

# Kinetic Analysis of Bulk Polymerization of Diisocyanate and Polyol

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## SYNOPSIS

The step addition polymerization between toluene diisocyanate and poly(oxypropylene) diol and triol was carried out in bulk in a closed batch reactor under vacuum and at isothermal conditions. The reactions have been examined under the influence of the catalysts *N*-phenyl- $\beta$ -naphthylamine, triethylene-tetraamine, and ferriacetylacetonate. The disappearance of the reactants and the appearance of one of the products were observed during the reaction. The kinetic analysis was brought about on the basis of the supposed reaction scheme and proposed kinetic model. The complex reaction was considered as serial-parallel. The experimental data fit well with the computed theoretical curves. The catalysts utilized were evaluated with respect to their selective catalysis of the primary diisocyanate-polyol reaction relative to the possible secondary reaction. The computed rate constants enabled the prediction of the composition of the reaction mixture. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The handling properties of polyurethane elastomers depend on the composition of the reaction mixture at the particular time of the reaction between isocyanates and alcohols. This composition is influenced by the reaction mechanism and kinetics, which are further influenced by the choice, purity, and the concentration of the main reaction components, by the presence and proper choice of the amount of catalyst and solvent, by the mode of the process-conducting, and by the reaction temperature. The mechanism and kinetics of these reactions have been investigated in the past as well as today.<sup>1-31</sup>

Baker et al.<sup>1-4</sup> were the first to show that isocyanate reactions with active hydrogen compounds are base catalyzed. They proposed the mechanism of these reactions and reported that these reactions are autocatalyzed by the urethane produced. Mechanistic features of autocatalytic effects were later the subject of considerable controversy.<sup>5,6</sup> Many authors have studied thoroughly both the catalyzed

and non-catalyzed reactions of aromatic, aliphatic, and furan-based isocyanates with alcohols in different solvents.<sup>7-14</sup> The most frequently employed catalysts were amine catalysts and organotin compounds.<sup>8-10,12-14,18</sup> The authors<sup>1-4,7-14</sup> have usually investigated both the mechanism and chemical kinetics of the reactions at the same time. They have supposed a variety of intermediates during the reaction, but only using modern methods can the authors<sup>12,14-16</sup> detect various intermediates as well as the final reaction products.

The kinetic data have been analyzed mostly according to the classical second order reaction rate equation.<sup>2-4,7,11,17,18</sup> The second order rate constant was found to be dependent upon the ratio of alcohol and isocyanate and the reaction order upon the H-bonding of the solvent.<sup>7</sup> The deviation from second order kinetics was often found<sup>2-4,7,11,12,18-21</sup> and was first explained as due either to the catalytic effect of the urethane group or due to solvent.<sup>3,10,22,23</sup> A great difference in reactivity between the different types of isocyanates<sup>19,24,25</sup> was also found. In those systems where diisocyanate with isocyanate groups of unequal reactivity<sup>26</sup> has been used, the deviation from second order kinetics occurred. Greenshields et al.<sup>27</sup> studied the kinetics of the reaction between alkyldiisocyanate and polyol of different character

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in various solvents. The results showed that the agreement between the tested kinetic equation and experiment differed from experiment to experiment. In the work,<sup>28</sup> the independence of the chain length and the functionality of the polymer glycols on the reaction rate constants was demonstrated. It was also found that primary alcohols react faster than secondary ones.

Because of the influence of branches and cross-links on the physico-chemical properties of polyurethane elastomers, it has been of particular interest to know the contribution of secondary reactions to the overall reaction between diisocyanates and polyether glycols under certain conditions. In the literature,<sup>11,29</sup> it was assumed that the main reactions are those between isocyanate and hydroxyl groups (primary reaction), and that the urethane with isocyanate groups is the so-called side reaction (secondary reaction). The rate constants reactions were calculated and it was shown to be possible to control the reaction between NCO and OH components by choosing the appropriate kind and the correct concentration of catalysts. The deviations from the second order kinetic curves was explained in the literature<sup>11,20,29,30</sup> in terms of secondary reactions and not in terms of other reasons. There are some new works where the deviation was explained to be due to the gel formation.<sup>30,31</sup>

Our best knowledge indicates that there are no works on kinetic data dealing with the systems employed in this work, on which basis one can predict with certainty the concentration of the reaction components and reaction products during the polymerization process. The establishing of the kinetic model and a knowledge of rate constants in complex reactions enables a production of final products with the desired handling properties, e.g., in this work, the desired casting properties of polyurethane matrix in polyurethane composite propellant.

## EXPERIMENTAL

### Materials

The polyol reactants were the mixture of poly(oxypropylene) glycol PPG-2025 and poly(oxypropylene) triol NP 16-46 in the ratio of 1.0 : 0.5 (by weight). The reason for this particular polyol ratio is because of the use of the same polyol mixture in the commercial production of polyurethane as a matrix in polyurethane composite propellant. The polyol mixture was dried before use at 353 K, under

vacuum of 1333 Pa. The polyols were analyzed according to Refs. 32-34. The moisture content in the mixture of polyol was less than 0.09 g H<sub>2</sub>O/100 g of polyol mixture according to the Karl Fischer method. The hydroxyl number of polyols mixture in mg KOH per g polyol mixture was 55.4.

The acid number of PPG 2025 was 0.04, and the number of NP 16-46 was 0.02 mg KOH per 100 g of the polyol. Toluene diisocyanate, TDI-80, was stored at 298 K. Employed TDI-80 had an isomer content of 80% 2.4 and 20% 2.6 and NCO content of 47.99%.<sup>36,37</sup>

The initial concentration of NCO groups was 1.084 mol, and of polyols was 0.877 mol per kg of reaction components. The [NCO]/[OH] ratio was 1.236. The total volume of reaction mixture was 142 cm<sup>3</sup>.

Three different catalysts in concentration of 0.048% based on the weight of reactants were used:  $1.21 \times 10^{-3}$  mol *N*-phenyl- $\beta$ -naphthyl amine (NF $\beta$ NA),<sup>37</sup>  $1.81 \times 10^{-3}$  mol triethylenetetra amine (TET),<sup>39</sup> and  $7.51 \times 10^{-4}$  mol ferriacetylacetonate (FeAA)<sup>20,38</sup> per kg of reaction mixture. All the materials used were supplied by Union Carbide Ltd.

### Procedure

The bulk polymerization was carried out in a batch reactor of 200 cm<sup>3</sup>, at isothermal condition ( $T = 295 \pm 0.5$  K), under vacuum of 1333 Pa and under a constant mixing speed of 200 rpm. The temperature of 295 K was selected because it provided the best conditions for following the reaction by titration and because of further urethane polymer application. The reactor was equipped with a system for sampling the reaction mixture. The preparation of the reaction mixture was different with the different catalysts used, depending on the reactivity and solubility of the components. FeAA was first dissolved in TDI and amine catalyst was dissolved in the mixture of polyols. Polymerization was carried out by a "one shot" procedure.

The reacting mixtures were withdrawn at fixed time intervals and the concentrations of the NCO groups were determined by a well-known method.<sup>35,36</sup> The concentration of hydroxyl groups was determined by titration<sup>32-34</sup> and the concentration of the allophanate and/or biuret by the method<sup>40</sup> specially developed for the allophanate and/or biuret determination in polyurethane products containing NCO groups, that is, for the promotion of isocyanate reactions. The reactions were not carried to completion.

## RESULTS AND DISCUSSION

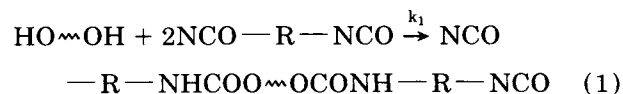
The progress of reactions is presented by the change in concentration of reactants and by the change of the reaction product, Figure 1(a), (b), and (c).

No change in the reactants' concentration was observed in uncatalyzed reaction under the same conditions, because the uncatalyzed reaction is extremely slow.

Results presented in Figure 1 show different changes in reactant and products' concentration in the systems catalyzed with different catalysts. The kinetic analysis was brought about on the basis of the supposed reaction scheme and proposed kinetic model.

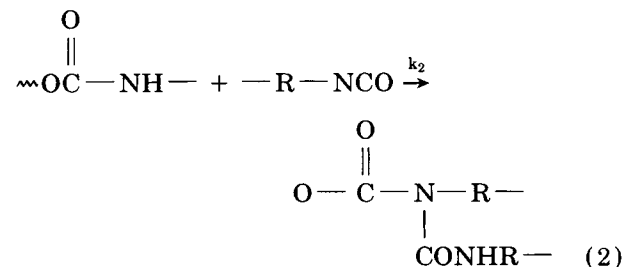
### Reaction Scheme and Kinetic Model

The polyurethane elastomers for liquid casting technique can be prepared by the reaction between diisocyanate and the mixture of polydiol and triol. The main, primary<sup>29</sup> reaction is

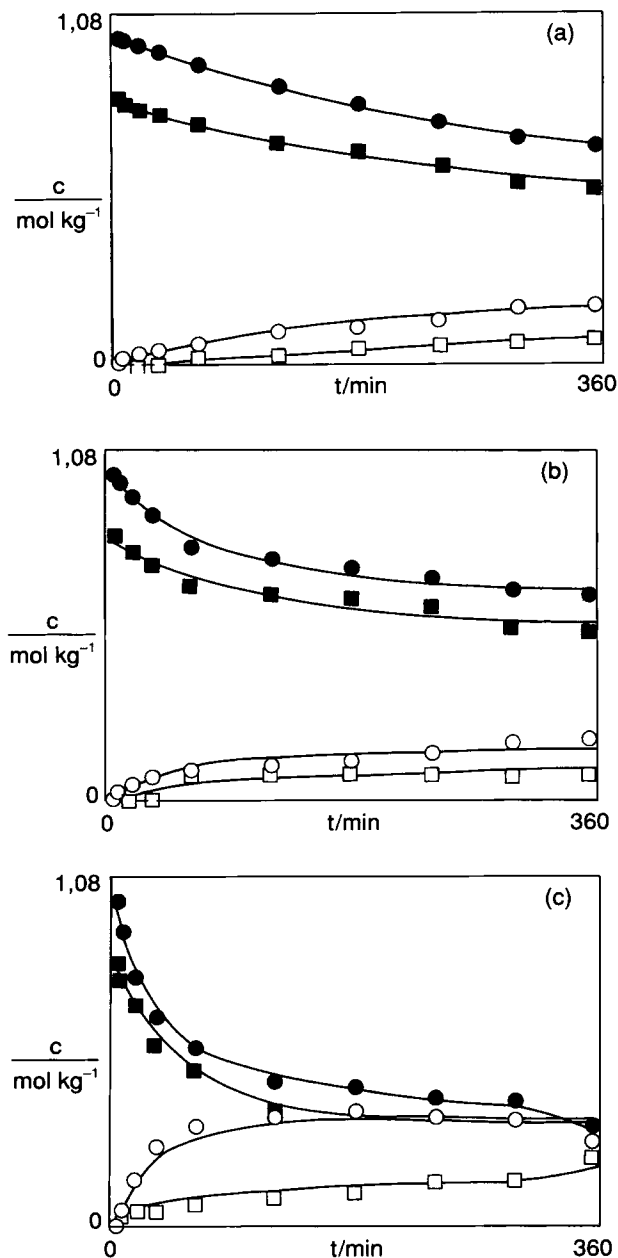


The reaction product has the functional groups on the ends of the molecules, which are able to step forward in reaction, to add the molecules present in the reaction mixture, yielded by step polyaddition the molecules of the higher and higher mol wt. Theoretically, the branched molecules of polyurethane rise from the diisocyanate and polydiol and triol by such a polyaddition.

However, the urethane group can also react in the next step with isocyanate group, (which is present in excess), yielding an allophanate in the so called secondary reaction<sup>29</sup>



The isocyanates can react also with water to form carbamic acid, which is unstable and decomposes to carbon dioxide and an amine. The amine can react with an additional isocyanate to form substituted



**Figure 1** Experimental points of concentration vs. time for (—●—) isocyanate groups ( $C_B$ ), (—■—) hydroxyl groups ( $C_A$ ), (—□—) allophanate ( $C_S$ ), and (—○—) the points for urethane groups ( $C_R$ ) vs. time, obtained by fitting to the kinetic model (full line). (a) catalyzed with  $\text{NF}\beta\text{NA}$ , (b) catalyzed with TET, and (c) catalyzed with FeAA.

urea and, finally, biuret. It is found in some other systems<sup>14</sup> that the allophanate and biuret were intermediates, yet could not be found at end of the reaction,



and it is the only unknown in eq. (11). Experimental data are tested according to eq. (11) by the method of nonlinear regression (modified Nelder–Mead optimization method). The success of fitting of experimental data to the model was estimated by the standard deviation,  $\sigma$ .

$$\sigma = \frac{1}{N-1} \left[ \sum (Y - Y_e)^2 \right]^{1/2}$$

- ( $N$ ) number of data,  
 ( $Y$ ) computed value of the function according to the theoretical model, and  
 ( $Y_e$ ) experimental value of the function.

The experimental data fit well the computed theoretical curves. This justifies the simplified reaction scheme and kinetic model. The fitting of the experimental and theoretical function, curve  $C_R$ , is also shown in Figure 1 (a), (b), and (c). The values of parameters  $K$  are listed in Table I.

The particular rate constants  $k_1$  and  $k_2$  were obtained by differential kinetic analysis. Rate constants  $k_1$  or  $k_2$  can be determined from eq. (7) or eq. (10), respectively. For these purposes, the experimental values of concentration ( $C_A$ ) – time curve were approximated by the appropriate monotonic function

$$f(C_A) = A' \exp(-B'C_A) + C' \quad (12)$$

$A'$ ,  $B'$ , and  $C'$  are the constants chosen on the basis of the mean square deviation. The reaction rate in the given time interval was obtained by analytic differentiation of the function in eq. (12). Further, the constant  $k_1$  was computed by testing the kinetic

model, eq. (7), using linear regression, Figure 2 (a), (b), and (c). With known values of  $K$  and  $k_1$ , the reaction constant of the secondary reaction,  $k_2$ , can be computed.

All the constants are listed in Table I.

*Selectivity and Activity of the Catalysts.* Table I provides a good comparison between different systems, although the catalyst concentrations differ slightly in each case.

The selectivity of the employed catalysts is in this work defined by the  $K$  (ratio of the rate constants,  $k_1/k_2$ ), and is represented by the higher acceleration of one of the two possible reactions. According to this criterion, the catalyst is selective if the rate constants ratio for the two reactions is different from 1. The selectivity is usually considered with respect to the preferred product/reaction from a practical standpoint. In the observed systems, in this work, for  $K < 1$ , the primary reaction is the more accelerated reaction. For  $K > 1$ , the secondary reaction is the more accelerated.

In the system catalyzed with FeAA,  $K = 0.717$ ,  $K < 1$ . The primary reaction resulting in polyurethane is preferred. In the system catalyzed with NF $\beta$ NA and TET,  $K > 1$  and the secondary reaction resulting in allophanate is more accelerated. The selectivity of TET is slightly higher than that of NF $\beta$ NA, with respect to the product of reaction, allophanate. It should be emphasized here that the amount of polyurethane or allophanate at the theoretical end of reaction depends on the  $C_{\text{NCO}}/C_{\text{OH}}$  ratio at the beginning of the reaction, but the amount of the reaction product during the reaction also depends on the activity of catalysts.

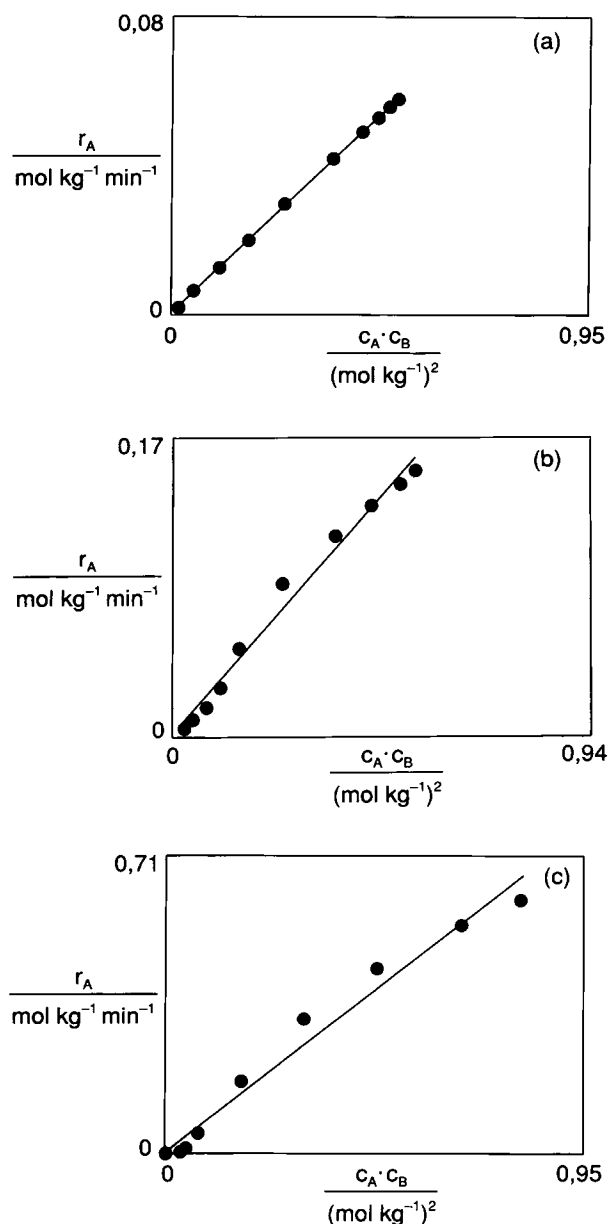
The activity of employed catalysts with respect to primary reaction, eq. (4a), or secondary reaction,

**Table I** Rate Constants of the Primary and Secondary Reaction,  $k_1^a$  and  $k_2^a$ , and the Selectivity of the Catalysts,  $K$

Catalysts (mol/kg)	$K = \frac{k_2^*}{k_1^*}$	Stand. Dev. ( $\sigma \times 10^2$ )	$k_1^*$ , ( $k_1$ )	Stand. Dev. ( $\sigma \times 10^2$ )	$k_2^*$ , ( $k_2$ )
(a) NF $\beta$ NA $1.21 \times 10^{-3}$	2.36	0.654	103.3 (0.125)	0.04	208.3 (0.252)
(b) TET $1.81 \times 10^{-3}$	2.70	1.890	163.5 (0.296)	0.67	441.9 (0.800)
(c) FeAA $0.75 \times 10^{-3}$	0.717	3.210	1143 (0.857)	3.81	820.0 (0.615)

<sup>a</sup>  $k_1$  and  $k_2$  are expressed in  $\text{kg mol}^{-1} \text{min}^{-1}$ .

<sup>b</sup>  $k_1^*$  and  $k_2^*$  are expressed in  $\text{kg mol}^{-1} \text{min}^{-1}$  per mol/kg of catalyst.



**Figure 2** Testing of the kinetic model [ eq. (7) ] (Computation of the rate constant  $k_1$ ). (a) catalyzed with  $\text{NF}\beta\text{NA}$ , (b) catalyzed with TET, (c) catalyzed with FeAA, (—●—) experimental data, and (—) theoretical function.

eq. (4b) is determined by the absolute value of the rate constants  $k_1$  and  $k_2$ , (or  $k_1^*$  and  $k_2^*$ , respectively. These constants are expressed in  $\text{kgmol}^{-1} \text{min}^{-1}$  per mol/kg of catalyst.). Considering Table I, one can conclude that, with respect to the primary reaction, FeAA is the most active catalyst with the highest value of  $k_1$ , but it is comparably selective for the primary and secondary reaction.

$\text{NF}\beta\text{NA}$  is about ten times and TET about six times less active than FeAA, but in the system catalyzed with  $\text{NF}\beta\text{NA}$  and TET it seems to be possible to have preferential catalysis of secondary reaction over the primary reaction.

Considering the rate constants divided by the concentration of the employed catalysts, the following order for both rate constants can be established:

$$k_{\text{FeAA}} > k_{\text{TET}} > k_{\text{NF}\beta\text{NA}}$$

The knowledge of the rate constants in the complex diisocyanate-polydiol (triol) reactions enables us, on the basis of the proposed reaction scheme and established kinetic model, to compute the concentration of all the reactants and products in the given reaction time. Furthermore, by choosing the proper catalysts or by an interruption of the reaction in the given time interval, the reaction could be directed to the desired branched or crosslinked product, moreover, to the desired properties, which is the most important for practical purposes.

## CONCLUSIONS

A reaction scheme for the bulk polymerization of diisocyanate with polydiol and triol into the polyurethane under the given reaction conditions is proposed. The reaction is considered as a complex serial-parallel reaction: serial with respect to the urethane groups, parallel with respect to the isocyanate groups.

A kinetic model consisting of a set of four equations is established.

The rate constants of primary and secondary reaction,  $k_1$  and  $k_2$ , are computed using the integral and differential methods of kinetic analysis.

The agreement between proposed theoretical model and experimental data enables the prediction of the reactants and products concentration in the given reaction time.

The selectivity and activity of employed catalysts are evaluated and established.

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