min)	\bar{M}_n	Concentration of Polymer Fraction (wt %)		
		F1 + F2	F3 + F4	F5 + F6			F1 + F2	F3 + F4	F5 + F6
20	261	64.7	30.2	4.5	10	287	56.2	36.1	6.8
40	320	47.8	37.9	11.2	20	352	39.5	40.9	14.3
60	363	38.0	38.3	16.0	30	399	31.0	39.3	18.9
90	413	30.1	35.7	20.0	45	456	23.6	34.8	22.1
120	456	24.8	32.0	21.9	60	506	18.9	30.3	23.1
180	533	18.3	25.5	22.4	75	552	15.6	26.4	23.0
240	603	14.2	20.5	21.4	90	596	13.2	23.1	22.2
300	669	11.5	16.8	19.3	105	638	11.4	20.4	21.2

which gave suitable consideration to kinetic effects resulting from substitution and to different reactivities of —NCO groups in 2,4-TDI. In addition to the rate constant for the most active —NCO group, this model contains also a "k" constant

which is responsible for the difference in reactivities of —NCO groups in diisocyanate and in isocyanate-urethane. It was found from the calculations performed that the value of "k" is close to the value of the a_1 constant in the "quasi-opti-

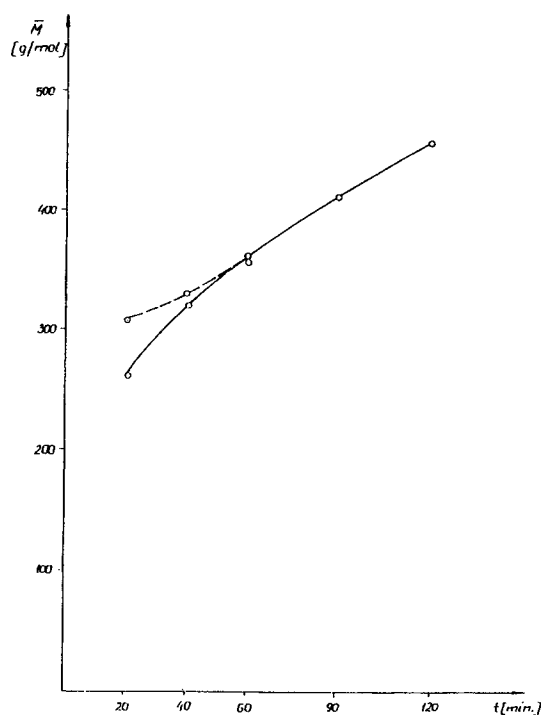


Figure 5 Graphical presentation of dependence: polyurethane mean molecular weight vs. reaction time, at 86°C : (—) profile calculated from "quasi-optimum" model ($k_{11} = 1.50 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $a_1 = 2.0$, $a_2 = 0.5$); (----) experimental profile.

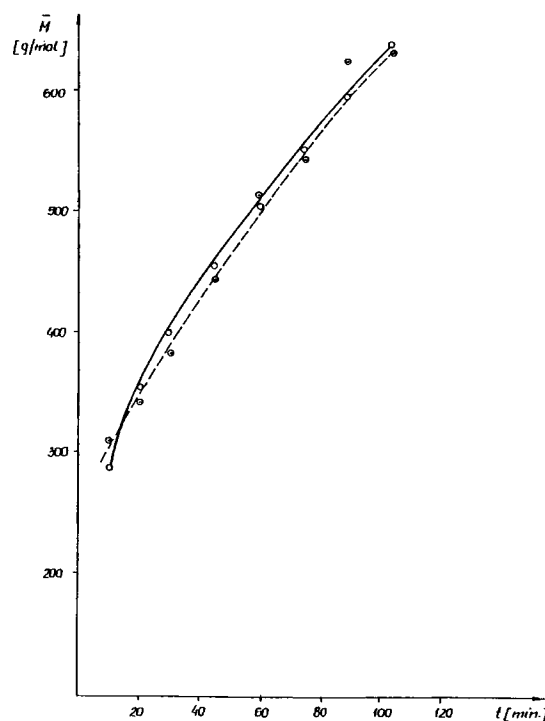


Figure 6 Graphical presentation of dependence: polyurethane mean molecular weight vs. reaction time, at 101°C : (—) profile calculated from "quasi-optimum" model ($k_{11} = 18 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $a_1 = 2.2$, $a_2 = 0.5$); (----) experimental profile.

mum" model. Also, the predictions obtained from this model are closer to experimental data than are predictions from the first model.³ These predictions, however, are not as good as those resulting from the model described in this article. Hence, it seems reasonable to accept the assumption that the molecule size—represented in a way by molecular weight—has some effect on the reactivity of urethane oligomers.

It can be commented on like this: Under the solely kinetic reaction conditions, the growing polyurethane molecule size can reduce self-reactivity due to an increased number of hydrogen bonds. Also, several types of hydrogen bridges can be present within polyurethanes, depending on the monomers employed. The donors of hydrogen bonds created are —NH— groups from urethane fragments, while there are many more acceptors of these bonds. These can be carbonyl groups within urethane fragments or oxygen atoms within polyether and/or polyester fragments.¹³ As the size of the polyurethane molecule increases, the network of hydrogen bonds becomes more and more complicated. This situation can reduce the degrees of freedom of the polymer molecule—hence, reducing its reactivity.

CONCLUSIONS

The mathematical model presented for the gradual polyaddition of diisocyanate and diol, which assumes the dependence of oligomer reactivity on the oligomer molecular weight, provides a much better description for the process studied than does a kinetic model based on equal reactivity of all urethane oligomers. This model can be employed to study the dynamics of the polymerization processes and to compare chemical compositions and molecular weight distributions of linear polyurethanes at early stages of the process, for reactions based on diisocyanates and diols, wherein the effects resulting from interactions between functional groups can be neglected. In the case of 2,4- and/or 2,6-TDI-based isocyanates, where such interactions have to be taken into consideration, a better correlation between experimental data and calculations could be achieved from a "quasi-optimum" model. Besides the influence of molecular weight, this model makes use of empirical coefficients to account for additional kinetic effects connected with interactions of functional groups within such diisocyanates.

Considering previous assumptions on reactivities of reaction intermediate products, which make a basis for developing stepwise polymerization process models, it appears essential to compare the model presented in this study with a model following the Flory's postulate. This model describes the process studied solely by the substitution effects.

NOTATION

A	hydroxyl substrate
B	isocyanate substrate
$A_n B_m$	urethane oligomers
$n, m, i, j, 1$	natural numbers
k_{mn}	reaction rate constants
k_n, k_m	"partial reaction rate constants" (19)
t	time
C_A	concentration of hydroxyl substrate
C_B	concentration of isocyanate
C_A^0	initial concentration of hydroxyl substrate
C_B^0	initial concentration of isocyanate
F_n	polymer fraction of "n" order
C_{F_n}	concentration of polymer fraction
$C_{F_n}^0$	initial concentration of polymer fraction
β'	empirical constant in eq. (20)
γ	constant calculated from eq. (25)
M_A, M_B	molecular weights of monomers
$M_{A_n B_m}$	molecular weight of $A_n B_m$ urethane oligomers
M_{F_n}	molecular weight of polyurethane fraction
M_n, M_w	mean molecular weight (numerical and by weight) of linear polyurethane
P	polydispersion degree of linear polyurethane molecular weight
W_S	total defined by eq. (42), referred to all polyurethane fractions
W_{SP}	total defined by eq. (43), referred to even polyurethane fractions
α_1	number present in eq. (48), found from (47)
S_j	value defined by (50), needed to calculate W_S and W_{SP} from (51) and (52)
a_1, a_2	empirical coefficients in "quasi-optimum" model (58) and (59)

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