Kinetic Study on the Reaction of 2,4- and 2,6-Tolylene Diisocyanate with 1-Butanol in the Presence of Styrene, as a Model Reaction for the Process that Yields Interpenetrating Polyurethane–Polyester Networks

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ABSTRACT: A classical method was utilized for determination of free isocyanates to study the kinetics of a model reaction of 2,4- and 2,6-tolylene diisocyanate (TDI) with 1-butanol, which was run in the reaction medium of liquid aliphatic hydrocarbons. Such conditions made it possible to find rate constants and activation energy values for the second-order reactions under isothermal conditions. Those reactions can be employed to produce isocyanate prepolymers, which make intermediates for downstream polyurethanes. The findings are commented upon against the background of earlier kinetic data that can widely be found in the research reports published. Further, part of our work utilized the findings to provide interpretation of kinetic parameters for analogous reactions, the kinetic data being found in the presence of styrene—the monomer employed when producing polyurethane–polyester interpenetrating polymer network (IPN) systems. The hypothesis was put forward that styrene and isocyanate component(s) could react at the final stages of the process when the system becomes short in the hydroxyl substrate. That hypothesis was based on disturbances observed in the reactivity of —NCO groups (in 2,4-TDI) in the reaction system studied. The rate constants and activation energy values were determined and presented for the urethanization reaction of 1-butanol. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 327–336, 2003

INTRODUCTION

From the formal point of view, interpenetrating polymer networks (IPN) are mixtures of two or more polymers, at least one of them having been polymerized or having been crosslinked in the presence of other components. The idea is that the polymer chains with different hydrophobic performance must interpenetrate each other. That makes it possible to produce new materials with macroscopically homogeneous structures that are to some extent analogous with solid solutions of low molecular weight compounds. The supermolecular structure of this type of polymer does not necessarily have to be so homogeneous. We deal with examples of thermodynamically immiscible systems at that level— phase separation is usually observed, then, which results from heterogeneity of polymeric structures that form IPNs, e.g., polyolefines and polyacrylates or polyurethanes and epoxy resins. Hence, the physical-mechanical properties of such multicomponent systems must be dependent on morphology of polymeric structures that form the systems. Said morphology, on the other hand, results from the processes employed to produce those materials, i.e., both the polymerization method adopted and the final product molding technique.[1]

One of the methods applicable to the synthesis of IPNs is the polymerization of a few monomers in a solvent. The polymerization processes must follow different mechanisms, e.g., chain-type free-radical copolymerization of styrene and unsaturated polyester resin with simultaneous step-growth polyaddition of urethane–isocyanate oligomers and diols. Styrene is employed in that case as a solvent that homogenizes the reaction system.[2]

It is therefore important to learn the kinetics for the reactions of isocyanates and polyols in the presence of styrene. We found it advisable to study the kinetics for the reaction of mixed 2,4- and 2,6-tolylene diisocyanate (TDI) isomers with a selected alcohol, 1-butanol in this case. That reaction was dealt with as a model reaction for step-growth polyaddition of those diisocyanates with oligodiols that have primary —OH end groups, which proceeded just in the presence of styrene. Thus, the purpose of our investigations was to find the kinetic parameters for the above-mentioned reactions vs styrene concentrations. The collected data would then be compared to the information previ-

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TABLE I
Kinetic Parameters for the Reaction of Phenyl Isocyanate or TDI and Hydroxyl Compounds

Isocyanate	Hydroxyl compound	Temp (°C)	Solvent	$k_{\mathrm{exp}} \cdot 10^4$ ($\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$)	E_a ($\mathrm{kJ\ mol}^{-1}$)	Ref.
C_6H_5NCO	1, 4-Ethanediol	35	1,4-Dioxane	0.091	—	3
	1,4-Butanediol	35	1,4-Dioxane	0.542	20	3
		50	Chlorobenzene	95.0		4
	1,4-Hexanediol	35	1,4-Dioxane	30.7	—	3
		50	Chlorobenzene	52.0	—	4
	1-Butanol	45	Chlorobenzene	117	—	4
	1-Hexanol	40	Chlorobenzene	7.94	34	6
		60		16.92		
		80		35.05		
	1-Octanol	60	chlorobenzene	10.89	32	6
		80		28.07		
		100		44.35		
	Suberin[a]	23	THF (catal. DBTL)	16.3	18.7	7
		35		22.8		
		45		27.5		
TDI	Ethanol	60	Chlorobenzene	5.59	38	6
		80		14.27		
	1-Hexanol	60	Chlorobenzene	6.08	39	
		80		13.05		
		100		27.77		
	1-Octanol	40	Chlorobenzene	3.28	39	
		60		7.51		
		80		18.21		
	1-Decanol	60	Chlorobenzene	6.47	48	
		80		15.49		
		100		36.84		
	Oligo(oxy-propylene-adipate)	60	Cycloheksanone	5.15	40.7	5
		80		11.84		
		100		24.91		
2,4-TDI	Suberin[a]	23	THF (catal. DBTL)	2.1 and 18.1	—	7
2,6-TDI				1.4 and 11.1[b]	—	

[a] Suberin: polyester-diol type macromonomer with 16–24 carbon atoms.

[b] The figures refer to the substitution effect and not reactivity of ±—NCO groups in 2,6-TDI.

ously published elsewhere for reactions carried out in different media.

The questions of catalysis and kinetics of the reaction between diisocyanates and polyols have been the point of interest for numerous researchers.[3–7] Their efforts were focused principally on finding kinetic parameters for the reactions of various mono- and diisocyanates with alcohols and diols in selected solvent systems. The solvents were inert materials like chlorobenzene, tetrahydrofurane (THF), or 1,4-dioxane (Table I). The following kinetic model was adopted for those investigations:

$$-\frac{d[\mathrm{NCO}]}{dt} = k_{\mathrm{exp}}\,[\mathrm{NCO}] \cdot [\mathrm{OH}] \qquad (1)$$

where [NCO] is the momentary concentration of free isocyanate groups, [OH] the momentary concentration of free hydroxyl groups, k_{exp} the experimental rate constant for the second-order reaction, and t the reaction time;

A number of research reports covered diisocyanates wherein —NCO groups are considered chemically equivalent (2,6-TDI, MDI (4,4-methylenebis (phenyl isocyanate))/(1,6-diisocyanatohexane), HDI). Kinetics was also studied for the reactions that involved the 2,4-TDI isomer in which — NCO groups offer different reactivity features.[8–11] Reactivity of the —NCO group at position 4 in that compound was found to be 1.2–5 times higher than that for the —NCO group on location 4, depending on the reaction conditions.[7,10,12] Moreover, it is always the case for diisocyanates, and in particular aromatic diisocyanates, that a substitution effect should be expected that will be responsible for lower activity of, for example, toluylene-2-isocyanate-6-carbamate in its reaction with an alcohol, as compared to that for the initial monomer—2,6-TDI. That effect is negligible in practice in such aromatic diisocyanates as MDI and NDI. In case of 2,4- and 2,6-TDI, however, it results in inferior activity of the "second" substituent group, which can be lower 2–5 times.[7,12] In case of monomers that contain three

—NCO groups in a molecule—for example, isocyanurate trimers of 2,4-TDI—the situation becomes even more complicated, which leads to considerable diversification of the chemical composition of polyurethane mixtures. That impacts, then, the reactivity specifications of those mixtures, which is critical, for example, in their hardening and/or crosslinking processes.

The findings from the kinetic studies were utilized when developing the kinetic model of the polyaddition process of those monomers. The model would make it possible to optimize the manufacturing process for polyurethane plastics.[12–14] From among the latest studies on that subject, we refer to the findings of N. Corderio et al.,[7] who investigated the kinetics for the reactions of various isocyanates with the oligoester compound that contained secondary —OH groups within its molecule. Table I presents also the kinetic parameters for the second-order reaction of that macromonomer and phenyl isocyanate with TDI. The parameters were determined in the presence of dibutyltin dilaurate (IV) (DBTL), at ambient temperature (23°C) and in the THF solvent. Although the findings for the mono-isocyanate conform to those published earlier by other researchers, the quoted authors specify the data for both TDI isomers, which differ considerably from each other. For example, the ratio of reactivities for both —NCO groups in 2,4-TDI was found to reach 8.6 while the reactivity for the —NCO groups in 2,6-TDI was supposed to be equal to that for the group at position 2 in 2,6-TDI ($k \approx 15 \cdot 10^{-4}$) and the substitution effect in the 2,6-isomer was close to 10.[7] We estimated those values in our earlier papers to be about 1.5 and 2–4, respectively.[12,13] We found it necessary to refer to that problem again in this article. The above information shows that the problem of reactivity of isocyanates in their reactions with the compounds that contain unstable hydrogen atoms—the fundamental issue for the polyurethane production processes—still causes controversy. The problem becomes even more complicated when one considers (which is indispensable) the effects from catalysts and solvents.

The investigations carried out in a few solvents with different polarities, from $\epsilon = 2.2$ for decalin to $\epsilon = 49.0$ for dimethyl sulfoxide, made it possible to correlate the rate constants of that reaction and the dielectric constants of the solvents employed. The Kirkwood equation was used for that purpose[15]:

$$\ln k = \ln k_0 - A \cdot \frac{\varepsilon - 1}{2 \cdot \varepsilon + 1} \tag{2}$$

where ϵ is the dielectric constant of the solvent used, k the rate constant of the reaction studied, k_0 the rate constant for the reaction proceeding in a solvent with $\epsilon = 1$, and A the constant value dependent on the temperature, on the Boltzmann constant, on the dipole moment of the solvent used, and on the Loschmidt number $N_L = 2.68 \cdot 10^{19}\ \mathrm{cm}^{-3}$.

The effect from polarity of solvent(s) on the kinetics of the reaction between diisocyanates and alcohols was assumed to result from the polar structure of the transient active complex formed. One can expect that in case of styrene, i.e., the solvent that has not been considered in the above study, the problem will become additionally complicated due to possible homopolymerization of that monomer. Polymerization can be prevented by adding adequate inhibitor for radical-type polymerization. Still, one should give consideration to potentially possible homocyclization reactions of isocyanate groups or to the reaction of those groups with the vinyl group of styrene, which will take place at temperatures above 120°C.[16]

It is necessary, moreover, for the proper interpretation of findings from kinetic studies to determine the catalytic activity of both external catalysts and autocatalytic urethane groups. One may assume in the most general approach that the rate of polyaddition reaction, as measured by reducing content of free —NCO groups, is dependent on the concentration of both acid and alkaline catalysts and on other compounds introduced to the process—for example, tertiary amines [1,4-diazabicyclo-(2,2,2)-octane] (DABCO), or organometallic compounds of Sn, Pb, or rather rarely Fe, e.g., highly active DBTL mentioned above. The last group affects the rate of formation of an active complex between isocyanate and suitable catalyst molecules. The contribution from the catalysts to the rate of the reaction considered can be presented by the general equation[17]:

$$\begin{aligned}\frac{d[\mathrm{NCO}]}{dt} = \frac{d[\mathrm{OH}]}{dt} = \\ - k_{\mathrm{OH}}\,[\mathrm{NCO}] \cdot [\mathrm{OH}]^2 - \eta \cdot k_{\mathrm{COOH}}[\mathrm{COOH}] \cdot \\ [\mathrm{NCO}] \cdot [\mathrm{OH}] - \eta \cdot k_{\mathrm{C}} \cdot [\mathrm{C}] \cdot [\mathrm{NCO}] \cdot [\mathrm{OH}]\end{aligned} \tag{3}$$

where k_{OH} is the total rate constant affected by the formation of a complex structure by the —NCO and —OH groups, by the reaction of that complex with diol, etc.; k_{COOH} the total rate constant dependent on the formation of a complex structure by a proton and —NCO, and on the reaction of that complex with diol; k_{C} the total rate constant influenced by the formation of a complex structure by —NCO and catalyst, and by the reaction of that complex with diol, etc.; and η the efficiency factor for the catalyst employed ($0 \leq \eta \leq 1$).

Having considered the above aspects, we restricted our research to only one system of reacting substances that were interesting to us: —TDI and 1-butanol. That reaction was carried out with no external catalyst, in solutions—in volatile aliphatic hydrocarbons and styrene at the concentrations of 25–75% as per the parent substances present in the system. In order to be able to control the reaction temperature and refer the values found for the constant k_{exp} to a precisely defined temperature, the measurements were taken at the boiling point of the reaction mixture. Adequate volumes of one of the low boiling aliphatic hydrocarbons (pentane, hexane, or 2,2-dimethylbutane) were additionally introduced for that purpose. Those components were understood as completely inert. We could precisely run the exothermic reaction of TDI and 1-butanol under isothermal conditions in that way. Moreover, our findings could be referred to the temperature employed by us for a two-stage production process of polyurethane–polyester IPN systems, said systems being synthesized by mixing two process solutions: a solution of unsaturated polyester resin in styrene and polyurethane synthesized in this solvent by extending isocyanate prepolymers with various polyols.[2]

EXPERIMENTAL

Employed Reagents

Tolylene Diisocyanate

A reagent from Aldrich was used, which was a mixture of 2,4- and 2,6-TDI isomers at the ratio of 80 and 20%, respectively (boiling point 121°C, $p = 10$ mm Hg).

Styrene

Producer: Allied Signal Riedel-de Haën (Germany)
Boiling point: 144–146°C
Purity: 99%
Stabilized with 4-*tert*-butylpyrocatechol

1-Butanol

Producer: CHEMPUR, Piekary Śląskie (Poland)
Boiling point: 117.7°C
Purity: 99.5
water content: 0.1%
After distillation, 1-butanol should be stored with molecular sieve (Zeolite 4A)

Pentane

Producer: POCh S.A., Gliwice (Poland)
Boiling point: 35.5°C
Purity: 99.5%
Water content: 0.1

Hexane

Producer: POCh S.A., Gliwice (Poland)
Boiling point: 69°C
Purity: 99%
Water content: < 0.02

2,2-Dimethylbutane (DMB)

Producer: Aldrich
Boiling point: 50°C
purity: 99%

Analytical Reagents

Dibutylamine, 99% (Merck), 0.5*N* solution in chlorobenzene
Chlorobenzene, pure (POCh S.A., Gliwice)
Methanol, pure (POCh S.A., Gliwice)
Weighed samples of hydrochloric acid, analytically pure (POCh S.A., Gliwice)
Bromophenol blue, (POCh S.A., Gliwice)

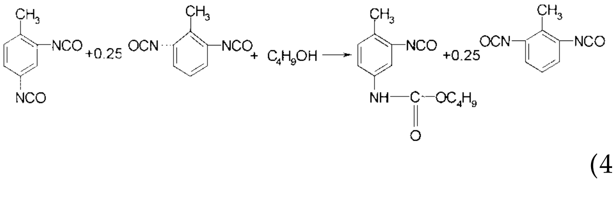
Methods for Kinetic Studies

The urethanization process of 1-butanol with TDI was carried out in a 50 cm^3 glass reactor provided with a reflux condenser, magnetic agitator, and sampling probe. After charging the reacting substances—TDI and alcohol—and solvent(s) (aliphatic hydrocarbon and/or styrene), nitrogen was passed over the liquid level to prevent any access of ambient moisture. Initially, the reaction was run at a few different concentrations of the reaction solution; the concentration was then fixed at 50 wt % (Table II).

Having regarded different reactivities of —NCO groups in both TDI isomers as well as their contents in TDI employed in our tests, the urethanization reaction was organized in two stages:

Stage I

1-Butanol was introduced to TDI and a selected mixture of solvents; the volume of the former was adjusted to reach the initial molar ratio $[\text{NCO}]_o : [\text{OH}]_o$ of 2.5 : 1. The addition process was run at constant temperature (at boiling point of the reaction mixture) until the concentration for —NCO groups was reached, which had been calculated from stoichiometry. Complete conversion was assumed for more reactive —NCO groups at position 4 in 2,4-TDI, as presented by the equation below:



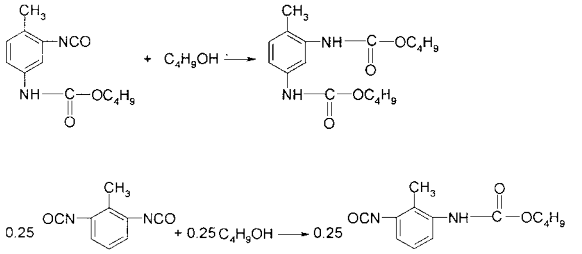
(4)

TABLE II
Rate Constants for the Reaction of TDI and 1-Butanol, Taking Place in Solutions—in Aliphatic Hydrocarbons with Styrene Added

Reaction no./no. of process stage	Type of aliphatic HC	Styrene-to-HC ratio (wt %)	Conc. of reaction solution (wt %)	Reaction temp. (°C)	$k_{exp} \cdot 10^4$ ($dm^3\ mol^{-1}\ s^{-1}$)	Linear correlation factor for Eq. (8)
1/I	Pentane	0	25	36	1.73	0.9898
2/I			50	36.5	3.52	0.9777
3/I			75	40	3.73	0.9823
1/II			25	36.5	0.86	0.9765
2/II			50	38	1.27	0.9985
3/II			75	52	2.97	0.9989
4/I	Hexane	0	25	66	16.2	0.9922
5/I			50	70.5	10.8	0.9999
6/I			75	75.5	40.8	0.9832
4/II			25	65	5.37	0.9837
5/II			50	70.5	4.27	0.9981
6/II			75	77	9.49	0.9981
7/I ≡ 2/I	Pentane	0	50	36.5	3.52	0.9777
8/I	DMB			52	7.19	0.9926
9/I	Hexane			70.5	10.8	0.9999
7/II = 2/II	Pentane			38	1.27	0.9985
8/II	DMB			51	4.28	0.9946
9/II	Hexane			70.5	4.27	0.9981
10/I	Pentane	1.00	50	50	4.15	0.9773
11/I	DMB			66	5.06	0.9745
12/I	Hexane			81	19.7	0.9675
10/II	Pentane			52.5	4.13	0.9981
11/II	DMB			64	5.71	0.9918
12/II	Hexane			83	43.9	0.9412
13/I	Pentane	0.45	50	43.5	3.84	0.9781
14/I		1.00		50	4.15	0.9773
15/I		1.64		62	12.6	0.9949
13/II		0.46		48.5	2.06	0.9977
14/II		1.00		52.5	4.13	0.9981
15/II		1.64		73.5	16.9	0.9923

Stage II

At the second stage, 1-butanol was added to the mixture obtained from Stage I and the volume was controlled to obtain the initial ratio $[NCO]_o : [OH]_o$ of 1.2 : 1, and adequate volume of solvent(s) was supplemented as well to maintain the assumed concentration of the reaction solution.



(5)

The initial concentrations of $[NCO]_0$ and $[OH]_0$ were calculated from the assumed amounts of parent substances. When the amounts of substrates followed the stoichiometric ratio as above, that certainly did not guarantee that the above reaction would proceed quantitatively exactly according to that model. Still, we could control in that way the process studied and to impose the required route to a considerable degree. The reaction mixture was sampled at predefined intervals and known volumes of dibutylamine were immediately added to samples to stop urethanization of butanol. Then, dibutylamine, which had not reacted with diisocyanate, was titrated by means of alcoholic HCl (to bromophenol blue indicator) to find the concentrations of —NCO groups that had not reacted with alcohol. The method required an earlier blank sample, i.e., determination of the volume of HCl solution needed to titrate the volume of amine introduced.[18]

The reactions studied in succession, referred to as Stage I and Stage II, respectively, are presented in Table II. As can be seen, the type of aliphatic hydrocarbon employed clearly defines the reaction temperature. Reactions 1–6 were run at a few selected concentrations of the reaction solution, while the concentration of 50 wt % was adopted for further reactions.

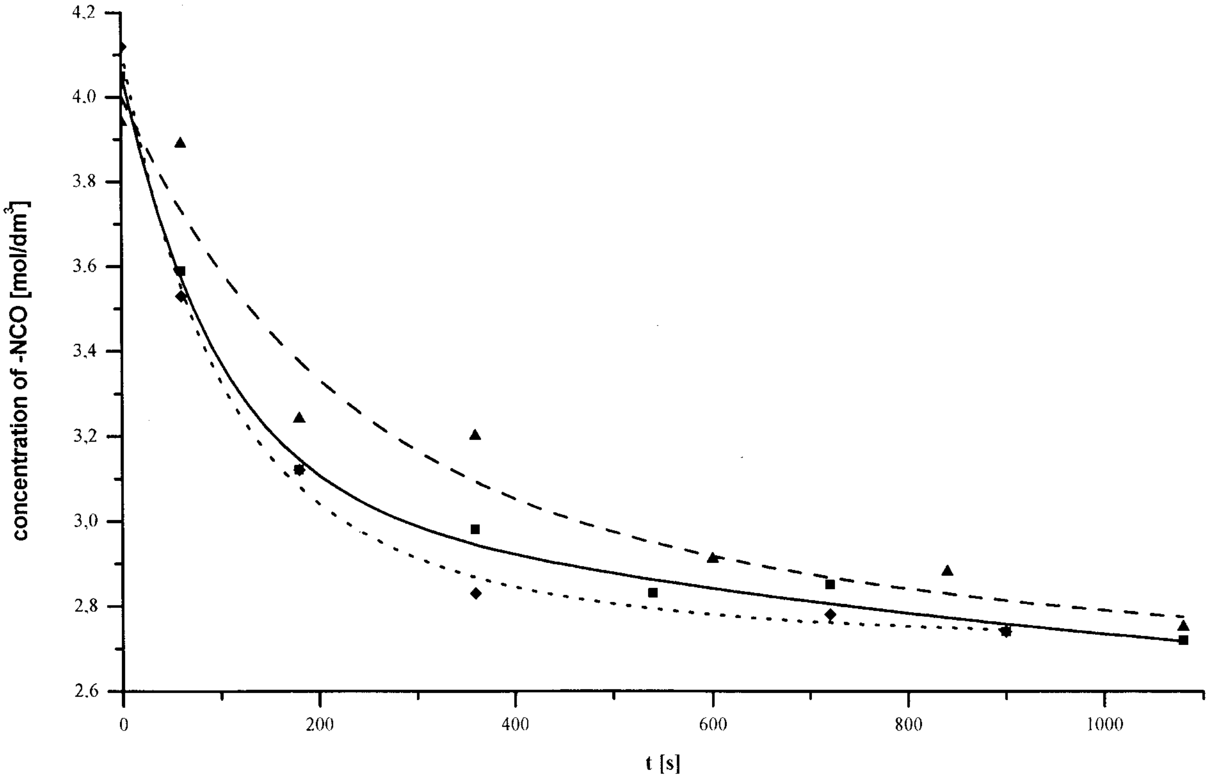


Figure 1 Concentration profiles for —NCO groups over the reaction time for TDI + 1-butanol in the medium composed of pentane and styrene (reactions 13/I, 14/I, and 15/I as per Table II). Concentration of process solution: 50 wt %. (□)T = 45°C; solvent: mixture 31% styrene and 62% pentane. (■) T = 50°C; solvent: mixture 50% styrene and 50% pentane. (◆) T = 59°C; solvent: mixture 62% styrene and 38% pentane.

The findings were analyzed on the basis of eq. (1), which describes the concentration profile for isocyanate in a batch reactor with constant volume and perfect mixing of reacting substances. In order to solve analytically that equation, the concentration of hydroxyl groups was expressed as follows:

$$[\mathrm{OH}]_{(t)} = [\mathrm{OH}]_0 - [\mathrm{OH}]_p = [\mathrm{OH}]_0 - ([\mathrm{NCO}]_0 - [\mathrm{NCO}]) = [\mathrm{NCO}]_0(1/\mathrm{r} - 1) + [\mathrm{NCO}] \qquad (6)$$

where r is $[\mathrm{NCO}]_0 : [\mathrm{OH}]_0$, the ratio of the initial concentrations of the functional groups. After solving analytically the differential eq. (1), and having considered the relation (6), we arrived at the following function, which describes the concentration profile for —NCO groups during the process:

$$[\mathrm{NCO}]_{(t)} = \frac{(1 - 1/r)[\mathrm{NCO}]_0\, e^{-(1/r-1)[\mathrm{NCO}]_0 k_{\mathrm{exp}} t}}{e^{-(1/r-1)[\mathrm{NCO}]_0 k_{\mathrm{exp}} t} - 1/\mathrm{r}} \qquad (7)$$

To provide an example, Figures 1 and 2 present the experimental charts for function (7) for some selected reactions. The rate constant k_{exp} was found from the integral form of the kinetic equation for a second-order reaction. Due consideration was given to different initial concentrations of substrates for which the notation made it possible to present every concentration as a linear profile:

$$\mathrm{W} = \mathrm{B}\cdot\mathrm{t} \qquad (8)$$

where W and B are alegebraic expressions, and where

$$W = \log \frac{([\mathrm{NCO}]_0\,(1/r - 1) + [\mathrm{NCO}]) \cdot r}{[\mathrm{NCO}]} \qquad (9)$$

$$B = \frac{[\mathrm{NCO}]_0\,(1/r)}{2.303} \cdot k_{\mathrm{exp}} \qquad (10)$$

Based on the experimental momentary concentrations o of —NCO groups, the values for W were each time calculated, which corresponded to the time of sampling, and then the least squares method was employed to find the values for B, and—from equation (10)—rate constants k_{exp} could be calculated for the reactions studied. Figures 3 and 4 illustrate the exemplary graphs for eq. (8) for the reactions of Stage I and Stage II, respectively. High values of linear correlation coefficients for the obtained dependencies confirm the conclusion learned from earlier investigations that urethanization of alcohols with isocyanates is a second-order reaction.[19] The rate constants obtained by

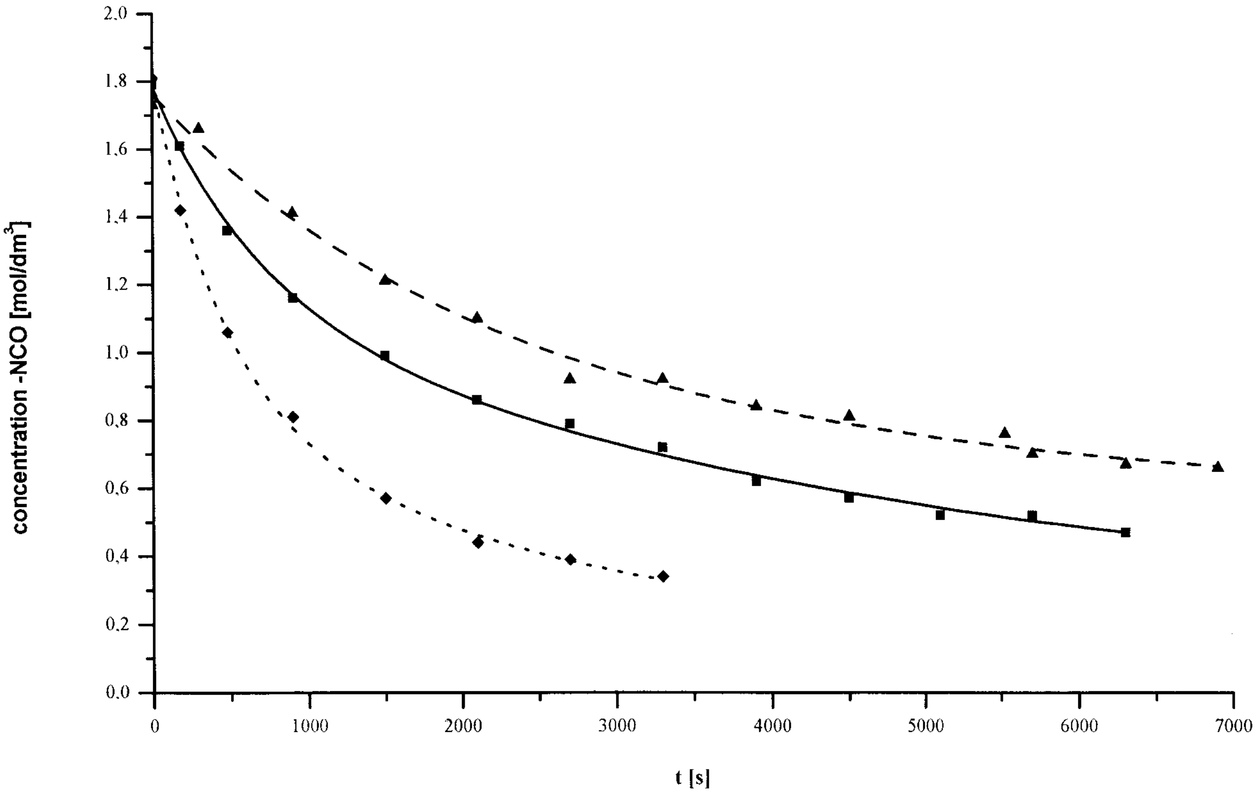


Figure 2 Concentration profiles for —NCO groups over the reaction time for butyl 2-isocyanate-4-toluylenecarbamate and 2,6-TDI + 1-butanol in the medium composed of pentane and styrene (reactions 13/II, 14/II, and 15/II as per Table II). Concentration of process solution: 50 wt %.(▲) $T = 48.5°C$; solvent : mixture 31% styrene and 62% pentane. (■) $T = 52.5°C$; solvent: mixture 50% styrene and 50% pentane. (◆) $T = 73°C$; solvent: mixture 62% styrene and 38% pentane.

that method for the reactions studied are presented in Table II together with linear correlation coefficients for the straight lines employed to arrive at the values k_{exp} reported. The diagrams were plotted on the basis of 6–10 experimental points, after their statistical verification. The ratio of rate constant for the reaction of —NCO groups substituted at position 4 in 2,4-TDI with 1-butanol (stage I) (k_I) and rate constant for the reaction of —NCO groups substituted at position 2 in 2,4- and 2,6-TDI (Stage II) (k_{II}) as calculated from the above data has been provided in Table III.

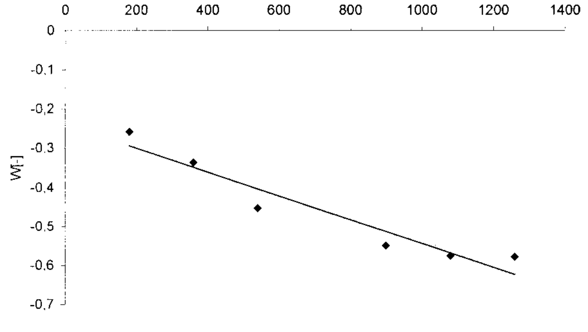


Figure 3 Profile for linear function (8) for the reaction of TDI and 1-butanol in the medium composed of pentane and styrene (reaction 14/I).

The activation energy for noncatalyzed reactions of TDI and 1-butanol that take place at both stages was found graphically on the basis of the Arrhenius equation:

$$\ln k = -\frac{E}{RT} + \ln A \qquad (11)$$

where T is the temperature, R the 8.314 J mol^{-1} K^{-1} universal gas constant, and A the frequency factor.

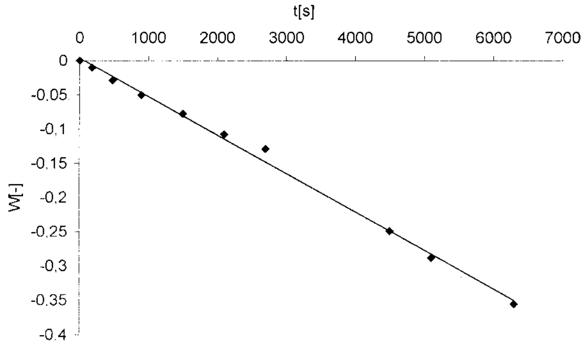


Figure 4 Profile for linear function (8) for the reaction of butyl 2-isocyanate-4-toluylenecarbamate and 2,6-TDI + 1-butanol in the medium composed of pentane and styrene (reaction 14/II).

TABLE III
Kinetic Parameters for the Reaction of TDI and 1-Butanol, Taking Place in Solutions—in Aliphatic Hydrocarbons with Styrene Added (Concentration of Process Solution = 50 wt %)

Type of solvent	Reaction temperature (°C)		$\ln k_{\text{exp}}$			Slope—linear correlation factor for eq. (11)		E_a (kJ mol^{-1})	
	Stage I	Stage II	Stage I	Stage II	$k_{\text{I}}/k_{\text{II}}$	Stage I	Stage II	Stage I	Stage II
Pentane	36.5	38	−7.95	−8.97	2.78	$-3.50 \cdot 10^3$	$-3.83 \cdot 10^3$	29.1	31.8
DMB	52	51	−7.24	−7.75	1.68	0.9883	0.8210		
Hexane	70.5	70.5	−6.83	−7.76	2.53				
50 % Mixture:									
(pentane + styrene)	50	52.5	−7.79	−7.75	1.00	$-5.62 \cdot 10^3$	$-9.24 \cdot 10^3$	46.7	76.8
						0.9255	0.9477		
50 % Mixture:									
(DMB + styrene)	66	64	−7.50	−7.47	0.89				
50 % Mixture:									
(hexane + styrene)	81	83	−6.23	−5.42	0.45				
Mixture:									
69 % pentane and 31 % styrene	43.5	48.5	−7.86	−8.48	1.86	$-8.31 \cdot 10^3$	$-8.98 \cdot 10^3$	69.1	75.6
						0.9255	0.9842		
50 % Mixture:									
(pentane + styrene)	50	52.5	−7.79	−7.75	1.00				
Mixture:									
38 % pentane and 62 % styrene	62	73.5	−6.68	−6.38	0.75				

Diagrams for eq. (11) were plotted on the basis of measurements of rate constants taken at three temperatures—those three temperatures resulted from the use of different hydrogen solvents. The data utilized in calculations and the results can be found in Table III. The study focused primarily on the effect of styrene on the activation energy values found.

RESULTS AND DISCUSSION

It seems necessary to start the discussion by referring to the findings of earlier kinetic studies of the urethanization reaction of hydroxyl compounds with diisocyanate feedstocks (most commonly used in the polyurethane manufacturing processes), i.e., 2,4- and 2,6-TDI isomers, which are present in commercial feedstocks at 80 and 20 wt %, respectively. The previously published reports show that the rate of any noncatalyzed urethanization reaction of any alcohol, diol, or polyol with those diisocyanates can be characterized within the temperatures of 50–80°C—the most frequently used temperatures in the production of isocyanate prepolymers—by the rate constant values k_{exp} within 5–15 dm^3 mol^{-1} s^{-1} and activation energy values within 20–40 kJ mol^{-1}. Those figures are also confirmed by the findings from the kinetic study that involved a model aromatic monoisocyanate—phenyl isocyanate.[3–7] Individual values for kinetic parameters, however, are dependent on the structure of the hydroxyl substrates, the order of their —OH groups, and other (apart from temperature) reaction conditions, e.g., type of reaction medium and in particular polarity of the solvent used.

Our findings presented herein also fell within those limits. The average kinetic parameters for urethanization of 1-butanol by means of TDI in nonreactive liquid aliphatic hydrocarbons, like pentane, DMB, and hexane, amount to $k_{\text{exp}} = (1\text{–}15) \cdot 10^{-4}$ dm^3 mol^{-1} s^{-1} and $E_a = 30$ kJ mol^{-1} (E_a is the activation energy for chemical reaction), depending on the type of hydrocarbon and concentration. The hydrocarbons referred to above made it possible to take measurements at 36–77°C. By carrying out the reaction at a precisely defined molar ratio of substrates, we fairly well managed to separate urethanization stage I and urethanization stage II. We found the chemical reactivity of —NCO groups at position 4 in 2,4-TDI to be 1.5–3 times higher on average under the conditions adopted for our study. That confirms the findings from ref. 10, which determined the ratio of $k_{\text{I}}/k_{\text{II}} = 1.15\text{–}1.63$,* depending on temperature. Much higher values were reported for that ratio from the kinetic study that involved urethanization of suberin.[7] Anyway, the simulation calculations for the increase of the molecular weight of linear polyurethane gave the results conforming to gel permeation chromatography (GPC) ex-

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*Despite the fact that we consider the ratio of rate constants $k_{\text{II}}/k_{\text{I}}$ as reported in ref. 10 to be correct, we think that the absolute rate constants reported in that paper for a second-order reaction are much too high against other findings: $k_{\text{I}} = 0.3306$ and $k_{\text{II}} = 0.2867$ dm^3 mol^{-1} s^{-1}.

perimental findings.[12] The diversification factor for reactivities of various —NCO groups within 2,4-TDI was assumed to be exactly 1.16–1.63. Hence, the findings obtained later for the reaction proceeding in the presence of styrene could also be referred to that level.

The liquid aliphatic hydrocarbons introduced to the reaction mixture will without any doubt have no essential effect on the rate of the reaction of TDI and 1-butanol. Any changed reaction rate will certainly result only from changing process temperatures for different hydrocarbon solvents. Our investigations, however, proved that any addition of styrene to the system would considerably alter reactivities of substrates and would most probably be responsible for disturbances in the expected course of reaction. In part, that could be accounted for by the change in polarity of the reaction system. Styrene is a bit more polar than pentane. Dielectric constants for styrene and pentane at 20–25°C equal to $\epsilon = 2.43$ and 1.84, respectively.

The data presented in Table II show that the 50 wt % share of styrene in the solvent mixture made it possible to run the reactions studied at 50–81°C (reaction of stage I) and at 52.5–83°C (for stage II), depending on the aliphatic hydrocarbon employed. And that, according to our method, led to finding the constant values: $k_{\mathrm{I}} = (4\text{–}20) \cdot 10^{-4}$ and $k_{\mathrm{II}} = (20\text{–}40) \cdot 10^{-4}$ dm^3 mol^{-1} s^{-1}. However, there are no reasonable grounds for any inverted performance (reactivity) for —NCO groups of 2,4-TDI in the presence of styrene. One should rather expect styrene to be responsible for some disturbances in stoichiometry defined by eqs. (4) and (5). Hence, the findings from kinetic measurements should not be referred to the expected reactions only. In order to verify that suggestion, further tests were run in the mixture of pentane and gradually increased share of styrene, from 31 up to 62%, which resulted in the following rate constants measured: $k_{\mathrm{I}} = (4\text{-}13) \cdot 10^{-4}$ ($T = 43.5$–62°C) and $k_{\mathrm{II}} = (2\text{-}17) \cdot 10^{-4}$ dm^3 mol^{-1} s^{-1} ($T = 48.5$–73.5°C). The values obtained for k_{I} are more or less compatible with the value of that constant for the reaction run at 50% styrene. Yet, the unjustifiable relation of $k_{\mathrm{II}} \geq k_{\mathrm{I}}$ is observed. That can be accounted for only by some change in reaction stoichiometry or by occurrence of some additional reaction(s) involving the 2,6-TDI isomer that is still present in the system–as results from eq. (5).

The values of activation energy for the reactions studied in the presence of styrene are about twice as high as those for the reactions proceeding in aliphatic hydrocarbons (Table III). Thus, introducing styrene modifies the course of the process, and its kinetic parameters observed could be interpreted from the formal point of view as slowing down the reaction of 2,4- and 2,6-TDI with 1-butanol, i.e., urethanization of every alcohol or polyol in a broader sense.

That conclusion is essential for the manufacturing process of urethane–isocyanate prepolymers from TDI and polyols in the presence of styrene. That solvent is not employed in polyurethane manufacturing processes. Still, as can be concluded from our earlier research and from other reports, it can be applicable in the IPN manufacturing processes—for example, polyurethane–polyester or polyurethane–polystyrene IPNs.[2,20, 21] When carrying out a polyaddition process, one should expect an apparently lower reactivity resulting most probably from side reactions. It is necessary to plan further studies to clarify what other products—apart from oligourethanes—can potentially be expected from such reaction systems. One can also infer that the rate of urethanization of alcohols with isocyanates, when carried out in the presence of solvents, is related in a complex way to many more parameters than it would appear from the Kirkwood equation mentioned. Styrene analyzed in our study makes just an example of that.

CONCLUSIONS

The kinetic parameters for the reaction of 2,4- and 2,6-TDI with hydroxyl compounds—alcohols, diols, and polyols—which are available in the research reports referred to, although controversial in some cases, create satisfactory grounds for the critical judgment of new data, which becomes necessary when developing polyurethane processes. That issue applies to a considerable degree to the findings presented herein for the kinetics of a model urethanization reaction of 1-butanol with diisocyanates, in the styrene solvent. That reaction can have great weight for developing production methods for polyurethane–polyester or polyurethane–polystyrene IPN compositions; styrene is employed at various stages of the synthesis of such systems. From the formal point of view, styrene is considered a neutral matter that can be employed as just a solvent. The issue of its effect on the kinetics of the reaction of isocyanate and alcohol has not been analyzed so far. The studies, however, were focused generally on the effect of polar nature of the solvents employed. The basic early studies on chemistry of isocyanates already reported the possible cyclization of those compounds, which admits the opinion that styrene would not make an absolutely inert medium for that reaction. The mechanism for such a cyclization reaction can be close to that of Diels–Alder cycloaddition.[4]

The presented study determined the kinetic parameters—rate constants and activation energy values—for the reaction of TDI and 1-butanol in the presence of styrene. Liquid aliphatic hydrocarbons introduced to the reaction system made it possible to carry out the reactions studied under isothermal conditions. The experimental findings obtained from the initial tests, when no styrene was employed, proved generally compatible with the literature reports. The process was split into two stages with different stoichiometry of the urethanization reactions occurring. That made it possible to determine the parameters for the reactions of —NCO groups substituted at positions 2 and 4 in TDI isomers. We confirmed in that way the known fact (although it is contested sometimes) that the reactivity of the —NCO group at position 4 in 2,4-TDI is only 1.5–3 times higher than that for the group at position 2, even if the kinetic effect of substitution is considered for both TDI isomers, which was not possible to evaluate directly in our measurements. After styrene is additionally introduced to the reaction system, the course of reactions becomes upset, although finding the kinetic parameters according to the method adopted faces absolutely no formal problems. That is confirmed by obtained detailed data for rate constants (at both stages of urethanization) and by the activation energy values found. Generally, styrene causes reduction of the reaction rate but it can also be expected to be responsible for side reactions that involve 2,6-TDI—in particular, at the final stage of the process when just that isomer was available unreacted in the system. The reaction temperature below 83°C and no external catalysts suggest that the side reactions are different from trimerization or formation of allophanate connections with the use of that diisocyanate. That problem, however, requires further investigation. First of all, it seems advisable to verify the progress of an analogous urethanization reaction in the presence of a solvent with its polarity similar to that of styrene, which, however, cannot undergo cyclization with isocyanate—for example, ethylbenzene ($\epsilon = 2.41$). The question is still open on the effect from commonly employed polyaddition catalysts on the process researched. The studies in that field are foundations for the process issues for the production new polymeric IPN-type materials wherein considerable contributions are made both by styrene (understood to be an inert solvent) and by aromatic diisocyanate, which reacts with a specific polyol compound.

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