Kinetic Study of the Urethane and Urea Reactions of Isophorone Diisocyanate

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ABSTRACT: Kinetic studies of the catalyzed urethane reactions between isophorone diisocyanate (IPDI) and alcohols and of the urea reactions between an isocyanate-terminated prepolymer [IPDI–PPG2000–IPDI, where PPG2000 is poly(propylene glycol) with a number-average molecular weight of 2000 g/mol] and water in the bulk state were performed with Fourier transform infrared (FTIR) spectroscopy. Dibutyltin dilaurate was used as the catalyst for the urethane reaction, and various tertiary amines were used as catalysts for the urea reactions. The reactions were followed through the monitoring of the change in the intensity of the absorbance band for NCO stretching at 2270 cm^{-1} in the FTIR spectra; the activation parameters were determined through the evaluation of the kinetic data obtained at various temperatures (within the range of 30–60°C). The kinetic data indicated that the catalyzed isocyanate/alcohol and isocyanate/water reactions both followed second-order kinetics during their initial stages but later followed third-order kinetics resulting from the autocatalytic effects of hydrogen bonding between the hydroxyl groups and the newly formed urethane and urea groups. Furthermore, activation energies of 64.88 and about 80 kJ/mol for the isocyanate/alcohol and isocyanate/water reactions, respectively, indicated that the urea-forming reactions were more sensitive to the reaction temperature than the urethane-forming reactions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3891–3902, 2008

Key words: compatibility; FTIR; kinetics (polym.); polyurethanes

INTRODUCTION

Polyurethanes are used in a variety of applications in several technological fields, such as coatings, elastomers, sealants, adhesives, and foams. The most important reactions in the preparation of polyurethane are those between isocyanates and alcohols (urethane reaction) and between isocyanates and water (urea reaction). In terms of industrial productivity, isocyanate groups react rather slowly with alcohols, water, and other isocyanate groups in the absence of catalysts. The choice of catalyst for the manufacture of a particular polyurethane is usually made toward obtaining an appropriate profile among the several reactions that can occur during the process. Many groups have studied extensively the catalyzed reactions of isocyanates with alcohols and water. They have found that the catalyst must be sufficiently nucleophilic to stabilize the isocyanate group through resonance or that it must activate the active hydrogen atom containing compound.[1] Metal cata-

lysts activate the isocyanate groups by making them more electrophilic, whereas bases make the hydroxyl groups more nucleophilic. The catalysts most commonly used are tertiary amines and metal catalysts, especially organotin derivatives. Organotin catalysts behave as Lewis acids that activate the isocyanate group through coordination to the carboxyl group.[2] Organotin catalysts are extremely effective for the isocyanate/alcohol reaction because they activate alcohols preferentially over water because of the higher nucleophilicity of the oxygen atoms of alcohols.[3] Tertiary amines are catalysts for both the isocyanate/alcohol reactions (especially for the reactions of aliphatic isocyanates, which are widely used for the preparation of light-stable, nonyellowing polyurethanes for outdoor applications) and the isocyanate/water reactions. The complex that forms through a single hydrogen bond between the nucleophilic reagent (alcohol or water) and the tertiary amine reacts with the isocyanate to form the urethane (gel reaction) or urea (blow reaction) product. Because the electronic accessibility of a tertiary amine is also usually measured by its basicity, the catalytic activity generally increases as the basicity increases.[4] Mixtures of the two types of catalysts are used very often in foam manufacturing because the tertiary amine based catalysts tend to catalyze the

blowing reaction preferentially, whereas metal salts such as dibutyltin dilaurate (DBTDL) and stannous octoate promote the gelling reaction preferentially. Moreover, it has been determined that these two types of catalysts exhibit a synergistic effect when used together. A number of equations have been suggested to describe the kinetics of the catalyzed isocyanate/alcohol and isocyanate/water reactions. It is generally accepted that these reactions follow pseudo-second-order kinetics,[5,6] but this kinetic model generally holds true only up to a medium-to-low degree of conversion because several physical phenomena (e.g., an increase in viscosity) or autocatalytic effects of the newly formed urea or urethane groups may occur subsequently. Although polyurethane reactions have been subjected to a great number of studies that have suggested various mechanisms for urethane or urea formation, very little attention has been paid to the mechanistic aspects of the autocatalytic effects themselves.[7] In particular, no previously proposed mechanism provides a satisfactory interpretation of the experimental results mentioned previously. In this article, a kinetic study, using quantitative Fourier transform infrared (FTIR) spectroscopy, is performed to gain insight into the mechanism of the autocatalytic effect of the reactions of urethane and urea in the bulk state. FTIR spectroscopy is a powerful technique for monitoring organic reactions and especially for conducting kinetic analyses, determining reaction orders, and obtaining real-time conversion information.[5,8–10] The particular advantage of using FTIR spectroscopy to monitor polyurethane and polyurea syntheses is the ability to examine, during the course of the reaction, the disappearance of the strong isocyanate stretching absorbance at 2270 cm^{-1} and the formation of strong carbonyl absorptions. The intensities of these absorbances allow quantitative data to be obtained even at low conversions.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI; >99.5%) was purchased from Air Products and Chemical Inc. (Allendown, PA). Poly(propylene glycol) with a number-average molecular weight of 2000 g/mol (PPG2000; OH value = 54–58 mg/g of KOH), which possesses the chemical structure
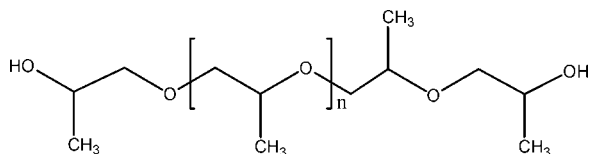
and 1,4-butanediol (1,4-BD) were purchased from Bayer Material Science (New Martinsville, WV) and

dried at 80°C for 3 h *in vacuo* before use. Analytical-grade DBTDL (95%) was purchased from Sigma-Aldrich (Shanghai, China) and dehydrated over 3-Å molecular sieves before use. 1,5-Diazabicyclo[4.3.0]-non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), N,N-dimethylcyclohexylamine (DMCHA), and pentamethyldiethylenetriamine (PMDETA) were purchased from Acros Organics (USA). Polyoxydimethylsilene (surfactant) was purchased from Goldschmidt Co. (Essen, Germany).

FTIR spectroscopy

A BIO-RAD FTS-3000 FTIR spectrometer was used to determine the kinetics of the isocyanate reaction. The instrument was situated in a thermostatic room maintained at room temperature (27°C). The kinetics were determined with a CaF$_2$ plate, which was kept in a thermostatic bath that was located close to the FTIR spectrometer to minimize thermal transients during the handling of the FTIR plate. The contents of the reaction mixture were fixed after the validity of the Lambert–Beer law was checked within the NCO concentration range considered. FTIR absorbance spectra were recorded at regular time intervals, measuring the progressive decrease of the NCO band at 2270 cm^{-1}. The reaction was monitored approximately up to the achievement of the gel point for every temperature/catalyst pair.

Urethane polymerization at different temperatures

Anhydrous PPG2000 (0.1 equiv) was placed in a 500-mL, round-bottom, four-necked reaction flask equipped with a thermometer, a stirrer, and an inlet and outlet for dry nitrogen; IPDI (0.05 equiv) was added to provide an [OH]/[NCO] ratio of 2 : 1. The reaction, which was performed under a dry nitrogen atmosphere in a constant-temperature oil bath, was followed through the monitoring of the change with time in the intensity of the absorption band at 2270 cm^{-1} (NCO stretching) in the FTIR spectra. A series of prepolymers were prepared, with DBTDL as the catalyst, at temperatures of 30, 40, and 60°C.

Urethane polymerization with different contents

1. Anhydrous PPG2000 (0.1 equiv) was placed in a 500-mL, round-bottom, four-necked reaction flask equipped with a thermometer, a stirrer, and an inlet and outlet for dry nitrogen; IPDI (0.1 equiv) was added to provide an [OH]/[NCO] ratio of 1 : 1. The reaction using DBTDL as the catalyst was performed under a dry nitrogen atmosphere in a constant-temperature oil bath; the reaction was monitored for the change with time in the intensity of the absorp-

tion band at 2270 cm^{-1} (NCO stretching) in the FTIR spectrum.

2. Anhydrous PPG2000 (0.05 equiv) and 1,4-BD (0.05 equiv) were placed in a 500-mL, round-bottom, four-necked reaction flask equipped with a thermometer, a stirrer, and an inlet and outlet for dry nitrogen; IPDI (0.1 equiv) was added to provide an [OH]/[NCO] ratio of 1 : 1. The reaction, which was conducted with DBTDL as the catalyst, was performed under a dry nitrogen atmosphere in a constant-temperature oil bath; the reaction was monitored for the change with time in the intensity of the absorption band at 2270 cm^{-1} (NCO stretching) in the FTIR spectrum.

Urea polymerization at different temperatures

The prepolymer was synthesized by the dissolution of anhydrous PPG2000 (0.05 equiv) with IPDI (0.1 equiv) in an [OH]/[NCO] ratio of 1 : 2 in a 500-mL, round-bottom, four-necked reaction flask equipped with a thermometer, a stirrer, and an inlet and outlet for dry nitrogen. The reaction, which was performed under a dry nitrogen atmosphere in a constant-temperature oil bath, was followed through the monitoring of the intensity of the absorption band at 2270 cm^{-1} (NCO stretching) in the FTIR spectrum to a constant value. The mixture was then charged with water (to provide an [OH]/[NCO] ratio of 1 : 1) and surfactant (0.5 g); the mixture was stirred for 20 s and monitored for the change with time in the intensity of the absorption band at 2270 cm^{-1} for NCO stretching in the FTIR spectrum. A series of reaction mixtures were prepared with various tertiary amines as catalysts and temperatures of 30, 40, and 50°C.

Kinetic study

Reaction kinetics for the formation of urethane and urea were investigated with *in situ* FTIR spectroscopy, which monitored the changes in the absorption band for the NCO stretching vibration. Our assay determined only the total amount of unreacted isocyanate because this provided only one absorption band for NCO stretching; the peak position remained essentially unaltered throughout the course of the reaction. For kinetic measurements, the FTIR spectroscopy absorbances were obtained with the Lambert–Beer law:

$$A = \varepsilon \cdot c \cdot d$$

where A is the absorbance, ε is the molar extinction coefficient, C is the concentration of the absorbent, and d is the thickness. C of the reacting group (here the NCO units) was available directly through the measurement of the absorbance peak area. The change in the intensity of the NCO stretching

absorption band of IPDI at 2270 cm^{-1} was monitored and divided by the intensity of the reference band [1372 cm^{-1} for the CH$_3$ stretching in poly(propylene glycol) (PPG)] to ensure that the quantitative results were independent of the thickness of the sample film:
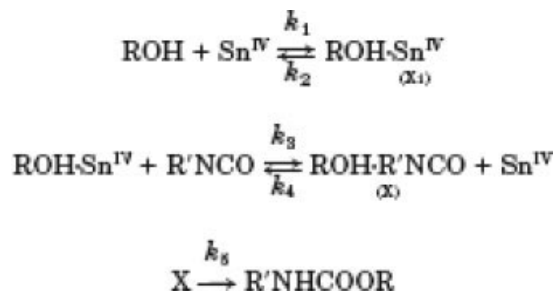
$$\left[\frac{\text{Area}_{-\text{reaction}-\text{group}}}{\text{Area}_{-\text{reference}-\text{group}}}\right]_1 = C_1$$

where C_1 is the reaction concentration independence on the thickness of the sample film.

Therefore, the degree of the catalyzed isocyanate reaction (X_{NCO}) can be written as follows:

$$X_{\text{NCO}}(\%) = \frac{\left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0} - \left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=t}}{\left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0}} \times 100\%$$
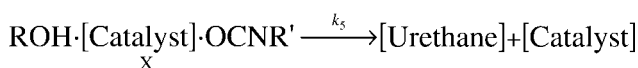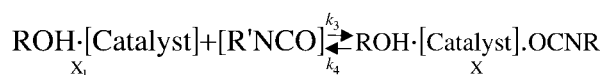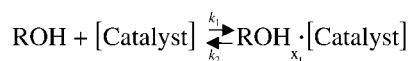
A number of equations have been proposed to describe the kinetics of the reactions between isocyanates and alcohols under catalysis. To describe the experimental data, the mechanism proposed by Frisch et al.[11–13] was considered to be valid (at first approximation):

$$\text{ROH} + \text{Sn}^{\text{IV}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{ROH·Sn}^{\text{IV}}_{(X_1)}$$

$$\text{ROH·Sn}^{\text{IV}} + \text{R'NCO} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{ROH·R'NCO} + \text{Sn}^{\text{IV}}_{(X)}$$

$$X \overset{k_5}{\longrightarrow} \text{R'NHCOOR}$$
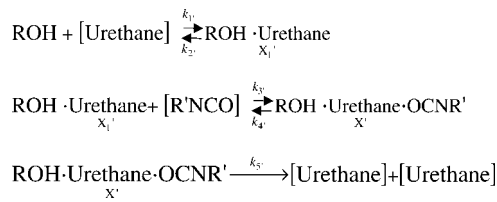
Urethane polymerization

On the basis of the previously discussed mechanism, a more elaborate mechanism to take into account the autocatalytic effect of the urethane groups is proposed:

1. The added catalyst mediates the initial reaction to produce urethane groups:

$$\text{ROH} + [\text{Catalyst}] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{ROH·[Catalyst]}_{X_1}$$

$$\text{ROH·[Catalyst]} + [\text{R'NCO}] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{ROH·[Catalyst]·OCNR}_X$$

$$\text{ROH·[Catalyst]·OCNR'}_X \overset{k_5}{\longrightarrow} [\text{Urethane}] + [\text{Catalyst}]$$

where k is the rate constant of the added catalyst mediates the initial reaction to produce urethane groups.

2. The urethane groups participate in catalyzing subsequent reactions:

$$\text{ROH} + [\text{Urethane}] \underset{k_{2'}}{\overset{k_{1'}}{\rightleftarrows}} \underset{X_{1'}}{\text{ROH} \cdot \text{Urethane}}$$

$$\underset{X_{1'}}{\text{ROH} \cdot \text{Urethane}} + [\text{R'NCO}] \underset{k_{4'}}{\overset{k_{3'}}{\rightleftarrows}} \underset{X'}{\text{ROH} \cdot \text{Urethane} \cdot \text{OCNR'}}$$

$$\underset{X'}{\text{ROH} \cdot \text{Urethane} \cdot \text{OCNR'}} \overset{k_{5'}}{\longrightarrow} [\text{Urethane}] + [\text{Urethane}]$$

where k' is the rate of constant of the urethane groups participate in catalyzing subsequent reactions.

The expression for the reaction rate is assumed to be as follows:

$$\frac{-d[\text{NCO}]}{dt} = k_5[\text{ROH} \cdot \text{Catalyst} \cdot \text{OCNR'}]$$
$$+ k_{5'}[\text{ROH} \cdot \text{Urethane} \cdot \text{OCNR'}]$$
$$= k_5[X] + k_{5'}[X'] \qquad (1)$$

where $[\text{ROH} \cdot \text{Catalyst} \cdot \text{OCNR'}] = [X]$ and $[\text{ROH} \cdot \text{Urethane} \cdot \text{OCNR'}] = [X']$.

The rate equation for $[X]$ is

$$\frac{d[X]}{dt} = k_3[\text{ROH} \cdot \text{Catalyst}] \cdot [\text{R'NCO}] - k_4[X] - k_5[X] \quad (2)$$

The existence of activated intermediate complex X is extremely transient:

$$[X] \cong 0 \rightarrow \frac{d[X]}{dt} = 0 \rightarrow 0 = k_3[X_1] \cdot [\text{R'NCO}] - k_4[X] - k_5[X]$$

where $[\text{ROH} \cdot \text{Catalyst}] = [X_1]$ and

$$[X] = \frac{k_3[X_1] \cdot [\text{R'NCO}]}{k_4 + k_5}.$$

The rate equation for $[X_1]$ is

$$\frac{d[X_1]}{dt} = k_1[\text{Catalyst}] \cdot [\text{ROH}] - k_2[X_1] - k_3[X_1]$$
$$\cdot [\text{R'NCO}] + k_4[X] \qquad (3)$$

The existence of activated intermediate complex X_1 is also extremely transient:

$$[X_1] \cong 0 \rightarrow \frac{d[X_1]}{dt} = 0 \rightarrow 0$$

$$= k_1[\text{Catalyst}] \cdot [\text{ROH}] - k_2[X_1] - k_3[X_1] \cdot [\text{R'NCO}]$$

$$+ k_4\left[\frac{k_3[X_1] \cdot [\text{R'NCO}]}{k_4 + k_5}\right]$$

$$[X_1] = \frac{k_1[\text{Catalyst}] \cdot [\text{ROH}]}{k_2 + (k_3 - \frac{k_3 k_4}{k_4 + k_5})[\text{R'NCO}]}$$

By introducing $[X_1]$ to $[X]$, we obtain

$$[X] = \frac{\left(\frac{k_1}{k_4 + k_5}\right)[\text{R'NCO}][\text{ROH}][\text{Catalyst}]}{\frac{k_2}{k_3} + \left(1 - \frac{k_4}{k_4 + k_5}\right)[\text{R'NCO}]}$$

Because $[X_1] \cong 0 \rightarrow k_2 \gg k_1$ and k_3

$$[X] = \frac{\left(\frac{k_1}{k_4 + k_5}\right)}{\frac{k_2}{k_3}}[\text{R'NCO}][\text{ROH}][\text{Catalyst}]$$

The rate equation for $[X']$ is

$$\frac{d[X']}{dt} = k_{3'}[\text{ROH} \cdot \text{Urethane}] \cdot [\text{R'NCO}] - k_{4'}[X'] - k_{5'}[X']$$

$$(4)$$

The existence of activated intermediate complex X' is also extremely transient:

$$[X'] \cong 0 \rightarrow \frac{d[X']}{dt} = 0 \rightarrow 0 = k_{3'}[\text{ROH} \cdot \text{Urethane}]$$
$$\cdot [\text{R'NCO}] - k_{4'}[X] - k_{5'}[X]$$

$$[X'] = \frac{k_{3'}[X_{1'}] \cdot [\text{R'NCO}]}{k_{4'} + k_{5'}}$$

where $[\text{ROH} \cdot \text{Urethane}] = [X_{1'}]$.

The rate equation for $[X_{1'}]$ is

$$\frac{d[X_{1'}]}{dt} = k_{1'}[\text{Urethane}] \cdot [\text{ROH}] - k_{2'}[X_{1'}] - k_{3'}[X_{1'}]$$
$$\cdot [\text{R'NCO}] + k_{4'}[X'] \qquad (5)$$

The existence of activated intermediate complex $(X_{1'})$ is also extremely transient:

$$[X_{1'}] \cong 0 \rightarrow \frac{d[X_{1'}]}{dt} = 0 \rightarrow 0 = k_{1'}[\text{Urethane}] \cdot [\text{ROH}]$$
$$- k_{2'}[X_{1'}] - k_{3'}[X_{1'}] \cdot [\text{R'NCO}] + k_{4'}[X'] \rightarrow$$
$$0 = k_{1'}[\text{Urethane}] \cdot [\text{ROH}] - k_{2'}[X_{1'}] - k_{3'}[X_{1'}]$$
$$\cdot [\text{R'NCO}] + \frac{k_{3'} k_{4'}[X_{1'}][\text{R'NCO}]}{k_{4'} + k_{5'}}$$

$$[X_{1'}] = \frac{k_{1'}[\text{Urethane}] \cdot [\text{ROH}]}{k_{2'} + \left(k_{3'} - \frac{k_{3'} k_{4'}}{k_{4'} + k_{5'}}\right)[\text{R'NCO}]}$$

By introducing $[X_{1'}]$ to $[X']$, we obtain

$$[X'] = \frac{\left(\frac{k_{1'}}{k_{4'} + k_{5'}}\right)[\text{R'NCO}] \cdot [\text{ROH}] \cdot [\text{Urethane}]}{\frac{k_{2'}}{k_{3'}} + \left(1 - \frac{k_{4'}}{k_{4'} + k_{5'}}\right)[\text{R'NCO}]}$$

By introducing $[X]$ and $[X']$ to eq. (1), we obtain

$$\frac{-d[\text{NCO}]}{dt} = k_5 \cdot [\text{X}] + k_{5'}[\text{X}']$$

$$= \left\{ \left[\frac{k_1 k_5 k_3}{(k_4 + k_5)k_2} \right][\text{Catalyst}] + \frac{(\frac{k_{1'}k_{5'}}{k_{4'}+k_{5'}})[\text{Urethane}]}{\frac{k_{2'}}{k_{3'}} + (1 - \frac{k_{4'}}{k_{4'}+k_{5'}})[\text{R'NCO}]} \right\}$$

$$[\text{R'NCO}][\text{ROH}] \qquad (6)$$

By denoting

$$k_{\text{cat}} = \left[\frac{k_1 k_5 k_3}{(k_4 + k_5)k_2} \right]$$

and

$$k_{\text{obs}} = k_{\text{cat}}[\text{Catalyst}]$$

where k_{cal} [Catalyst] is considered as apparent rate constant k_{obs} for the catalyzed urethane forming reactions, we obtain the final equation as follows:

$$\frac{-d[\text{NCO}]}{dt} = \left\{ k_{\text{obs}} + \frac{\left(\frac{k_{1'}}{k_{4'}+k_{5'}}\right)[\text{Urethane}]}{\frac{k_{2'}}{k_{3'}} + \left(1 - \frac{k_{4'}}{k_{4'}+k_{5'}}\right)[\text{R'NCO}]} \right\}$$

$$[\text{R'NCO}] \cdot [\text{ROH}] \qquad (7)$$

This kinetic equation, which takes into account the auto-catalytic effect, is immensely complex. To integrate eq. (7), we first simplified it, using the following considerations:

1. When the reaction is at its initial stage, the concentration of urethane is low $\left(\frac{(\frac{k_{1'}}{k_{4'}+k_{5'}})[\text{Urethane}]}{\frac{k_{2'}}{k_{3'}}+(1-\frac{k_{4'}}{k_{4'}+k_{5'}})[\text{R'NCO}]} \ll k_{\text{obs}} \right)$ and [R'NCO] is high; eq. (7) can then be written as

$$\frac{-d[\text{NCO}]}{dt} = k_{\text{obs}} \cdot [\text{R'NCO}][\text{ROH}] \qquad (8)$$

2. When the concentration of urethane is high $\left(\frac{(\frac{k_{1'}}{k_{4'}+k_{5'}})[\text{Urethane}]}{\frac{k_{2'}}{k_{3'}}+(1-\frac{k_{4'}}{k_{4'}+k_{5'}})[\text{R'NCO}]} \gg k_{\text{obs}} \right)$ and [R'NCO] is low, eq. (7) can then be written as

$$\frac{-d[\text{NCO}]}{dt} = \left\{ \frac{\left(\frac{k_{1'}k_{5'}}{k_{4'}+k_{5'}}\right)}{\frac{k_{2'}}{k_{3'}}} \right\}[\text{Urethane}] \cdot [\text{R'NCO}] \cdot [\text{ROH}]$$

$$(9)$$

By denoting

$$k_{\text{urethane}} = \left[\frac{k_{1'} k_{5'} k_{3'}}{(k_{4'} + k_{5'})k_{2'}} \right]$$

we can rewrite eq. (9) as follows:

$$\frac{-d[\text{NCO}]}{dt} = k_{\text{urethane}} \cdot [\text{Urethane}] \cdot [\text{R'NCO}] \cdot [\text{ROH}]$$
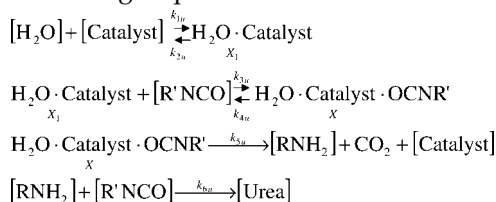
$$(10)$$

Equation (8) represents the second-order kinetics of the catalyst-mediated initial stage, which is accompanied by the autocatalytic effect of the urethane groups, as indicated in the subsequent third-order kinetics in eq. (10).
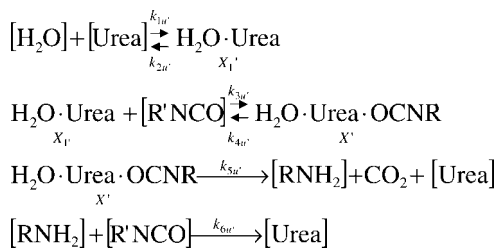
Urea polymerization

Similarly, the following mechanism is proposed for the reaction between the isocyanate and water, mediated by the catalyst, to produce urea groups, which provide autoacceleration:

1. The catalyst mediates the initial reaction to produce urea groups:

$$[\text{H}_2\text{O}] + [\text{Catalyst}] \underset{k_{2u}}{\overset{k_{1u}}{\rightleftharpoons}} \underset{X_1}{\text{H}_2\text{O} \cdot \text{Catalyst}}$$

$$\underset{X_1}{\text{H}_2\text{O} \cdot \text{Catalyst}} + [\text{R'NCO}] \underset{k_{4u}}{\overset{k_{3u}}{\rightleftharpoons}} \underset{X}{\text{H}_2\text{O} \cdot \text{Catalyst} \cdot \text{OCNR'}}$$

$$\underset{X}{\text{H}_2\text{O} \cdot \text{Catalyst} \cdot \text{OCNR'}} \overset{k_{5u}}{\longrightarrow} [\text{RNH}_2] + \text{CO}_2 + [\text{Catalyst}]$$

$$[\text{RNH}_2] + [\text{R'NCO}] \overset{k_{6u}}{\longrightarrow} [\text{Urea}]$$

where k_u is the rate constant of the catalyst mediates the initial reaction to produce urea groups.

2. These urea groups behave as additional catalysts for the reaction.

$$[\text{H}_2\text{O}] + [\text{Urea}] \underset{k_{2u'}}{\overset{k_{1u'}}{\rightleftharpoons}} \underset{X_1'}{\text{H}_2\text{O} \cdot \text{Urea}}$$

$$\underset{X_1'}{\text{H}_2\text{O} \cdot \text{Urea}} + [\text{R'NCO}] \underset{k_{4u'}}{\overset{k_{3u'}}{\rightleftharpoons}} \underset{X'}{\text{H}_2\text{O} \cdot \text{Urea} \cdot \text{OCNR}}$$

$$\underset{X'}{\text{H}_2\text{O} \cdot \text{Urea} \cdot \text{OCNR}} \overset{k_{5u'}}{\longrightarrow} [\text{RNH}_2] + \text{CO}_2 + [\text{Urea}]$$

$$[\text{RNH}_2] + [\text{R'NCO}] \overset{k_{6u'}}{\longrightarrow} [\text{Urea}]$$

where $k_{u'}$ is rate constant of the urea groups behave as additional catalysts for the reaction.

The expression for the reaction rate is assumed to be

$$\frac{-d[\text{R'NCO}]}{dt} = k_{5u} \cdot [\text{X}] - k_{6u}[\text{R'NH}_2] \cdot [\text{R'NCO}]$$

$$+ k_{5u'} \cdot [\text{X}'] - k_{6u'}[\text{R'NH}_2] \cdot [\text{R'NCO}] \qquad (11)$$

where $[\text{ROH} \cdot \text{Catalyst} \cdot \text{OCNR'}] = [\text{X}]$ and $[\text{ROH} \cdot \text{Urea} \cdot \text{OCNR'}] = [\text{X}']$.

The rate equation for [X] is

$$\frac{d[\text{X}]}{dt} = k_{3u}[\text{H}_2\text{O} \cdot \text{Catalyst}] \cdot [\text{R'NCO}] - k_{4u}[\text{X}] - k_{5u}[\text{X}]$$

$$(12)$$

The existence of activated intermediate complex X is extremely transient:

$$[\text{X}] \cong 0 \rightarrow \frac{d[\text{X}]}{dt} = 0 \rightarrow 0$$

$$= k_{3u}[\text{H}_2\text{O} \cdot \text{Catalyst}] \cdot [\text{R'NCO}] - k_{4u}[\text{X}] - k_{5u}[\text{X}]$$

where $[\text{H}_2\text{O} \cdot \text{Catalyst}] = [\text{X}_1]$ and

$$[\text{X}] = \frac{k_{3u}[\text{X}_1] \cdot [\text{R'NCO}]}{k_{4u} + k_{5u}}$$

The rate equation for $[X_1]$ is

$$\frac{d[X_1]}{dt} = k_{1u}[\text{Catalyst}] \cdot [\text{H}_2\text{O}] - k_{2u}[X_1] - k_{3u}[X_1]$$
$$\cdot [\text{R}'\text{NCO}] + k_{4u}[X] \qquad (13)$$

The existence of activated intermediate complex X_1 is also extremely transient:

$$[X_1] \cong 0 \rightarrow \frac{d[X_1]}{dt} = 0 \rightarrow 0 = k_{1u}[\text{Catalyst}] \cdot t[\text{H}_2\text{O}]$$
$$- k_{2u}[X_1] - k_3[X_1] \cdot [\text{R}'\text{NCO}] + k_{4u}[X] \rightarrow$$
$$0 = k_{1u}[\text{Catalyst}] \cdot [\text{H}_2\text{O}] - k_{2u}[X_1] - k_{3u}[X_1] \cdot [\text{R}'\text{NCO}]$$
$$+ \frac{k_{3u}k_{4u}[X_1][\text{R}'\text{NCO}]}{k_{4u} + k_{5u}} \left([X] = \frac{k_{3u}[X_1] \cdot [\text{R}'\text{NCO}]}{k_{4u} + k_{5u}} \right)$$

$$[X_1] = \frac{k_{1u}[\text{Catalyst}] \cdot [\text{H}_2\text{O}]}{\left[k_{2u} + (k_{3u} - \frac{k_{3u}k_{4u}}{k_{4u}+k_{5u}})[\text{R}'\text{NCO}] \right]}$$

The rate equation for $[\text{R}'\text{NH}_2]$ is

$$\frac{d[\text{R}'\text{NH}_2]}{dt} = k_{5u}[X] - k_{6u}[\text{R}'\text{NH}_2] \cdot [\text{R}'\text{NCO}] \qquad (14)$$

The primary aliphatic amine reacts immediately:

$$[\text{R}'\text{NH}_2] \cong 0 \rightarrow \frac{d[\text{R}'\text{NH}_{21}]}{dt} = 0 \rightarrow 0$$
$$= k_{5u}[X] - k_{6u}[\text{R}'\text{NH}_2] \cdot [\text{R}'\text{NCO}]$$

$$[\text{R}'\text{NH}_2] = \frac{k_{5u}}{k_{6u}[\text{R}'\text{NCO}]} \cdot [X] = \frac{k_{5u}}{k_{6u}[\text{R}'\text{NCO}]}$$
$$\times \frac{\frac{k_{5u}k_{1u}k_{3u}}{k_{4u}+k_{5u}}[\text{R}'\text{NCO}] \cdot [\text{Catalyst}] \cdot [\text{H}_2\text{O}]}{\left[k_{2u} + (k_{3u} - \frac{k_{3u}k_{4u}}{k_{4u}+k_{5u}})[\text{R}'\text{NCO}] \right]}$$

$$[\text{R}'\text{NH}_2] = \frac{\frac{k_{5u}k_{5u}k_{1u}k_{3u}}{k_{6u}(k_{4u}+k_{5u})}[\text{Catalyst}] \cdot [\text{H}_2\text{O}]}{\left[k_{2u} + (k_{3u} - \frac{k_{3u}k_{4u}}{k_{4u}+k_{5u}})[\text{R}'\text{NCO}] \right]}$$

By introducing $[X']$ and $[\text{R}'\text{NH}_2]$ into $k_{5u}[X] - k_{6u}[\text{R}'\text{NH}_2][\text{R}'\text{NCO}]$, we obtain

$$k_{5u} \cdot [X] - k_{6u}[\text{R}'\text{NH}_2] \cdot [\text{R}'\text{NCO}]$$
$$= \frac{\left[\frac{k_{5u}k_{1u}k_{6u}-k_{5u}^2k_{1u}}{k_{6u}(k_{4u}+k_{5u})} \right][\text{R}'\text{NCO}] \cdot [\text{Catalyst}] \cdot [\text{H}_2\text{O}]}{\left[\frac{k_{2u}}{k_{3u}} + (1 - \frac{k_{4u}}{k_{4u}+k_{5u}})[\text{R}'\text{NCO}] \right]}$$

Because $[X_1] \cong 0 \rightarrow k_2 \gg k_1$ and k_3

$$k_{5u} \cdot [X] - k_{6u}[\text{R}'\text{NH}_2] \cdot [\text{R}'\text{NCO}]$$
$$= \frac{\left[\frac{k_{5u}k_{1u}k_{6u}-k_{5u}^2k_{1u}}{k_{6u}(k_{4u}+k_{5u})} \right]}{\left[\frac{k_{2u}}{k_{3u}} \right]}[\text{R}'\text{NCO}] \cdot [\text{Catalyst}] \cdot [\text{H}_2\text{O}] \qquad (15)$$

The rate equation for $[X']$ is

$$\frac{d[X']}{dt} = k_{3u'}[\text{H}_2\text{O} \cdot \text{Urea}] \cdot [\text{R}'\text{NCO}]$$
$$- k_{4u'}[X'] - k_{5u'}[X'] \qquad (16)$$

The existence of activated intermediate complex X' is also extremely transient:

$$[X'] \cong 0 \rightarrow \frac{d[X']}{dt} = 0 \rightarrow 0 = k_3[\text{H}_2\text{O} \cdot \text{Urea}] \cdot [\text{R}'\text{NCO}]$$
$$- k_4[X'] - k_5[X']$$

where $[\text{H}_2\text{O} \cdot \text{Urea}] = [X_1']$ and

$$[X'] = \frac{k_{3u'}[X_1'] \cdot [\text{R}'\text{NCO}]}{k_{4u'} + k_{5u'}}.$$

The rate equation for $[X_1']$ is

$$\frac{d[X_1']}{dt} = k_{1u'}[\text{Urea}] \cdot [\text{H}_2\text{O}] - k_{2u'}[X_1'] - k_{3u'}[X_1']$$
$$\cdot [\text{R}'\text{NCO}] + k_{4u'}[X'] \qquad (17)$$

The existence of activated intermediate complex X_1' is also extremely transient:

$$[X_1'] \cong 0 \rightarrow \frac{d[X_1']}{dt} = 0 \rightarrow 0 = k_{1u'}[\text{Urea}] \cdot [\text{H}_2\text{O}]$$
$$- k_{2u'}[X_1'] - k_{3u'}[X_1'] \cdot [\text{R}'\text{NCO}] + k_{4u'}[X'] \rightarrow 0$$
$$= k_{1u'}[\text{Urea}] \cdot [\text{H}_2\text{O}] - k_{2u'}[X_1'] - k_{3u'}[X_1'] \cdot [\text{R}'\text{NCO}]$$
$$+ \frac{k_{3u'}k_{4u'}[X_1'][\text{R}'\text{NCO}]}{k_{4u'} + k_{5u'}} \left([X'] = \frac{k_{3u'}[X'] \cdot [\text{R}'\text{NCO}]}{k_{4u'} + k_{5u'}} \right)$$

$$[X_1'] = \frac{k_{1u'}[\text{Urea}] \cdot [\text{H}_2\text{O}]}{\left[k_{2u'} + (k_{3u'} - \frac{k_{3u'}k_{4u'}}{k_{4u'}+k_{5u'}})[\text{R}'\text{NCO}] \right]}$$

The rate equation for $[\text{R}'\text{NH}_2]$ is

$$\frac{d[\text{R}'\text{NH}_2]}{dt} = k_{5u'}[X] - k_{6u'}[\text{R}'\text{NH}_2] \cdot [\text{R}'\text{NCO}] \qquad (18)$$

The primary aliphatic amine reacts immediately:

$$[\text{R}'\text{NH}_2] \cong 0 \rightarrow \frac{d[\text{R}'\text{NH}_2]}{dt} = 0 \rightarrow$$
$$0 = k_{5u'}[X'] - k_{6u'}[\text{R}'\text{NH}_2] \cdot [\text{R}'\text{NCO}]$$

$$[\text{R}'\text{NH}_2] = \frac{\frac{k_{5u'}k_{5u'}k_{1u'}k_{3u'}}{k_{6u'}(k_{4u'}+k_{5u'})}[\text{Urea}] \cdot [\text{H}_2\text{O}]}{\left[k_{2u'} + (k_{3u'} - \frac{k_{3u'}k_{4u'}}{k_{4u'}+k_{5u'}})[\text{R}'\text{NCO}] \right]}$$

By introducing $[X']$ and $[\text{R}'\text{NH}_2]$ into $k_{5u'}[X'] - k_{6u'}[\text{R}'\text{NH}_2][\text{R}'\text{NCO}]$, we obtain

$$k_{5u'} \cdot [X'] - k_{6u'}[\text{R}'\text{NH}_2] \cdot [\text{R}'\text{NCO}]$$
$$= \frac{\left[\frac{k_{5u'}k_{1u'}k_{6u'}-k_{5u'}^2k_{1u'}}{k_{6u'}(k_{4u'}+k_{5u'})} \right][\text{R}'\text{NCO}] \cdot [\text{Urea}] \cdot [\text{H}_2\text{O}]}{\left[\frac{k_{2u'}}{k_{3u'}} + (1 - \frac{k_{4u'}}{k_{4u'}+k_{5u'}})[\text{R}'\text{NCO}] \right]} \qquad (19)$$

TABLE I
Kinetic Data for the DBTDL-Catalyzed Reaction Between IPDI and PPG2000 (OH/NCO = 2 : 1)

Temperature (°C)	Catalyst	[Catalyst] (mol/L)	k_{obs} (L mol^{-1} S^{-1})	R^{2a}	k_{cat} (L^2 mol^{-2} S^{-1})
30	DBTDL	0.00033	0.00263	0.990	13.87
30	DBTDL	0.00066	0.00721	0.994	

[a] Correlation coefficient of the mean-square linear regression.

By introducing eqs. (15) and (19) into eq. (11), we obtain

$$-\frac{d[R'NCO]}{dt} = \left\{ \frac{\left[\frac{k_{5u}k_{1u}k_{6u}-k_{5u}^2k_{1u}}{k_{6u}(k_{4u}+k_{5u})}\right]}{\left[\frac{k_{2u}}{k_{3u}}\right]}[\text{Catalyst}] \right.$$
$$\left. + \frac{\left[\frac{k_{5u'}k_{1u'}k_{6u'}-k_{5u'}^2k_{1u'}}{k_{6u'}(k_{4u'}+k_{5u'})}\right][\text{Urea}]}{\left[\frac{k_{2u'}}{k_{3u'}}+(1-\frac{k_{4u'}}{k_{4u'}+k_{5u'}})[R'NCO]\right]} \right\} [R'NCO]\cdot[H_2O]$$

By denoting

$$k_{cat} = \frac{\left[\frac{k_{5u}k_{1u}k_{6u}-k_{5u}^2k_{1u}}{k_{6u}(k_{4u}+k_{5u})}\right]}{\left[\frac{k_{2u}}{k_{3u}}\right]}$$

and

$$k_{obs} = k_{cat}[\text{Catalyst}]$$

we obtain the final equation as follows:

$$-\frac{d[R'NCO]}{dt} = \left\{ k_{obs} + \frac{\left[\frac{k_{5u'}k_{1u'}k_{6u'}-k_{5u'}^2k_{1u'}}{k_{6u'}(k_{4u'}+k_{5u'})}\right][\text{Urea}]}{\left[\frac{k_{2u'}}{k_{3u'}}+(1-\frac{k_{4u'}}{k_{4u'}+k_{5u'}})[R'NCO]\right]} \right\}$$
$$[R'NCO]\cdot[H_2O] \quad (20)$$

This kinetic equation, which takes into account the autocatalytic effect, is immensely complex. To integrate eq. (20), we first simplify the equation by taking into account the following considerations:

1. When the reaction is at the initial stage

$$\frac{\left[\frac{k_{5u'}k_{1u'}k_{6u'}-k_{5u'}^2k_{1u'}}{k_{6u'}(k_{4u'}+k_{5u'})}\right][\text{Urea}]}{\left[\frac{k_{2u'}}{k_{3u'}}+(1-\frac{k_{4u'}}{k_{4u'}+k_{5u'}})[R'NCO]\right]} \ll k_{obs}$$

Equation (20) may then be written as

$$-\frac{d[R'NCO]}{dt} = k_{obs} \cdot [R'NCO] \cdot [H_2O] \quad (21)$$

2. When the concentration of urea is high

$$\frac{\left[\frac{k_{5u'}k_{1u'}k_{6u'}-k_{5u'}^2k_{1u'}}{k_{6u'}(k_{4u'}+k_{5u'})}\right][\text{Urea}]}{\left[\frac{k_{2u'}}{k_{3u'}}+(1-\frac{k_{4u'}}{k_{4u'}+k_{5u'}})[R'NCO]\right]} \gg k_{obs}$$

and [R'NCO] is low, eq. (20) may then be written as follows:

$$-\frac{d[R'NCO]}{dt} = \left\{ \frac{\left[\frac{k_{5u'}k_{1u'}k_{6u'}-k_{5u'}^2k_{1u'}}{k_{6u'}(k_{4u'}+k_{5u'})}\right]}{\left[\frac{k_{2u'}}{k_{3u'}}\right]} \right\}[\text{Urea}]$$
$$\cdot [R'NCO] \cdot [H_2O] \quad (22)$$

By denoting

$$k_{urea} = \frac{\left[\frac{k_{5u'}k_{1u'}k_{6u'}-k_{5u'}^2k_{1u'}}{k_{6u'}(k_{4u'}+k_{5u'})}\right]}{\left[\frac{k_{2u'}}{k_{3u'}}\right]}$$

we can rewrite eq. (22) as follows:

$$-\frac{d[R'NCO]}{dt} = k_{urea} \cdot [\text{Urea}] \cdot [R'NCO] \cdot [H_2O] \quad (23)$$

The kinetic equation [eq. (20)], which takes into account the autocatalytic effect of the urea groups, will follow third-order kinetics when the urea groups participate in the reaction. Furthermore, if the initial concentrations of the hydroxyl and isocyanate groups are equal (i.e., [OH]$_0$ = [NCO]$_0$ = [C]) and the functional groups (OH and NCO) are both consumed at the same rate (i.e., no side reactions occur), then the second-order equations [eqs. (18) and (21)] can be integrated to retrieve the following concentration–time profile:

TABLE II
Kinetic Data for the DBTDL-Catalyzed Reactions of IPDI with PPG2000 (OH/NCO = 2 : 1) at Various Temperatures

Temperature (°C)	Catalyst	[Catalyst] (mol/L)	k_{obs} (L mol^{-1} S^{-1})	R^{2a}	E_a (kJ/mol)[b]	Frequency factor
30	DBTDL	0.00033	0.0026	0.990	64.88	1.06×10^9
40	DBTDL	0.00033	0.0105	0.995		
60	DBTDL	0.00033	0.0429	0.991		

[a] Correlation coefficient of the mean-square linear regression.
[b] Activation energy.
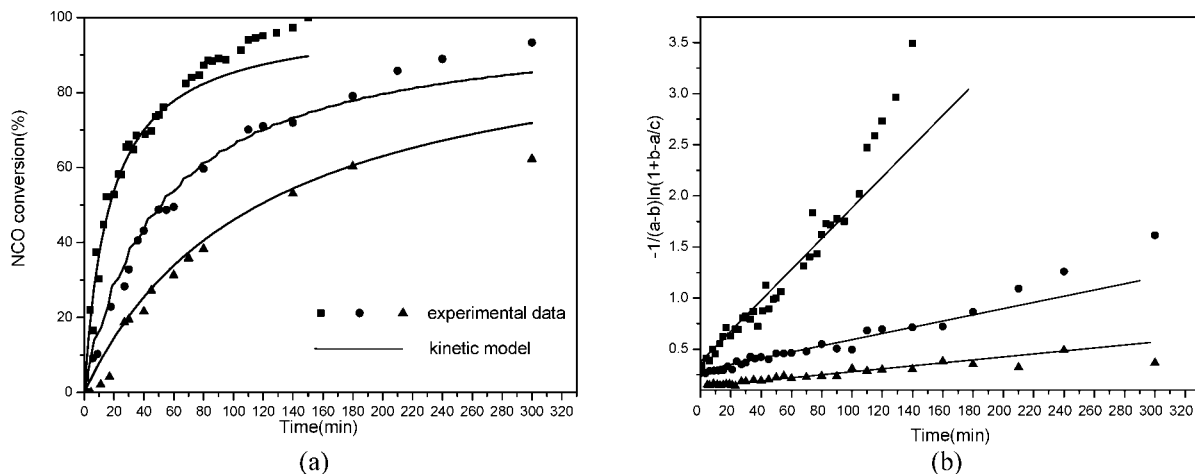
Figure 1 (a) Plots of the conversion versus time for the DBTDL-catalyzed reactions of IPDI with PPG2000 (OH/NCO = 2 : 1) at different temperatures: (—) second-order kinetic model and experimental data at (■) 30, (▲) 40, and (◆) 60°C. (b) Second-order plots for the DBTDL-catalyzed reactions of IPDI with PPG2000 (OH/NCO = 2 : 1) at different temperatures: (—) second-order kinetic model and experimental data at (■) 30, (▲) 40, and (◆) 60°C.

$$\frac{1}{\left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=t}} - \frac{1}{\left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0}} = k_{\text{obs}}.t \quad (24a)$$

If the initial concentrations of the hydroxyl and isocyanate groups are unequal (i.e., $[\text{OH}]_0/[\text{NCO}]_0 = M$) and the functional groups (OH and NCO) are both consumed at the same rate (i.e., no side reactions), eq. (24a) can be integrated to retrieve the following concentration–time profile:

$$\frac{1}{\left[\frac{\text{Area}_{-\text{OH}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0} - \left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0}}$$

$$\times \ln \frac{\left[\frac{\text{Area}_{-\text{OH}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0} - \left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0} + \left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=t}}{M\left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=t}}$$

$$= k_{\text{obs}}.t \quad (24b)$$

where $\left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0}$ is the starting concentration of the diisocyanate, $\left[\frac{\text{Area}_{-\text{OH}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=0}$ is the initial concentration of the polyol, and $\left[\frac{\text{Area}_{-\text{NCO}}}{\text{Area}_{-\text{CH}_3}}\right]_{t=t}$ is the running concentration of the diisocyanate. The catalyst concentration can be considered constant; as a result, a new apparent constant, $k_{\text{obs}} = k_{\text{cat}}[\text{Catalyst}]$, is obtained. The third-order equations [eqs. (10) and (23)] can be integrated with respect to the degree of isocyanate (X_A) as follows:
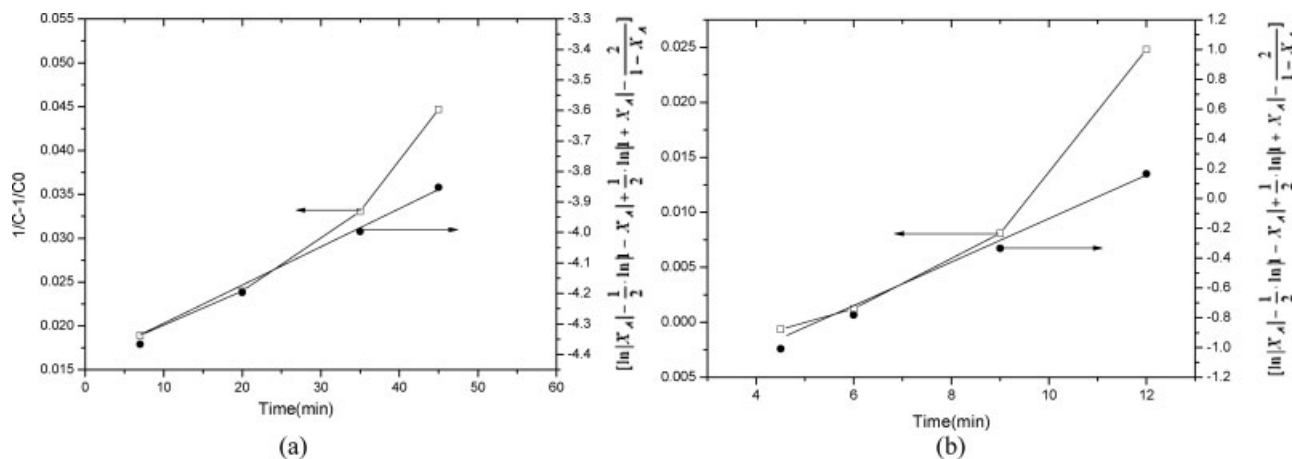
$$\left[\ln|X_A| - \frac{1}{2}.\ln|1 - X_A| + \frac{1}{2}.\ln|1 + X_A| - \frac{2}{1 - X_A}\right]$$

$$= k_{\text{obs}}.C_{A0}^2.t \quad (24c)$$

where C_{A0} is the starting concentration of the diisocyanate.
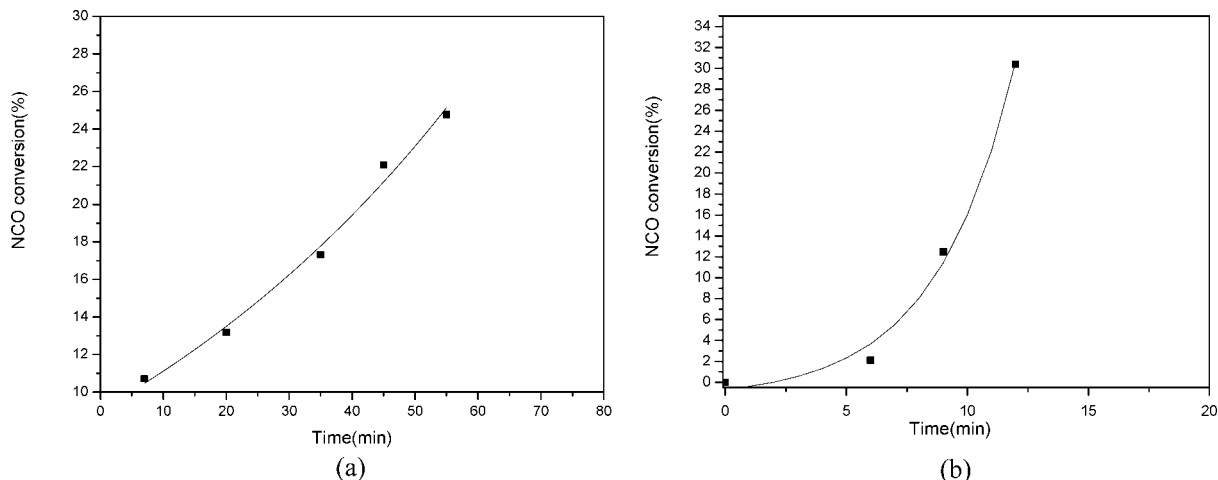
Figure 2 Plot of the conversion versus time for the DBTDL-catalyzed reactions of (a) IPDI with PPG2000 (OH/NCO = 1 : 1) at 30°C and (b) IPDI with PPG2000 and 1,4-BD (OH/NCO = 1 : 1) at 30°C.

Figure 3 (□) Second-order and (●) third-order plots for the DBTDL-catalyzed reactions of (a) IPDI with PPG2000 (OH/NCO = 1 : 1) at 30°C and (b) IPDI with PPG2000 and 1,4-BD (OH/NCO = 1 : 1) at 30°C.

Therefore, the catalytic rate constants (the slope of the straight line obtained by the plotting of the reciprocal concentration versus time) for each reaction were determined according to eqs. (24a)–(24c). The rate constant k_{cat} was thus determined from two or three independent experiments. The conversion–time data were first expressed as the percentage of NCO consumed as a function of time, and the thermodynamic parameters were obtained with the Arrhenius equation.

RESULTS AND DISCUSSION

### Kinetic study of IPDI in the urethane reaction

Tables I and II present the results of the alcohol/isocyanate reaction, at an OH/NCO ratio of 2 : 1, that forms the hydroxyl-terminated prepolymer under DBTDL catalysis. Figure 1 presents some examples of plots as a function of time, together with the calculated second-order kinetic model [with eq. (24b)] and experimental reaction profiles. It is evident that the reaction is described well by the second-order kinetics during the catalyst-mediated initial-to-middle stages (Fig. 1, curves for 30°C), but we observe some positive deviations from linearity (autoacceleration) during the later stages [Figs. 1(a,b)]. Similar autoacceleration effects were observed at an OH/NCO ratio of 1:1 for the reactions between IPDI and PPG2000 [Fig. 2(a)] and between IPDI and PPG2000 in the presence of 1,4-BD [Fig. 2(b)]; the autoacceleration intensity depended on the concentration of urethane groups produced. Clearly, the isocyanate/alcohol reaction is catalyzed by the newly formed urethane groups. Applying the autocatalytic model of eq. (24c) to the experimental results, Figure 4 (shown later) presents some examples of plots versus time, together with the second-order kinetic model and autocatalytic model. Our suggested kinetic model, which takes into account the autocatalytic effect of the urethane groups, fits the experimental data much better at low to high conversions than the second-order kinetic model does (cf. Figs. 3 and 4). The plots display a rather significant deviation from the autocatalytic model, even at a low conversion. It is evident that the urethane groups provide an autoacceleration of the isocyanate/alcohol reaction. Luo and Tan[4] proposed that the formation of a hydrogen-bonded complex between the hydroxyl and resulting urethane groups is the cause of the autocatalysis of this reaction. Therefore, the pathway proposed for the urethane-catalyzed reaction of isocyanate groups with hydroxyl compounds is presented in Scheme 1.

The hydroxyl group is activated by the urethane through the formation of a hydrogen bond in which the urethane moiety acts as a basic catalyst (much like a tertiary amine) to increase the nucleophilicity of the oxygen atom of the complexed hydroxyl
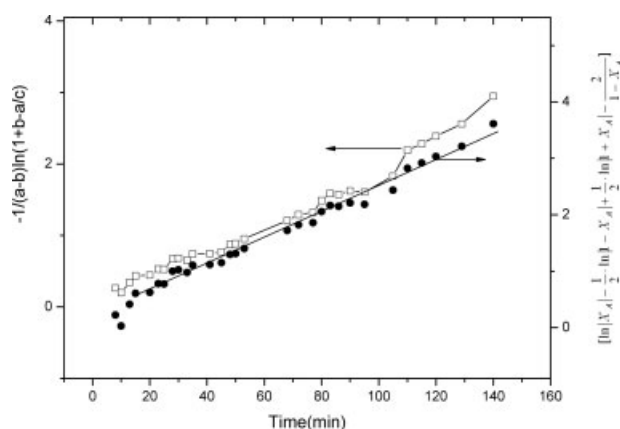
Figure 4 (□) Second-order and (●) third-order plots for the DBTDL-catalyzed reactions of IPDI with PPG2000 (OH/NCO = 2 : 1) at 60°C.
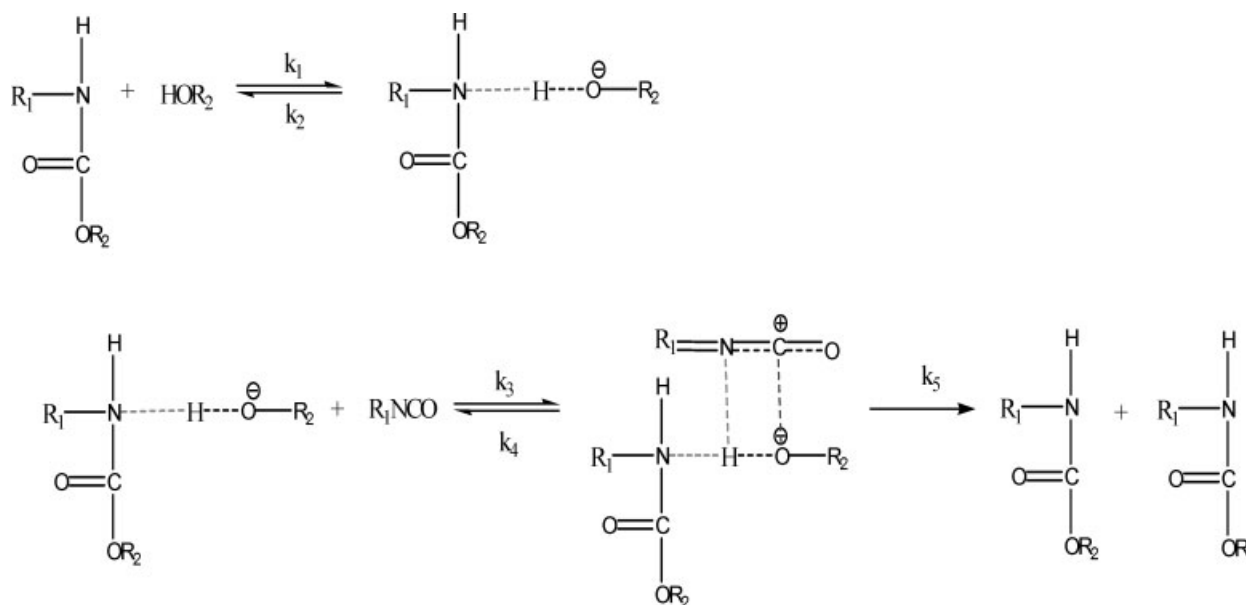
Scheme 1 Proposed pathway of the urethane-catalyzed reaction of isocyanate groups with hydroxyl compounds.

group. This complex then reacts with the isocyanate; that is, the polymerization occurs to produce a new urethane group, with regeneration of the previously complexed urethane moiety.

Kinetic study of IPDI in the urea reaction

The kinetics of the reactions of isocyanates with alcohols to form urethanes have been studied widely; in contrast, the reactions of isocyanates with water are relatively little studied.[6] Tables III and IV display the kinetic results of the isocyanate/water reactions between isocyanate-terminated oligomers (IPDI–PPG2000–IPDI) and water at an OH/NCO ratio of 1 : 1 that principally form polyurea under catalysis with various tertiary amines at various temperatures.

An interesting tendency is noted: the activation energy for the isocyanate/alcohol reaction was 64.88 kJ/mol, but those for the isocyanate/water reactions were about 80 kJ/mol, indicating that the urea-forming reaction is more sensitive to the reaction temperature than the urethane-forming reaction. Furthermore, it is also observed that the autoacceleration effect came into effect at an earlier degree of conversion (Fig. 5). Preliminary experiments have indicated that this autoacceleration effect is due to the presence of the urethane group; therefore, the newly formed urea groups should also catalyze the reaction between the isocyanate and water. Indeed, the autocatalytic model in eq. (24c) describes the experimental results for the isocyanate/water reaction very well (Fig. 6). It is evident that the urea groups

TABLE III
Kinetic Data for the Reactions of the IPDI–PPG–IPDI Prepolymer with Water (OH/NCO = 1 : 1)
Catalyzed by Various Tertiary Amines

Temperature (°C)	Catalyst	[Catalyst] (mol/L)	k_{obs} (L mol^{-1} S^{-1})	R^{2a}	k_{cat} (L^2 mol^{-2} S^{-1})
30	DBU	0.0032	0.000295	0.991	0.110
30	DBU	0.0064	0.000450	0.992	
30	DBU	0.0096	0.001010	0.992	
30	DBN	0.0039	0.000185	0.999	0.010
30	DBN	0.0079	0.000227	0.999	
30	DBN	0.0118	0.000267	0.990	
30	DMCHA	0.0038	0.000118	0.999	0.062
30	DMCHA	0.0077	0.000317	0.993	
30	DMCHA	0.0115	0.000598	0.988	
30	PMDETA	0.0028	0.000073	0.971	0.103
30	PMDETA	0.0056	0.000248	0.992	
30	PMDETA	0.0085	0.000662	0.999	

[a] Correlation coefficient of the mean-square linear regression.

TABLE IV
Kinetic Data for the Reactions of the IPDI–PPG–IPDI Prepolymer with Water (OH/NCO = 1 : 1) Catalyzed by Various Tertiary Amines at Various Temperatures

Temperature (°C)	Catalyst	[Catalyst] (mol/L)	k_{obs} (L mol^{-1} S^{-1})	R^{2a}	E_a (kJ/mol)[b]	Frequency factor
30	DBU	0.0032	0.000295	0.992	79.15	1.23×10^{10}
40	DBU	0.0032	0.000769	0.991		
50	DBU	0.0032	0.001320	0.999		
30	DBN	0.0039	0.000185	0.999	70.33	3.06×10^{8}
40	DBN	0.0039	0.000391	0.996		
50	DBN	0.0039	0.002000	0.988		
30	DMCHA	0.0038	0.000118	0.999	76.4	1.94×10^{9}
40	DMCHA	0.0038	0.000422	0.996		
50	DMCHA	0.0038	0.000701	0.998		
30	PMDETA	0.0028	0.000073	0.971	94.0	2.23×10^{3}
40	PMDETA	0.0028	0.000328	0.991		
50	PMDETA	0.0028	0.001270	0.998		

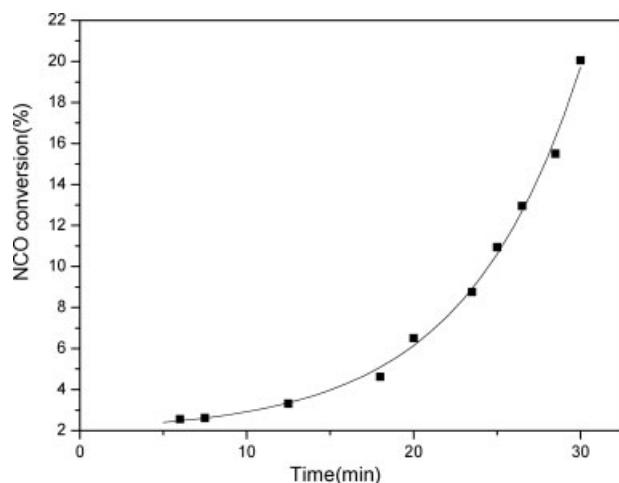[a] Correlation coefficient of the mean-square linear regression.
[b] Activation energy.

provide an autoacceleration effect in addition to the effect of the urethane groups. Similarly, it is proposed that the autocatalysis pathway of the isocyanate/water reaction occurs through the formation of hydrogen bonds between water molecules and the newly formed urea groups (Scheme 2).

These activated water molecules exhibit increased nucleophilicity of their oxygen atoms. These complexes then react with the isocyanate to form a carbamic acid intermediate, which is unstable and decarboxylates spontaneously to form an amine and carbon dioxide, with regeneration of the urea group; this amine reacts further with another isocyanate to produce a new urea group.
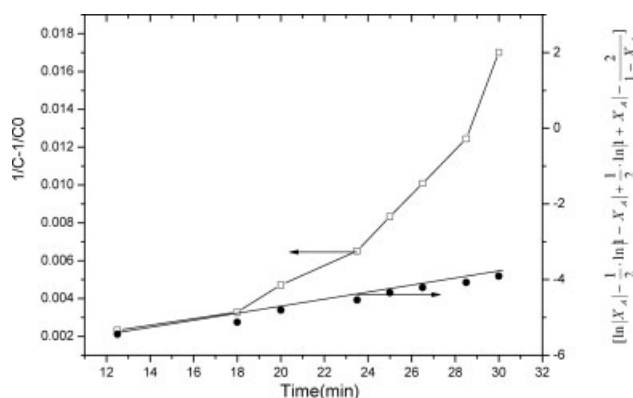
CONCLUSIONS

FTIR spectroscopy is a powerful analytical technique for monitoring the syntheses of polyurethanes and polyureas because the disappearance of the strong isocyanate absorption and the appearance of highly intense absorbances for the products allow quantitative measurements to be conducted, even at low conversions. The analysis of the kinetic data leads us to the following conclusions:

1. Global kinetic models that take into account the autocatalytic contributions of the urethane and urea groups are effective for describing the catalyst-mediated isocyanate/alcohol and isocyanate/water reactions. These global models describe second-order kinetics during the initial stages of the catalyst-mediated reaction but subsequently describe autocatalytic third-order kinetics arising from the formation of hydrogen bonds between the alcohol or water and the resulting urethane or urea groups.

2. Activation energies of 64.88 and about 80 kJ/mol for the isocyanate/alcohol and isocyanate/water reactions, respectively, indicate that the

Figure 5 Plot of the conversion versus time for the DBN-catalyzed reaction of the IPDI–PPG–IPDI prepolymer with water (OH/NCO = 1 : 1) at 30°C.

Figure 6 (□) Second-order and (●) third-order plots for the DBN-catalyzed reaction of the IPDI–PPG–IPDI prepolymer with water (OH/NCO = 1 : 1) at 30°C.
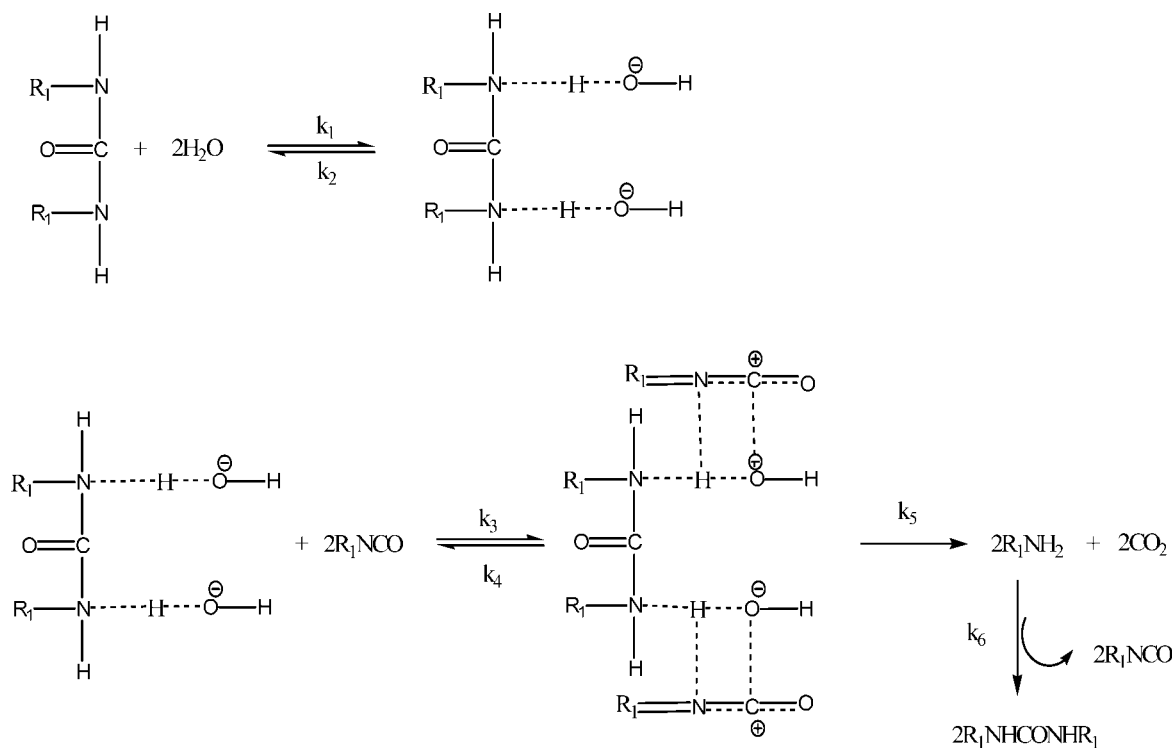
Scheme 2 Proposed pathway for the urea-catalyzed reaction of isocyanates with water.

influence of the temperature during the urea-forming reaction is higher than that during the urethane-forming reaction.

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