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Mechanism of a Chain-Extending Reaction in the Synthesis of Segmented Poly(urethane–urea) Using Blocked Ethylenediamine

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An attempt was made to clarify the mechanism of a chain-extending reaction of NCO-terminated prepolymers in the synthesis of segmented poly(urethane–urea) using blocked ethylenediamine (EDA) with acetone (ACE). For this purpose, an ACE/EDA mixture was allowed to react with phenyl isocyanate (PhNCO) as a model of the prepolymer. The reaction of PhNCO with the ACE/EDA mixture, which was proved to contain ketimine and imidazolidine compounds by NMR measurements, gave 1,1′-ethylenebis[3-phenylurea] (M-Ur-1) as the main product; at the same time 1,3-diphenylurea (1,3-DPU) was assumed to be formed as a side-reaction product between PhNCO and H_2O, inevitably existing in the mixture as the result of condensation. From a considerable increase in the yield of M-Ur-1 upon the addition of an excess amount of H_2O to the reaction system, H_2O was elucidated to participate in the acceleration of the main reaction, giving M-Ur-1 as well as in the side reaction, yielding 1,3-DPU. The excess H_2O added to the system might preferentially facilitate the former reaction, rather than the latter.

Segmented poly(urethane–urea) (PUU) is one important class of polymer materials used for resins, paints, coatings, adhesives, and fibers.[1] Generally, PUU is synthesized by a chain-extending reaction of a prepolymer which carries an isocyanato group (–NCO) at two chain ends.[2] As chain-extending reagents, polyvalent aliphatic, aromatic, and alicyclic amines are commonly used. Although alkanediamine, such as ethylenediamine (EDA), has for many years been employed in practical PUU yarn manufacturing, its reaction control has been said to be very hard, due to its extremely high reaction rate with a considerable exothermic nature.[3] To avoid this, the reaction is carried out in such solvents as *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide.[4] On the other hand, in the field of coatings, some studies have been reported on methods for a controllable reaction procedure of isocyanates with amines using blocked amines with aldehydes and ketones.[5,6] It has been known that monoamine and diamine compounds form monoketimine or bisketimine by a condensation reaction with ketones, and EDA or *N,N*′-dialkylethylenediamines form imidazolidine derivatives by condensation with cyclohexanone or acetone (ACE).[7,8] Kushioka[9] studied the reactions between ACE and *N,N*′-dialkylethylenediamines, and discussed the effect of the *N*-alkyl groups of the EDA derivatives on the imidazolidine formation mechanism from both electronic and steric standpoints.

Recently, we have prepared a segmented PUU film using 1,1′-methylenebis[4-isocyanatobenzene] (MDI), poly(tetramethylene oxide) (PTMO), and the blocked EDA with ACE without using DMAc, and examined its morphology and amorphous structure in comparison with the conventional PUU film prepared using DMAc as a reaction media, suggesting that the former method gave a new type of phase-separated structure.[10] Concerning the blocking reaction of EDA with ACE, the formation of *N,N*′-diisopropylideneethylenediamine (i.e., bisketimine) and 2,2-dimethylimidazolidine has been shown by a ^{1}H NMR measurement; however, owing to the difficulties in isolating the reaction products, their detailed identification and quantitative analysis have remained untouched until now.[9] In addition, the reaction mechanism between the NCO-terminated prepolymer and the blocked-EDA mixture has not yet been understood in view of ketimine and imidazolidine formation. Although Dieterich[11] dealt with the reaction between the NCO-terminated prepolymer and blocked diamines (i.e., ketimines and ketazine), he never referred to the formation of imidazolidines.

In this study, we attempted to clarify the mechanism of segmented PUU formation based on the use of blocked EDA with ACE. For this purpose a detailed identification and quantitative analysis of the reaction products contained in the mixture of ACE and EDA was carried out as the first step by the ^{1}H NMR, ^{13}C NMR, and 2D ^{13}C–^{1}H COSY spectra. Subsequently, the effect of the compounds contained in the above reaction mixture on the chain-extending reaction of the NCO-terminated prepolymer was examined using phenyl isocyanate (PhNCO) as a model of the prepolymer.

Experimental

General. ^{1}H, ^{13}C, and 2D ^{13}C–^{1}H COSY NMR spectra were obtained with a JEOL GSX-400 spectrometer (^{1}H frequency of

399.78 MHz or ^{13}C frequency of 100.54 MHz) in a $CDCl_3$ or DMSO-d_6 solution with $SiMe_4$ as an internal standard (0 ppm). Special-grade acetone (ACE), cyclohexanone (CYH), ethylenediamine (EDA), butylamine (BA), and phenyl isocyanate (PhNCO), purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan), were used without further purification. *N*,*N*-Dimethylacetamide (DMAc), supplied as extra-pure grade by Wako Pure Chemical Industries Ltd., was used after storing over a molecular sieve (4-A). H_2O was used after purification with an ion-exchanged regin.

Procedure for Reaction of EDA with PhNCO. A solution of PhNCO (8.92 g, 74.9 mmol) in 15 ml of DMAc was added dropwise to EDA (1.80 g, 30.0 mmol) at 20 °C with stirring. The reaction started immediately, and a white precipitate was produced. After allowing to continue the reaction at 20 °C for 30 min, the reaction mixture was poured into $CHCl_3$ (250 ml). The precipitated compound was collected by filtration through a glass filter, washed with methanol, and dried in vacuo. The obtained white precipitate (8.83 g) was proved to be 1,1′-ethylenebis[3-phenylurea] (M-Ur-1, see Scheme 1) by ^1H and ^{13}C NMR measurements, and the yield of M-Ur-1 based on EDA was 100%. M-Ur-1: ^1H NMR (DMSO-d_6, 50 °C) $\delta = 3.20$ (2H, s), 6.15 (1H, s), 6.88 (1H, t, $J = 7.5$ Hz), 7.20 (2H, t, $J = 7.8$ Hz), 7.39 (2H, d, $J = 7.8$ Hz), 8.41 (1H, s); ^{13}C NMR (DMSO-d_6, 50 °C) $\delta = 39.6$, 118.0, 121.1, 128.8, 140.6, 155.4.

Typical Procedure for Reaction of Ketone/EDA Mixture with PhNCO. A mixture of ACE and EDA (hereafter referred to as 'ACE/EDA mixture') was prepared by mixing EDA (1.80 g, 29.9 mmol) with ACE (2.61 g, 44.9 mmol) in a reaction vessel. After keeping the ACE/EDA mixture at 50 °C for 4.0 h with stirring, PhNCO (8.92 g, 74.8 mmol) in a DMAc (15.0 ml) solution was added drop-wise with stirring. A white precipitate was gradually produced. After the reaction was allowed to continue for 30 min, the reaction mixture was poured into $CHCl_3$ (250 ml). After filtration, washing with methanol, and drying, M-Ur-1 was obtained in a 59% yield. The reaction of a CYH/EDA mixture with PhNCO was also carried out in the same manner using CYH (4.41 g, 44.9 mmol) in the place of ACE; the yield of M-Ur-1 was 69%.

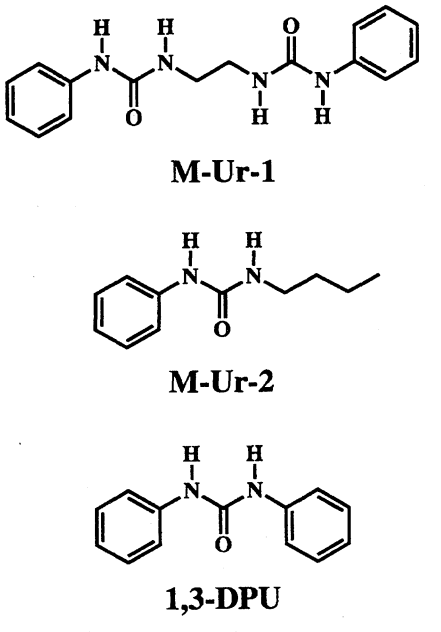
Typical Procedure for Reaction of Ketone/EDA/H_2O Mixture with PhNCO. An ACE/EDA/H_2O mixture was prepared by mixing EDA (1.80 g, 29.9 mmol) with ACE (2.61 g, 44.9 mmol) and H_2O (0.539 g, 29.9 mmol) at 50 °C for 4.0 h. To the ACE/EDA/H_2O mixture was added a solution of PhNCO (8.92 g, 74.9 mmol) in 15 ml of DMAc dropwise with stirring; the reaction was allowed to continue for 30 min. The workup described above gave M-Ur-1 in a 73% yield. The reaction of a CYH/EDA/H_2O mixture with PhNCO was also carried out in the same manner using CYH (4.41 g, 44.9 mmol) in the place of ACE; the yield of M-Ur-1 was 88%.

^1H NMR Analysis of Reaction of ACE/BA Mixture with PhNCO. An ACE/BA mixture was prepared by mixing BA (108 mg, 1.47 mmol) with ACE (128 mg, 2.20 mmol) in an NMR sample tube (5 mmφ) at 50 °C for 4.0 h. Then, PhNCO (175 mg, 1.47 mmol) in a DMSO-d_6 (0.5 ml) solution was added with stirring. After keeping the reaction mixture in the sample tube at 50 °C for 30 min, an ^1H NMR measurement was started for the identification and quantification of the reaction products. As a control experiment, an analysis of the reaction of PhNCO (175 mg, 1.47 mmol) with an ACE/BA/H_2O mixture prepared from ACE (128 mg, 2.20 mmol), BA (108 mg, 1.47 mmol), and H_2O (26.6 mg, 1.47 mmol) was also conducted in the same manner. In both cases, the ^1H NMR spectra showed the production of 1-butyl-3-phenylurea (M-Ur-2, see Scheme 1) and 1,3-diphenylurea[12] (1,3-DPU, see Scheme 1), and PhNCO was not observed. The yields of M-Ur-2 (Y_{MU2}) and 1,3-DPU (Y_{DPU}) based on PhNCO used (%) were estimated from the intensities in the ^1N NMR spectra as

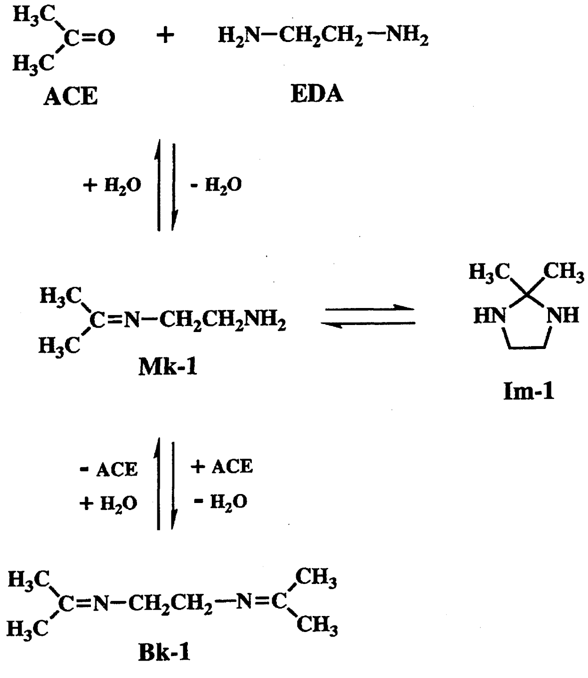
$$Y_{\mathrm{MU2}} = 100 I_{\mathrm{MU2}} / (I_{\mathrm{MU2}} + I_{\mathrm{DPU}}), \qquad (1)$$

$$Y_{\mathrm{DPU}} = 100 I_{\mathrm{DPU}} / (I_{\mathrm{MU2}} + I_{\mathrm{DPU}}), \qquad (2)$$

where I_{MU2} and I_{DPU} are the integral values of the peaks assigned to the imino proton adjacent to the phenyl group of M-Ur-2 (8.41 ppm) and those of 1,3-DPU (8.94 ppm), respectively. The formation of M-Ur-2 was confirmed by a direct comparison with an authentic sample prepared independently from BA and PhNCO. M-Ur-2: ^1H NMR (DMSO-d_6, 30 °C) δ=0.89 (3H, t, J=6.8 Hz), 1.31 (2H, m), 1.42 (2H, m), 3.10 (2H, q, J=6.2 Hz), 6.01 (1H, br s), 6.86 (1H, t, J=7.3 Hz), 7.19 (2H, t, J=7.8 Hz), 7.37 (2H, d, J=7.8 Hz), 8.25



Scheme 1. Model compounds.



Scheme 2. Reactions occurring in the ACE/EDA mixture.

(1H, s); ^{13}C NMR δ=13.6, 19.5, 31.9, 38.7, 117.7, 120.8, 128.5, 140.6, 155.2.

Results and Discussion

Identification and Quantitative Analysis of Compounds in an ACE/EDA Mixture. Scheme 2 illustrates the possible reactions occurring in a mixture of acetone (ACE) and ethylenediamine (EDA) (hereafter referred to as ACE/EDA mixture) proposed so far. 2,2-Dimethylimidazolidine, *N*-isopropylideneethylenediamine, and *N*,*N'*-diisopropylideneethylenediamine are called Im-1, Mk-1, and Bk-1, respectively. Due to difficulties in the isolation of all the compounds shown in Scheme 2, a quantitative analysis was carried out by direct NMR measurements on the ACE/EDA mixture.

Figure 1 shows the ^{1}H (a) and ^{13}C NMR (b) spectra

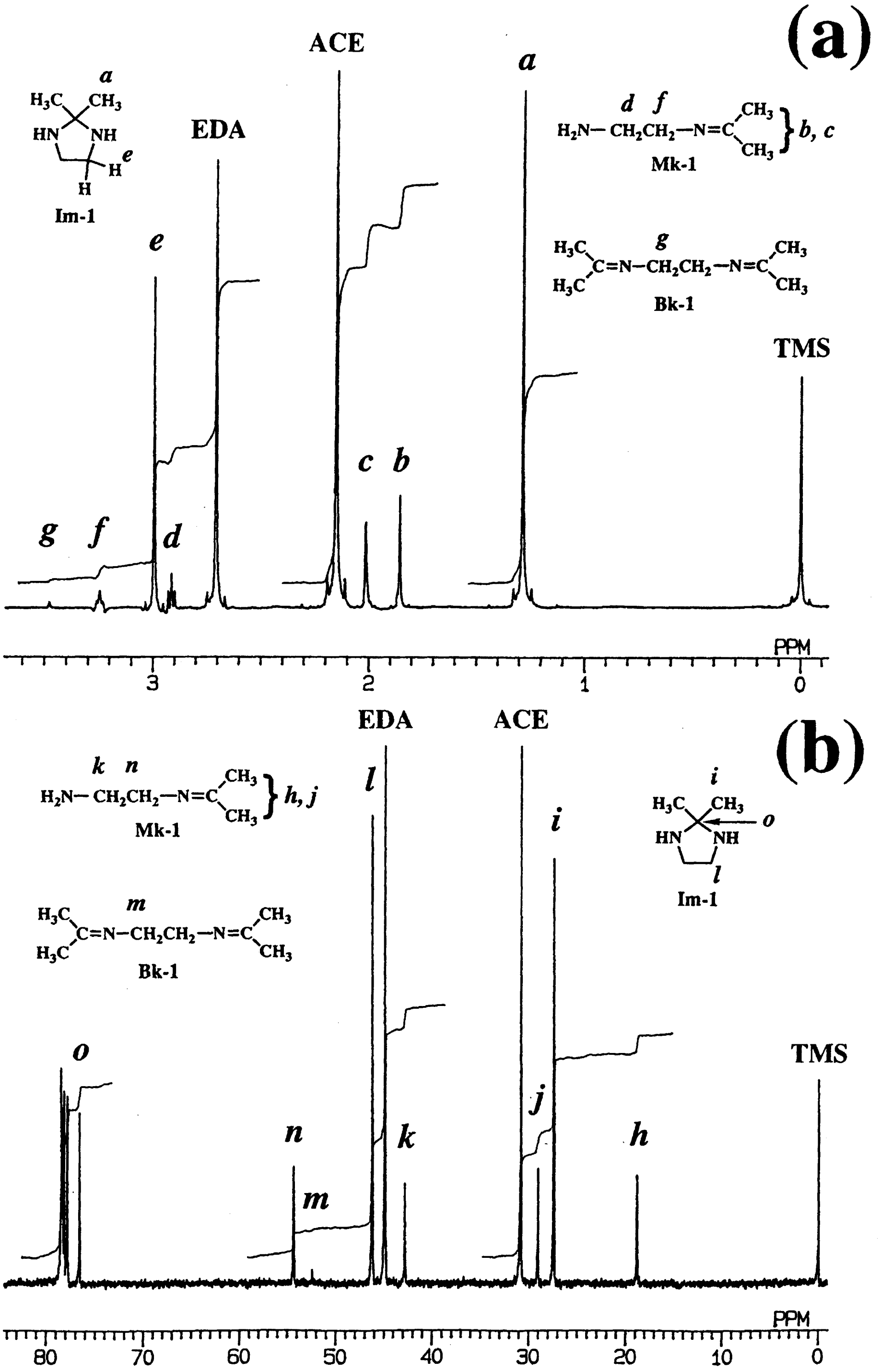


Fig. 1. ^{1}H (a) and ^{13}C NMR (b) spectra measured at 30 °C for the ACE/EDA mixture in $CDCl_3$ (initial molar ratio, $[ACE]_0/[EDA]_0$ = 1.8 mol/mol; initial ACE+EDA concentration, 22 wt%).

measured at 30 °C for the ACE/EDA mixture in $CDCl_3$ (initial molar ratio, $[ACE]_0/[EDA]_0=1.8$ mol/mol; initial ACE+EDA concentration, 22 wt%), and ^{13}C–^1H COSY spectrum is shown in Fig. 2. Peaks at 1.29 (Peak *a*) and 3.00 ppm (Peak *e*) in Fig. 1(a) were assigned to the methyl and methylene protons of Im-1, respectively. These peaks were found to correlate with ^{13}C Peak *i* and *l*, respectively, in Fig. 1(b) with the help of Fig. 2. Peak *o* in Fig. 1(b), which has no correlated ^1H peak, was assigned to the quarternary carbon of Im-1. Two peaks centered at 2.92 (Peak *d*) and 3.25 ppm (Peak *f*) with the same coupling constant ($J=5.8$ Hz) in Fig. 1(a) were both triplet, and were assigned to two kinds of the methylene protons of Mk-1. The former might be the methylene protons adjacent to the amino group. The small singlet Peak *g* (3.48 ppm) is attributed to the methylene protons of Bk-1. Two kinds of quarternary carbons of Mk-1 and Bk-1 were found at 168.3 and 168.5 ppm on the ^{13}C NMR spectrum, the former (168.3 ppm) being attributed to that of Bk-1 by a comparison of the peak intensities of the two. All of the results mentioned above in turn reconfirmed the reactions shown in Scheme 2, and the peak intensities in the ^1H NMR spectrum give some basis for a quantitative analysis of the compounds formed in the mixture.

Figure 3 shows the reaction-time dependence of the molar fractions of the compounds (EDA, Mk-1, Im-1, and Bk-1) in the ACE/EDA mixture with $[ACE]_0/[EDA]_0=5.8$ (closed symbols) and 1.0 mol/mol (open symbols) at 50 °C (initial ACE+EDA concentration, 43 wt%). Both cases exhibit some reaction equilibrium state after an appropriate reaction time, being ca. 1 h for the former and a little longer for the latter. Bk-1 occupied as large as 28 mol% of the mixture at the equilibrium for the former case (◆), decreasing to ca. 6 mol% for the latter case (◇). In contrast, the molar fraction of Im-1 (● and ○) in equilibrium did not appreciably depend on the value of $[ACE]_0/[EDA]_0$.

Reaction of the ACE/EDA Mixture with PhNCO. Although Fig. 3 omits ACE and H_2O, the ACE/EDA mixture consisted of an equilibrated composition between ACE, EDA, Mk-1, Im-1, Bk-1, and H_2O. Table 1 compiles the experimental results of the reactions of phenyl isocyanate (PhNCO) as a model compound of an NCO-terminated prepolymer with the ACE/EDA mixture ($[ACE]_0/[EDA]_0=1.5$ mol/mol, Run 2) and with EDA alone as a control reaction (Run 1); at the same time the effect of the addition

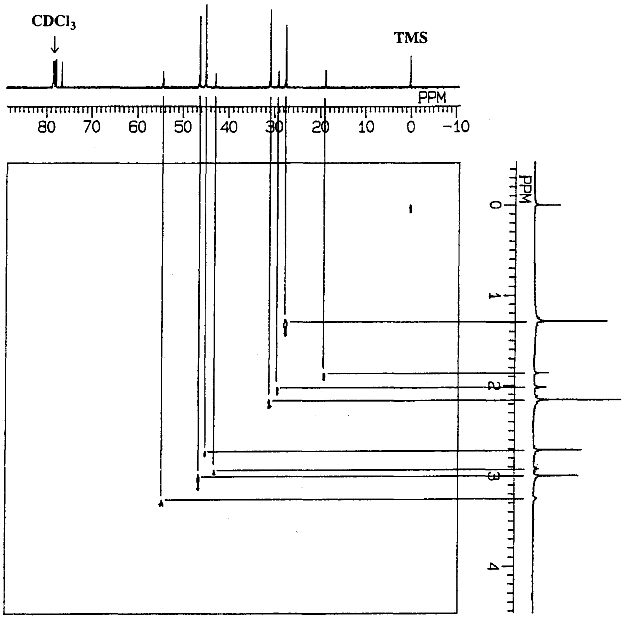


Fig. 2. 2D ^{13}C–^1H COSY NMR spectrum measured at 30 °C for the ACE/EDA mixture in $CDCl_3$ (initial molar ratio, $[ACE]_0/[EDA]_0=1.8$ mol/mol; initial ACE+EDA concentration, 22 wt%).

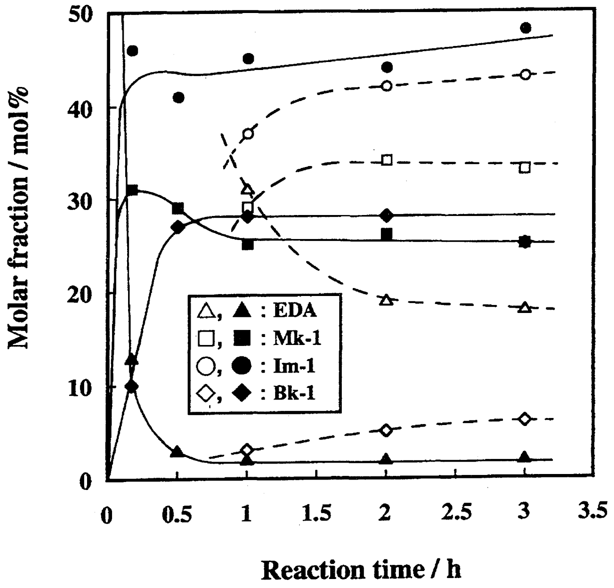


Fig. 3. Reaction time dependence on the molar fractions of the compounds (EDA, Mk-1, Im-1, and Bk-1) in the ACE/EDA mixture with $[ACE]_0/[EDA]_0=5.8$ (▲, ■, ●, and ◆) and 1.0 mol/mol (△, □, ○, and ◇) at 50 °C (initial ACE+EDA concentration, 43 wt%).

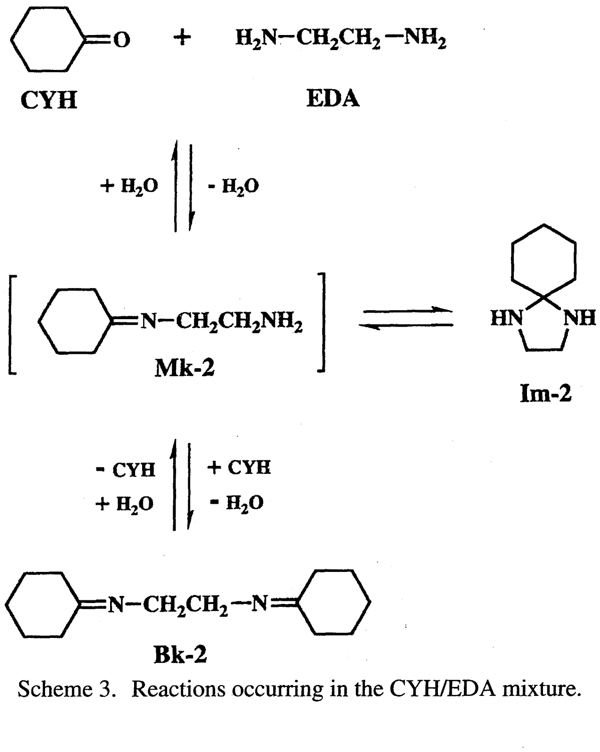
Table 1. Molar Fractions of EDA, Im-1, Mk-1, and Bk-1 in the ACE/EDA and ACE/EDA/H_2O Mixtures at 50 °C and the Yield of M-Ur-1 in the Reactions of These Mixtures with PhNCO[a)]

Run	Mixture system	$[H_2O]_0/[EDA]_0$ mol/mol	Molar fraction (mol%)				Yield of M-Ur-1[b)]
			EDA	Im-1	Mk-1	Bk-1	%
1	EDA[c)]	0.0	100	0	0	0	100
2	ACE/EDA	0.0	5	51	25	19	59
3	ACE/EDA/H_2O	1.0	6	46	37	11	73

a) $[ACE]_0/[EDA]_0/[PhNCO]_0=1.5/1.0/2.5$ (molar ratio). b) Based on EDA used. c) $[ACE]_0/[EDA]_0=0.0$ (mol/mol).

of H_2O on the former reaction was examined using the H_2O-added ACE/EDA mixture ($[ACE]_0/[EDA]_0[H_2O]_0=1.5/1.0/1.0$, molar ratio; Run 3). Here, PhNCO was charged so as to give $[PhNCO]_0/[EDA]_0=2.5$ (mol/mol), and the molar fractions of EDA, Im-1, Mk-1, and Bk-1 at the equilibrium state in Table 1 were determined independently from the ^1H NMR spectra measured immediately after the addition of DMSO-d_6 as an NMR lock solvent to the different ACE/EDA and ACE/EDA/H_2O mixtures prepared in the same manner; the initial concentration of ACE+EDA is regarded as 30 wt%. This procedure for the determination of the molar fractions of each component at an equilibrium state was employed throughout all experiments afterwards. The yield of 1,1′-ethylenebis[3-phenylurea] (M-Ur-1, Scheme 1) as a main reaction product in Run 1 was confirmed to be 100%. Run 2, in which the ACE/EDA mixture was an equilibrium between EDA, Im-1, Mk-1, Bk-1 (EDA/Im-1/Mk-1/Bk-1=5/51/25/19, molar ratio), ACE, and H_2O, gave M-Ur-1 in a yield of 59%, indicating that the main reaction was hindered to a great extent by a certain reason. This means that a stoichiometric chain extending reaction of NCO-terminated prepolymers with EDA with can never be carried out in the synthesis of segmented poly(urethane–urea) (PUU) using the blocked EDA with ACE. The most probable reason is either prohibition by Im-1 (or Mk-1+Bk-1) or the consumption of PhNCO by H_2O inevitably existing in the ACE/EDA mixture as a result of condensation. Run 3 was made to examine this aspect. However, despite the excess addition of H_2O to the system ($[H_2O]_0/[EDA]_0=1.0$ mol/mol) the yield of M-Ur-1 unexpectedly increased by 14%, compared with that for Run 2. This means that an excess H_2O could catalyze the formation reaction of the M-Ur-1. Thus, an inhibitory action of the each component (Mk-1, Im-1, Bk-1, and H_2O) and the catalytic action of H_2O in the reaction of the ACE/EDA mixture with PhNCO should be clarified in more detail. For this purpose, two contrast blocked amine mixtures were chosen as model systems: an ACE/butylamine (ACE/BA) mixture characterized by no imidazolidine compound in the system and a cyclohexanone/EDA (CYH/EDA) mixture characterized by a high molar fraction (ca. 93 mol%) of an imidazolidine compound in the system.

From a similar ^1H NMR analysis carried out for the ACE/EDA mixture, the CYH/EDA mixture ($[CYH]_0/[EDA]_0=1.5$ mol/mol) in DMSO-d_6 was confirmed to consist of CYH, EDA, *N*,*N*′-dicyclohexylideneethylenediamine (Bk-2), spiro[cyclohexane-1,2′-imidazolidine][7] (Im-2), and H_2O, as shown in Scheme 3. The four methylene protons adjacent to the imino groups of Im-2 were found at 2.78 ppm as singlet, and the ethylene protons of Bk-2 owing to EDA was found at 3.41 ppm. Note that the existence of *N*-cyclohexylideneethylenediamine (Mk-2) was not affirmed in the present case. Table 2 includes the result of the reaction of the CYH/EDA mixture ($[CYH]_0/[EDA]_0=1.5$ mol/mol) with PhNCO ($[PhNCO]_0/[EDA]_0=2.0$ mol/mol). As shown in Run 5, the yield of M-Ur-1 based on PhNCO used was 69%, even when as much as 93 mol% of Im-2 was contained in the CYH/EDA mixture, indicating that the inhibitory action of Im-2 (i.e., imidazolidine compound) on the M-Ur-1 formation was very small. Moreover, the addition of an excess amount of H_2O to the CYH/EDA mixture ($[H_2O]_0/[EDA]_0=1.0$ mol/mol) did not change the equilibrated composition but again proved to increase the yield of M-Ur-1 (Run 6), as seen for the ACE/EDA system (Runs 2 and 3 in Table 1). The full line in Fig. 4 (●) shows the yield of M-Ur-1 based on EDA plotted against the molar ratio of $[H_2O]_0/[EDA]_0$ in the reaction of the CYH/EDA mixture ($[CYH]_0/[EDA]_0=1.5$ mol/mol) with PhNCO ($[PhNCO]_0/[EDA]_0=2.5$ mol/mol).



Scheme 3. Reactions occurring in the CYH/EDA mixture.

Table 2. Effect of Addition of H_2O on the Yield of M-Ur-1 in the Reaction of PhNCO with the CYH/EDA Mixture[a)]

Run	Mixture system	$[H_2O]_0/[EDA]_0$ mol/mol	Molar fraction (mol%) EDA	Im-2	Mk-2	Bk-2	Yield of M-Ur-1[b)] %
4	EDA[c)]	0.0	100	0	0	0	100
5	CYH/EDA	0.0	1	93	Trace	6	69
6	CYH/EDA/H_2O	1.0	1	95	Trace	4	88

a) $[CYH]_0/[EDA]_0/[PhNCO]_0=1.5/1.0/2.0$ (molar ratio). b) Based on PhNCO used. c) $[CYH]_0/[EDA]_0=0.0$ (mol/mol).

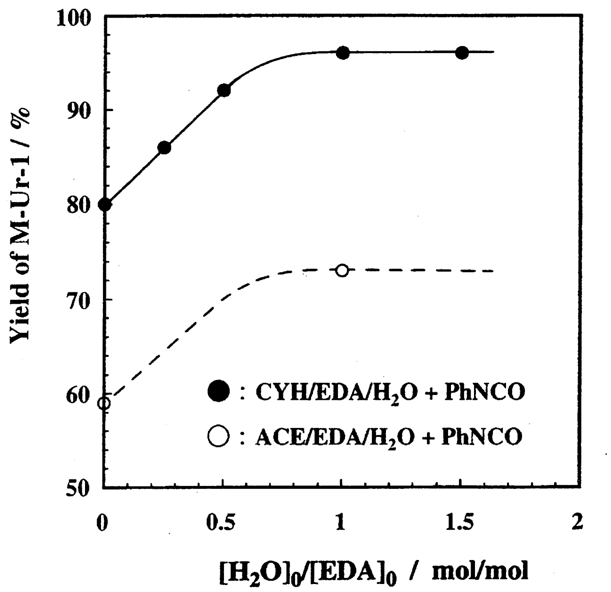
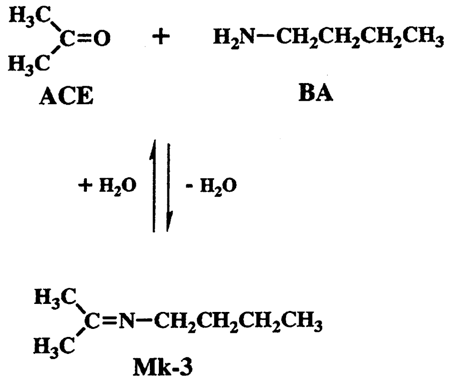


Fig. 4. Yield of M-Ur-1 based on EDA plotted against the initial molar ratio, $[H_2O]_0/[EDA]_0$, in the reactions of PhNCO with the CYH/EDA/H_2O mixture (●) and the ACE/EDA/H_2O mixture (○) ($[\text{ketone}]_0/[EDA]_0/[PhNCO]_0=1.5/1.0/2.5$, molar ratio).



Scheme 4. Reactions occurring in the ACE/BA mixture.

The yield of M-Ur-1 increased by 16% to 96% when the ratio, $[H_2O]_0/[EDA]_0$, increased from 0.0 to 1.0 (mol/mol). This degree of increase in the yield by the addition of excess H_2O was nearly equal to that observed for the ACE/EDA system, indicated by the broken line in Fig. 4 (○), indicating that the catalytic feature of H_2O had the same origin.

On the other hand, an ^{1}H NMR analysis showed that the ACE/BA mixture did not contain the imidazolidine compound, and comprised only ACE, BA, *N*-isopropylidenebutylamine (Mk-3), and H_2O, as shown in Scheme 4. The methylene protons adjacent to the nitrogen atom of Mk-3 were found at 3.14 ppm as a triplet. Table 3 lists the molar fractions of BA and Mk-3 in the ACE/BA and ACE/BA/H_2O mixtures ($[ACE]_0/[BA]_0=1.5$ mol/mol) and the results of reactions of these mixtures with PhNCO ($[PhNCO]_0/[BA]_0=1.0$ mol/mol) in the NMR sample tube. The reaction products of the ACE/BA mixture with PhNCO were revealed by a ^{1}H NMR measurement to be 1-butyl-3-phenylurea (M-Ur-2, see Scheme 1) as the main reaction product and 1,3-diphenylurea (1,3-DPU, see Scheme 1) as a side-reaction product. In this case, using a mixture including 83 mol% of Mk-3, the yield of M-Ur-2 based on PhNCO, estimated from the intensities in the ^{1}H NMR spectrum (Y_{MU2}), was 75%, also indicating a very small inhibitory action of Mk-3 (i.e., ketimine compound) on the production of M-Ur-2. Although the addition of H_2O to this mixture changed the equilibrium (BA/Mk-3=30/70, molar ratio), Y_{MU2} (76%, Run 8) was almost the same as that (75%, Run 7) observed without the addition of H_2O. This result means that an excess amount of H_2O could not play the role of a catalyst on the formation of M-Ur-2, in contrast to the CYH/EDA system (Runs 5 and 6 in Table 2).

The yields of 1,3-DPU, based on PhNCO (Y_{DPU}), were estimated to be 25% (Run 7) and 24% (Run 8) from ^{1}H NMR measurements, as shown in Table 3. It is known that 1,3-DPU is formed by a reaction of 2 moles of PhNCO with 1 mole of H_2O through decarboxylation.[13] Since some evolution of gaseous products was observed during both the reactions of PhNCO with the ACE/EDA and CYH/EDA mixtures, a similar side reaction producing 1,3-DPU might also take place in both cases. Therefore, the low yields of M-Ur-1 in Runs 2 (Table 1) and 5 (Table 2) are considered to be caused by an unavoidable consumption of PhNCO by H_2O inevitably existing in the ACE/EDA and CYH/EDA mixtures. Consequently, H_2O was clarified to participate in both the acceleration of the main reaction and the consumption of PhNCO as a side reaction. Note that the excess amount of H_2O added to the ACE/EDA and CYH/EDA mixtures contributes to an increase in the yield of M-Ur-1, as described above. Thus, the excess H_2O might preferentially accelerate the production of M-Ur-1, not the reaction of H_2O with PhNCO giving 1,3-DPU.

In these reactions of PhNCO with blocked diamine mixtures, carried out without removing H_2O from the systems,

Table 3. Results of ^{1}H NMR Analysis of the ACE/BA and ACE/BA/H_2O Mixtures and the Reactions of These Mixtures with PhNCO[a]

Run	Mixture system	$[H_2O]_0/[EDA]_0$ mol/mol	Molar fraction (mol%) BA	Mk-3	Y_{MU2}[b] %	Y_{DPU}[c] %
7	ACE/BA	0.0	17	83	75	25
8	ACE/BA/H_2O	1.0	30	70	76	24

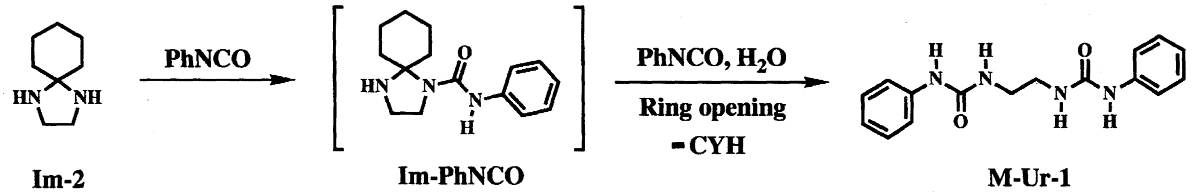
a) $[ACE]_0/[BA]_0/[PhNCO]_0=1.5/1.0/1.0$ (molar ratio). b) Yield of M-Ur-2 based on PhNCO estimated by Eq. 1. c) Yield of 1,3-DPU based on PhNCO estimated by Eq. 2.

it is very difficult to prove the existence of direct reactions of PhNCO with ketimine and imidazolidine compounds experimentally, due to some reversible reactions in the mixture, as shown in Schemes 2, 3, and 4. In fact, a direct ^{1}H NMR measurement for the reaction mixture of PhNCO with the CYH/EDA mixture ($[\mathrm{CYH}]_0/[\mathrm{EDA}]_0/[\mathrm{PhNCO}]_0 =$ 1.5/1.0/0.5, molar ratio) could show the M-Ur-1 formation accompanying the reproduction of CYH, but not detect a possible intermediate, such as 1′-(phenylcarbamoyl)spiro-[cyclohexane-1,2′-imidazolidine] (Im-PhNCO) illustrated in Scheme 5. Although the molar fraction of EDA (only 1 mol%) in the CYH/EDA mixture did not change upon the addition of H_2O, the yield of M-Ur-1 increased considerably due to excess H_2O in the reaction between the mixture and PhNCO. It may therefore be considered that M-Ur-1 is produced via a direct reaction of PhNCO with Im-2, rather than by the reaction with EDA reproduced by hydrolysis of the blocked diamine compounds (i.e., Im-2 and Bk-2), and that an excess amount of added H_2O accelerates the ring-opening reaction of Im-PhNCO, as shown in Scheme 5. Such a direct reaction of the imidazolidine compound with PhNCO can be supported by the experimental results reported by Witek et al.,[14] in which the formation of *N*-methyl-*N*′-substituted (substituent R=CONHPh) imidazolidines was shown in reactions of PhNCO with some imidazolidine compounds prepared from *N*-methylethylenediamine and 4-substituted benzaldehydes. In addition, Harada et al., demonstrated that 1,3-DPU (i.e., urea derivative) was obtained by the hydrolysis of 1-(1-cyclohexen-1-yl)-1,3-diphenylurea synthesized by the reaction of cyclohexanone anil (i.e., ketimine) with PhNCO. This result implies that M-Ur-1 (or M-Ur-2) can also be produced via both the direct reaction of PhNCO with ketimines and the hydrolysis of the resulting products in our cases.

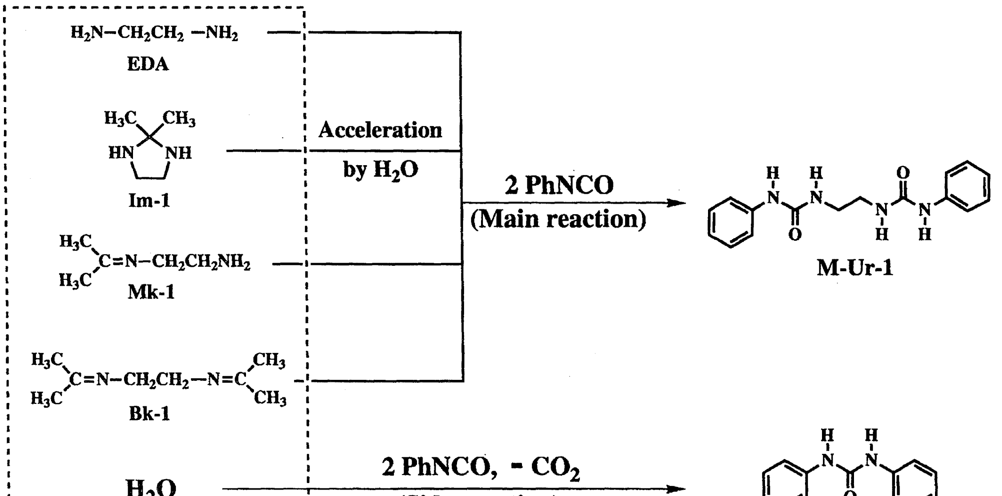
From all of these results mentioned above, the reaction between PhNCO and the ACE/EDA mixture might be summerized as in Scheme 6. The reaction system may include at least four pathways for the production of M-Ur-1 as the main reactions and a path affording 1,3-DPU as a side reaction, competing with those main reactions. The introduction of excess H_2O to the system speeded up only the formation of M-Ur-1 via the direct reaction of PhNCO with Im-1, resulting in an increase in the yield of M-Ur-1. It should be noted here that the addition of H_2O comes into effect, provided that the ring-opening reaction of Im-PhNCO (Scheme 5) forming M-Ur-1 is a rate-determining step. In addition, the use of CYH in place of ACE as a blocking reagent gave a better yield of M-Ur-1. In other words, preferred chain-extending reactions of NCO-terminated prepolymers with EDA in the synthesis of segmented PUU using the blocked EDA system are expected to take place by using excess H_2O and CYH, rather than ACE, as a blocking reagent.

Conclusions

In order to clarify the mechanism of the chain-extending reaction of NCO-terminated prepolymers in the synthesis of



Scheme 5. Possible pathway for the production of M-Ur-1 via the hydrolysis of intermediate (Im-PhNCO) formed by direct reaction of Im with PhNCO.



Scheme 6. Schematic representation of total reactions of the ACE/EDA mixture with PhNCO.

segmented PUU using blocked EDA with ACE, the reaction of the ACE/EDA mixture with PhNCO was investigated as a model reaction. The ACE/EDA mixture was found to comprise ACE, EDA, Mk-1, Im-1, Bk-1, and H_2O based on NMR measurements (Scheme 2); also, the reaction between the mixture and PhNCO ($[\mathrm{ACE}]_0/[\mathrm{EDA}]_0/[\mathrm{PhNCO}]_0 = 1.5/1.0/2.5$, molar ratio) afforded 1,1′-ethylenebis[3-phenylurea] (M-Ur-1) as an expected product in a 59% yield based on the EDA used. On the basis of a direct NMR analysis of the reaction mixture of PhNCO with the ACE/BA mixture, the low yield of M-Ur-1 (i.e., 59%) was considered to be associated with an unavoidable consumption of PhNCO by the H_2O existing in the ACE/EDA mixture as a result of condensation, producing 1,3-diphenylurea (1,3-DPU). On the other hand, the addition of excess H_2O to the mixture unexpectedly increased the yield of M-Ur-1 in the reaction of PhNCO with the mixture. H_2O was clarified to participate in not only the side reaction yielding 1,3-DPU, but also in the acceleration of the main reaction, giving M-Ur-1 via a direct reaction of PhNCO with imidazolidine compound (i.e., Im-1). The excess H_2O charged to the reaction system might preferentially accelerate the formation reaction of M-Ur-1, rather than the side-reaction.

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