Kinetic Study of the Polycondensation of Diisocyanates with Polyols

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SYNOPSIS

On the basis of kinetic studies of noncatalyzed synthesis of carbamates in chlorobenzene solution, a kinetic model of polyurethane synthesis has been proposed. The model was built on a set of elementary, sequential–parallel reactions between functional groups of the main reagents involved in polyurethane synthesis. The assumption that reactivity of reagents did not depend of their mol wt allowed simulation of the kinetics of formation of allophanate branches for various process parameters. It has been found that the process temperature and initial ratio of reagents are of primary importance. A set of equations, describing the synthesis of linear polyurethanes, has been derived. The equations afford calculation of the degree of polymer chain branching and their application yields results similar to those obtained by the more general method based on numerical solution of the differential equations involved. Advantages resulting from the mathematical modeling of the process kinetics have been pointed out. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Addition polymerization of diisocyanates with polyols is the basic process used for synthesis of polyurethanes, which are applied for the production of polyurethane foams, elastomers, and protective coatings. The comprehension of the process kinetics allows the prediction of the polyurethane structure, the mol wt distribution, the contents of soft and hard segments of the polymer chain, and the degree of branching and crosslinking.[1,2] Moreover, the kinetics are helpful for the planning and controlling of the polymerization process.[3] Among a large number of works related to polyurethane synthesis, we have concentrated on those attempting to formulate a general model of the addition polymerization of diisocyanates with polyols.[1,4] Such a model would afford computer simulation of the polymerization process and prediction of various properties of the polymeric product (e.g., the mol wt distribution). The model describing initial steps of the polymerization process has already been proposed by Johnson and O'Driscoll.[5]

In this article, the results of kinetic studies of the addition polymerization of diisocyanates with polyols are presented. An approximate kinetic model, derived on the basis of the experimental data, is proposed and the model is verified by results of simulation calculations. This article is an initial attempt at a more comprehensive generalization of the process studied. The more complex model, which affords prediction of the polyurethane structure, is to be presented.

KINETICS OF THE POLYURETHANE SYNTHESIS PROCESS

The basic reaction involved in polyurethane synthesis is the reaction of a diisocyanate with an oligomeric diol that leads to the formation of an oligourethane (i.e., a macromolecular equivalent of carbamate):

$$R_1 - NCO + R_2OH \rightarrow R_1 - NHCOOR_2 \quad (1)$$
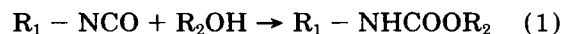
The formation of a polyurethane requires at least two functional groups in each reagent. Side reactions often accompany the polyurethane formation. These

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are: trimerization of the isocyanate component to yield an isocyanurate or dimerization to a carbodiimide and, sometimes, allophanate or biuret crosslinking. Some of the side reactions occur only in the presence of catalysts (e.g., the diisocyanate trimerization requires the Friedel–Crafts catalyst). Some other side reactions, however, such as the allophanate crosslinking, occur spontaneously at elevated temperatures.[6] The appropriate side reactions, occurring at every particular reaction condition and with every particular reagent or catalyst, have to be taken into account while designing the kinetic model.

It is well established that the reaction (1) is second order and irreversible.[7,8] However, there are many of deviations from that rule. The deviations are a result of some differences in reactivity of particular functional groups and from the autocatalytic properties of carbamates. Moreover, the polymerization rate is affected by the tendency for hydrogen bonding, which depends of the kind and polarity of the solvent used.[9,10] The rate of reaction[1] is particularly dependent on the presence of catalysts.[11–13] Medium viscosity is also an important factor in the kinetics. Phenomena, resulting from viscosity changes, can significantly limit the rate of the polymerization process.[4,14] The influence of viscosity is often observed in the systems of high gelation tendency, where a lot of crosslinking covalent bonds are formed. The kinetics of the systems crossing the gelation point have been described by Flory.[15]

Many methods of controlling the kinetics of polyurethane synthesis are known. The most popular methods rely on application of chemical or spectrophotometric methods.[16,17]

Study of highly viscous systems requires more sophisticated methods.[18] Application of calorimetric methods for that purpose, reported by Tudos and Boros-Gyevi, is an example.[19]

Exemplified kinetic data for the reaction of isocyanates with polyols are collected in Table I. It is apparent (Table I) that the reaction rate depends on the reagents structure, kind of solvent, and the ratio of the reacting functional groups. The building of a kinetic model of a chemical reaction requires specification of the effect of reagent structure on the reagent reactivity. When the chemical structure of reagents is similar, other factors, such as the reagent mol wt, has to be taken into account as well. The data in the literature available do not allow such generalizations, because most of the kinetic studies were done at conditions that were not comparable. Moreover, some of the articles report unusually high reaction rates, in spite of similar reaction conditions.[20] Therefore, we decided to reinvestigate the kinetics of reaction (1) at the conditions far from the gelation point in order to acquire comparable data. The results obtained have become the basis for further generalizations and for development of the simplest possible kinetic model.

EXPERIMENTAL
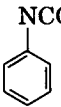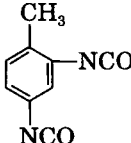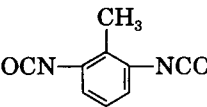
Starting Materials

Phenyl isocyanate (Merck).

Izocyn T-80 [i.e., the mixture of toluylene 2,4-diisocyanate (20% wt) and toluylene 2,6-diisocyanate (80% wt), which is equivalent to

Table I Kinetic Data for the Reaction of Diisocyanates with Polyols

Isocyanate	Polyol	P	Solvent	T [°C]	k_1 [dm^3 mol^{-1} s^{-1}]	E_a [kJ mol^{-1}]	References
C_6H_5NCO	HO-$(CH_2)_2$-OH	0.25	1,4-dioxane	35	0.91×10^{-5}	—	7
		1.00	C_6H_5Cl	50		—	9
	HO-$(CH_2)_4$-OH	0.196	1,4-dioxane	35	5.42×10^{-5}	20.0	7
		1.00	C_6H_5Cl	50	9.5×10^{-3}	—	9
	C_4H_9OH	1.00	C_6H_5Cl	45	1.17×10^{-3}	—	9
	HO-$(CH_2)_6$-OH	1.5	1,4-dioxane	35	3.07×10^{-5}	—	7
		1.00	C_6H_5Cl	50	5.2×10^{-3}	—	9
2,4-TDI	Polyoxypropylene Glycol (M.W.1000)	2.00	—	30	1.20×10^{-4}	35.0	21
				50	2.84×10^{-4}		
	Oxyethylene-Oxypropylene Glycol Adipate	1.00	Cyclohexanone	60	5.15×10^{-4}		
				80	11.84×10^{-4}	40.7	22
				100	24.91×10^{-4}		

Table II   Results of the Kinetic Studies

Isocyanate	No.	Polyol	$k_1 \times 10^4$ dm^{3}mol^{-1}s^{-1}			E_a [kJ mol^{-1}]
			60°C	80°C	100°C	
NCO (benzene ring)	1	1-Octadecanol	13.7	23.4	32.4	22
	2	DGMB	1.7	3.6	8.5	40
	3	PEG 400	2.8	6.8	15.0	43
	4	ROKOPOL D2002	0.5	1.0	2.2	35
CH$_3$ / NCO / NCO (toluene diisocyanate)	5	Ethanol	5.6	14.3	25.3	38
	6	1,4-Butanediol	9.8	19.3	26.6	26
	7	1-Octanol	7.5	18.2	38.5	39
	8	1-Decanol	6.5	15.5	36.8	48
CH$_3$ / OCN—NCO	9	1-Octadecanol	10.0	17.6	22.2	21
	10	ROKOPOL D2002	1.1	1.9	4.8	30

60% NCO groups at the position 6 and 40% at the position 4] was received from the "Zachem" Chemical Plant in Bydgoszcz and was purified by fractional distillation; fraction boiling at 150°C/20 Tr was collected.

Ethanol (pure, POCH-Gliwice).

1,4-Butanediol (Merck).

n-Octanol (Fluka).

n-Decanol (Reachim).

Diethylene glycol monobutyl ether, DGMB (Fluka).

Polyoxyethylene glycol 400, PEG 400 ("Blachownia" Chemical Plant in Kedzierzyn-Kozle).

n-Octadecanol [the fraction of fatty alcohols (bp 184–198/10 Tr), made in the Nitrogen Fertilizers Plant in Kedzierzyn-Kozle, was used instead; the fraction contained octadecyl alcohol (78%), cetyl alcohol (17%), and unsaturated C_{14} and C_{20} alcohols (about 5%)].

Polyoxypropylene glycol 2000, ROKOPOL D2002 (techn., NZPO "Organika–Rokita" in Brzeg Dolny).

Chlorobenzene (pure, POCH-Gliwice).

Procedures

The rate constants for reaction (1) were determined on the basis of the integral form of the second order kinetic equation [eq. (2)], derived on the assump-

tion of equimolar course of the reaction and equal initial concentration of the reagents:

$$\frac{C_B^0 - C_B}{C_B^0 C_B} = k_1^t \tag{2}$$

The activation energy of the reaction (1) was determined by measurement of the rate constants at different temperatures using the Arrhenius equation [eq. (3)]:

$$k_1 = k_0 \exp\left(-\frac{E}{RT}\right) \tag{3}$$

The concentration of isocyanate groups was analyzed by the standard procedure using di(n-butyl)amine; the excess of the amine was titrated with ethanolic HCl solution in the presence of bromophenol blue as an indicator.[23]

The reaction of isocyanates with polyols was carried out in a 500 cm^3 glass thermostated reactor equipped with a mechanical stirrer, condenser, and thermometer. About 50% wt solution of reagents in chlorobenzene was used for the kinetic studies.* The reactor was charged with a 1 : 1 molar ratio of isocyanate and alcohol. Initial concentration of the isocyanate component was 0.45 mol dm^{-3} when RO-KOPOL D2002 was used as the polyol component,

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* In the case of the reaction of Izocyn T-80 with 1,4-butanediol, five-fold dilution of the solution turned out to be necessary, because the polyurethane fractions with high mol wt precipitated at higher concentrations.

and 4.16 mol dm^{-3} in the case of the reaction with ethanol. Viscosity of the reaction medium did not exceed a few cP in the case of monofunctional reagents. The viscosity of the polyurethane solutions obtained from TDI and ROKOPOL D2002 was 25–40 cP at 20°C, and was dependent on the synthesis temperature. In the case of 1,4-butanediol, the viscosity was less, appropriately, due to the lower concentration of the reagents. The reaction conditions described neglected diffusion effects; it was assumed that the rate of the processes studied depended only on the kinetics of the reactions involved. The results are collected in Table II.

The carbamates formed in reactions 1, 5, 7, 8, and 9 (Table II) were precipitated from the chlorobenzene solution with hexane. After washing and drying, they formed crystalline solids. The carbamate obtained in reaction 2 (Table II) was an exception; it was a yellowish liquid with viscosity of about 50 cP.

DISCUSSION

The experimental results confirmed that the kinetic data for the reactions studied followed the second order reaction kinetics up to 60–70% conversion. At higher conversions, a slight decrease of the rate constants was usually observed, which probably resulted from influence of side reactions (i.e., formation of allophanate bonds). In some cases (i.e., in the reactions 2, 3, and 4, Table II), the rate constant started increasing after 50% conversion had been reached; this can be explained by autocatalytic effect of carbamates. When the kinetics data are analyzed, additional factors have to be taken into account as well, such as the varying number of etheric oxygen atoms in the polyol components. Those atoms are active centers for hydrogen bonding [eq. (4)].

$$-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{R_1}{|}}{N}-H\cdots\underset{\underset{R_2}{|}}{\overset{\overset{R_2}{|}}{O}} \qquad (4)$$
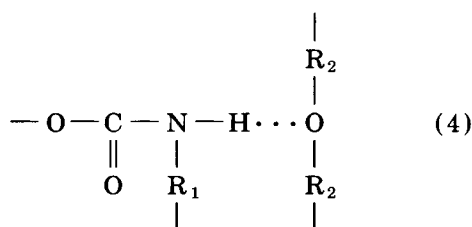
Although the structure shown [eq. (4)] is only one of the possibilities of hydrogen bonding, a large number of etheric oxygen atoms in a particular polyol may cause this bonding to dominate, which in turn may stabilize the structure of the carbamates

formed.[24] Hence, the presence of hydrogen bonding may affect the reaction kinetics. Similar reasoning was proposed to explain changes in reactivity of methylene glycols in their reaction with phenyl isocyanate.[9]

In the case of reactions 1–4 (Table II) a distinct decrease of polyol reactivity with an increase of the polyol mol wt was observed. This tendency was less marked in the other reactions. It is likely that the behavior observed was caused by apparent equalization of the reactivity of NCO groups in IZOCYN T-80, in which only 40% of the NCO groups are in the more reactive position 4 of toluylene diisocyanate.

The activation energies of the reactions studied were 20–40 kJ mol^{-1}. The activation energy depends more on the reagents' structure rather than the size of reacting molecules. For example, the reaction of phenyl isocyanate with DGMB has two times higher activation energy than the reaction of the same isocyanate with octadecanol. This cannot be explained only in terms of the different sizes of the reagents, but in terms of the structure of the carbamates formed in both cases. In particular, the tendency for hydrogen bonding was different.

On the basis of the data discussed, we assumed, as the first approximation, that under the conditions far from the gelation point, where the diffusional effects were negligible, the rate of the addition polymerization of diisocyanates with polyols did not depend on the reagent structure and that the rate could be described by the Arrhenius equation [eq. (5)].

$$\ln k = 7.0 - \frac{40}{RT} \qquad (5)$$

where k is expressed in (dm^3 mol^{-1} s^{-1}).

The preexponential factor, k_o, of the Arrhenius equation is consistent with that reported by Dorozhkin et al.[22] We have obtained the same result for reactions 2, 4, 5, 7, 9, and 10 (i.e., for most of the reactions studied). Application of the active complex theory, and the k_o value so determined, afforded the entropy of activation for the reactions studied. Equation (6) has been used for that purpose.[25]
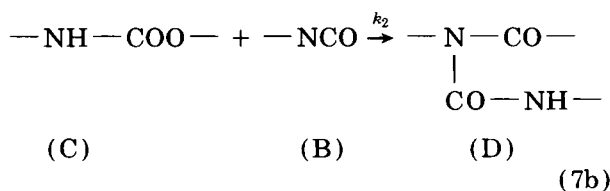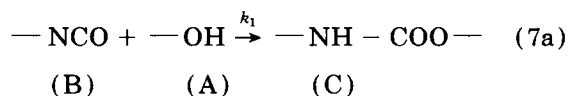
$$k_0 = \frac{ek_BT}{h} \exp\left(\frac{\Delta S_0^{\neq}}{R}\right) \qquad (6)$$

The activation entropy for reaction 5, for example, was -200 J mol^{-1} K^{-1}. In comparison, the corre-

sponding entropy at a highly viscous medium was approximately $-147 \text{ J mol}^{-1} \text{ K}^{-1}$.[18] Different values of k_o for the particular reactions studied indicate that the transient complexes for those reactions have different structures.

A SIMPLIFIED KINETIC MODEL OF THE ADDITION POLYMERIZATION OF DIISOCYANATES WITH POLYOLS

At this stage of research, we have taken into account the fundamental propagation step of the addition polymerization, as well as the possibility of allophanate branching. We have assumed that the key step in the polymerization process is the reaction between functional groups, which can be described by the model built on a sequential–parallel set of reactions [eqs. (7a) and (7b)].

$$-NCO + -OH \xrightarrow{k_1} -NH-COO- \quad (7a)$$
$$\text{(B)} \qquad \text{(A)} \qquad \text{(C)}$$

$$-NH-COO- + -NCO \xrightarrow{k_2} -N-CO- \\ \hspace{5.5cm} | \\ \hspace{5cm} CO-NH-$$
$$\text{(C)} \hspace{2cm} \text{(B)} \hspace{1.5cm} \text{(D)}$$
$$\hspace{7cm} (7b)$$

The model assumes that the reactivity of functional groups is similar. The assumption is usually met in the case of polyol component if the hydroxyl groups in the polyol are of equal order (i.e., all primary or all secondary), such as in polyoxymethylene glycol. In the case of the isocyanate component, the reactivity of NCO groups should be similar, such as in 2,6-TDI or in hexamethylene diisocyanate.

If it is assumed that reactions (7a) and (7b) follow simple, second order reactions, their rate can be described by the following equations:

$$r_1 = k_1 C_A C_B \qquad (8)$$

$$r_2 = k_2 C_B C_C \qquad (9)$$

The mass balance for a periodic reactor with ideal stirring at a constant volume leads to the following differential equations:

$$-\frac{dC_B}{dt} = k_1 C_A C_B + k_2 C_B C_C \qquad (10)$$

$$-\frac{dC_A}{dt} = k_1 C_A C_B \qquad (11)$$

$$\frac{dC_C}{dt} = k_1 C_A C_B - k_2 C_B C_C \qquad (12)$$

$$\frac{dC_D}{dt} = k_2 C_B C_C \qquad (13)$$

Technology of polyurethane production delivers initial conditions for the eqs. (10)–(13). We have assumed the following initial conditions:

$$C_B^0 = P C_A^0$$
$$C_C^0 = C_D^0 = 0 \qquad (14)$$

The examples of polyurethane technologies, subjected to computer simulation using the model described, are shown in Table III. On the basis of the results obtained (Table II), it has been assumed that the rate constant k_1 changes with temperature according to eq. (5). There were no data for the rate constant k_2, therefore, the Arrhenius equation reported in literature [eq. (15)] was assumed.[22]

$$\ln k_2 = 19 - \frac{60}{RT} \qquad (15)$$

The units used in eq. (15) are identical with those in eq. (5).

The set of differential equations, eqs. (10)–(13), has been solved by a numerical method for the processes 1, 2, and 3, using eqs. (5) and (15) and the initial conditions [eq. (14)]; the well known Runge–Kutta integration method was applied for this purpose. The following functions have been determined:

$$S = \frac{C_A^0 - C_A^0}{C_A^0} \qquad (16)$$

$$R = \frac{r_2}{r_1 + r_2} \qquad (17)$$

Plots of the functions R and S [eqs. (16) and (17)] are shown in Figure 1. The R and S plots allow prediction of the monomer conversion and the tendency for formation of branched structures at any given reaction time. Moreover, the R and S functions plotted for various reaction conditions can be used for controlling and optimization of the polyurethane production processes. For any given process (e.g., a polyurethane synthesis in the presence of an external catalyst), it is only necessary to determine appropriate kinetic parameters to apply them as input data for the model. The simulation method described may turn out to be particularly useful for processes

Table III Examples of Polyurethane Technologies

No.	Technology	Reaction Medium	T (°C)	C_A^0 (mol dm^{-3})	P	Product Application	References
1	Production of urethane-isocyanate oligomers prepolymers	Excess of the diisocyanate (e.g., 2.6 TDI)	70	0.8	7.0	Half-product for preparation of sealants, glues, and two-component lacquers	26
2	Production of polyfunctional branched allophanate-isocyanate prepolymers	—	120	0.5	10.0	Intermediate for production of foams and elastomers	27
3	Production of linear polyurethanes from bifunctional reagents	Inert solvent (e.g., chlorobenzene)	132	0.3	1.05	Impregnates for wood concrete and fabrics	28

carried out at nonisothermal conditions; the R and S functions will then describe the nonstationary state of the process and its effect on the properties of the final product.

In some cases, it is possible to get analytical functions for C_A and C_B by analytical solutions of the differential eqs. (10)–(13). Then, however, additional simplifying assumptions are necessary. For example, in some addition polymerization processes studied, only a small portion of urethane groups were converted to allophanate compounds, which was evidenced by a small content (less than a few percent) of tertiary nitrogen atoms in the polymer. In the case of the polyurethane synthesized by a two-step method from 2,4-TDI, 2,6-TDI, polyoxypropylene glycol, and the oligomeric diol obtained by oxyethylation of BISPHENOL A, for instance, the amount

of allophanate nitrogen atoms did not exceed 10%.[29] The following relationships between concentrations of functional groups can then be assumed:

$$C_B = (1 - \alpha)[C_B^0 - (C_A^0 - C_A)] \qquad (18)$$

$$C_A = C_A^0 - [(1 - \alpha)(C_B^0 - C_B)] \qquad (19)$$

$$C_C = (1 - \alpha)(C_B^0 - C_B) \qquad (20)$$

The coefficient α in eqs. (18)–(20) represents the fraction of the isocyanate groups that reacted to allophanates. In general, α is a function of time, which usually is not explicit. At the first approximation, we have assumed α to be constant and we have determined an average amount of the allophanate groups in the polymer, which yielded $\alpha = 0.05$.
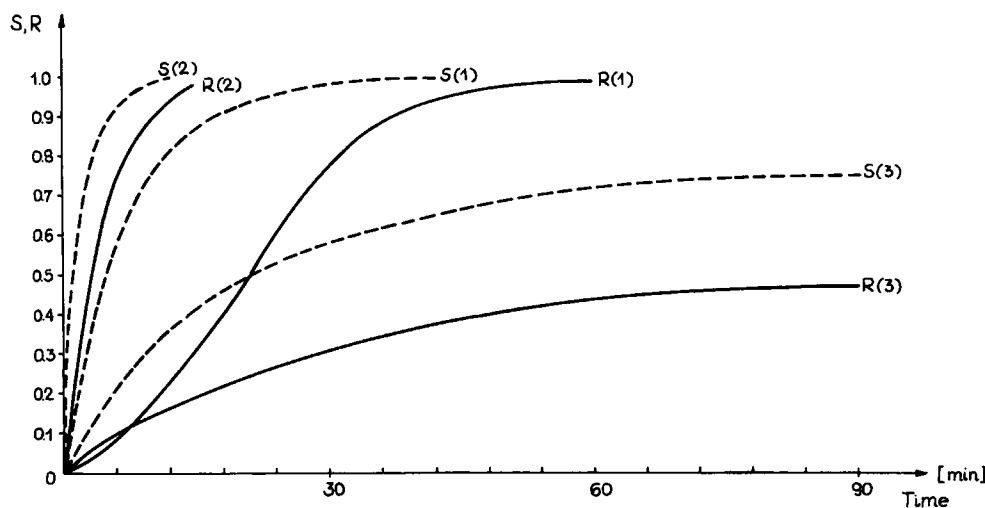

Figure 1 Plots of the S and R functions for processes 1–3.

Table IV   Simulation Results for the Synthesis of Linear Polyurethanes

	Analytical Method					Numerical Method				
(Min)	C_A (mol dm^{-3})	C_B (mol dm^{-3})	C_C (mol dm^{-3})	S	R	C_A (mol dm^{-3})	C_B (mol dm^{-3})	C_C (mol dm^{-3})	S	R
0	1.500	1.650	0.000	0.000	0.000	1.500	1.650	0.000	0.000	0.000
15	1.024	1.148	0.477	0.317	0.026	1.021	1.165	0.474	0.319	0.026
30	0.769	0.879	0.733	0.487	0.052	0.753	0.886	0.732	0.499	0.053
45	0.611	0.711	0.892	0.593	0.078	0.591	0.714	0.881	0.606	0.079
60	0.503	0.596	1.001	0.665	0.103	0.492	0.605	0.970	0.672	0.102
75	0.425	0.513	1.080	0.717	0.128	0.421	0.524	1.032	0.719	0.124
90	0.366	0.450	1.140	0.756	0.153	0.363	0.467	1.081	0.758	0.147
105	0.319	0.400	1.188	0.787	0.177	0.319	0.405	1.117	0.787	0.169
120	0.282	0.360	1.226	0.812	0.201	0.286	0.365	1.143	0.809	0.188

The analytical solution of eqs. (10)–(13), using the assumptions (18)–(20) and the initial conditions (14), afforded the following functions for C_A and C_B:*

C_A

$$= \frac{C_A^0(P-1)\exp[-C_A^0(P-1)(1-\alpha)k_1 t]}{P - \exp[-C_A^0(P-1)(1-\alpha)k_1 t]} \quad (21)$$

$$C_B = \frac{\exp(-bt)}{\frac{a}{b}[1-\exp(-bt)] + \frac{1}{C_B^0}} \quad (22)$$

where:

$$a = (1-\alpha)(k_1 - k_2) \quad (23)$$

$$b = k_1 C_A^0 - (k_1 - k_2)(1-\alpha)C_B^0 \quad (24)$$

Next, eqs. (21) and (22) were used for calculation of the R and S functions according to eqs. (16) and (17). The calculation results are summarized in Table IV. It is evident from Table IV that the simulation of the linear polyurethane synthesis at a slight excess of NCO groups ($P = 1.1$, 60°C), by the numerical integration method or by the analytical solution, yield similar results. Hence, in some cases, it may be more convenient to apply analytical eqs. (21)–(24) instead of the numerical integration of eqs. (18)–(20).

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* Equations (10)–(11) were solved for $P > 1$. Hence, Eqs. (21)–(24) can be applied only for the processes occurring at an initial excess of the isocyanate component.

CONCLUSIONS

It can be concluded from the data presented in this article that simulation calculations may prove useful in polyurethane technology. Even a simple kinetic model affords a set of analyses of the process studied. A significant limitation of the model described is the assumption that the addition polymerization occurs essentially between the functional groups, which leads to far-reaching generalizations that are sometimes difficult to rationalize in terms of the kinetic data. Our model does not allow simulation of the kinetics of carbamate formation that becomes more and more complex with conversion. However, the model is useful for analysis of the synthesis of linear polyurethanes, in which allophanate branching has to be controlled.

The experimental data obtained indicate that kinetics of the reaction of isocyanates with polyols depends on the reagent's structure. There is no direct relationship between the reaction kinetics and the size of the carbamates formed. A significant influence on the reaction kinetics is exerted by such factors as the tendency for formation of hydrogen bonds or the presence of etheric oxygen atoms in the carbamate molecule. The experimental data allow some generalizations, which will be helpful for development of a more complex kinetic model of the addition polymerization process by supplementing our model with additional elementary reactions. The more sophisticated model should allow prediction of various molecular parameters of polyurethane products, such as mol wt, mol wt distribution, or degree of branching. Such information is necessary both for the initial steps of technology development and upscaling of the technology from a laboratory

scale to an industrial plant. For example, the kinetic model may be helpful for the selection of an appropriate reactor in function of the product developed.

NOTATION

r_1	rate of reaction (7a)
r_2	rate of reaction (7b)
k_1	rate of carbamate formation by reaction (1) or (7a)
k_2	rate of allophanate formation by reaction (7b)
$C_A, C_B,$ C_C, C_D	instantaneous concentrations of hydroxyl, isocyanate, urethane and allphanate groups, respectively
$C_A^0, C_B^0,$ C_C^0, C_D^0	initial concentrations of hydroxyl, isocyanate, urethane, and allophanate groups, respectively
k_0	preexponential factor of the Arrhenius equation for the formation of carbamate [eq. (3)]
T	temperature
R	gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
e	the base of natural logarithm ($e = 2.718 \cdots$)
h	Planck constant ($h = 6.63 \times 10^{-34} \text{ J s}$)
k_B	Boltzman constant ($k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$)
$\Delta S_0^{\neq}$	activation entropy [eq. (6)]
E_a	activation energy
S	conversion of hydroxyl groups
R	probability of branching of the polymer chain
α	empirical coefficient,
t	time
P	concentration ratio (C_B^0/C_A^0)

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