

Generalization of Kinetics in the Reaction of Isocyanates and Polyols for Modeling a Process-Yielding Linear Polyurethane, 1

PIOTR KRÓL

Institute of Heavy Organic Synthesis, ul. Energetyków 9, 47-220 Kędzierzyn-Koźle, Poland

SYNOPSIS

A general kinetic reaction network has been suggested for the gradual chain growth polyaddition process for the synthesis of linear chain polyurethane. Based on the results from the kinetic investigation of the reactions of model aromatic/aliphatic isocyanates and alcohols and hydroxyethers, some methods were set forth to provide rate-constant values for the reactions included in this network. Model equations were derived from the collision theory, giving dependencies of reaction rate constant values on the molecular weights of the reacting substances. It was found that it was the structure of the reactants that had the most significant effect on the rate of carbamate-yielding reactions; the effects derived from temperature, catalyst, and size of reacting molecules follow. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In an earlier article,¹ the simplest possible kinetic model was provided for synthesis of polyurethanes. This model assumed that propagation of a polymer chain is based entirely on the reaction between hydroxyl and isocyanate groups of difunctional reactants, and chain branching involves allophanate groups. The derived equations presented the degree of substrate conversion and the degree of branching for the polyurethane backbone chain, depending on the initial ratio of monomers and on temperature. It is also important for a commercial process that the kinetic model should enable forecasting of the most important molecular parameters of polymers, i.e., mean molecular weight and degree of molecular weight distribution and, for a linear polyurethane of segmental structure, distribution of soft and hard segments along the backbone chain.²

Those parameters are decisive for numerous application features of polyurethanes, e.g., rheological properties of melted thermoplastic polyurethanes and of concentrated solutions utilized as fabric-impregnating agents.³ Structure of polyurethane segments is a requisite of physical-mechanical prop-

erties of polyurethanes and influences their viscosity-elasticity specifications and glass transition temperatures.^{4,5}

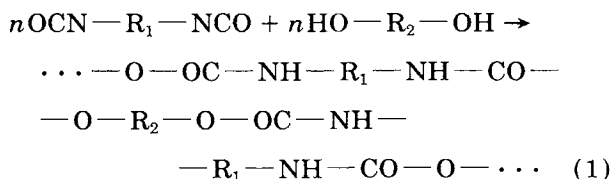
The principal purpose of this article is to develop a kinetic scheme for the gradual polyaddition process involving diols and diisocyanates. This scheme will make a base for the development, at further stages of investigations, of generalized mathematical models for the linear polyurethanes manufacturing process. Those models will comprise differential equations that can be solved with the use of numerical methods. The equations will represent changes in concentrations of urethane oligomers that are formed and subsequently disappear following the adopted kinetic scheme. Also, they will allow predicting distributions of linear polyurethane molecular weights at the successive stages of the polyaddition process. Then, they will undergo experimental verification for a selected reaction system, with the use of suitable methods for analyses to be carried out. As can be found in the available literature and results from our own simultaneous investigations, the GPC method can be very useful in such studies.⁶⁻⁹ The attempts to provide generalized models for the process tested should not be understood as an idea of mathematical unification for all the processes capable of yielding linear polyurethanes. That would not be possible to perform due

to numerous factors affecting the reaction rate in the process concerned, e.g., the use of various catalysts, polar nature of solvents employed, etc.^{10,11} However, the model sought could be some mathematical algorithm, observing the rules of chemical kinetics, and providing a way for describing any process giving linear polyurethanes; provided that proper kinetic parameters are introduced thereto. The data could possibly be derived, for example, from investigations on model reactions or from direct experimental findings obtained from the reactions between diisocyanates and diols.^{12,13}

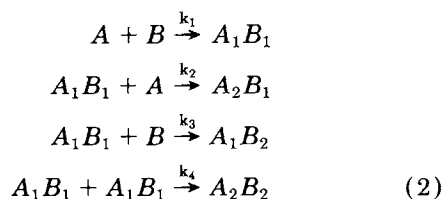
Another purpose of this study, not any less important, is to perform kinetic investigations for the reaction of isocyanates with alcohols and hydroxyethers and derive coefficients for the equation resulting from the collision theory. This equation is expected to make rate constants in the scheme being developed dependent on urethane oligomer molecular weights. Once set up, the equation could provide a basis for further studies, allowing for the development of models wherein rate constants would change to follow the growth of urethane oligomers.

KINETIC REACTION NETWORK FOR THE PROCESS YIELDING LINEAR POLYURETHANES

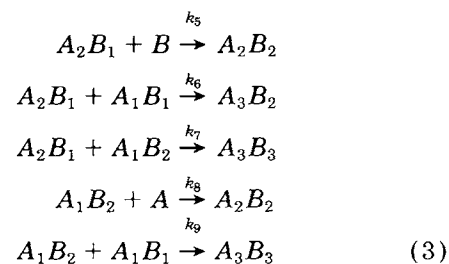
A general polyaddition reaction of difunctional isocyanates with diols/polyols such as polyethers or polyesters is shown below.



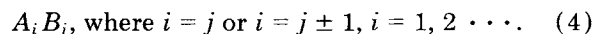
This can be represented by means of the following kinetic model, wherein A stands for difunctional polyol and B stands for any diisocyanate:



Oligourethanes created in the first stage, with denotations of A_2B_1 , A_1B_2 , and A_2B_2 can further react with each other and/or with starting materials, developing step by step the polyurethane molecule:



In general, any urethane oligomer created in this method can be expressed by the formula:



When $i = j$, the formula (4) presents an oligomer with $-\text{NCO}$ group at its one end and with $-\text{OH}$ group on the other end. So this compound can at subsequent stages react with both monomers and/or any products resulting from previous reactions. When $i = j + 1$ or $i = j - 1$, the created oligomer has got groups $-\text{OH}$ or $-\text{NCO}$, respectively, at both its ends. Hence, in the first case, it can react with monomer B or with oligomers A_iB_i and $A_{i-1}B_i$, and in the second case, it can react with monomer A or with oligomers A_iB_i and $A_{i+1}B_i$. The presented scheme illustrates step growth addition polymerization.

Unique notation for rate constants k_n will be necessary in further investigations so that individual rate constant values can be attributed to corresponding reactions.

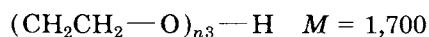
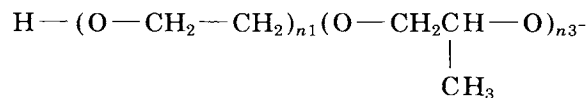
It is known from previous investigations that the reactions (2) and (3) are irreversible, and their rates conform in general to a second order kinetic eq. (4). Assuming constant volume of the mixture, and based on the material balance most convenient for a batch reactor, and perfect mixing, it is possible to set up a system of differential equations making a kinetic model for the studied process. This model could take the presence of all mixture components into consideration.

EXPERIMENTAL

Employed Reagents and Raw Materials

Phenyl isocyanate (from Merck); Izocyn T-80 (mixture of isomers: 80% wt of 2,4- and 20% wt of 2,6-tolylenediisocyanate (TDI), (produced by the "ZACHEM" Chemical Works in Bydgoszcz, purified directly before use by means of vacuum distillation); butyl isocyanate (Merck); 1,6-hexamethylenediisocyanate (HDI), (Merck); ethanol, pure (POCh Gliwice); 1-hexanol, (Fluka);

1-octanol, (Fluka); 1-decanol, (Fluka); 1-hexadecanol, (Fluka); diethylene glycol monobutyl ether, $C_4H_9O-(CH_2CH_2O)_2H$ (DGMB), (Fluka); polyoxyethylene glycol 400 (PEG 400), (from the "BLACHOWNIA" Chemical Works at Kędzierzyn-Koźle, dewatered by azeotropic distillation with benzene); poly(oxypropylene-oxyethylene) glycol, (Rokopol 30p5),



$$L_{OH} = 65.6 \text{ mg KOH g}^{-1}$$

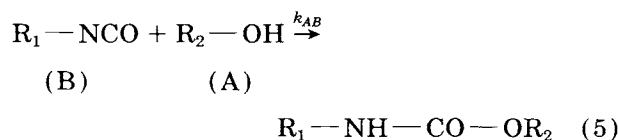
where: $n_1 + n_2 = 5$

$$n_3 = 25.48$$

(from the "ORGANIKA-ROKITA" Chemical Works, dewatered like PEG 400). 1,4-Diazabicyclo[2,2,2]octan (DABCO) (Fluka); and chlorobenzene, pure, purified by distillation (POCh Gliwice).

Method for Taking Kinetic Measurements

A reaction of isocyanate and a compound with the hydroxyl group (e.g., alcohol, hydroxyether, phenol, etc.) yields carbamates:



It is most convenient to express the rate of reaction (5) as changes in the concentration of isocyanate reactant, because it is easy to determine free isocyanates:

$$r = -\frac{dC_B}{dT} = k_{AB}C_A C_B \quad (6)$$

Concentration of isocyanate groups was determined by means of a standard method employing di(*n*-butyl)amine. Excess amine is then titrated with an ethanolic solution of HCl, in the presence of bromophenol blue indicator.¹⁴

Rate-constant values for the reactions studied were found from linear regression, based on integrated eq. (6), and assuming that initial concentrations of isocyanate and alcohol were equal ($C_B^0 = C_A^0$):

$$L = \frac{C_B^0 - C_B}{C_B^0 C_B} = k_{AB}t \quad (7)$$

Activation energy values for reactions considered were determined from measurements taken at three temperature values. As the reactivities of reactants employed were different, it was necessary to apply temperatures within 40–120°C.

The Arrhenius equation was used for this purpose:

$$k = k_0 e^{(-E_a/RT)} \quad (8)$$

Additional measurements were taken for selected isocyanates, alcohols, and ethers, in the presence of DABCO as a catalyst. The amount of the latter was 0.1% wt, based on the hydroxyl substrate.

The reaction was carried out in a 500 cm³ glass reactor provided with a heating system and a thermostat, agitator, reflux condenser with inlet for nitrogen, thermometer, and sampling probe.

Amounts of initial materials were adjusted in such a way that the product final concentration should reach about 50% wt. Viscosity for the reaction solutions, found by means of a Höppler viscometer at 25°C, amounted to 25–40 mPa s, depending on starting materials employed. This enabled us to neglect any inhibiting effect from diffusion.

Kinetic parameters for the studied reactions are provided in Tables I–V. Table I shows data for noncatalyzed reactions of aromatic isocyanates with alcohols, Table II refers to noncatalysed reactions of phenyl isocyanates with various hydroxyethers, Table III refers to noncatalysed reactions of aliphatic isocyanates with alcohols, while Table IV provides findings for noncatalyzed reactions of *n*-butyl isocyanate with two selected hydroxyethers. Kinetic parameters for aromatic isocyanates reacting with alcohols and hydroxyethers in the presence of DABCO as a catalyst are shown in Table V. The investigation revealed only a slight impact of DABCO on the rates of reactions of aliphatic isocyanates with the hydroxyl compounds studied. This confirms the previously observed fact that tertiary amines are not effective catalysts for the reactions of hydroxyl compounds with aliphatic isocyanates.¹⁵

Carbamates obtained from the reactions (1–7) and (12–15), after being separated from the reaction solution, were crystalline solids, while products from the reactions 8, 11, and 16 were liquids. Oligourethanes produced in the reactions 9, 10, and 17, after distilling chlorobenzene off, were thick and viscous liquids.

All products, after their purification, were subjected to elemental analysis. C, H, and N contents were found and compared to those calculated on the basis of expected molecular formulae for the compounds studied. The carbamates obtained were also subjected to IR investigation.¹⁶

Table I Kinetic Parameters for Reactions of Aromatic Isocyanates and Alcohols

Reaction No.	Isocyanate Reactant (M_B)	Alcohol Reactant (M_A)	Temp. [$^{\circ}\text{C}$]	$k_{AB} 10^4$ [$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$]	E_a [kJ mol^{-1}]	$\ln k_o$	$\beta' 10^4$ in Eq. (12)
1	$\text{C}_6\text{H}_5\text{NCO}$ (119.2)	1-Hexanol (102.18)	40	7.94	34	5.94	58.9
			60	16.92			
			80	35.05			
2		1-Octanol (130.23)	40	10.89	32	5.68	85.9
			60	28.07			
			80	44.35			
3	TDI (174.16)	Ethanol (46.07)	60	5.59	38	6.40	33.7
			80	14.27			
			100	24.34			
4		1-Hexanol (102.18)	60	6.08	39	6.61	48.9
			80	13.05			
			100	27.77			
5		1-Octanol (130.23)	40	3.28	39	16.28	28.3
			60	7.51			
			80	18.21			
6		1-Decanol (158.29)	60	6.47	48	9.75	59.2
			80	15.49			
			100	36.84			
7		1-Hexadecanol (242.45)	60	8.18	33	4.95	82.6
			80	14.53			
			100	30.44			

No catalyst employed.

Carbamates (1–7) and (11–15) obtained during the kinetic study were separated from reaction mixtures and were subjected to additional investigation by x-ray diffraction (XRD) and thermal analysis (DSC and TG). Structural investigations revealed that the products derived from monoisocyanates and alcohols were unary compounds and their purity reached about 99%, while products resulting from the reaction of diisocyanates and alcohols, besides position isomers in case of employing Izocyn T-80, contain small amounts of not fully substituted carbamate-isocyanates.¹⁶

DISCUSSION OF RESULTS

It is important for proper inferences within the field of kinetics that the reactions studied should run selectively and yield carbamates or urethane oligomers in accordance with eq. (5). Side reactions giving, for example, allophanates, isocyanate cyclization, and dimerization reactions are undesirable in this case.¹⁷ From the structural study performed, the reactions of aromatic and aliphatic isocyanates with varying chain length alcohols in chlorobenzene solvent, proceed selectively to carbamates, in accordance with eq. (5). Hence, those reactions can be

considered model reactions for the linear polyurethanes manufacturing process. Under such conditions, the possible presence, under such conditions, of unreacted isocyanates did not exceed the level of 0.1%. The findings from DSC and XRD analyses confirmed for reactions (3–7), wherein isocyanate initial material was a mixture of 2,4- and 2,6-TDI, that carbamates obtained were also mixtures of corresponding isomers.¹⁶ Kinetic parameters for the reactions involving Izocyn T-80 should, thus, be understood as averaged values for the reactions of both isomers, i.e., 2,4- and 2,6-TDI, with alcohols and/or hydroxyethers.

It can be concluded from the comparison of reaction kinetic parameters provided in Tables I–V that it is the chemical structure of the reacting substances that is decisive for the rate of the reaction (5). The aromatic structure of isocyanates has the most significant impact in this case. This can be accounted for by the resonance influence between the —NCO group and π electrons of the aromatic ring in phenyl isocyanate or in TDI isomers.¹⁸ The resonance effect stabilizes the mesomeric structures of aromatic isocyanates, hence, making it easier for the nucleophilic agents to attack the electrophilic carbon atom within the isocyanate group. There is no possibility of such a stabilizing effect for aliphatic

Table II Kinetic Parameters for Reactions of Phenyl Isocyanates and Hydroxyethers

Reaction No.	Isocyanate Reactant (M_B)	Hydroxyether Reactant (M_A)	Temp. [°C]	$k_{AB} 10^4$ [$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$]	E_a [kJ mol $^{-1}$]	$\ln k_o$	$\beta' 10^4$ in Eq. (12)
8	C ₆ H ₅ NCO (119.2)	DGMB (162.23)	60	1.67	40	5.81	14.1
			80	3.58			29.8
			100	8.47			70.5
9		PEG 400 (400)	50	1.74	43	7.24	16.7
			70	4.68			44.8
			90	9.97			95.5
10		Rokopol 30p5 (1700)	60	2.18	51	9.94	23.0
			80	6.93			73.1
			100	15.78			166.5

No catalyst employed.

isocyanates, which give much lower rates for the reactions of C₄H₉NCO and HDI with the same hydroxyl compounds under similar conditions (Tables III and IV). This is evident for the reactions of TDI and butyl isocyanate with 1-hexadecanol at the temperature of 80°C: $k_{AB} = (14.53 \text{ and } 7.65) \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Activation energy values for those reactions amount to 33 and 85.1 kJ mol $^{-1}$, respectively. Reaction rate constants for these isocyanates reacting with 1-octanol amount to $k_{AB} = (18.21 \text{ and } 30.96) \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, while their activation energy values $E_a = 39 \text{ and } 95 \text{ kJ mol}^{-1}$ are close to those specified above. Hence, in the reactions of isocyanates and alcohols, the reaction rate proves not to be dependent solely on the chemical structures involved. Some contribution is likely to

come, among others, from the size of combining molecules, in conformity with collision theory. In my opinion, this can account for the experimentally observed considerable differences in the rates of the reactions involving the two aliphatic isocyanates studied and alcohols. For illustration, at the temperature of 80°C, the rate constant for the reaction of 1-hexadecanol with butyl isocyanate is 7.65×10^{-4} , while for the reaction with MDI it is $1.97 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Corresponding activation energy values are 85.1 and 43.6 kJ mol $^{-1}$, respectively. The presence of the DABCO catalyst reveals an additional stabilizing effect on the structure of the active complex created. For example, at 80°C, the value of k_{AB} for the reaction of TDI and 1-octanol was increased by the application of a catalyst from

Table III Kinetic Parameters for Reactions of Aliphatic Isocyanates with Alcohols

Reaction No.	Isocyanate Reactant (M_B)	Alcohol Reactant (M_A)	Temp. [°C]	$k_{AB} 10^4$ [$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$]	E_a [kJ mol $^{-1}$]	$\ln k_o$	$\beta' 10^4$ in Eq. (12)
11	C ₄ H ₉ NCO (99.13)	1-Octanol (130.23)	40	1.88	95.0	27.30	14.1
			60	8.45			63.4
			80	30.96			232.5
12		1-Hexadecanol (242.45)	60	1.84	85.1	24.40	15.4
			80	7.65			64.2
			100	52.04			436.5
13	HDI (168.20)	1-Hexanol (102.18)	80	1.13	59.1	9.46	8.8
			100	3.23			25.5
			120	8.82			70.3
14		1-Decanol (158.29)	80	1.53	55.3	10.05	13.5
			100	4.06			37.0
			120	10.73			96.9
15		1-Hexadecanol (242.45)	80	1.97	43.6	6.28	19.9
			100	3.59			35.9
			120	9.14			91.0

No catalyst employed.

Table IV Kinetic Parameters for Reactions of *n*-Butyl Isocyanate with Hydroxyethers

Reaction No.	Isocyanate Reactant (M_B)	Hydroxyether Reactant (M_A)	Temp. [°C]	$k_{AB} 10^4$ [dm ³ mol ⁻¹ s ⁻¹]	E_a [kJ mol ⁻¹]	ln k_o	$\beta' 10^4$ in Eq. (12)
16	C ₄ H ₉ NCO (99.13)	DGMB (162.23)	60	13.8	61.0	13.18	108.2
			80	50.0			394.2
			100	150.0			1176.6
17		Rokopol 30p5 (1700)	80	3.51	141	38.28	33.9
			100	5.88			56.9
			120	23.79			230.2

No catalyst employed.

18.21 to 30.67, while the activation energy decreased from 39 to 35 kJ mol⁻¹. Generally, the catalytic effect is stronger for the reaction of phenyl isocyanate with hydroxyethers than with alcohols. This supports increased rates in the reactions of aromatic isocyanates with the hydroxyl compounds studied (Table V).

As can be seen from the data provided in Tables I-IV, among the hydroxyl substrates studied it is the simple alcohols that have considerably higher rates for the reactions with isocyanates. When considering reactions involving DGMB ether (its mo-

lecular weight is close to that for 1-decanol), one can find that the observed differences do not result from molecular weight values of the alcohols and hydroxyethers employed, but from the chemical nature of those compounds. Ethers, for example, have a much higher ability to create hydrogen bonds with reaction products and with some transient compounds, which affects the structure of the active complexes formed.

As can be found from the experiments, the activation energy for the reaction of aromatic isocyanates with simple alcohols amounts to 32-48 kJ

Table V Kinetic Parameters for Reactions of Aromatic Isocyanates with Alcohols (1-6) and Hydroxyethers (8, 10): Reactions Catalyzed by DABCO

Reaction No.	Isocyanate Reactant (M_B)	Alcohol or Hydroxyether Reactant (M_A)	Temp. [°C]	$k_{AB} 10^4$ [dm ³ mol ⁻¹ s ⁻¹]	E_a [kJ mol ⁻¹]	ln k_o	$\beta' 10^4$ in Eq. (12)
1	C ₆ H ₅ NCO (119.2)	1-Hexanol (102.18)	40	5.94	46	11.35	44.1
			60	16.00			118.7
			80	43.28			321.0
3	TDI (174.16)	Ethanol (46.07)	40	9.83	28	3.91	59.3
			60	38.90			234.8
			80	54.10			326.5
4		1-Hexanol (102.18)	40	5.76	37	6.67	46.2
			60	12.98			104.3
			80	28.69			230.3
5		1-Octanol (130.23)	40	6.71	35	11.34	57.9
			60	16.16			139.8
			80	30.67			265.0
6		t1-Decanol (158.29)	40	7.01	36	6.72	63.8
			60	17.86			163.0
			80	33.96			309.6
8	C ₆ H ₅ NCO (119.2)	DGMB (162.23)	40	21.37	40	9.05	195.9
			60	46.58			386.3
			80	121.34			1,005.5
10		Rokopol 30p5 (1700)	60	23.96	35	6.50	252.9
			80	30.51			322.0
			100	95.98			1,013.0

mol⁻¹, and for the reaction with hydroxyethers amounts to 40–51 kJ mol⁻¹. Specifically, the energy value does not depend on the alcohol chain length, in case of reactions with alcohols, while in the case of reactions involving hydroxyethers, some distinct increase can be observed in activation energy when higher molecular weight compounds are used. This can be explained by the higher number of hydrogen bonds/bridges created when higher molecular weight hydroxyethers are employed.¹⁹ As the data show in Table V, the presence of DABCO speeds up the reactions studied and makes the rates of reactions of aromatic isocyanates with alcohols and with hydroxyethers equal. The activation energy is lower in this case, compared to reactions employing no catalyst.

The above conclusions result from the investigation employing one solvent only—chlorobenzene—with medium polarity (dipole moment of 1.7 D), and taking no part in forming hydrogen bonds. Some different results could be expected when applying neutral solvents like 1,4-dioxane or tetrahydrofuran, wherein oxygen atoms with their free pairs of electrons make potential electron donor centres.²⁰

MATHEMATICAL MODEL FOR RATE-CONSTANT VALUES OF ELEMENTARY REACTIONS IN THE POLYADDITION PROCESS

As shown in the above analysis, the decisive factors affecting the rate of carbamate yielding reactions are: structure of the reacting substances, process temperature, and, in the case of aromatic isocyanates, also the presence of a catalyst. Some significant effects can also result from the type of solvent employed and from the viscosity of the reaction medium. When the above parameters remain unchanged for a given process, an attempt can be made to find dependencies between the rate of reaction (5) and molecular weights of isocyanate and hydroxyl compounds.

Assuming that the addition reaction results from a collision of two molecules with suitable orientation, collision theory can be employed for quantitative interpretation of this process.²¹ Despite the fact that this theory is based on the kinetic theory of gases, in some special cases its statements and conclusions can be transferred to liquids. In accordance with this theory, the number of collisions of molecules A and B taking part during 1 s in 1 dm³ is described by the equation as follows:

$$Z = \left(\frac{d_A + d_B}{2} \right)^2 \frac{N^2}{10^6} \sqrt{8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} C_A C_B \quad (9)$$

For linear molecules with functional groups at the ends of their chains, the element $\frac{(d_A + d_B)}{2}$ should be constant in practice, and independent of molecular weight.

Under constant temperature, the number of collisions can, hence, be given by the following equation:

$$Z = \beta \sqrt{\left(\frac{1}{M_A} + \frac{1}{M_B} \right)} C_A C_B \quad (10)$$

Because the reaction rate is proportional to the number of collisions, the expression may be presented in a form analogous to that for eq. (10):

$$r_i = Z_i e^{(-E_a/RT)} = \beta' \sqrt{\left(\frac{1}{M_A} + \frac{1}{M_B} \right)} C_A C_B \quad (11)$$

When this is compared to eq. (6), which defines reaction rate:

$$r_i = k_{AB} C_A C_B \quad (6')$$

one can obtain directly:

$$k_{AB} = \beta' \sqrt{\left(\frac{1}{M_A} + \frac{1}{M_B} \right)} = \frac{\beta' \sqrt{M_A + M_B}}{\sqrt{M_A M_B}} \quad (12)$$

After its suitable transformation, the expression (12) converts to the form of an equation for equiaxial hyperbola in the (M_A , M_B) coordinate system:

$$\frac{1}{M_A} + \frac{1}{M_B} = c \quad (13)$$

where:

$$c = \left(\frac{k_{AB}}{\beta'} \right)^2 \quad (14)$$

The constant value of β' is dependent on temperature only and, if the model (12) is valid, it can be derived experimentally with the use of a linear regression method. Equation (12) presents a straight line in the (k_{AB} , $\sqrt{\frac{M_A + M_B}{M_A M_B}}$) coordinate system.

The values of β' for studied model reactions found by means of this method are provided in Tables I–V.

Hence, eq. (13) is a mathematical model describing the dependence of rate-constant values on

Table VI Interpretation of Mathematical Model of Kinetics for Reactions of Aromatic Diisocyanates with Hydroxyl Compounds

Type of Isocyanate	Type of Hydroxyl Compound	Catalyst	Temp. [°C]	β'_{av} 10 ⁴	Model Rate Constant k_{AB} 10 ⁴ [dm ³ mol ⁻¹ s ⁻¹]	$C = \left(\frac{k_{AB}}{\beta'_{av}}\right)^2$	Asymptotes of Equiaxial Hyperbola $M_A = M_B = c^{-1}$
TDI	Alcohol	—	60	64.0	3.0	2.20 10 ⁻³	455
					5.0	6.10 10 ⁻³	164
					10.0	0.0244	41
			80	137.0	10.0	5.33 10 ⁻³	188
					15.0	0.0199	83
					20.0	0.0213	47
	100	299.0	20.0	4.47 10 ⁻³	224		
			30.0	0.01007	99		
			40.0	0.0179	56		
	DABCO	—	60	165.0	15.0	8.26 10 ⁻³	121
					20.0	0.0147	68
					25.0	0.0230	44
80			420.0	30.0	5.10 10 ⁻³	196	
				45.0	0.0115	87	
				60.0	0.0204	49	
C ₆ H ₅ NCO	Hydroxyether	—	60	21.4	1.5	4.91 10 ⁻³	204
					2.0	8.73 10 ⁻³	114
					2.5	0.0136	73
			80	56.1	3.5	3.89 10 ⁻³	257
					5.5	9.61 10 ⁻³	104
					7.5	0.0179	56
	100	127.0	8.0	3.97 10 ⁻³	252		
			12.0	8.93 10 ⁻³	112		
			16.0	0.0159	63		
	DABCO	—	60	320.0	20.0	3.91 10 ⁻³	256
					35.0	0.0120	84
					40.0	0.0244	41

molecular weights of substrates in the reaction (5). Because the constant value β' has to be found experimentally, this model has got a quasi-theoretical nature. The hyperbola provided by eq. (13) has two asymptotes:

$$M_A = M_B = \frac{1}{c} = \left(\frac{\beta'}{k_{AB}}\right)^2 \quad (15)$$

and its vertex crosses the straight line $M_A = M_B$, which is the symmetry axis, at the point of coordinates (2/c, 2/c).

Based on data collected in Tables I–V, more thorough analysis was carried out on model reactions for the manufacture of carbamates. The model utilized was based on eq. (13).

Results from those calculations are provided in Tables VI and VII, for reactions involving aromatic and aliphatic isocyanates, respectively. The values for β' given in columns 6 in those tables are derived from Tables I–V as mean values calculated after rejecting extreme values. Such β'_{av} depends solely on the type of isocyanate and hydroxyether as well as

on temperature. So, values for k_{AB} shown in columns 7 in those tables for a given temperature depend also on the substrate molecular weight, in accordance with eq. (13). Figures 1–4 provide charts obtained for model dependencies. The diagrams are theoretical pictures of the dependence of the rate constant k_n for the reaction (2) on molecular weights of urethane oligomers A_iB_j . They have been based on the values of β'_{av} found experimentally. Figure 1 shows a two-dimensional projection of the eq. (13) for the reaction giving urethane oligomers, which have the widest span of β'_{av} at the temperature of 80°C: 0.042 for the reaction of TDI-based oligourethanes, catalyzed by means of DABCO, and 0.0014 for the reaction of HDI-based oligourethanes. The charts obtained are hyperbolae, which characterize the range of variability for k_{AB} in the studied extent of molecular weights of urethane oligomers. For the needs of simplified representation, the lines are continuous ones although, in fact, molecular weight changes stepwise as further monomers are added to the polyurethane chain. Figures 2–4 show three-dimensional representations of the model eq.

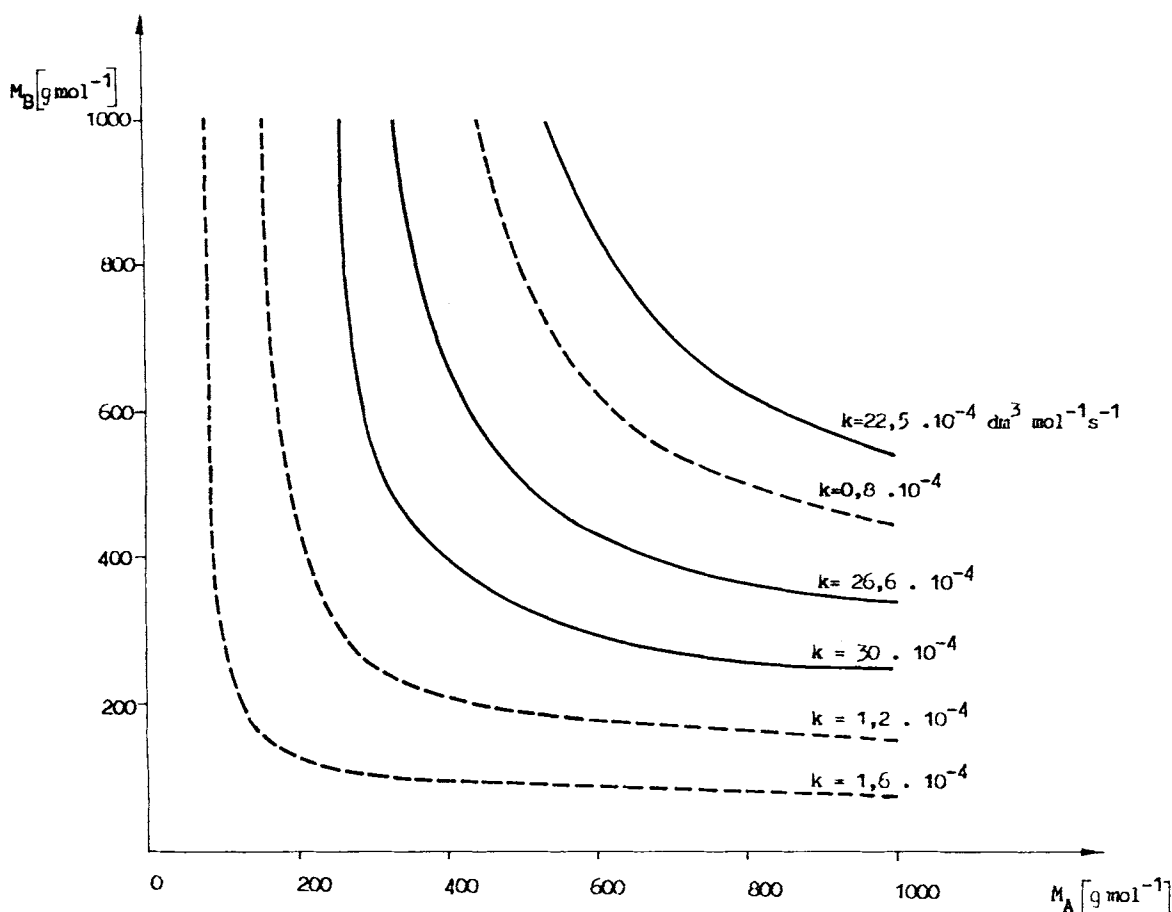


Figure 1 Two-dimensional projection of the Eq. (13), for the reaction of alcohols and isocyanate oligomers (temperature 80°C). ----- reaction of TDI-based oligomers, catalyzed by DABCO ($\beta'_{av} = 0.042$); - - - - - reaction of HDI-based oligomers ($\beta'_{av} = 0.0014$).

Table VII Interpretation of Mathematical Model of Kinetics for Reactions of Aliphatic Isocyanates with Hydroxyl Compounds

Type of Isocyanate	Type of Hydroxyl Compound	Temp. [°C]	β'_{av} 10^4	Calculated Rate Constant $k_{AB} 10^4$ [$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$]	$C = \left(\frac{k_{AB}}{\beta'_{av}}\right)^2$	Asymptotes of Equiaxial Hyperbola $M_A = M_B = c^{-1}$
HDI	Alcohol	80	14.0	1.0	$5.10 \cdot 10^{-3}$	196
				1.5	0.0115	87
				2.0	0.0204	49
		100	33.0	2.5	$5.74 \cdot 10^{-3}$	174
				3.5	0.0112	89
				4.5	0.0186	54
$\text{C}_4\text{H}_9\text{NCO}$	Hydroxyether	80	37.0	3.0	$6.57 \cdot 10^{-3}$	152
				4.0	0.0117	86
				5.0	0.0183	55
		100	87.0	5.0	$3.30 \cdot 10^{-3}$	303
				10.0	0.0132	76
				15.0	0.0297	34

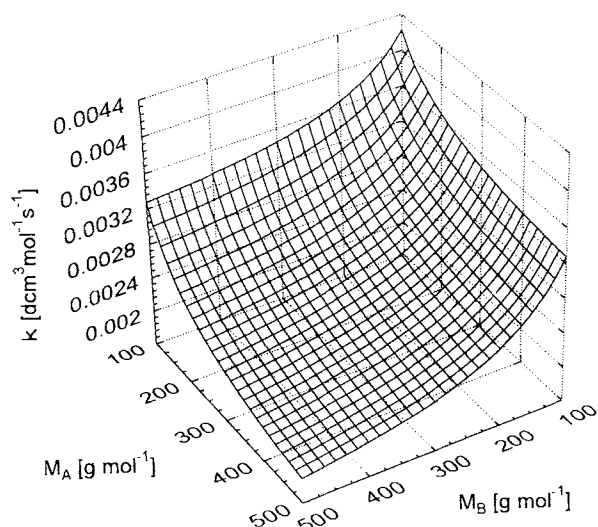


Figure 2 Three-dimensional projection of the Eq. (13), for the reaction of alcohols and TDI-based isocyanate oligomers (temperature 60°C, $\beta'_{av} = 0.0064$).

(13) for different reactions. Corresponding values of β'_{av} are provided in Tables VI and VII. The real range of variability for k_{AB} must be, and is shown, as a surface. As can be seen in these figures, the highest value of the rate constant is available for the reactions of monomers, and then it decreases following a hyperbolic dependence. Hence, the reactivity of oligourethanes depends considerably on the molecular weights of the reactants at the initial stages of the polyaddition process only, and then it becomes more linear. The charts obtained allow for the comparison of various effects like: structure of reacting substances, temperature, presence of a catalyst, and reacting substance molecular weight, on the rate of carbamate-yielding reactions. Those data confirm the earlier conclusion on the decisive effect of structure of reacting substances on the kinetics of the reactions studied; the effects derived from temperature, catalyst, and molecule size follow.

CONCLUSIONS

The findings obtained from a kinetic study of model reactions of isocyanates and hydroxyl compounds enable the quantification of rate constants k_n for reactions (2) and (3) of the kinetic scheme providing linear polyurethanes.

Polyurethane, resulting from reaction (1), is a set of macromolecules having the same structure and different molecular weights. Taking into consideration the fact that it is the structure of the reacting substances that are rate determining for reactions

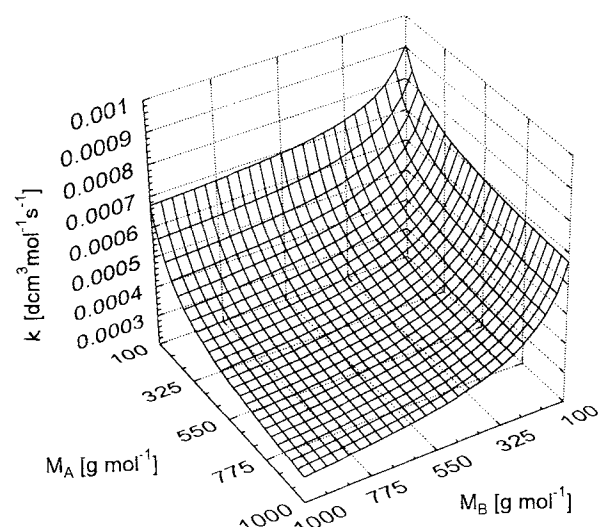


Figure 3 Three-dimensional projection of the Eq. (13), for the reaction of alcohols and TDI-based isocyanate oligomers (temperature 100°C, $\beta'_{av} = 0.0299$).

(2) and (3), it is reasonable to assume, in the first approximation, invariability of k_n at successive process stages. The study gives support for the application of the Arrhenius equation for k_n utilized earlier in analyzing this process:¹

$$\ln k = 7.0 - \frac{40}{RT} \quad (16)$$

The next approximation should be more precise and should find dependencies of k_n on molecular weights of reacting substances, in accordance with

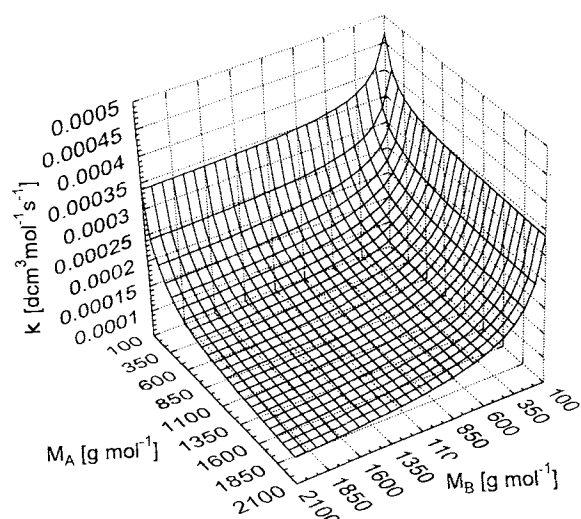


Figure 4 Three-dimensional projection of the Eq. (13), for the reaction of alcohols and HDI-based isocyanate oligomers (temperature 100°C, $\beta'_{av} = 0.0033$).

the model based on collision theory. The polymerization process will then be characterized by a specified value of β' , which will depend solely on temperature, and rate-constant values for successive reactions will follow the relationship (13).

The mathematical model (13) is relatively hard to verify by direct kinetic investigations because it is difficult to synthesize and separate urethane oligomers $A_i B_j$ with accurately defined chemical structure. This was done in Ref. 9, wherein such compounds were employed for the identification of components of linear polyurethane with the use of the GPC method.

However, eq. (13) will be used in further investigations intended to construct a generalized model for the linear polyurethane manufacturing process. The model will be based on the kinetic scheme provided in this article. Such a model would comprise a system of differential equations wherein rate constants for successive reactions are changed in accordance with (13). After its decomposition, the model could be verified experimentally on the basis of a reaction of diisocyanate and diol. The method shown in this study for the assessment of variability of rate constants, in the linear polyurethane yielding process, could then be evaluated indirectly.

The author wishes to thank Mr. Witold Pękala, M.Sc., who translated this study into English, hence, enabling it to be read by a broader group of researchers involved in polyurethanes. This study was carried out within the Project No. 3 1250 91 01 financially supported by the Committee for Scientific Investigations in Warsaw.

NOTATION

A —hydroxyl substrate
 B —isocyanate substrate
 $A_i B_j$ —urethane oligomers
 n, i, j —natural numbers
 L_{OH} —hydroxyl number
 k_{AB}, k_n —reaction rate constant factors
 t —time
 C_A —concentration of hydroxyl substrate
 C_B —concentration of isocyanate
 L —value provided by equation (7)
 C_A^0 —initial concentration of hydroxyl substrate
 C_B^0 —initial concentration of isocyanate
 k_0 —preexponential factor of the Arrhenius equation (8)
 E_a —activation energy
 T —absolute temperature
 R —gas constant ($R = 8.13 \text{ J mol}^{-1} \text{ K}^{-1}$)
 M, M_A, M_B —molecular weight
 Z —number of collisions defined by eq. (10)
 β —factor in Eq. (10).

$$\beta = \left(\frac{d_A + d_B}{2} \right)^2 \frac{N^2}{10^6} \sqrt{8\pi RT}$$

where:

d_A, d_B —diameters of molecules undergoing collisions
 N —Avogadro's number
 β' —factor in Eq. (12)

$$\beta' = \beta e^{(-E_a/RT)}$$

c —constant for hyperbola (13).

REFERENCES

1. P. Król, B. Atamańczuk, and J. Pielichowski, *J. Appl. Polym. Sci.*, **46**, 2139 (1992).
2. A. F. Johnson and K. F. Driscoll, *Eur. Polym. J.*, **10**, 979 (1984).
3. Y. M. Lee and L. J. Lee, *Polymer*, **28**, 2304 (1987).
4. M. K. Jain, *Man-Textiles India*, **26**, 9 (1983).
5. J. J. Marcinko, A. A. Parker, Y. T. Shien, and W. M. Ritchey, *J. Polym. Sci., Part C*, **28**, 301 (1990).
6. C. M. Thompson, S. G. Taylor, and W. W. McGee, *J. Polym. Sci., Part A*, **28**, 333 (1990).
7. M. Lesar, M. Žigon, and T. Malavašić, *J. Appl. Polym. Sci.*, **47**, 805 (1993).
8. C. M. Thompson, S. G. Taylor, and W. W. McGee, *J. Polym. Sci., Part A*, **32**, 113 (1994).
9. P. Król and R. Chrzęszcz, *Polimery*, **39**, 683 (1994).
10. S. C. Chong-Shyan Chern, *J. Appl. Polym. Sci.*, **40**, 2189 (1990).
11. J. J. Tondeur, G. Vandendunghen, and M. Watelet, *Chimie Nouvelle*, **10**, 1148 (1992).
12. G. D. Tickij, P. Garkusha-Bozhko, and V. A. Savelova, *Zhurn. Organ. Khim.*, **25**, 938 (1989).
13. Park Kang Choo and Chul Kim Sung, *J. Appl. Polym. Sci.*, **39**, 639 (1990).
14. H. E. Stagg, *Analyst*, **71**, 557 (1966).
15. L. Mandasescu, A. Petrus, and I. Matei, *Revue Roumaine Chim.*, **9**(8-9) (1964).
16. P. Król and Z. Wietrzyńska-Lalak, *Eur. Polym. J.*, to appear.
17. L. Thiele, *Acta Polym.*, **30**, 323 (1979).
18. J. H. Sanders and K. C. Frisch, *High Polymers, XVII, Polyurethanes: Chemistry and Technology, Part I: Chemistry*, New York Interscience Pubs. (Div. of J. Wiley), New York, 1962.
19. Yu. S. Lipatov, *Struktura i svojstva poliuretanov*, Izd. Naucova Dumca, Kiev, 1970.
20. Y. Iwakura, H. Okada, and S. Yamashiro, *Makromol. Chem.*, **58**, 237 (1962).
21. N. M. Emanuel and D. G. Knoree, *Kinetyka chemiczna w układach jednorodnych*, PWN, Warszawa, 1983.

Received July 16, 1992

Accepted January 27, 1995