

Kinetic Model for the Process Giving Linear Polyurethanes, with Consideration of Substitution Effects and Different Chemical Reactivities of Functional Groups in Toluene 2,4-diisocyanate

PIOTR KRÓL

Faculty of Chemistry, Department of Polymer Science, Rzeszów University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

Received 7 July 1997; accepted 24 November 1997

ABSTRACT: Based on an expanded kinetic scheme for 32 subsequent and parallel reactions that yield linear polyurethane, a mathematical model was developed for a gradual polyaddition process involving toluene 2,4-diisocyanate and 1,4-butanediol. Unlike the earlier models, this one followed Flory's assumption and made the reactivities of the oligomers dependent solely on the chemical environment of their functional groups. Also, —NCO groups in this compound were considered to offer different chemical values. The model developed was presented in the form of a complex system of ordinary differential equations that describe changes in concentrations of both monomers, dimers, and oligomers making up the successive fractions of linear polyurethane. Two essential kinetic constants for this model were calculated: the rate constant for the most reactive —NCO group within toluene 2,4-diisocyanate and the constant responsible for the substitution effect. At further stages, the model developed was subjected to experimental verification. Calculated number-average molecular weights of polyurethane were compared to gel permeation chromatography-determined values for sequenced steps of the polyaddition process conducted in chlorobenzene and tetrahydrofuran solvents, at temperatures of 86° and 101°C, and under conditions where diffusion effects could be neglected. The newly developed model was found to provide better fit for the process description as compared with the model that assumed the same rate constant at individual stages of the polyaddition process. However, the simulation results as compared with the so-called "quasi-optimum" model, which assumed reactivities of oligomers to be dependent on their molecular weights, were in general inferior. The impact was discussed from the structures of reacting substances on their reactivities with the influences from other factors considered, too (e.g., the possibility of creating a system of hydrogen bonds can contribute to reactivity specifications of urethane oligomers with different molecular weights). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 169–181, 1998

Key words: polyurethane; kinetic model; simulation; verification; gel permeation chromatography

INTRODUCTION

In earlier studies,^{1–3} kinetic models were provided that made it possible to describe, at a con-

siderable level of generalization, a process for the synthesis of linear polyurethanes. These models were based on a kinetic scheme of successive-parallel reactions that formed a synthesis system for urethane oligomers. Said models covered the polyaddition process proceeding under isothermal conditions, in a batch reactor that provided ideal mixing of the reactants. The progress of the reac-

Correspondence to: P. Król.

Journal of Applied Polymer Science, Vol. 69, 169–181 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/010169-13

tions was studied in a solution, hence the diffusion effects could be neglected.

The first of those models assumed unchanged rate constants at successive stages/reactions of the oligourethane-yielding process, which started from a defined pair of monomers—diisocyanate and diol. This model was subjected to verification: calculated instantaneous concentrations of urethane oligomer fractions formed in the reaction of toluene 2,4-diisocyanate (2,4-TDI) and 1,4-butanediol (1,4-BD) were compared with experimental concentrations determined with the gel permeation chromatography (GPC) method. Also, calculated and experimental values of average molecular weights were compared for linear oligourethanes. The model based on this assumption was found not to follow the experimental data.²

Much better conformance was found for new models that make further steps of approximation. Reaction rate constants for sequenced process stages of the gradual polyaddition were in these cases made dependent on molecular weights of the reacting oligomers, as per an equation derived from the collision theory.¹ Resulting from this assumption, urethane oligomers with increasingly higher molecular weights had lower and lower reactivities. These models can be considered to be quasitheoretical ones, as respective kinetic constants have to be determined experimentally.³ Their most important feature is that they do not adopt the assumption of no dependence between the oligomer reactivities and the molecular size. This assumption was not criticized before, and it is known as the Flory's paradigm. It binds the reactivity of compounds in gradual polymerization solely with functionalities in the reactants.⁴ In other words, the reactivity of an oligomer does not depend on its chain length, but only on the arrangement of the functional groups along this chain. In the case of linear polyurethanes, the groups are basically isocyanate groups and—to a lesser extent and varying with molecular structures—hydroxyl groups. In this way, an approximate kinetic analysis was conducted for the polyaddition process at the time of modeling the allophanate crosslinking process.⁵ However, the suggested model assumed no change in the reactivity of the second isocyanate group within 2,4-TDI after the first group turns into a carbamate group. Such an assumption is generally accepted for aliphatic diisocyanates (e.g., 1,6-hexamethylenediisocyanate), because no coupling effects between two isocya-

nate groups or between an isocyanate and carbamate groups are transferred across methylene groups. The effect(s) of different functional groups at the same aromatic ring on the reactivity of an isocyanate group is, however, considerable.^{6–8} It results from the comparison of the rate constants for reactions 5 and 6 (Fig. 1) that one can expect a few times lower reactivity of the second —NCO group within toluene 2,6-diisocyanate (2,6-TDI) or 2,4-TDI after the first group is converted. The —NCO group is a stronger electron acceptor than the —NHCOOH group. Thus, the isocyanate-carbamate forming reaction is faster than the reaction giving a corresponding dicarbamate compound.

When developing a kinetic model, one must also consider (apart from the substitution effect) that isocyanate groups within 2,4-TDI are not chemically equivalent. It is well known that the —NCO group at the 4-position offers—depending on temperature—approximately 1.15–1.63 times higher reactivity.⁹

It is characteristic that, in aromatic diisocyanates, wherein isocyanate groups are located at two aromatic rings connected with a methylene group (4,4'-diphenylmethanediisocyanate), and even in the case of condensed rings (naphthylene-1,5-diisocyanate), the substitution effect is not considerable, and under specific modeling conditions it can be neglected.¹⁰

The purpose of this study is to verify how far the kinetic model for the process of gradual polyaddition of 2,4-TDI and 1,4-BD, wherein the specific substitution effect and different reactivities of isocyanate groups were assumed, is consistent with experimental data and the findings obtained earlier from the model simulation that assumed the influence from the size of oligourethane molecules on their reactivities.³ To achieve this, it was found necessary to develop a new kinetic model for the process under investigation; the model had to follow Flory's postulate and had to have such a mathematical form that its experimental verification should be possible on the basis of GPC measurements.²

Generalized Kinetic Scheme for the 2,4-TDI and 1,4-BD Polyaddition Process

As in refs. 2 and 3, the kinetic scheme for this process was based on subsequent and parallel reactions that start from a pair of monomers: 2,4-TDI (denoted as **EF**, wherein **E** stands for the 4-positioned —NCO group and **F** stands for the 2-

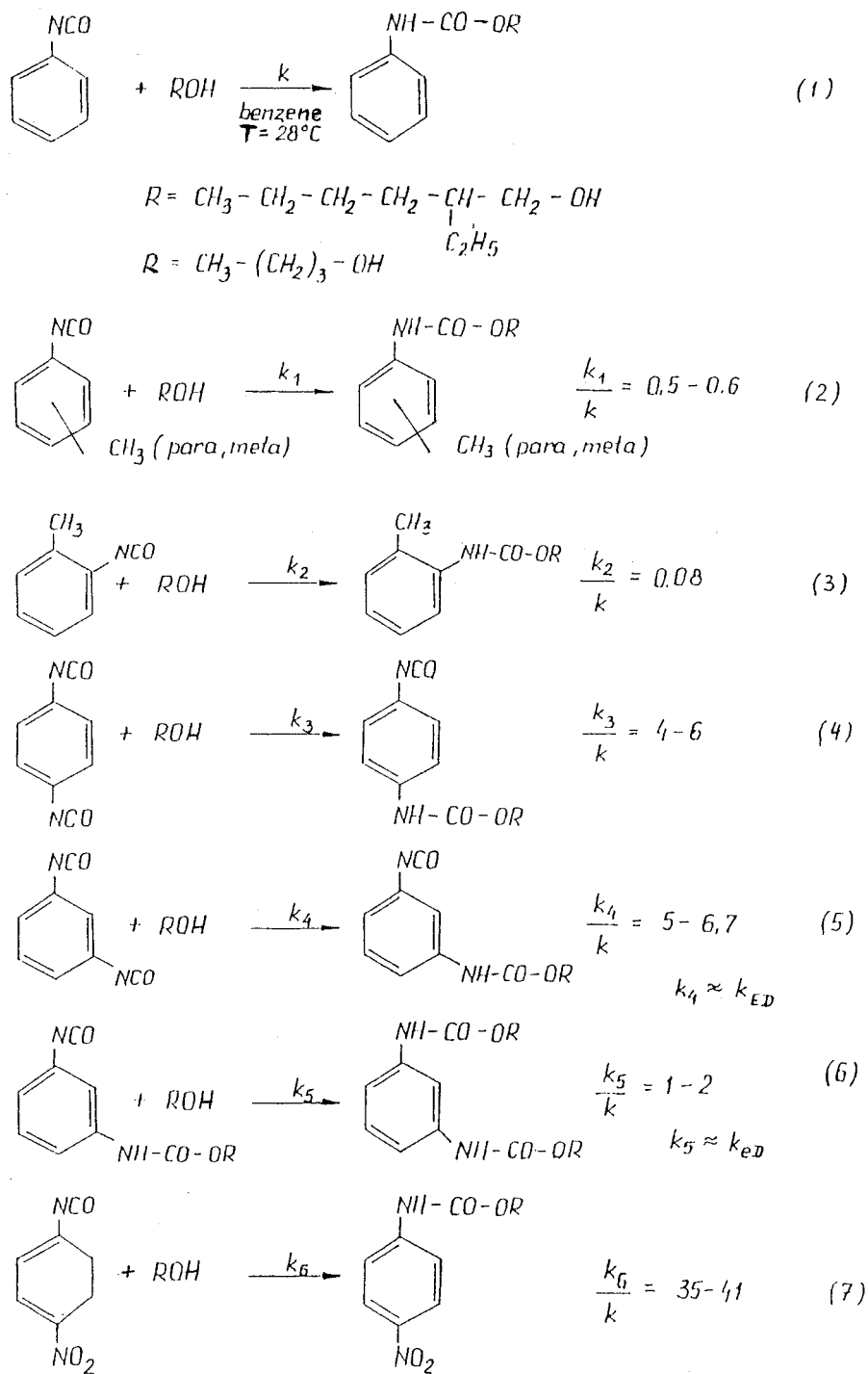


Figure 1 Comparison of effects from various substituent groups on reactivities of phenyl isocyanate derivatives in the reactions with alcohols.⁶⁻⁸

positioned $-\text{NCO}$ group at the benzene ring), and 1,4-BD with chemically equivalent $-\text{OH}$ groups (denoted as **DD**) (Fig. 2).

The following denotation system was adopted. The reaction between an **E** group of 2,4-TDI and

one of $-\text{OH}$ groups of 1,4-BD (**D** group) gives a dimer that is denoted as **fd**. This symbol defines that there is one $-\text{NCO}$ group in the dimer, at position 2 (i.e., group of type **f**), and one $-\text{OH}$ group of type **d**. No capital letters have been

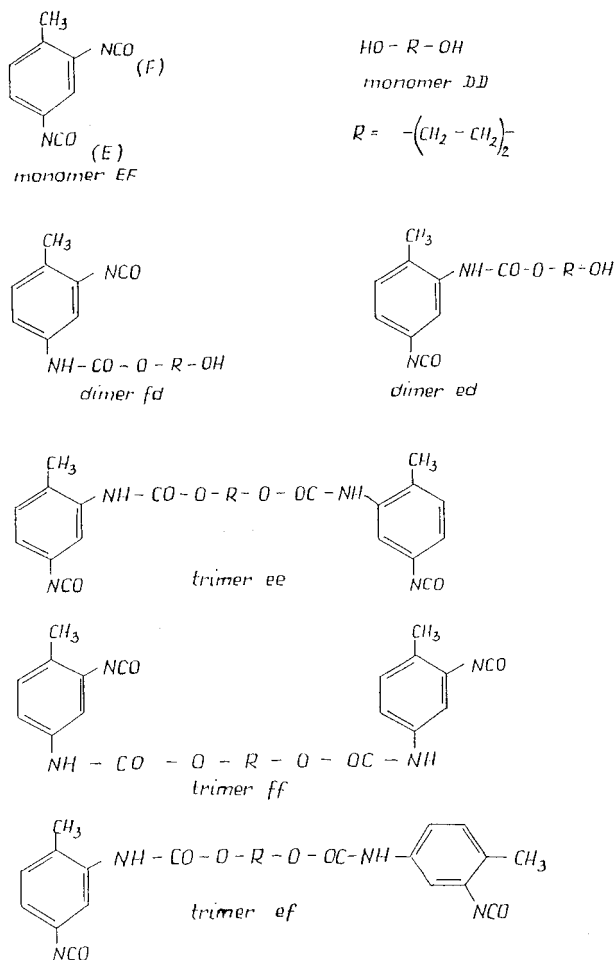


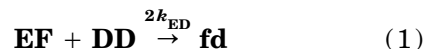
Figure 2 Chemical structure of urethane oligomers.

used herein to stress that the reactivity of the group **e** or **f** in the oligomer is not the same as the reactivity of the group **E** or **F** in the monomer, what results just from the substitution effect.

Similarly—in a generalized case—the reactivity of group **d** in the polymer can be different from that of group **D** in the monomer. Hence, two compounds (**ed** and **fd**) can result from the reaction of 2,4-TDI and 1,4-BD, with different chemical structure and the same molecular weight of 264, which cannot be distinguished by means of GPC.

Higher oligomers with the structures presented in Figure 2 will be denoted in the same way. For example, the reaction of dimer **fd** with monomer **EF** can yield trimers **ff** or **ef**, and the reaction of dimer **ed** with monomer **EF** will give trimers **ef** or **ee**. So, the kinetic scheme for the whole process can be presented as a system of 32 chemical reactions. Their rate constants were

provided in Table I. For example, the rate constant for the reaction yielding dimer **fd** will have the subscript of the groups involved in the reaction:



(2 at the rate constant results from the symmetry of monomer **DD**).

The scheme presented in Table I follows Flory's rule and assumes equal reactivities for functional groups in a given type of molecules. Thus, 8 rate constants are present in the kinetic scheme developed, with the following denotations:

$$k_{ED}, k_{Ed}, k_{eD}, k_{ed}, k_{FD}, k_{Fd}, k_{fD}, k_{fd} \quad (2)$$

For the need of simplicity, it was further assumed that the relative reactivities of isocyanate groups in 2,4-TDI are not dependent on temperature; their ratio is 1.5, and substitution at one —NCO group changes equally the reactivity of the other group, independently on the molecule size. This leads to the following assumption:

$$\frac{k_{ED}}{k_{FD}} = \frac{k_{Ed}}{k_{Fd}} = \frac{k_{eD}}{k_{fD}} = \frac{k_{ed}}{k_{fd}} = \text{const.} = 1.5 \quad (3)$$

The key factor for this model (i.e., the substitution effect) can, in this case, be defined by constants k_1 and k_2 , which characterize relative reactivities of functional groups in monomers and oligomers. Both isocyanate groups were assumed to change their reactivities equally, resulting from changes in their chemical environments. Consequently, the following equations were obtained:

$$\frac{k_{ED}}{k_{eD}} = \frac{k_{FD}}{k_{fD}} = k_1 \quad (4)$$

$$\frac{k_{ED}}{k_{Ed}} = \frac{k_{FD}}{k_{Fd}} = k_2 \quad (5)$$

It follows from the data presented in Figure 1 (reactions 5 and 6) that $k_1 = 2.5-4.5$. The substitution effect in the case of 1,4-BD can be neglected ($k_2 = 1$).

Additional assumption on additivity of activation energies for the reactions involved in substitution of functional group makes it possible to derive the following equation:

$$k_{ED}/k_{ed} = k_{FD}/k_{fd} = k_1 k_2 \quad (6)$$

Table I General Kinetic Scheme for Gradual Polyaddition Process Involving 2,4-TDI and 1,4-BD

No. for Reaction Type	Isocyanate Substrate	Hydroxyl Substrate	Denotation for Rate Constant	Product
1	EF	DD	$2k_{ED}$	fd
2	EF	DD	$2k_{FD}$	ed
3	EF	ed	k_{Ed}	ef
4	EF	ed	k_{Fd}	ee
5	EF	fd	k_{Ed}	ff
6	EF	fd	k_{Fd}	ef
7	EF	dd	$2k_{Ed}$	fd
8	EF	dd	$2k_{Fd}$	ed
9	ed	DD	$2k_{eD}$	dd
10	fd	DD	$2k_{fD}$	dd
11	ee	DD	$4k_{eD}$	ed
12	ef	DD	$2k_{eD}$	fd
13	ef	DD	$2k_{fD}$	ed
14	ff	DD	$4k_{fD}$	fd
15	ed	ed	$2k_{ed}$	ed
16	ed	fd	k_{ed}	fd
17	fd	ed	k_{fd}	ed
18	ee	ed	$2k_{ed}$	ee
19	ef	ed	k_{ed}	ef
20	ef	ed	k_{fd}	ee
21	ff	ed	$2k_{fd}$	ef
22	ed	dd	$2k_{ed}$	dd
23	fd	fd	$2k_{fd}$	fd
24	ee	fd	$2k_{ed}$	ef
25	ef	fd	k_{ed}	ff
26	ef	fd	k_{fd}	ef
27	ff	fd	$2k_{fd}$	ff
28	fd	dd	$2k_{fd}$	dd
29	ee	dd	$4k_{ed}$	ed
30	ef	dd	$2k_{ed}$	fd
31	ef	dd	$2k_{fd}$	ed
32	ff	dd	$4k_{fd}$	fd

[This follows from the approximation of taking the reactivities of functional group as being independent of each other. Hence, from eqs. (4)–(6) one may conclude about equality of the sums of activation energies: $E_{FD} + E_{ed} = E_{Fd} + E_{eD}$.]

For the needs of experimental verification of a newly developed model, the kinetic scheme provided in Table I must be presented in a convention that is in accordance with the earlier notation system for the 2,4-TDI and 1,4-BD polyaddition process. Thus, monomers were attributed the symbols of **A** and **B**, and the oligourethanes resulting from the process were described as A_iB_i . The reactants were organized in even and odd fractions.² In such a modified kinetic model, 32 reactions presented in Table I were assigned to successive stages of the polyaddition process (Table II). That

enabled a new kinetic model to be developed which—adhering to Flory’s idea—defined reactivity of oligomers dependent solely on the environment of functional groups.

Kinetic Model for the Reactions Giving Linear Polyurethanes

Like the earlier models, the kinetic model developed covers the processes taking place in a batch reactor, with constant volume and perfect intermixing of the reacting substances. It was assumed that the rate of changes in the concentrations of the reacting substances can be described by a second-order kinetic equation. This model is composed of a system of ordinary differential equations that describe changes in concentra-

Table II Detailed Kinetic Scheme for Gradual Polyaddition Process Involving 2,4-TDI and 1,4-BD

No. of Reaction	Isocyanate Substrate	Hydroxyl Substrate	No. for Reaction Type as per Table I	Rate Constant	Product	No. of Oligomer Fraction
1	B	A	1	$2k_{ED}$	A_1B_1	F2
			2	$2k_{FD}$		
2	B	A_1B_1	3	k_{Ed}	A_1B_2	F2
			4	k_{Fd}		
			5	k_{Ed}		
			6	k_{Fd}		
3	A_1B_1	A	9	$2k_{eD}$	A_2B_1	F3
			10	$2k_{fD}$		
4	B	A_2B_1	7	$2k_{Ed}$	A_2B_2	F4
			8	$2k_{Ed}$		
5	A_1B_2	A	11	$4k_{eD}$	A_2B_2	F4
			12	$2k_{eD}$		
			13	$2k_{fD}$		
			14	$4k_{fD}$		
6	A_1B_1	A_1B_1	15	$2k_{ed}$	A_2B_2	F4
			16	k_{ed}		
			17	k_{fd}		
			23	$2k_{fd}$		
7	A_2B_2	A	9	$2k_{eD}$	A_3B_2	F5
			10	$2k_{fD}$		
8	A_1B_1	A_2B_1	22	$2k_{eD}$	A_3B_2	F5
			28	$2k_{fD}$		
9	B	A_2B_2	3	k_{Ed}	A_2B_3	F5
			4	k_{Fd}		
			5	k_{Ed}		
			6	k_{Fd}		
10	A_1B_2	A_1B_1	18	$2k_{ed}$	A_2B_3	F5
			19	k_{ed}		
			20	k_{fd}		
			21	$2k_{fd}$		
			24	$2k_{ed}$		
			25	k_{ed}		
			26	k_{fd}		
27	$2k_{fd}$					
11	B	A_3B_2	7	$2k_{Ed}$	A_3B_3	F6
			8	$2k_{Fd}$		
12	A_2B_3	A	11	$4k_{eD}$	A_3B_3	F6
			12	$2k_{eD}$		
			13	$2k_{fD}$		
			14	$4k_{fD}$		
13	A_1B_1	A_2B_2	15	$2k_{ed}$	A_3B_3	F6
			16	k_{ed}		
			17	k_{fd}		
			23	$2k_{fd}$		
14	A_1B_2	A_2B_1	28	$2k_{fd}$	A_3B_3	F6
			29	$4k_{ed}$		
			30	$2k_{ed}$		
			31	$2k_{fd}$		
			32	$4k_{fd}$		

tions of monomers **A** and **B**, dimer **A₁B₁**, oligourethanes type **A_iB_i** that make even fractions, as well as those of types **A_{i-1}B_i** and **A_iB_{i-1}** that make odd fractions. Also, algebraic equations resulting from initial conditions were incorporated.

The rate of decreasing monomer (**A** and **B**) concentrations, within the **F1** fraction, can be described by the following differential equation:

$$-d[A]/dt = [A] \left\{ c_1[B] + c_2 \sum_{i=1}^n [A_i B_i] + c_3 \sum_{i=2}^n [A_{i-1} B_i] \right\} \quad (7)$$

$$-d[B]/dt = [B] \left\{ c_1[A] + c_3 \sum_{i=1}^n [A_i B_i] + c_4 \sum_{i=2}^n [A_{i-1} B_i] \right\} \quad (8)$$

The rate of changes in the concentration of dimer **A₁B₁**, which makes an **F2** fraction, is shown by the equation:

$$d[A_1 B_1]/dt = c_1[A][B] - [A_1 B_1] \left\{ c_4[B] + c_2[A] + c_5 \sum_{i=1}^n [A_i B_i] + c_6 \sum_{i=2}^n [A_i B_{i-1}] + c_7 \sum_{i=2}^n [A_{i-1} B_i] \right\} \quad (9)$$

The rate of changes in the concentrations of oligourethanes **A_iB_i**—which are components of **F4**, **F6**, \dots , fractions—can be presented as follows:

$$d[A_i B_i]/dt = c_4[B][A_i B_{i-1}] + c_3[A][A_{i-1} B_i] + c_5 \sum_{k=1}^{i-1} ([A_k B_k][A_{i-k} B_{i-k}]) + c_8 \sum_{k=2}^{i-1} ([A_{k-1} B_k] \cdot [A_{i-k+1} B_{i-k}]) - [A_i B_i] \left\{ c_4[B] + c_2[A] + c_5 \sum_{k=1}^n [A_k B_k] + c_6 \sum_{k=2}^n [A_k B_{k-1}] + c_7 \sum_{k=2}^n [A_{k-1} B_k] \right\} \quad (10)$$

The rate of changes in the concentrations of oli-

gourethanes **A_{i-1}B_i** and **A_iB_{i-1}**, which make fractions **F3**, **F5**, \dots , can be presented as follows:

$$d[A_{i-1} B_i]/dt = c_4[B][A_i B_i] + c_7 \sum_{k=1}^{i-2} ([A_k B_k] \times [A_{i-k} B_{i-k-1}]) - [A_{i-1} B_i] \left\{ c_3[A] + c_7 \sum_{k=1}^n [A_k B_k] + c_8 \sum_{k=2}^n [A_{k+1} B_k] \right\} \quad (11)$$

$$d[A_i B_{i-1}]/dt = c_2[A][A_i B_i] + c_6 \sum_{k=1}^{i-2} ([A_k B_k] \times [A_{i-k+1} B_{i-k}]) - [A_i B_{i-1}] \left\{ c_4[B] + c_6 \sum_{k=1}^n [A_k B_k] + c_8 \sum_{k=2}^n [A_k B_{k+1}] \right\} \quad (12)$$

Constant values **c₁** through **c₈**, which can be found in eqs. (6)–(11), are functions of rate constants (2) (this results directly from Table II). These functions can be simplified with the use of eqs. (3)–(6):

$$\mathbf{c}_1 = 2\mathbf{k}_{ED} + 2\mathbf{k}_{FD} = 3.34\mathbf{k}_{ED} \quad (13)$$

$$\mathbf{c}_2 = 2\mathbf{k}_{eD} + 2\mathbf{k}_{fD} = 3.34\mathbf{k}_{ED}/\mathbf{k}_1 \quad (14)$$

$$\mathbf{c}_3 = 4\mathbf{k}_{eD} + 2\mathbf{k}_{eD} + 2\mathbf{k}_{fD} + 4\mathbf{k}_{fD} = 6\mathbf{k}_{ED}(1 + 0.67/\mathbf{k}_2)/\mathbf{k}_1$$

for $\mathbf{k}_2 = 1$

$$\mathbf{c}_3 = 10.02\mathbf{k}_{ED}/\mathbf{k}_1 \quad (15)$$

$$\mathbf{c}_4 = \mathbf{k}_{Ed} + \mathbf{k}_{Fd} + \mathbf{k}_{Ed} + \mathbf{k}_{Fd} = 3.34\mathbf{k}_{ED}/\mathbf{k}_2$$

for $\mathbf{k}_2 = 1$

$$\mathbf{c}_4 = 3.34\mathbf{k}_{ED} = \mathbf{c}_1 \quad (16)$$

$$\mathbf{c}_5 = 2\mathbf{k}_{ed} + \mathbf{k}_{ed} + \mathbf{k}_{fd} + 2\mathbf{k}_{fd} = 5.01\mathbf{k}_{ED}/\mathbf{k}_1\mathbf{k}_2$$

for $\mathbf{k}_2 = 1$

$$\mathbf{c}_5 = 5.01 \mathbf{k}_{ED}/\mathbf{k}_1 \quad (17)$$

$$\mathbf{c}_6 = 2\mathbf{k}_{ed} + 2\mathbf{k}_{fd} = 3.34\mathbf{k}_{ED}/\mathbf{k}_1\mathbf{k}_2$$

for $\mathbf{k}_2 = 1$

$$\mathbf{c}_6 = 3.34\mathbf{k}_{ED}/\mathbf{k}_1 = \mathbf{c}_2 \quad (18)$$

$$\mathbf{c}_7 = 2\mathbf{k}_{ed} + \mathbf{k}_{ed} + \mathbf{k}_{fd} + 2\mathbf{k}_{fd} + 2\mathbf{k}_{ed} + \mathbf{k}_{ed} + \mathbf{k}_{fd} + 2\mathbf{k}_{fd} = 10.02\mathbf{k}_{ED}/\mathbf{k}_1\mathbf{k}_2$$

for $\mathbf{k}_2 = 1$

$$\mathbf{c}_7 = 10.02\mathbf{k}_{ED}/\mathbf{k}_1 = \mathbf{c}_3 \quad (19)$$

$$\begin{aligned}
 \mathbf{c}_8 &= 2\mathbf{k}_{fd} + 4\mathbf{k}_{ed} + 2\mathbf{k}_{ed} + 2\mathbf{k}_{fd} + 4\mathbf{k}_{fd} \\
 &= 11.36\mathbf{k}_{ED}/\mathbf{k}_1\mathbf{k}_2 \\
 \text{for } \mathbf{k}_2 &= 1 \\
 \mathbf{c}_8 &= 11.36\mathbf{k}_{ED}/\mathbf{k}_1 \quad (20)
 \end{aligned}$$

Dependencies (13) through (20) make it possible to present in a more simple form eqs. (7)–(12) in the kinetic model developed. As a result, instead of having 8 rate constants (2), the model contains only the \mathbf{k}_{ED} constant for the reaction of the most reactive —NCO group in 2,4-TDI with the —OH group in 1,4-BD, and the \mathbf{k}_1 constant that represents the substitution effect in 2,4-TDI.

The initial conditions for the differential equations presented are as follows:

$$\begin{aligned}
 [\mathbf{A}](\mathbf{0}) &= [\mathbf{B}](\mathbf{0}) = [\mathbf{A}]_0 \\
 [\mathbf{A}_i\mathbf{B}_j](\mathbf{0}) &= \mathbf{0} \quad \text{for } i, j = 1, 2, \dots \quad (21)
 \end{aligned}$$

EXPERIMENTAL

The model developed was verified on the basis of measured concentration changes for fractions and number-average molecular weights of urethane oligomers formed in the reaction between 2,4-TDI and 1,4-BD, which was run in 1 : 1 and 1 : 3 tetrahydrofuran-chlorobenzene solution and at the boiling points of these solutions (i.e., 86° and 101°C, respectively). These conditions correspond more or less to those used in technology. Polyurethane chemical compositions at subsequent stages of the polyaddition reaction and numerical-average molecular weights of urethane oligomers were found by GPC. Components in the kinetic model suggested (Table II) were identified from a calibration curve that was developed with the use of model carbamates synthesized in the reaction of 2,4-TDI, with alcohols having various chain lengths. Quantitative determinations were obtained from chromatograms with the use of the internal standardization method and numerical processing of GPC findings. Detailed procedures for kinetic investigations, numeric calculations, and GPC analysis were described in refs. 2, 11, 12, and 13.

RESULTS AND DISCUSSION

The mathematical model provided in eqs. (7)–(12) and in eq. (21) was used in numerical simulation of the process studied. The results obtained

were interpreted in the same terms as for models developed earlier (i.e., in terms of sums of concentrations of fractions and their average molecular weights).^{2,3}

At the first stage of calculations, certain values for rate constant \mathbf{k}_{ED} were assumed, which could correspond to the progress of the process studied at 86° and 101°C. The actual value of this rate constant for the reaction of 2,4-TDI and alcohols is not known. Analysis of data provided in Figure 1 suggests that its value can be even five times higher than the rate constant for the reaction between phenyl isocyanate and corresponding alcohol. Hence, the preliminary model calculations should allow for a relatively wide span for its variation interval.

The range for rate constant k_1 was investigated in three levels. The results of such a simulation have been presented in Tables III and IV. In qualitative terms, the model presented describes the polyaddition process just like earlier models,^{2,3} because they all were based on similar differential equations. However, quantitative differences between these models are considerable.

The model developed was then subjected to experimental verification, wherein values for k_{ED} and k_1 were found. The least-squares method was used for the determination of these values. The kinetic parameters were searched for to give the minimum sum of squares for deviations in molecular weights found in experiments and model calculations. In fact, this procedure was to find the minimum for the following function:

$$F = 1/n \sum_{l=1}^n (M_{l\text{calc}} - M_{l\text{exp}})^2 \quad (22)$$

where n is the number of measuring points, wherein average molecular weight of the sample taken from the reactor was analyzed ($n = 8$ for polyaddition at the temperature of 86°C, $n = 7$ for 101°C).

Table V presents kinetic parameters of the process studied and corresponding values of the function (22). As can be seen, at 86°C, the function F goes down to its minimum for the following conditions:

$$\begin{aligned}
 \mathbf{k}_{ED} &= 6 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\
 \mathbf{k}_1 &= 4, 3.
 \end{aligned}$$

Similar calculations for the temperature of 101°C failed; no optimum value for the rate constant k_1 could be found within the suggested range of 2.5–

Table III Results from Numerical Simulation of 2,4-TDI and 1,4-BD Polyaddition Process Conducted at a Temperature of 86°C

Time (min)	Concentration of Oligomer Fraction (wt %)																							
	$k_{ED} = 3 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$						$k_{ED} = 15 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$						$k_{ED} = 40 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$											
	$k_1 = 2.5$		$k_1 = 3.5$		$k_1 = 4.5$		$k_1 = 2.5$		$k_1 = 3.5$		$k_1 = 4.5$		$k_1 = 2.5$		$k_1 = 3.5$		$k_1 = 4.5$							
	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6				
20	181	86.1	9.1	3.9	177	89.6	7.4	2.6	175	91.7	6.2	1.9	422	26.1	16.4	18.1	342	35.9	21.5	18.2	303	43.5	24.0	16.5
40	237	61.8	17.9	12.4	219	69.8	16.9	9.2	209	75.1	15.5	7.1	668	12.3	8.7	12.8	492	19.5	14.5	17.0	416	25.4	18.7	18.6
60	298	44.5	19.6	17.1	262	54.3	21.1	14.1	242	61.2	20.9	11.5	855	7.9	5.4	9.6	614	13.1	9.7	14.4	513	17.5	13.3	17.0
90	388	29.7	17.4	18.2	321	39.8	21.9	17.6	287	47.4	23.7	15.6	1059	5.1	3.1	7.3	769	8.4	5.8	11.4	643	11.5	8.4	14.0
120	471	21.8	14.4	17.0	372	31.2	20.1	18.5	325	38.6	23.2	17.6	1208	3.7	2.0	6.1	898	6.0	3.7	9.6	755	8.2	5.6	12.0
180	617	14.0	9.8	13.8	461	21.8	15.8	17.6	392	28.0	19.9	18.6	1402	2.4	0.9	4.9	1086	3.7	1.8	7.5	983	5.0	2.8	9.4
240	741	10.2	7.1	11.3	538	16.6	12.3	16.0	452	21.9	16.3	18.1	1511	1.8	0.5	4.4	1203	2.7	1.0	6.5	1057	3.6	1.6	8.0
300	846	8.0	5.4	9.7	608	13.2	9.7	14.5	508	17.7	13.3	17.1	1572	1.5	0.3	4.1	1274	2.3	0.6	6.0	1140	2.9	1.0	7.2

Table IV Results from Numerical Simulation of 2,4-TDI and 1,4-BD Polyaddition Process Conducted at a Temperature of 101°C

Time (min)	Concentration of Oligomer Fraction (wt %)																							
	$k_{ED} = 8 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$						$k_{ED} = 40 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$						$k_{ED} = 80 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$											
	$k_1 = 2.5$		$k_1 = 3.5$		$k_1 = 4.5$		$k_1 = 2.5$		$k_1 = 3.5$		$k_1 = 4.5$		$k_1 = 2.5$		$k_1 = 3.5$		$k_1 = 4.5$							
	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6	\bar{M}_n	F1 +F2	F3 +F4	F5 +F6
10	199	77.4	13.2	6.9	191	82.8	11.3	4.8	187	86.1	9.7	3.5	526	18.3	13.0	16.1	407	27.2	19.3	18.5	352	34.3	23.0	18.2
20	279	49.1	19.8	16.1	249	58.6	20.5	12.9	233	65.1	19.8	10.3	819	8.7	6.1	10.2	588	14.3	10.9	15.1	492	19.1	14.7	17.5
30	361	33.4	18.5	18.4	303	43.5	22.2	16.9	274	51.0	23.4	14.6	1022	5.6	3.6	7.7	736	9.4	6.7	12.1	614	12.7	9.5	14.8
45	473	21.7	14.4	17.0	374	31.0	20.2	18.5	327	38.4	23.4	17.6	1232	3.6	1.9	6.0	916	5.8	3.7	9.4	772	8.0	5.5	14.7
60	573	15.8	11.1	14.7	434	24.1	17.2	18.1	372	30.8	21.2	18.6	1373	2.6	1.2	5.1	1053	4.1	2.2	7.8	900	5.7	3.5	9.8
75	663	12.3	8.8	12.8	489	19.6	14.5	17.1	414	25.6	18.7	18.6	1471	2.1	0.7	4.6	1154	3.2	1.4	6.9	1001	4.3	2.3	8.6
90	774	10.2	7.1	11.3	540	16.5	12.3	16.0	453	21.8	16.3	18.1	1537	1.8	0.5	4.3	1227	2.6	1.0	6.4	1078	3.5	1.6	7.8
105	816	8.6	5.9	10.2	588	14.1	10.5	15.0	491	18.8	14.3	17.4	1583	1.5	0.3	4.1	1279	2.3	0.7	6.0	1140	3.0	1.1	7.2

Table V Kinetic Parameters for the Model That Takes Substituent Effects and Different Reactivities of Functional Groups Within 2,4-TDI into Consideration

$k_{ED} \cdot 10^4$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	5.0		6.0		7.0				
Temperature = 86°C									
k_1	3.6	3.7	3.8	4.2	4.3	4.4	4.4	4.5	4.6
$F \cdot 10^{-3}$	2.51	2.38	2.45	2.05	1.95	2.09	2.97	2.50	2.18
$k_{ED} \cdot 10^4$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	13.0		14.0		15.0				
Temperature = 101°C									
k_1	3.9	4.0	3.8	4.1	4.2	4.3	4.5	4.6	4.7
$F \cdot 10^{-3}$	1.70	1.60	1.61	1.51	1.48	1.53	1.39	1.37	1.48

4.5. The minimum value for F could be found for the following kinetic parameters:

$$k_{ED} = 15 \cdot 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_1 = 4, 6.$$

Table VI provides kinetic parameters for the model developed earlier, which was found to be a quasioptimum model.³

Figures 3 and 4 show the dependence between average molecular weight of linear polyurethanes and reaction time in the polyaddition processes studied. Apparently, after taking into account kinetic effects from substitution within 2,4-TDI, the model results are not in much better conformance with experimental values than those from the quasioptimum model.³ However, consistency of the findings from the model wherein substitution effects have been involved and experimental findings is much better than for the model, assuming constant reaction rates at subsequent polyaddition stages.² In general, the quasioptimum model provides better mapping for the actual process, and in particular for its initial and final stages. As results from the data collected in Tables V and

Table VI Kinetic Parameters for the Quasioptimum Model

$k_{11} \cdot 10^4$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	Temperature = 86°C	Temperature = 101°C
	8.0	18.0
a_1	2.0	2.2
a_2	0.5	0.5
$F \cdot 10^{-3}$	3.17	0.27

VI, the value for (22) gives no definite decision which way is better: the simulation presented herein and based on Flory's paradigm, or the sim-

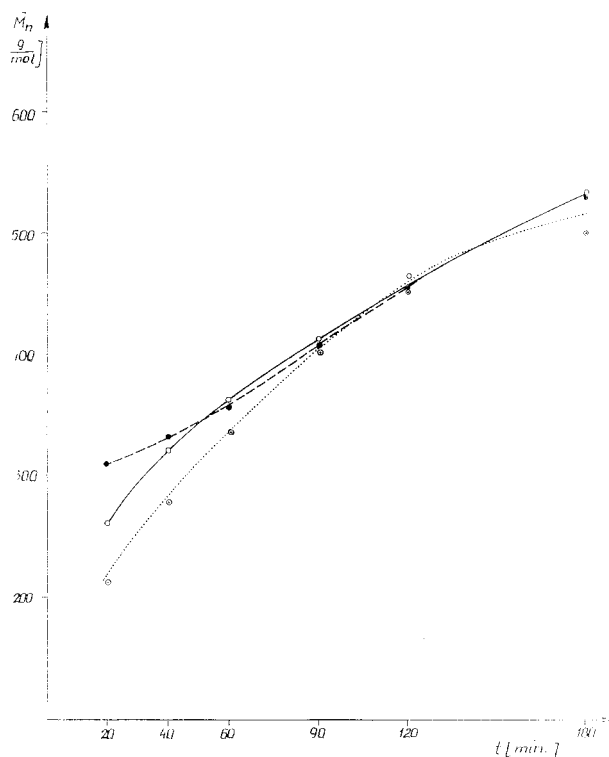


Figure 3 Graphic representation for dependence of mean molecular weight of linear polyurethanes on time, in reaction between 2,4-TDI and 1,4-BD (temperature = 86°C). - - -, experimental values obtained from GPC²; · · ·, values calculated from the model assuming substitution effect for 2,4-TDI ($k_1 = 4.3$); and —, values calculated from the quasioptimum model.²

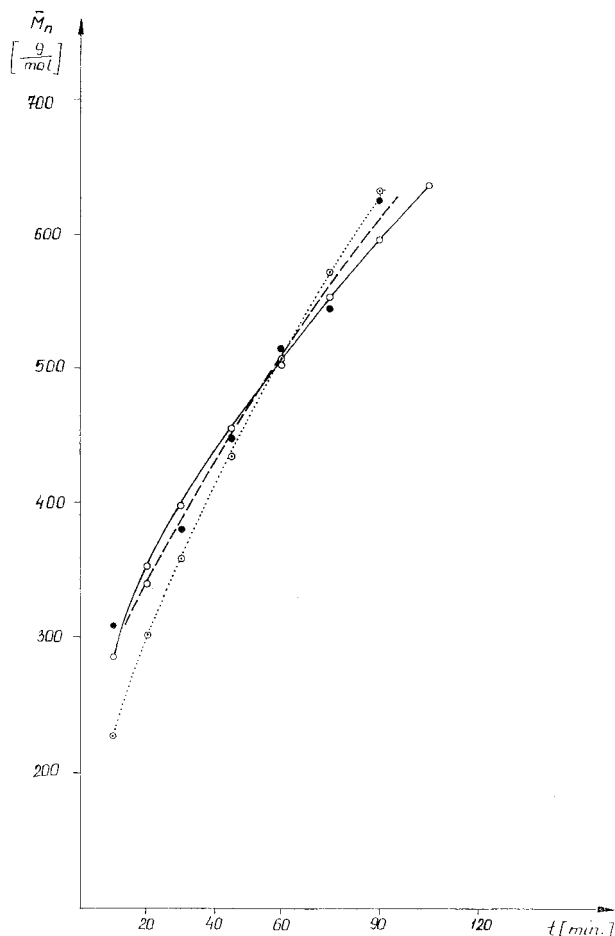


Figure 4 Graphic representation for dependence of mean molecular weight of linear polyurethanes on time, in reaction between 2,4-TDI and 1,4-BD (temperature = 101°C). - - -, experimental values obtained from GPC²; · · ·, values calculated from the model assuming substitution effect for 2,4-TDI ($k_1 = 4.6$); and —, values calculated from the quasioptimum model.²

ulation assuming oligomer reactivity to be dependent predominantly on molecule size.

Our calculations suggest that the kinetic effect from substitution, which reveals in the reaction of 2,4-TDI and alcohol, can be considerably high and amounts to about $k_1 = 4$. As can be expected, it increases with temperature and when this is not incorporated into a kinetic model, some other compensation must be introduced in the form of a value that changes in the course of polyaddition (e.g., average molecular weight of polymer). The quasioptimum model provides a better description for the total progress of the process: in addition to changing molecular weights—through introducing coefficients a_1 and a_2 —it also gives con-

sideration to substitution effects, although solely in the numeric form. Making allowance for two contributions [i.e., from molecular weight and from substitution effect(s)] gives a more reliable model for the reaction of 2,4-TDI with 1,4-BD.

Nevertheless, Flory's postulate—which has been generally accepted for gradual polymerization processes—is shaken. This has resulted from the confrontation of models developed and experimental data obtained from GPC analysis of polyurethanes. As stated in ref. 2, the GPC method is used in most studies of high molecular weight polymers. For its applicability in quantitative evaluation of urethane oligomers to be out of any question, we performed earlier check tests on model urethane oligomers that had been synthesized in the reaction of 2,4-TDI and 1,4-BD with stoichiometric excess of one monomer.^{11,12} In our opinion, accuracy and precision offered by GPC procedures are good enough to find the analytical results for urethane oligomers satisfactory to support the above conclusion. Doubts, if any, can arise from currently wider possibilities of performing complex numerical calculations, compared with instrumental methods available to verify the models developed. Considerable problems in GPC can be encountered especially for a very complex system of polar polymers. In such a case, the main mechanism of spatial elimination is accompanied by a number of secondary processes (e.g., adsorption processes) that upset the course of analysis.

What is left now is to explain the effect of molecular weight on reactivity of urethane oligomers.

Molecular weight of a linear polyurethane, which is present in a solution in the form of a ball with specific diameter, represents molecule size (i.e., also the distance between both molecule ends with functional groups). Hence, molecular weight can indirectly affect the chemical activity of the molecules discussed.

Oligomer molecule size can also reduce the molecule reactivity, and also under conditions for the kinetic area of chemical reaction, through increased number of hydrogen bonds. In the case of polyurethanes, there can exist a few types of such bonds.¹⁴ Urethane or urea —NH— groups are active donors for such bonds, wherein carbonyl and ether oxygen atoms are acceptors, with carbonyl and ether groups being numerous in polyurethane chains. Resulting spatial structures become expanded, and translation movements of molecules become limited.

Van der Waals forces cannot be neglected, either. These forces are dependent on the polar nature of molecules that can be affected not only by the presence of functional end groups but by the presence of other polar groups as well. Polyurethane molecular size influences, among others, the number of urethane groups. These groups are generally known to have a considerable contribution to the physical, mechanical, and thermal properties of polymers.

CONCLUSIONS

A mathematical model has been presented for the process of gradual polyaddition of 2,4-TDI and 1,4-BD. The model follows Flory's assumption for the dependence of oligomer reactivity on the chemical environment of its functional groups, and additionally gives consideration to different reactivities of —NCO groups within 2,4-TDI. The model presented offers a better description for the process studied than the model presented earlier,² which assumed equal reactivities for all functional groups within the reacting compounds.

However, the same conclusion for the models assuming oligomer reactivity dependent on molecule size, as described in ref. 2, is not that obvious. In general, the best conformity with actual number-average molecular weights for linear polyurethanes was found for the data from the so-called quasioptimum model.

It is essential that the kinetic effect from substitution, which is revealed in the reactions of 2,4-TDI and 2,6-TDI with diols, is relatively high so that it makes it possible to correctly present the gradual polyaddition process investigated. The best conformance with experimental data was obtained only after considering two factors: kinetic effect from substitution in 2,4-TDI, together with different value of its isocyanate groups; and dependence of oligomer reactivity on oligomer molecular weight, as adopted in the quasioptimum model. What was observed is in contrast with Flory's postulate, which assumes no dependence between the polymer molecule reactivity and polymer molecule size. This can be accounted for with the fact that the polymer molecular weight reflects the molecule size, inclusive of the distance between the molecule ends, and also polymer-polymer and polymer-solvent interactions, which result, among others, from the presence of hydrogen bonds and different numbers of polar urethane groups. They can indirectly affect reactivity

of polyurethane macromolecules, even in the areas where diffusion phenomena are negligible.

This study was conducted within Research Project 3T 09B 151 10, which was financially supported by the state Committee for Scientific Research.

NOMENCLATURE

A, DD	hydroxyl substrate (1,4-BD)
B, EF	isocyanate substrate (2,4-TDI)
$A_i B_j$, fd, ed, ef, ee, ff, dd	urethane oligomers
i, j, n, k	natural numbers
$k_{ED}, k_{Ed}, k_{eD}, k_{ed}, k_{FD}, k_{Fd}, k_{fD}, k_{fd}$	reaction rate constant factors (2)–(6)
k_1, k_2	constants responsible for substitution effects (4) and (5)
t	time
T	temperature
$[A], [B], [A_n B_m], [Fn]$	concentration of hydroxyl substrate, isocyanate substrate, oligomers, and fraction of polymer
$[A]_0, [B]_0, [A_n B_m]_0$	initial concentration of hydroxyl substrate, isocyanate, and oligomers
Fn	polymer fraction of n order (Table II)
$c_1, c_2, c_3, c_4, c_5, c_6, c_7, c_8$	functions of rate constants (15)–(20)
M_n	number-average molecular weights of urethane oligomer
F	sum of squares of deviations for experimental (M_{exp}) and calculated (M_{calc}) molecular weights (22)
α_1, α_2	empirical factors of the quasioptimum model ² (Table VI).

REFERENCES

1. P. Król, *J. Appl. Polym. Sci.*, **57**, 739 (1995).
2. P. Król and A. Gawdzik, *J. Appl. Polym. Sci.*, **58**, 729 (1995).
3. P. Król, *J. Appl. Polym. Sci.*, **61**, 220 (1996).
4. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.

5. P. Król, B. Atamańczuk, and J. Pielichowski, *J. Appl. Polym. Sci.*, **46**, 2139 (1992).
6. M. E. Bailey, V. Kirss, and Spaunburgh, *Ind. Eng. Chem.*, **48**, 794 (1956).
7. M. Kaplan, *J. Chem. Eng. Data*, **6**, 272 (1961).
8. J. Burkus and C. F. Eckert, *J. Am. Chem. Soc.*, **80**, 4958 (1958).
9. G. Sh. Papava, N. A. Maisuradze, N. S. Dokhturishvili, Z. M. Sarishvili, G. B. Razmadze, S. V. Vini-gradova, and V. V. Korsak, *Acta Polym.*, **39**, 445 (1980).
10. X. Y. Huang, W. Yu, and C. S. P. Sung, *Macromolecules*, **23**, 390 (1990).
11. P. Król and R. Chrzaszcz, *Polimery*, **39**, 683 (1994).
12. P. Król and M. Dejnega, *Polimery*, **40**, 94 (1994).
13. P. Król, *Polimery*, **42**, 458 (1997).
14. K. V. Zharkov, A. V. Zhitargina, and F. A. Zhokhova, *Zh. Fiz. Khim.*, **44**, 223 (1970).