Segmented Poly(urethane–urea)s Synthesized Directly from Isocyanate-Terminated Prepolymers and Masked Diamines III. Kinetic and Mechanistic Study on Polymerization Reactions

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ABSTRACT: The direct synthesis of segmented poly(urethane–urea)s (DSPUU) from an isocyanate-terminated prepolymer (ITPP) and reaction products (AE) from acetone and ethylenediamine consisting of N-isopropylideneethylenediamine (1), N,N'-diisopropylideneethylenediamine (2), 2,2-dimethylimidazolidine (3), water and the unreacted diamine was kinetically investigated. The following elementary reactions forming the desired urea structure linkage take place simultaneously in the absence of an acid at 40°C; (i) reaction of NCO groups with amino groups of the unreacted diamine and (1), (ii) direct reaction of NCO groups with (3), (iii) ring opening reaction of (3), and (iv) reaction of NCO groups with the ketimine groups in (1) and (2). The side reactions of NCO groups with water (Urea II formation reaction) catalyzed by both the ketimine groups and the imino groups occurred. Dramatic decrease of the yield of Urea II in the presence of acetic acid is attributed to the acid-catalyzed ring opening of the imino groups of (3) in particular and acid-catalyzed hydrolysis of the ketimine groups.
    KEY WORDS   Poly(urethane–urea)s / Bulk Polymerization / Isocyanate-Terminated Prepolymer / Masked Diamines / Polymerization Kinetics / Demasking Reactions / Direct Reactions /

For clarification of the mechanism of the direct synthesis of segmented poly(urethane-urea)s (DSPUU reaction) from an isocyanate-terminated prepolymer (ITPP) and acetone-masked ethylenediamine (AE),[1] consisting of N-isopropylideneethylenediamine (1), N,N'-diisopropylideneethylenediamine (2), 2,2-dimethylimidazolidine (3), and water ([☐] in Scheme 1),[2] we found that significant reactions involved in DSPUU reactions in the ab-

sence of an acid catalyst are direct reactions of isocyanate (NCO) groups with (1) and (2) as well as with (3)[1,2] (see ☐ in Scheme 1). These reactions were classified into the first category. The preceding paper[3] elucidated the kinetics of masking and demasking reactions for AE. Important reactions belonging to the second category were found to be the water- and acid-catalyzed ring opening of (3) and acid-catalyzed hydrolysis reactions of
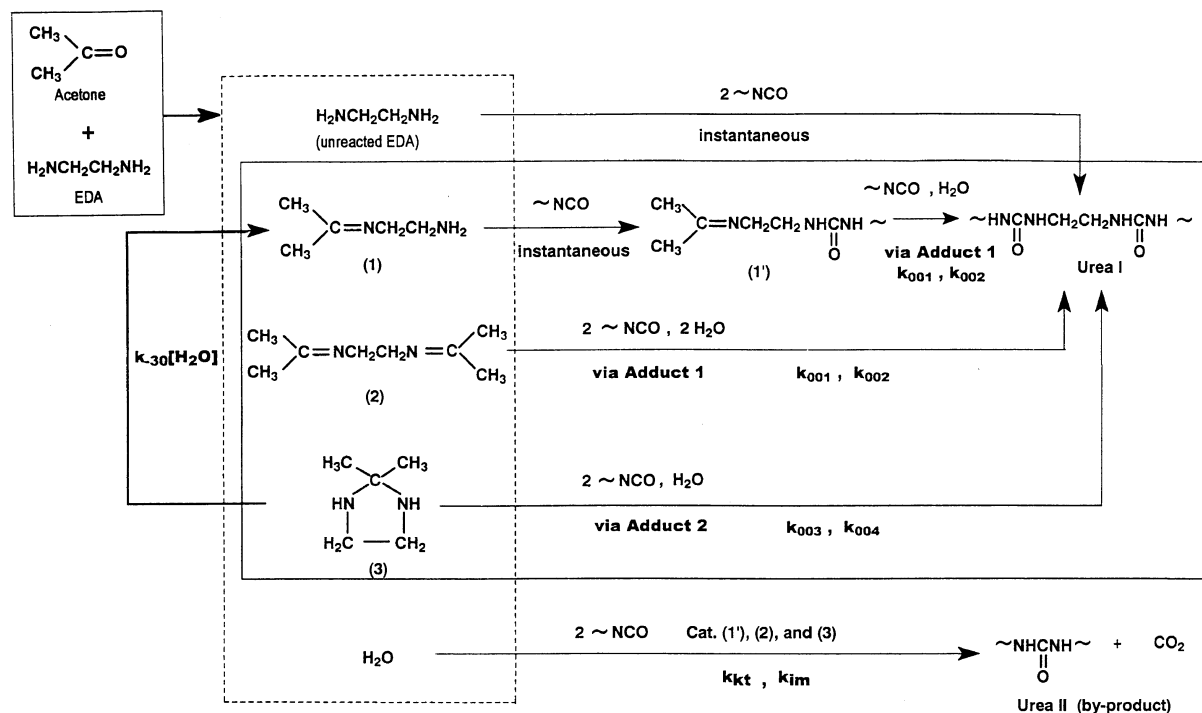
Scheme 1. Elementary DSPUU reactions in the absence of acid catalyst.

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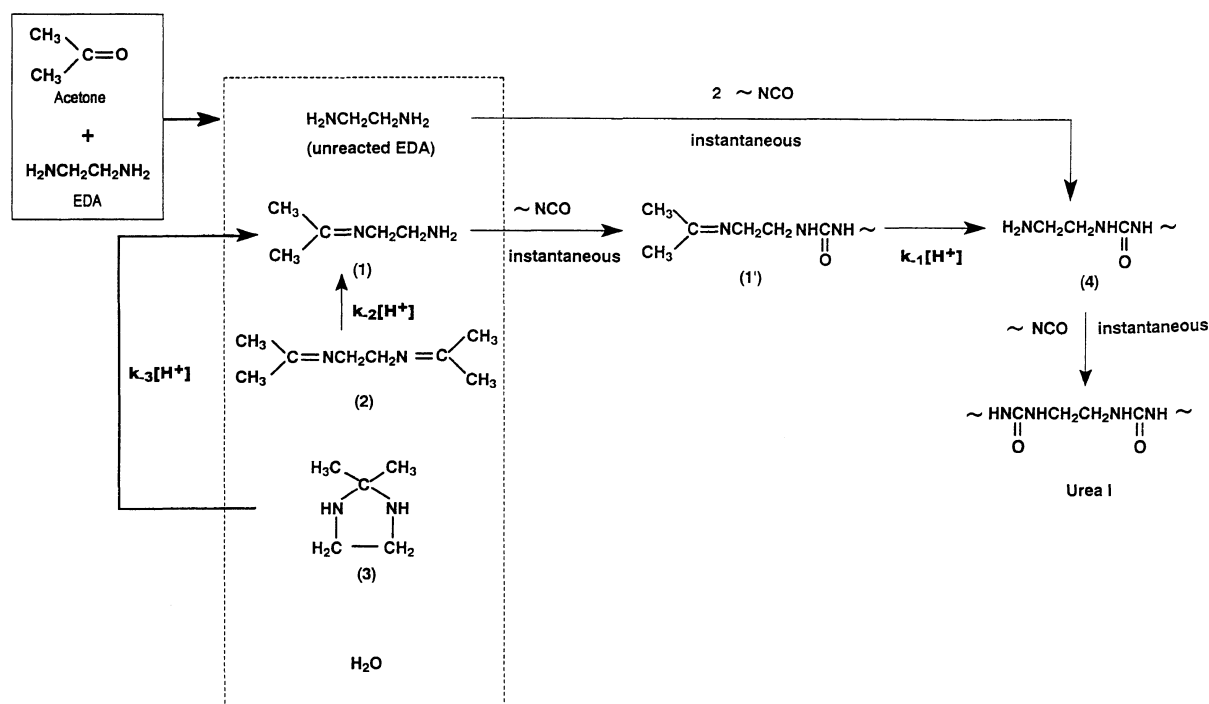
Scheme 2. Urea I formation through acid-catalyzed hydrolysis reaction of ketimine groups.

(1) and (2) (Schemes 1 and 2).[3]

This paper estimates the rate and catalyst constants of elementary reactions in the first category. The dominant and simultaneous elementary reactions belonging to the first and second categories in DSPUU reactions are made clearer by comparing ① experimental rates of consumption of NCO groups during the DSPUU reactions and ② the yields of the by-product (Urea II) formed from the reaction of NCO groups with water, to the corresponding values ①′ and ②′ calculated by solving numerically a set of simultaneous rate equations including all elementary reactions belonging to the above two categories. The roll of an acid for vanishing the yield of Urea II[1] is also clarified, finally leading to clarification of overall mechanism of DSPUU reactions in the absence and presence of the acid catalyst.

EXPERIMENTAL

Model Reactions of ITPP with Ketimine or Imidazolidine

For estimating the rate and catalyst constants of the reactions of the isocyanate-terminated prepolymer (ITPP) with (1), (2), and (3), the following two model reactions were examined. Since it was impossible to isolate the reaction products (AE) from acetone with EDA, N-isopropylidenebutylamine and 2-pentamethylenoimidazolidine were used as the model of ketimine and imidazolidine in an AE sample, respectively.

Reaction of ITPP with N-Isopropylidenebutylamine. One hundred grams of ITPP (NCO content, 0.679 mol) obtained from the reaction of excess molar of 4,4′-methylenediphenyl diisocyanate (MDI) with poly(tetramethylene oxide) (PTMO, $\overline{M}_n = 2010$) were mixed with 7.08 g (0.0625 mol as 91% purity) of N-isopropylidene-butylamine[4] and 1.13 g (0.0625 mol) of water using a mixing device[1] for 5 s, followed by tracing the concentration change of NCO groups at 40°C for 400 s by FT-IR

described later. By ^{13}C NMR, the reaction product was found to contain 58.3 mol% of Urea I′, the urea linkage formed by the reaction of an NCO group of ITPP with n-butylamine. The rest (41.7 mol%) was Urea II. The detailed preparation procedure of the above ITPP and operating conditions of ^{13}C NMR were described in ref 1.

Since the rate of hydrolysis reaction of a ketimine analogue is negligibly slow[3] for the reaction pathway of Urea I′ formation, it should be recognized that an intermediate compound is formed first from the direct reaction of the ketimine group with NCO groups[2,5] (corresponding rate constant is defined as k_{001}), followed by the hydrolysis reaction (rate constant of k_{002}), giving Urea I′. Urea II is formed by the reaction of ITPP with water, supported by the ketimine catalysis[1] (the catalyst constant of k_{kt}).

k_{001}, k_{002}, and k_{kt} were estimated by fitting the calculated plots of [NCO]/[NCO]$_0$ and calculated molar fraction of Urea II (see, APPENDIX) to the above experimental plots and the molar fraction by the least-square fitting method.

Reaction of ITPP with 2-Pentamethylenoimidazolidine. The model reaction of 100.0 g of ITPP (0.679 mol), 10.63 g of the reaction products from cyclohexanone with EDA containing 0.0625 mol of 2-pentamethylenoimida-zolidine as 93% purity, and 0.0625 mol of water was carried out in chloroform (109.9 g), giving a mixture of Urea I′ and Urea II. The preparation procedure of the reaction products is shown in ref 2. Kinetic measurements by FT-IR were also performed during this reaction. The molar fraction of Urea II was 26.0% in this case. Note that this reaction was inevitably carried out in chloroform solution due to the extremely fast reaction in bulk.

Subject to the analogy of this reaction pathway to that of the above model ketimine-ITPP reaction,[2,6] rate constants such as k_{003} for the addition reaction and k_{004}

for the hydrolysis reaction as well as the catalyst constant k_{im} of the imino groups were estimated in the similar manner to the case of model ketimine–ITPP reaction.

Kinetic Measurements

Figure 1 schematically shows an ATR (attenuated total reflection) holder for kinetic measurements in DSPUU reactions. The holder is composed of an IRE (ZnSe crystalline rod, 45°, 84-mm long × 9-mm wide × 6-mm high) and a lid for sealing a sample with nitrogen gas. The consumption of NCO groups at various reaction times was measured when DSPUU samples (DSPUU2— 11) were synthesized in the literature.[1] The temperature rise during the measurements for all DSPUU reactions was within 5% owing to the relatively low concentrations of NCO and amino groups. It was inaccurate to detect concentrations of other functional groups such as the ketimine and imino groups by this FT-IR method since the characteristic ketimine peak (1665 cm^{-1}) was close to those of Urea I (1635 cm^{-1} (hydrogen-bonded)) and Urea II (1639 cm^{-1} (hydrogen-bonded)) and the extremely weak peak of the imino group (1600 cm^{-1}).

RATE EQUATIONS

DSPUU reactions in the absence and presence of an acid catalyst are the elementary reactions shown in Schemes 1 and 2, respectively. The Urea I formation reaction of NCO groups (i) with the amino groups of unreacted EDA and (1) which is instantaneously transformed to (1')[7] and (ii) with the ketimine groups of (1') and (2) as well as the imidazolidine (3) in the presence
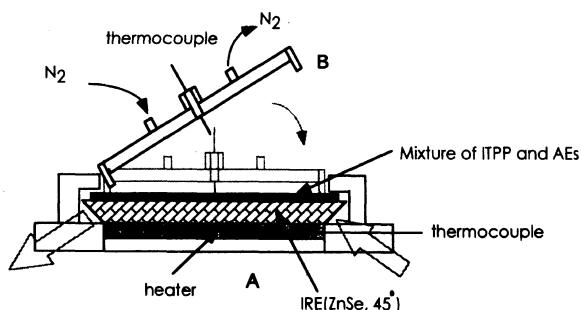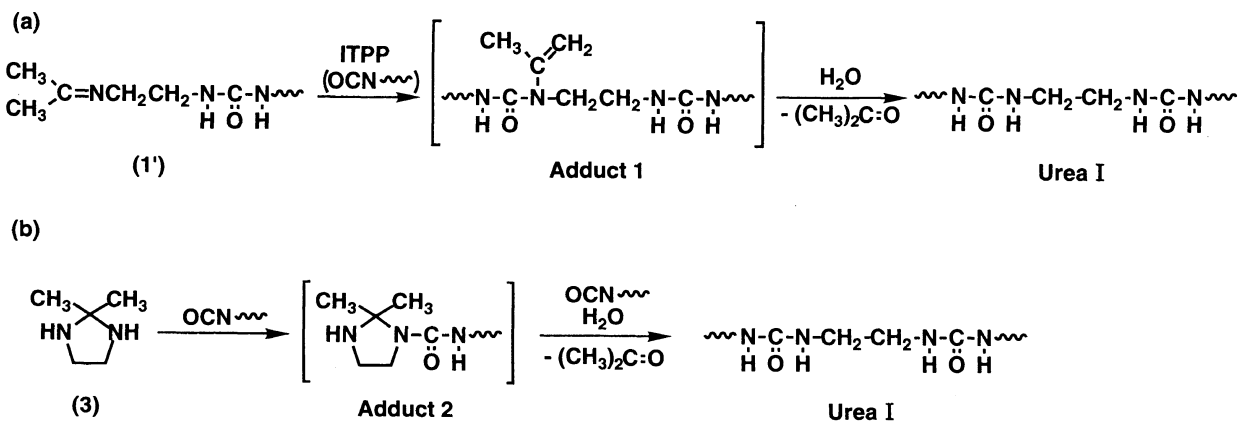

Figure 1. Schematic diagram of the ATR (attenuated total reflection) holder for kinetic measurements; A, ZnSe crystalline rod with heating elements and temperature controller; B, a lid for sealing a sample by nitrogen gas.

of water *via* Adducts 1 and 2 (Scheme 3), respectively[1,2] (these reactions belong to the category of the direct reactions). The water-catalyzed ring opening of (3) to form (1) also takes place at the same time.[3] (iii) the side reaction of NCO groups with water to form Urea II catalyzed by the ketimine groups of (1') and (2) as well as the imino groups of (3) and the Adduct 2 also occurs.[1,2]

In the presence of the acid catalyst, (iv) the reactions of NCO groups with the amino groups reformed from the ketimine groups of (1') and (2) as well as the imidazolidine (3) and (v) the acid-catalyzed ring opening of (3) are significant (these reactions belong to the category of the demasking reactions in Scheme 2).[3] It should be noted that the acid-catalyzed hydrolysis of the above Adducts 1 and 2 are neglected in this simulation because formation reactions of these adducts were found to be rate determining as described later.

Taking into account the extremely fast reactions of NCO groups with amino groups[7] regenerated from (1'), (2), and (3), it can be assumed in the rate equations for the model of DSPUU reaction that the reverse reactions do not principally occur (that is, negligible) and therefore the regeneration rates of the amino groups from (1'), (2), and (3), respectively, may be regarded as the rate determining reactions to form the main product (Urea I). The reformation rate of amino groups from (1') may be considered the same as that of (1).

The simultaneous rate equations (eq 1—11) could be solved by a computer after substituting the six rate and catalyst constants estimated in EXPERIMENTAL, together with four constants previously determined[3] (all listed in Table I) and the initial concentrations of the functional groups in AE samples and NCO groups of ITPP (Table II). All numerical calculations were performed using the Runge–Kutta fourth order method on a work station Model INDY, manufactured by Silicon Graphics Inc., U.S.A.

The rate of increase in the concentrations of the amino groups reformed from (1'), (2), and (3) is expressed in eq 1, neglecting the rate constants of the hydrolysis reactions of the ketimine groups in the absence of the acid.[1] Note again that the amino groups thus formed are consumed instantaneously by reactions with NCO groups, forming Urea I. EDA contained in AE samples is also consumed at the beginning of the reactions.

(a)

(1')   Adduct 1   Urea I

(b)

(3)   Adduct 2   Urea I

Scheme 3. Formation pathways of Adducts 1 and 2 from (1') and (3), respectively.

$$d[NH_2]/dt = k_{-1}[H^+][(1')][H_2O]$$
$$+ 2k_{-2}[H^+][(2)][H_2O] + (k_{-30}[H_2O]$$
$$+ k_{-3}[H^+])[(3)]$$

(1)

where $[NH_2]$, $[(1')]$, $[(2)]$, $[(3)]$, and $[H_2O]$ represent the concentrations of the amino groups, $(1')$, (2), (3), and water, respectively. The catalyst constants of hydrolysis reactions of $(1')$ and (2) are denoted as k_{-1} and k_{-2}. The catalyst constants of k_{-30} and k_{-3} are those for the water- and acid-catalyzed reformation reactions of (1) from (3) by tautomeric relation.

Similarly, the rate of increase in the concentration of acetone is given by eq 2.

$$d[acetone]/dt = k_{-1}[H^+][H_2O][(1')]$$
$$+ 2k_{-2}[H^+][(2)][H_2O] + 2k_{002}[Add1][H_2O]$$
$$+ k_{004}[Add2][H_2O]$$

(2)

where k_{002} and k_{004} denote the rate constants of the hydrolysis reactions of the Adduct 1 and Adduct 2; the former is derived from the addition reaction of NCO groups with the ketimine groups of $(1')$ and (2) and the latter with (3), respectively.

Next the rates of decrease in the concentrations of $(1')$, (2), and (3) (subject to water catalysis[8]), respectively, can be expressed as follows, considering that $(1')$ is formed instantaneously from (1);

$$-d[(1')]/dt = k_{-1}[H^+][(1')][H_2O]$$
$$- 2k_{-2}[H^+][(2)][H_2O] + k_{001}[(1')][NCO]$$
$$- (k_{-30}[H_2O] + k_{-3}[H^+])[(3)]$$

(3)

$$-d[(2)]/dt = 2k_{-2}[H^+][(2)][H_2O]$$
$$+ 2k_{001}[(2)][NCO]$$

(4)

$$-d[(3)]/dt = (k_{-30}[H_2O] + k_{-3}[H^+])[(3)]$$
$$+ 2k_{003}[(3)][NCO]$$

(5)

where k_{001} and k_{003} denote the rates of addition reactions of NCO groups with the ketimine groups of $(1')$ $((2))$ and imino group of (3), forming the Adducts 1 and 2 (Scheme 3), respectively.

The rate of decrease in a water concentration is given by eq 6, considering the catalysis of the ketimine and the imino groups of (3) and Adduct 2 for the NCO–water reaction (k_{kt} and k_{im} are the catalyst constants by the ketimine group and imino group, respectively). The rate constant $(5.9 \times 10^{-5} \, kg\,mol^{-1}\,s^{-1})$ of ITPP and water[9] was small and therefore neglected.

$$-d[H_2O]/dt = k_{-1}[H^+][H_2O][(1')]$$
$$+ 2k_{-2}[H^+][H_2O][(2)] + \{k_{kt}([(1')]$$
$$+ 2[(2)]) + k_{im}(2[(3)] + [Add2])\}[NCO][H_2O]$$
$$+ k_{002}[Add1][H_2O] + k_{004}[Add2][H_2O]$$

(6)

The rate of decrease in the concentrations of the Adducts 1 and 2 can be written in eq 7 and 8 as,

$$-d[Add1]/dt = k_{001}(2[(2)] + [(1')])[NCO]$$
$$- k_{002}[Add1][H_2O]$$

(7)

$$-d[Add2]/dt = 2k_{003}[(3)][NCO]$$
$$- k_{004}[Add2][H_2O]$$

(8)

By considering eq 1, A5 (see APPENDIX), 7, and 8, the rate of increase in Urea I concentration is given by eq 9.

$$d[Urea\ I]/dt = k_{002}[Add1][H_2O]$$
$$+ 2k_{004}[Add2][H_2O] + k_{-1}[H^+][(1')][H_2O]$$
$$+ 2k_{-2}[H^+][(2)][H_2O] + (k_{-30}[H_2O]$$
$$+ k_{-3}[H^+])[(3)]$$

(9)

The formation rate of Urea II is written in eq 10, referring to eq 6.

$$d[Urea\ II]/dt = \{k_{kt}([(1')] + 2[(2)])$$
$$+ k_{im}(2[(3)] + [Add2])\}[NCO][H_2O]$$

(10)

The rate of NCO consumption is expressed by eq 11, taking into account the above all the equations (eq 1—10) except for eq 2;

$$-d[NCO]/dt = k_{-1}[H^+][(1')][H_2O]$$
$$+ 2k_{-2}[H^+][(2)][H_2O] + (k_{-30}[H_2O]$$
$$+ k_{-3}[H^+])[(3)] + k_{001}([(1')]$$
$$+ 2[(2)])[NCO] + 2k_{003}[(3)][NCO]$$
$$+ 2\{k_{kt}([(1')] + 2[(2)]) + k_{im}(2[(3)]$$
$$+ [Add2])\}[NCO][H_2O]$$

(11)

RESULTS AND DISCUSSION

DSPUU Reactions in the Absence of Acid Catalyst

Determination of ① Rate Constants (k_{001}, k_{001}, k_{003}, and k_{004}) for Reactions of ITPP with $(1')$ $((2))$ or (3) and ② Catalyst Constants (k_{kt} and k_{im}) for Reactions of ITPP with Water. Figure 2 shows the experimental plots of the concentration ratio of the unreacted NCO groups to initial NCO groups, $[NCO]/[NCO]_0$ vs. reaction time for the model reactions of ITPP with the mixture of N-isopropylidenebutylamine and water (●) or mixture of 2-pentamethylenoimidazolidine and water (■). The best-fitted plots by the least-square fitting method are also shown in the figure. Table I lists rate and catalyst constants such as k_{001}, k_{002}, and k_{kt} as well as k_{003}, k_{004}, and k_{im} estimated by the fitting procedures. The reactivity
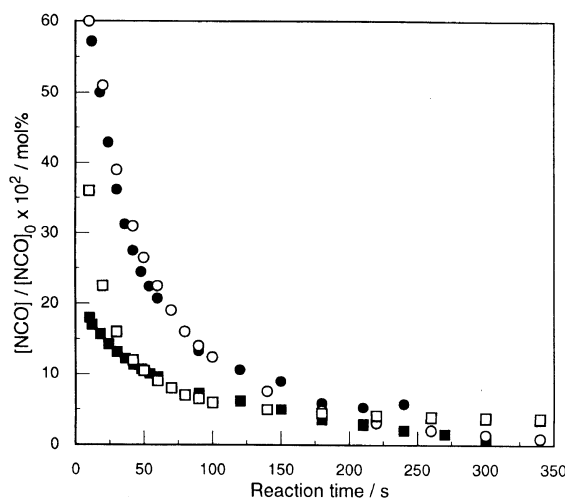

Figure 2. Plots of $[NCO]/[NCO]_0$ vs. reaction time for the model reactions of ITPP with the mixture of N-isopropylidenebutylamine and water (●, experimental; ○, calculated) as well as with the mixture of 2-pentamethylenoimidazolidine and water in chloroform (■, experimental; □, calculated).

Table I. Estimated rate and catalyst constants of elementary DSPUU reactions

Catalyst constants of reformation reactions of amino groups[a]				Rate constants of direct reactions				Catalyst constants of NCO–water reaction	
$kg^2 mol^{-2} s^{-1}$				$kg mol^{-1} s^{-1}$				$kg^2 mol^{-2} s^{-1}$	
k_{-1}	k_{-2}	k_{-30}[b]	k_{-3}[b]	k_{001}	k_{002}	k_{003}	k_{004}	k_{kt}	k_{im}
8.5×10^{-2}	5.2×10^{-2}	2.4×10^{-2}	4.3×10^{-3}	5.0×10^{-3}	0.32	5.0×10^{-2} $(0.2)^c$	0.61 $(1.2)^c$	2.1×10^{-2}	6.8×10^{-2} $(2.3 \times 10^{-1})^c$

[a] Estimated in ref 3. [b] $kg mol^{-1} s^{-1}$. [c] Uncorrected values for the model reaction. See the text.

Table II. Calculation conditions for DSPUU reactions and mol fractions of by-product (Urea II) in PUUs

Sample code	Preparation conditions for AEs			Initial concentrations of each compound in AEs and ITPP/mol kg⁻¹						[Acid]ᵃ × 10³	Mol fraction of Urea IIᵇ
	Sample code	[Acetone]₀/ [EDA]₀	[H₂O]₀/ [EDA]₀	AE					ITPP	mol kg⁻¹	mol%
				EDA	(1)	(2)	(3)	H₂O	NCO		
DSPUU2	AE2	1.4	—	0.0117	0.0573	0.0483	0.2067	0.3606	0.6479	—	28
DSPUU3	AE3	1.8	—	0.0068	0.0569	0.0794	0.1916	0.4073	0.6431	—	36
DSPUU4	AE4	2.5	—	0.0041	0.0590	0.0946	0.1597	0.4079	0.6348	—	42
DSPUU5	AE5	3.0	—	0.0022	0.0478	0.1245	0.1400	0.4368	0.6290	—	50
DSPUU6	AE6	1.4	0.5	0.0149	0.0581	0.0391	0.2109	0.5087	0.6460	—	36
DSPUU7	AE7	2.5	0.5	0.0074	0.0583	0.0567	0.1981	0.5303	0.6412	—	36
DSPUU8	AE6	1.4	0.5	0.0149	0.0581	0.0391	0.2109	0.5087	0.6460	0.70	16
DSPUU9	AE6	1.4	0.5	0.0149	0.0581	0.0391	0.2109	0.5087	0.6460	1.05	12
DSPUU10	AE6	1.4	0.5	0.0149	0.0581	0.0391	0.2109	0.5087	0.6460	1.75	4
DSPUU11	AE6	1.4	0.5	0.0149	0.0581	0.0391	0.2109	0.5087	0.6460	3.50	0

Note: Reaction conditions including raw materials, reaction temperature (time) and the by-product contents are originated from ref 1. ᵃ Acetic acid. ᵇ $10^2 [Urea II]/([Urea I] + [Urea II])$ (mol%).

of the direct reaction of ITPP with (1′), (2), and (3) as well as the catalytic effects of these compounds on the side reaction of ITPP with water were quantified in terms of rate and catalyst constants. In Table I, k_{-1} and k_{-2} are known catalyst constants of the acid-catalyzed reformation reactions of amino groups from the ketimine groups of (1′) and (2), respectively. k_{-30} and k_{-3} are the catalyst constants of water- and acid-catalyzed ring opening reaction of (3).

Using the six rate and catalyst constants estimated from the model reactions as well as k_{-30}, the $Y_{Urea II}$ for DSPUU2 was first calculated by substituting these constants in eq 1—11 and solving the equations simultaneously. The concentration of [H⁺] is zero in this case. $Y_{Urea II}$ was 13.1%, far smaller than the experimental $Y_{Urea II}$ of 28% (Table II). Explanation for this discrepancy can be found by comparing the calculated [NCO]/[NCO]₀ plots with the experimental ones (Figure 3); the calculated plots (□) deviated downwards from the experimental plots (●) up to *ca.* 75 s of t_{DS} and then turned upwards till the end of the DSPUU reaction (400 s). This suggests that ① the rate constants of k_{001} and/or k_{003} must be larger compared to the 'real' constants of the corresponding elementary reactions in the DSPUU reaction and ② consequently other constants such as k_{002} and k_{kt} (k_{004} and k_{im}) should also be changed. Taking into account the similarity of the chemical structures between *N*-isopropylidenebutyl-amine and (1′) ((2)) rather than between 2-pentamethyl-enoimidazolidine and (3), we decided to fix k_{001}, k_{002}, and k_{kt} and adjust k_{003}, k_{004}, and k_{im} so as to fit the calculated $Y_{Urea II}$s as well as the calculated [NCO]/
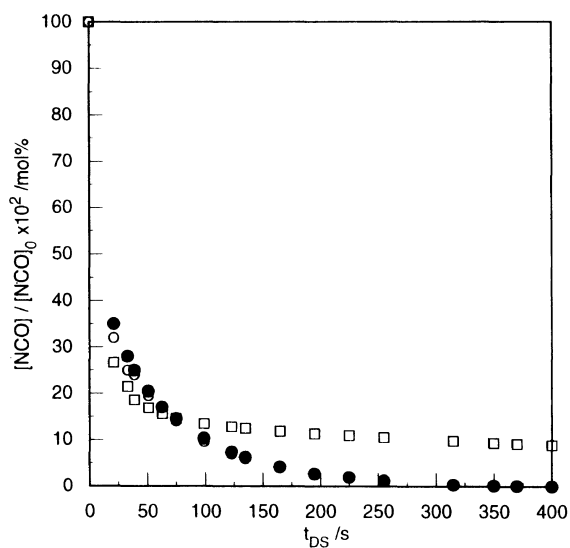

Figure 3. Reaction time (t_{DS})–NCO consumption plots for DSPUU2 reaction (□, calculated plots by using k_{003}, k_{004}, and k_{im} estimated by the model reaction; ○, fitted plots; ● experimental plots).

[NCO]₀ plots to the experimental data. Using the adjusted k_{003}, k_{004}, and k_{im} listed in Table I, the recalculated $Y_{Urea II}$ was 27.89% and calculated [NCO]/[NCO]₀ plots (○) fit the experimental plots (Figure 3). For further validation of these constants adjusted, other $Y_{Urea II}$s were calculated for DSPUU3—5. The calculation conditions are listed in Table II. Figure 4 shows the calculated plots of $Y_{Urea II}$ *vs.* initial concentration ratio of acetone to EDA, [acetone]₀/[EDA]₀ for the preparation of AE samples (AE2—5), together with the ex-
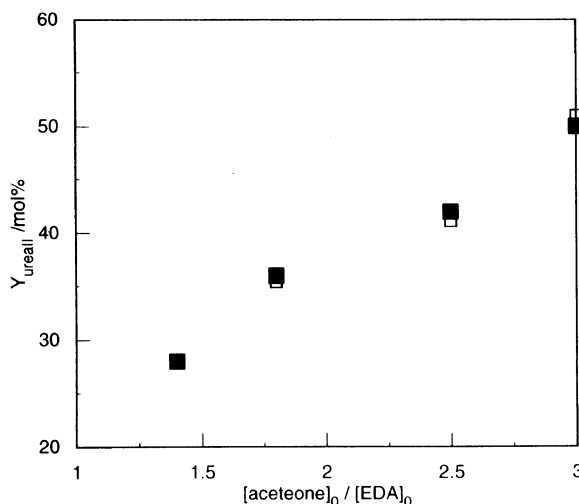
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Figure 4. $[acetone]_0/[EDA]_0$ dependence of $Y_{Urea\,II}$ for DSPUU2—5 reactions (■, experimental plots; □, calculated plots).

perimental plots. With increasing ratio, calculated $Y_{Urea\,II}$s increased, agreeing quite well with the experimental data for all DSPUU reactions.

From the above results we may reasonably conclude that the elementary reactions involving in the DSPUU reaction in the absence of an acid are aligned in the order of magnitude of the rate constants; (i) direct reaction of an NCO group with (3) ($k_{003} = 5.0 \times 10^{-2}$ kg mol^{-1} s^{-1}), (ii) reformation reaction of an amino group from (3) (water-catalyzed ring opening reaction) ($k_{-30} = 2.4 \times 10^{-2}$ kg mol^{-1} s^{-1}), and (iii) reaction of an NCO group with the ketimine groups of (1') and (2) ($k_{001} = 5.0 \times 10^{-3}$ kg mol^{-1} s^{-1}). The side reactions of an NCO group with water, subject to catalysis of the ketimine groups and the imino groups of (3) and Adduct 2 (catalyst constants of $k_{kt} = 2.1 \times 10^{-2}$ and $k_{im} = 6.8 \times 10^{-2}$ kg^2 mol^{-2} s^{-1}, respectively) take place simultaneously. The reactions are summarized in Scheme 1.

Effects of Concentration of Ketimine or Imino Group in DSPUU Reactions on $Y_{Urea\,II}$ Figures 5a, b, and c show concentration changes of the ketimine groups, water, and the imino groups during DSPUU2—5 reactions, respectively. Note that the concentrations of the ketimine groups and imino groups were equivalent to $[(1')] + 2[(2)]$ and $2[(3)] + [Add2]$, respectively. With increasing ratio of $[acetone]_0/[EDA]_0$ (see AE2—5 samples in Table II), the concentrations of the ketimine groups and water during the DSPUU reactions were kept higher (Figures 5a and b), while the concentrations of the imino groups were lower (Figure 5c). These results clearly explain the positive correlation between $[acetone]_0/[EDA]_0$ and $Y_{Urea\,II}$ depicted in Figure 4. $Y_{Urea\,II}$s may thus be mainly controlled by the initial concentration of the ketimine groups (or water). From the rapid disappearance of the imino groups shown in Figure 5c, the catalytic effect of the imino groups on the $Y_{Urea\,II}$ appears to be smaller than that of the ketimine groups, as also described in the previous paper.[1] However, Figure 6a shows that the Urea II was formed rapidly up to 100 s by the strong catalytic effect ($k_{im} = 6.8 \times 10^{-2}$ kg^2 mol^{-2} s^{-1}) of the imino groups and immediately faded away due to the rapid disappearance of the imino groups ($k_{-30} = 2.4 \times 10^{-2}$ kg mol^{-1} s^{-1}). In the case of the
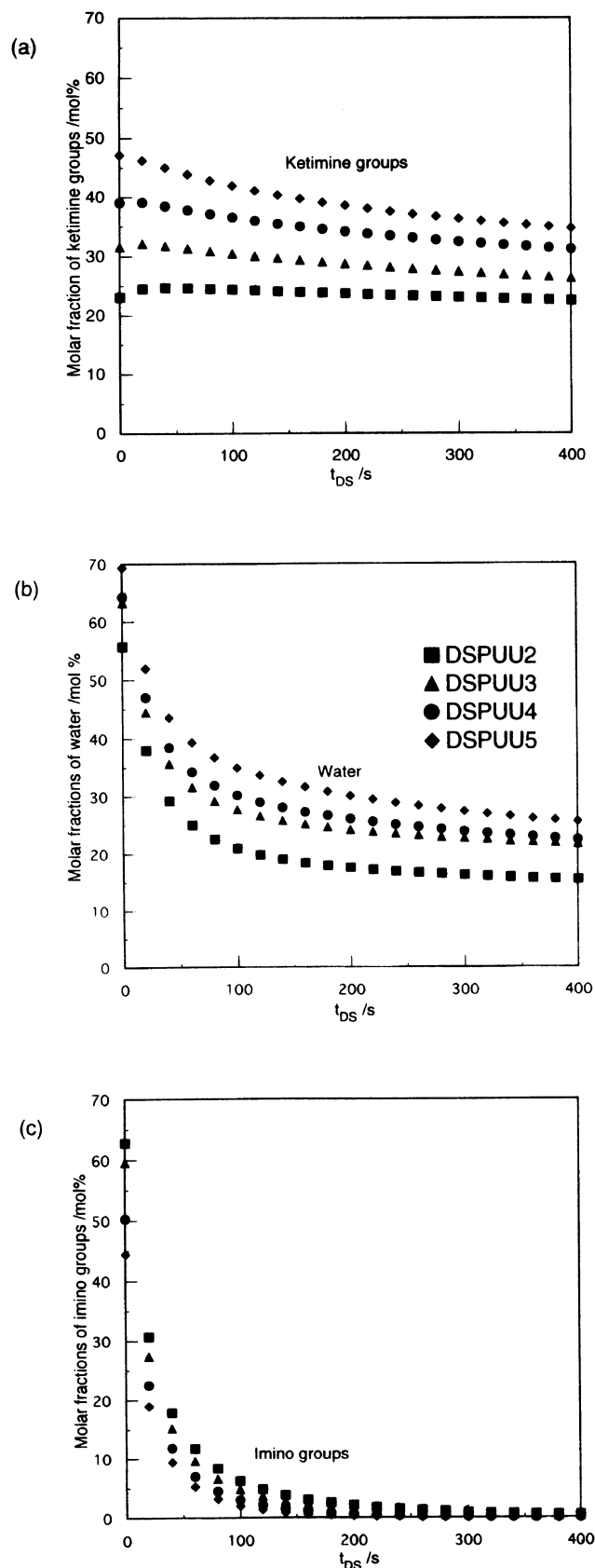

Figure 5. Calculated changes of molar fractions of (a) ketimine groups, (b) water, and (c) imino groups with t_{DS} for DSPUU2—5 reactions.

DSPUU2 reaction, Urea II formed by the imino group catalyst reached 75.3% in terms of $Y_{Urea\,II}$ (at 400 s). Since $Y_{Urea\,II}$ depends on the products of the first and second
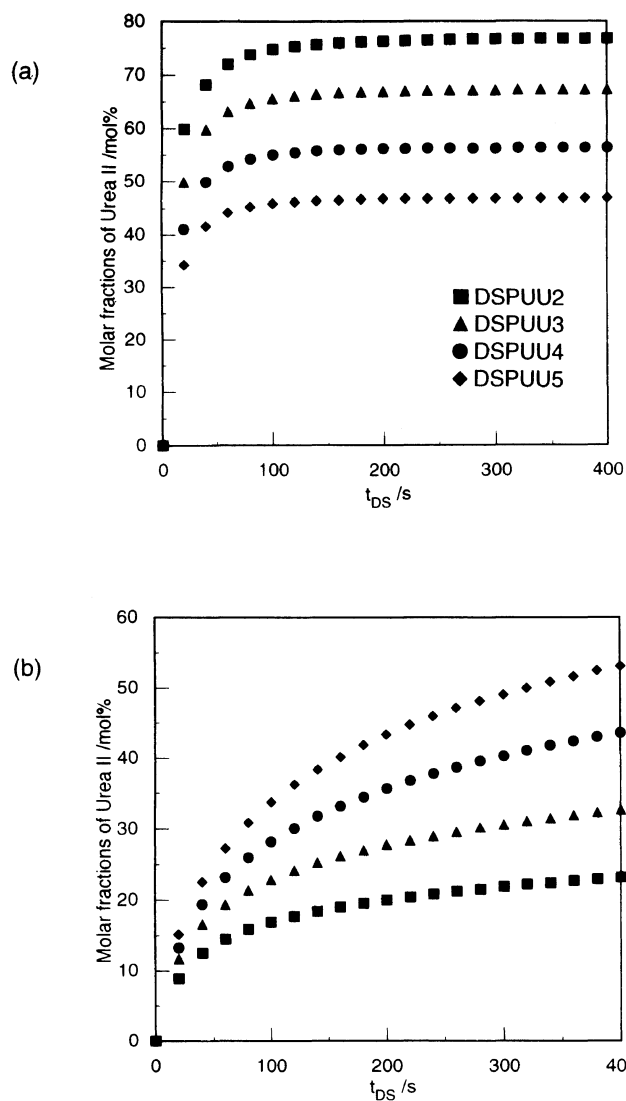
Figure 6. Calculated changes of molar fractions of Urea II formed with t_{DS} (a) by imino catalyst and (b) by ketimine catalyst.

terms of eq 10, with decreasing initial concentrations of the imino groups (corresponding to decrease of the contribution of the first term), the catalytic effect fades away and the ketimine catalyst becomes important (Figure 6b). For example, when the initial concentration ratio of the ketimine groups to the imino groups of (3) was 2/3, corresponding to that in the equilibrated composition of the AE prepared at $[\text{acetone}]_0/[\text{EDA}]_0$ of 1.8, about half the resultant Urea II was formed by the ketimine catalyst (the imino catalyst). The formation rate of Urea II by the ketimine catalyst was slow and amount of Urea II gradually increased in accordance with the comparably small catalytic effect of the ketimine $(k_{kt} = 2.1 \times 10^{-2}\,\text{kg}^2\,\text{mol}^{-2}\,\text{s}^{-1})$ and slow consumption rate of the ketimine $(k_{001} = 5.0 \times 10^{-3}\,\text{kg}\,\text{mol}^{-1}\,\text{s}^{-1})$.

Effects of Addition of Water on $Y_{\text{Urea II}}s$. The effects of addition of water to the AE samples on $Y_{\text{Urea II}}s$ can also be explained similarly. In the case of DSPUU6 reaction in which the AE6 sample was prepared by adding a certain amount of water to the AE2, the experimental $Y_{\text{Urea II}}$ (36% in Table II) is in agreement with that calculated (36.96%) for the DSPUU6. The concentra-
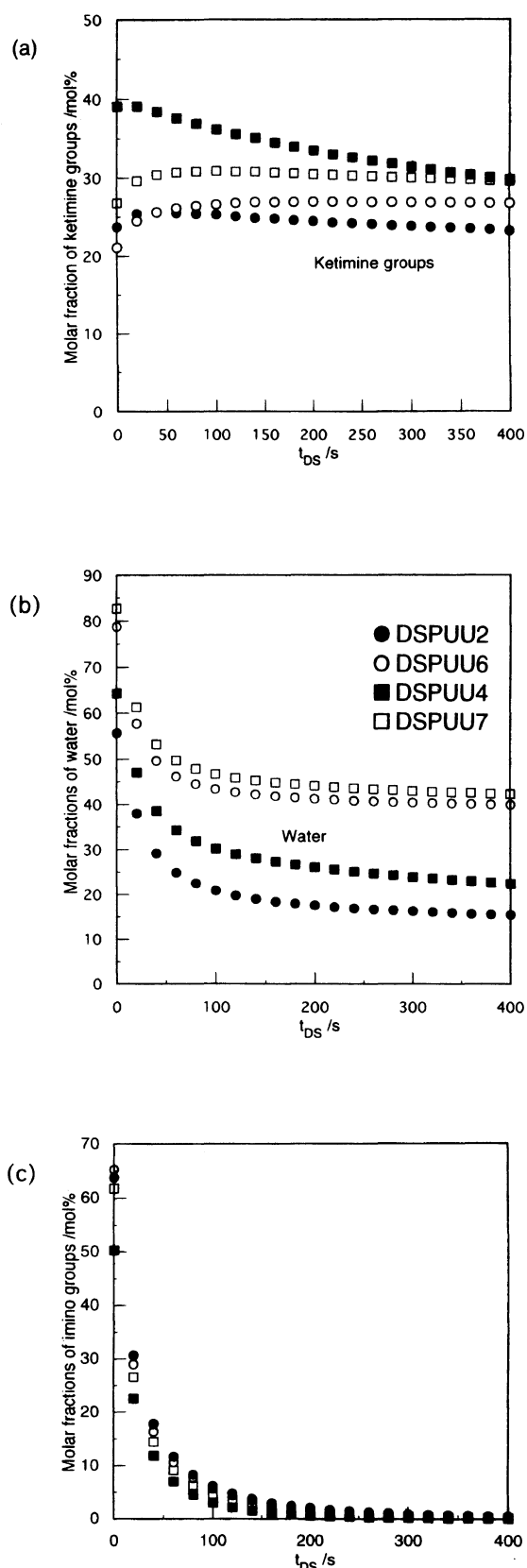
Figure 7. Calculated changes of molar fractions of (a) ketimine groups, (b) water, and (c) imino groups with t_{DS} for DSPUU2, 4, 6, and 7.

tions of the ketimine groups and water were kept higher during the DSPUU6 reaction (Figures 7a and b) than those of the DSPUU2 except for the reaction time up to *ca.* 50 s with respect to the ketimine groups. The

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concentration of the imino groups for the DSPUU6 was lower throughout the reaction except at the beginning of the reaction. Thus, increase in $Y_{\text{Urea II}}$ for the DSPUU6 by 8% in comparison to that for the DSPUU2 should be attributable to increase in the ketimine and water concentrations at the later reaction stage. The slightly higher increase in concentration of the imino group in the DSPUU6 reaction at the very first stage would also contribute to increase in $Y_{\text{Urea II}}$.

In similar reactions of DSPUU4 and 7 the experimental $Y_{\text{Urea II}}$s were 42 and 36% (the calculated value, 38.93%), respectively. The difference of the experimental $Y_{\text{Urea II}}$ by 6% is ascribed to the significant decrease in the concentrations of the ketimine groups throughout the DSPUU7 reaction (Figure 7a), not to the increase in the concentrations of water and strong catalyst, the imino groups (Figures 7b and c).

Similar effect of water on decrease in $Y_{\text{Urea II}}$ was observed in the case of the DSPUU model reactions of phenylisocyanate in replace of MDI with AE samples in chloroform.[2] 1,3-Diphenylurea which corresponds to Urea II in DSPUU reaction was formed in 41 mol% using an AE sample consisting of 51 mol% of imino (NH) groups and 31.5 mol% of ketimine groups. When an AE sample was prepared in the presence of water and contained 46 and 29.5 mol% of NH and ketimine groups, respectively, the yield of 1,3-diphenylurea decreased to 27 mol%. The latter result is attributable to the decrease in the initial concentrations of NH and ketimine groups. In a somewhat different model reaction where the AE sample was prepared from cyclohexanone and EDA, containing 93 mol% of NH groups of 2-pentamethyleno-imidazolidine and only 6 mol% of ketimine groups of N,N'-dicyclohexylideneethylenediamine, the yield of 1,3-diphenylurea was 31 mol%. Similar reaction products prepared in the presence of water resulted in the significant decrease of $Y_{\text{Urea II}}$ (12%), although there was little change in the composition (95 and 4 mol% of NH and ketimine groups, respectively). Since both reaction products from the ketone-EDA involved little ketimine groups, water might have accelerated the rate of the disappearance of the imino groups of the Adduct 2, leading to lower yield of 1,3-diphenylurea.[2]

DSPUU Reactions in the Presence of Acid Catalyst

In the DSPUU reaction in the presence of an acid, the following acid-catalyzed reactions ought to be considered in addition to elementary reactions that take place in the absence of the acid: (i) the acid-catalyzed reformation reactions (Scheme 2) of the amino groups from the ketimine groups of (1') and (2) (catalyst constants of k_{-1} and k_{-2}, respectively in Table I), (ii) ring opening reaction of (3) supported by acid catalysis, and (iii) there is the possibility of acid-catalyzed direct reactions of NCO groups with the ketimine groups and also with (3). In the case of (iii), the addition reaction of NCO groups with the ketimine groups or (3) occurs first, followed by the hydrolysis reaction of Adduct 1 for the former reaction or of Adduct 2 for the latter. As mentioned previously,[1] acid-catalysis for these addition reactions seems unlikely, while expected for the hydrolysis of the Adducts. However, since the addition reactions are the rate-determining steps for ITPP–ketimine and ITPP–NH
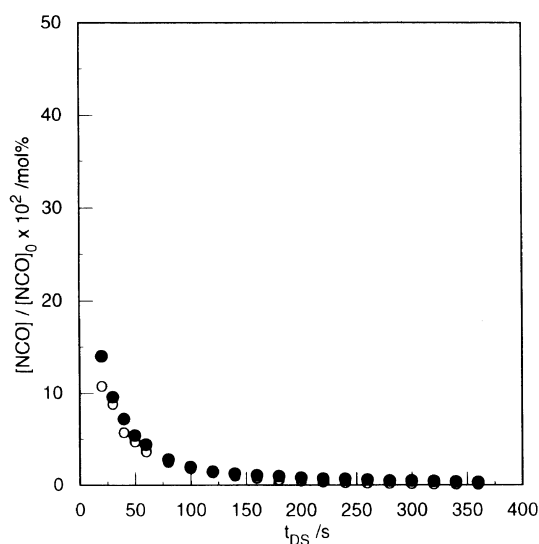
Figure 8. Reaction time (t_{DS}) vs. NCO consumption plots for DSPUU11 in the presence of acid catalyst (●, experimental; ○, calculated).

reactions (Table I), the acid-catalyzed hydrolysis reactions influence much less the yield of Urea II than the acid-catalyzed reformation reactions of amino groups of (1') above mentioned (Scheme 2).

Acid-Catalyzed Regeneration Reactions of Amino Groups from (1'), (2), *and* (3). To make the acid-catalyzed DSPUU reaction more complicated, the acid species in the AE preparation reactions are different[3] from that in DSPUU reactions. The protonated amine $(H_3{}^+N-R)$ is the active species for the former and proton and/or acid itself is for the latter. Assuming that the active acid species is H^+ only, the concentration of H^+ is expressed in eq 12.

$$[H^+] = \sqrt{K_{\text{HA}}[CH_3COOH]} \qquad (12)$$

where K_{HA} and $[CH_3COOH]$ are the dissociation constant of acetic acid added and its concentration, respectively. The catalyst constants for the hydrolysis reaction of (1') as a representative in the DSPUU reaction can be written in eq 13

$$k_{-1} = \gamma k_{-1(\text{NH}_3\text{R})} \qquad (13)$$

where γ is the proportion constant and $k_{-1(\text{NH}_3\text{R})}$ is the catalyst constant in the case of the AE reaction. Combining eq 12 and 13 simply gives

$$k_{-1}[H^+] = \gamma \sqrt{K_{\text{HA}}} k_{-1(\text{NH}_3\text{R})} \sqrt{[CH_3COOH]} \qquad (14)$$

$k_{-1(\text{NH}_3\text{R})}$ and $\sqrt{[CH_3COOH]}$ are known and thus, the left side can be estimated, provided that the parameter $\gamma \sqrt{K_{\text{HA}}}$ is determined. A similar relation as eq 14 holds for other catalyst constants such as k_{-2} and k_{-3}. An attempt was made to determine the above parameter by fitting the calculated plots of $[NCO]/[NCO]_0$ as a function of t_{DS} to the experimental plots (Figure 8) for the DSPUU11 reaction. The calculated plots were obtained by substituting the $k_{-1}[H^+]$, $k_{-2}[H^+]$, and $k_{-3}[H^+]$ into eq 1—11 and solving them. In a similar way, the parameters were estimated for DSPUU8—10 and averaged. By using the average value, the calculated $Y_{\text{Urea II}}$s for DSPUU8—11 are plotted in Figure 9. The
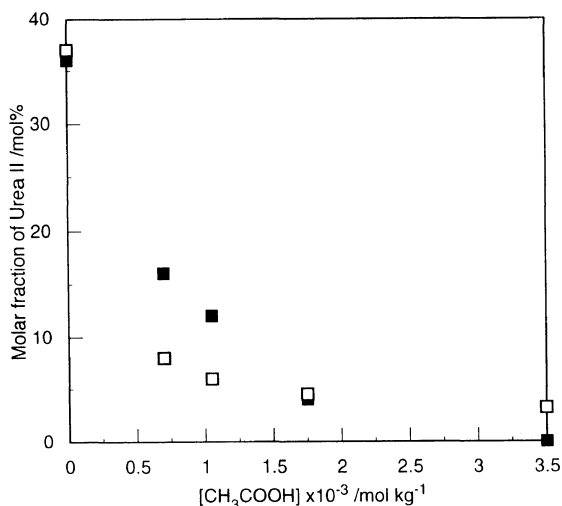
Figure 9. Acid concentration dependence of $Y_{Urea\,II}$ for DSPUU6, 8, 9, 10, and 11 (■, experimental; □, calculated).
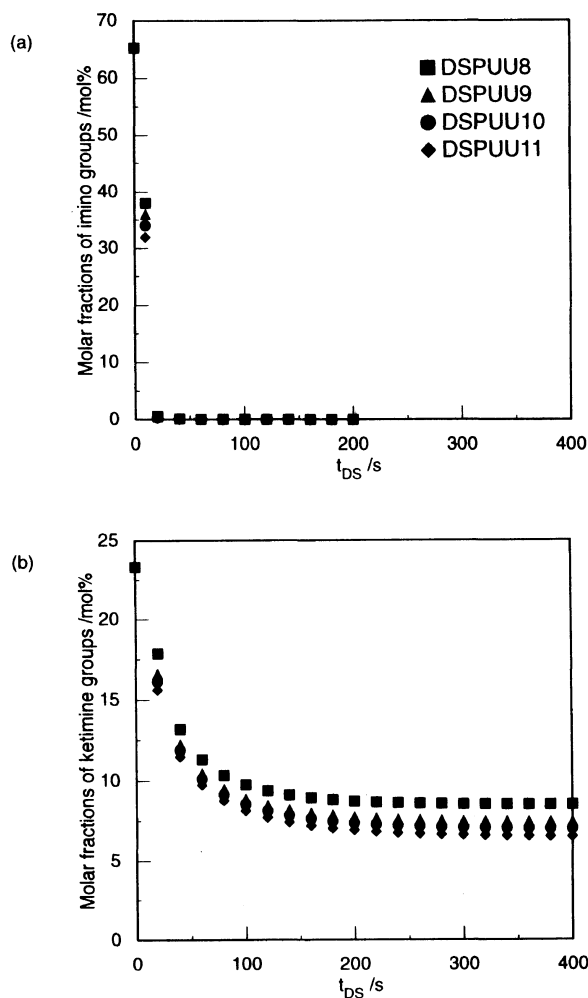

Figure 10. Calculated changes of molar fractions of (a) imino groups and (b) ketimine groups with t_{DS} for DSPUU8—11.

calculated $Y_{Urea\,II}$ for the DSPUU6 in the absence of acid is also plotted in Figure 9. The calculated $Y_{Urea\,II}$s abruptly decreased and almost leveled off. There is no serious discrepancy between the calculated and experimental data, indicating that acid catalyzed reformation reactions principally take place. Figures 10a and b show the

time-dependence plots of the calculated concentration of the residual imino groups and ketimine groups for the DSPUU8—11 reactions, respectively. By comparing these results with those for the DSPUU6 in Figures 7c and a, it is clear that the presence of the acid is very effective for accelerating the rates of the disappearance of the imino groups in particular and also the ketimine groups, leading to lower $Y_{Urea\,II}$s. Contrary to the complete disappearance of the imino groups, the calculated concentrations of the ketimine groups gradually leveled off even in the latter half of the DSPUU11 reaction. This may be caused by the fact that the NCO groups were consumed by the side reaction with water before reacting with the ketimine groups, forming Urea II (Figure 9). The reason that $Y_{Urea\,II} = 0$ for the DSPUU11 is not clarified yet, but possibly associated with the neutralization of significant amounts of ketimine groups by acetic acid at that acid concentration so that the NCO—water reaction is completely suppressed.

The calculated concentration (7.3 mol%) of the ketimine groups at the chain ends of the polymer after completion of the DSPUU10 ($t_{DS} = 400$ s) is comparable to the experimental value (8.2%) measured by the end-group analysis.[1] This indirectly shows that the acid catalyzed reformation reactions take place and the end groups are ketimine groups.

APPENDIX

According to the reaction pathway for the direct reaction of ITPP with the ketimine groups in the presence of water in the Experimental, the rates of decrease in the concentration of the NCO and ketimine groups can be written in eq A1

$$-d[Ket]/dt = k_{001}[Ket][NCO] \qquad (A1)$$

where [Ket] and k_{001} are the concentration of the ketimine groups of N-isopropylidenebutylamine and rate constant for the corresponding adduct formation reaction, respectively. The rates of consumption of the adduct, NCO groups, and water can be written in eq A2, A3, and A4, respectively.

$$-d[Add1_0]/dt = -k_{001}[Ket][NCO]$$
$$+ k_{002}[Add1_0][H_2O] \qquad (A2)$$

$$-d[NCO]/dt = k_{001}[Ket][NCO]$$
$$+ 2k_{kt}[Ket][NCO][H_2O] \qquad (A3)$$

$$-d[H_2O]/dt = k_{002}[Add1_0][H_2O]$$
$$+ k_{kt}[Ket][NCO][H_2O] \qquad (A4)$$

where $[Add1_0]$, k_{002}, and k_{kt} are the concentration of the adduct, rate constant for Urea I' formation, and catalyst constant of the NCO—water reaction. Here, the rate constant $(5.9 \times 10^{-5}\,kg\,mol^{-1}\,s^{-1})$ of NCO—water reaction was neglected.[9] Similarly the rate of formation of Urea I' and Urea II are written in eq A5 and A6, respectively.

$$d[\text{Urea I}']/dt = k_{002}[\text{Add1}_0][H_2O] \qquad (A5)$$

$$d[\text{Urea II}]/dt = k_{kt}[\text{Ket}][\text{NCO}][H_2O] \qquad (A6)$$

Equations A1—A6 were solved numerically by substituting arbitrary values for k_{001}, k_{002}, and k_{kt} into these equations to calculate $[\text{NCO}]/[\text{NCO}]_0$ as a function of t_{DS} and the molar ratio of Urea II at the end of the reaction ($t_{DS} = 400$ s).

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4. A reaction of 10.0 g (0.17 mol) of extra pure acetone and 6.2 g (0.085 mol) of extra pure *n*-butylamine, both of which were purchased from Wako Pure Chemical Industries, Ltd. (Kyoto, Japan) was carried out in a 0.1 L round-bottomed flask (with a seal cap) over 10 g of molecular sieve (4A) obtained from the same manufacturer at 50°C for 15 h. The unreacted raw materials and water were removed *in vacuo* (70°C 200 Pa^{-1}). The light yellow liquid was characterized as the desired product (91% purity based on the amine) by ^{1}H NMR.
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