

Sequence Distribution of Segmented Polyurethane-Urea

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ABSTRACT: Segmented polyurethane-urea (SPU) elastomer was prepared from polytetramethyleneglycol (PTMG), 4,4'-diphenylmethane diisocyanate (MDI), and ethylenediamine (EDA). The SPU is a kind of block copolymer composed of soft and hard segments. ^{13}C NMR spectra of the SPU were measured and the mean sequence lengths of polyurethane block and polyurea block were estimated from the signals of aromatic carbons. The mean polyurea sequence length was shorter than the hard segment as estimated by X-ray diffraction (Kimura *et al.*) or by other methods (Suzuki *et al.*). This polymer was found to be almost a random copolymer. The reactivity of the isocyanate group in MDI decreases slightly when the other side of isocyanate has reacted. The hard segment observed by X-ray diffraction or by other methods might only be the longer fraction of polyurea sequences.

KEY WORDS Polyurethane-urea / Sequence Distribution / Isocyanate / 4,4'-Diphenylmethane Diisocyanate / Reactivity Ratio / ^{13}C NMR /

Segmented polyurethane-urea (SPU) elastomer is a kind of block copolymer composed of soft and hard segments. The soft segment usually consists of aliphatic polyether or polyester urethane block and the hard segment is a polyurea block. SPU is usually prepared in two-stage reactions as shown in Figure 1. A diisocyanate compound is reacted with a hydroxy terminated prepolymer (I). The amount of the isocyanate compound exceeds that of prepolymer (I) so that the unreacted isocyanate compound remains after the reaction. The resultant polymer (prepolymer (II)) is then extended with a diamine (chain extender). The mechanical properties of SPU depend on (1) the composition of soft and hard segments, (2) the length of soft and hard segments, or in other words, the molecular weight of prepolymer (I) (polyether or polyester) and the sequence length distribution, (3) anomalous linkages (branching, cross-linking), (4) molecular weight of SPU. The hydrogen-bonding in the crystal of the hard

segment plays important roles in the elasticity of this polymer.¹⁻³ The estimation of the lengths of soft and hard segments is essential for the investigation of SPU. Kimura *et al.* observed the length of hard segment directly by wide angle X-ray diffraction and by small angle X-ray scattering when the chain extender was 4,4'-diphenylmethanediamine (MDA).^{4,5} They estimated the length of the hard segment composed of the polyurea block to be about four monomer units in the case of the molar ratio of prepolymer (I)/chain extender = 1 : 1. Suzuki *et al.* measured the length of the polyurea block in a similar SPU (chain extender; hydrazine) by selective degradation.⁶ The length of the polyurea block agreed with the length of the hard segment estimated by Kimura *et al.* This suggests that the polyurea block is identical to the hard segment.

The length of polyurea block depends on the reactivity ratio of isocyanate groups of diisocyanate compounds.⁷ In the case of 4,4'-diphenylmethane diisocyanate (MDI), the re-

EXPERIMENTAL

Materials

SPU was prepared from 4,4'-diphenylmethane diisocyanate (MDI), polytetramethyleneglycol (PTMG; $M_w \approx 1800$), and ethylenediamine (EDA) as shown in Figure 1. PTMG and an excess amount of MDI were mixed under nitrogen atmosphere at 60–65°C for 2 h. Then, the reactant prepolymer (II) was dissolved in dimethylacetamide (DMAc) together with EDA at ambient temperature. The polymer was precipitated in water and dried.

Some model compounds were prepared by the reaction of alcohol or amine with isocyanate compounds in DMAc. *n*-Butyl phenylcarbamate (PUT) was prepared from *n*-butyl alcohol and phenyl isocyanate (PHI). Di-*n*-butyl 4,4'-diphenylmethane dicarbamate (MUT) was prepared from *n*-butyl alcohol and MDI. 1-Phenyl-3-*n*-propyl urea (PUA) was prepared from *n*-propyl amine and PHI. 4,4'-Bis(3-*n*-propylureido)-diphenylmethane

(MUA) was prepared from *n*-propyl amine and MDI.

DMAc was dried by molecular sieves before use. The other materials were used as received.

NMR Measurement

^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (^{13}C ; 75.5 MHz) at 80°C. SPU was dissolved in DMAc and dimethylsulfoxide- d_6 (ca. 10:1, v/v) at about 25%. Spin-lattice relaxation times (T_1 s) were measured by inversion recovery method and nuclear Overhauser effects (NOEs) were measured by gated decoupling method. Quantitative measurement was conducted by the gated decoupling method of NOE free mode.

RESULTS AND DISCUSSION

Assignment of Signals

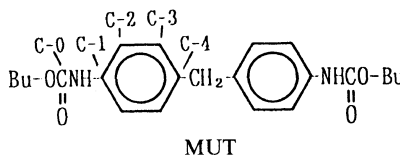
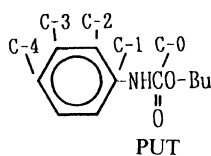
The ^{13}C NMR chemical shifts of carbonyl and aromatic carbons of model compounds in DMAc are listed in Table I. These signals are

Table I. ^{13}C NMR chemical shifts (ppm from TMS) of model compounds

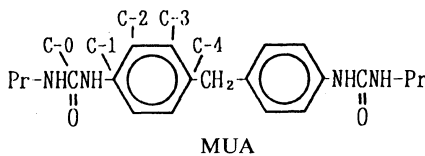
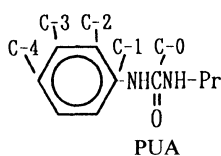
	C-0	C-1	C-2	C-3	C-4
Urethane					
PUT	153.9	139.6	118.4	128.7	122.3
MUT	153.6	137.1	118.4	128.7	135.3
Urea					
PUA	155.3	141.1	117.3	128.4	120.6
MUA	155.2	138.8	117.5	128.4	134.0

Solvent, *N,N*-dimethyl acetamide/DMSO- d_6 (ca. 90:10); temperature, 50°C.

Urethane models,



Urea models,



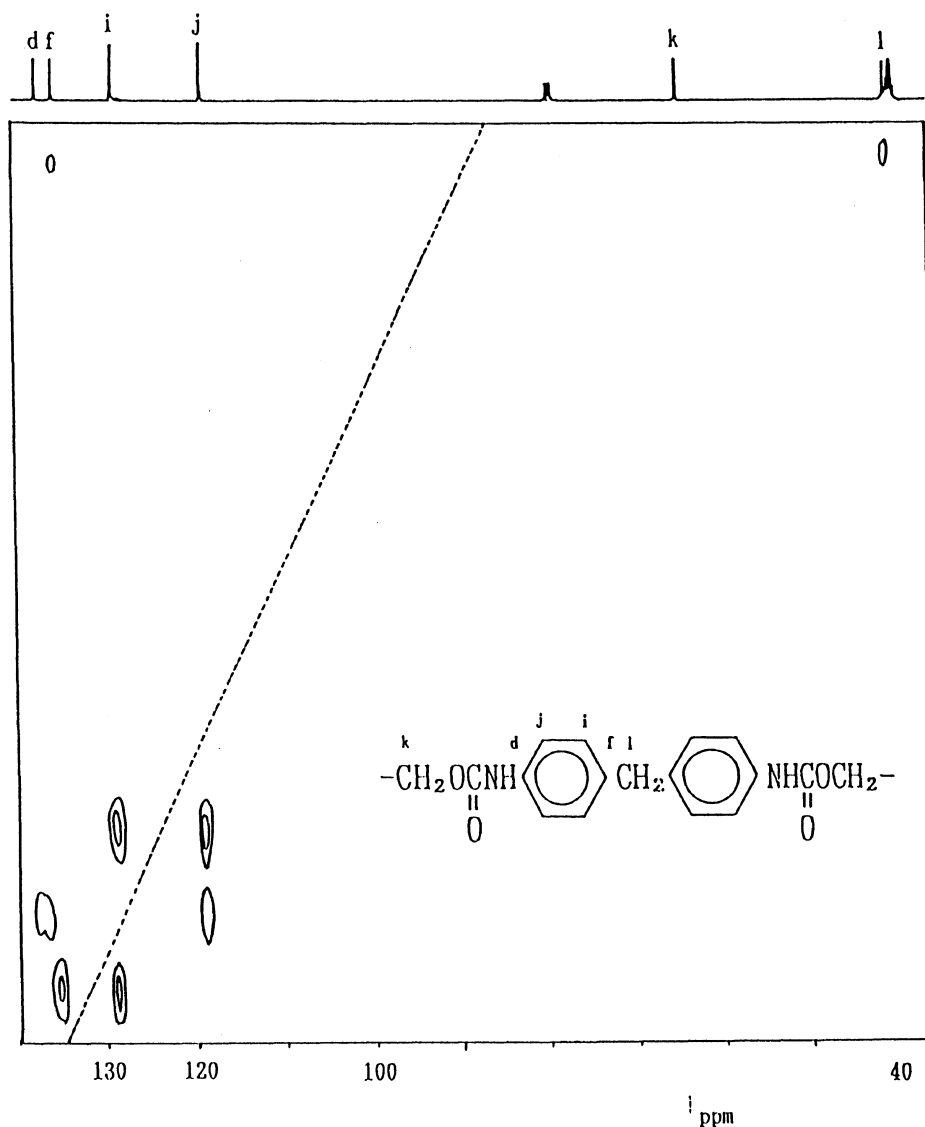
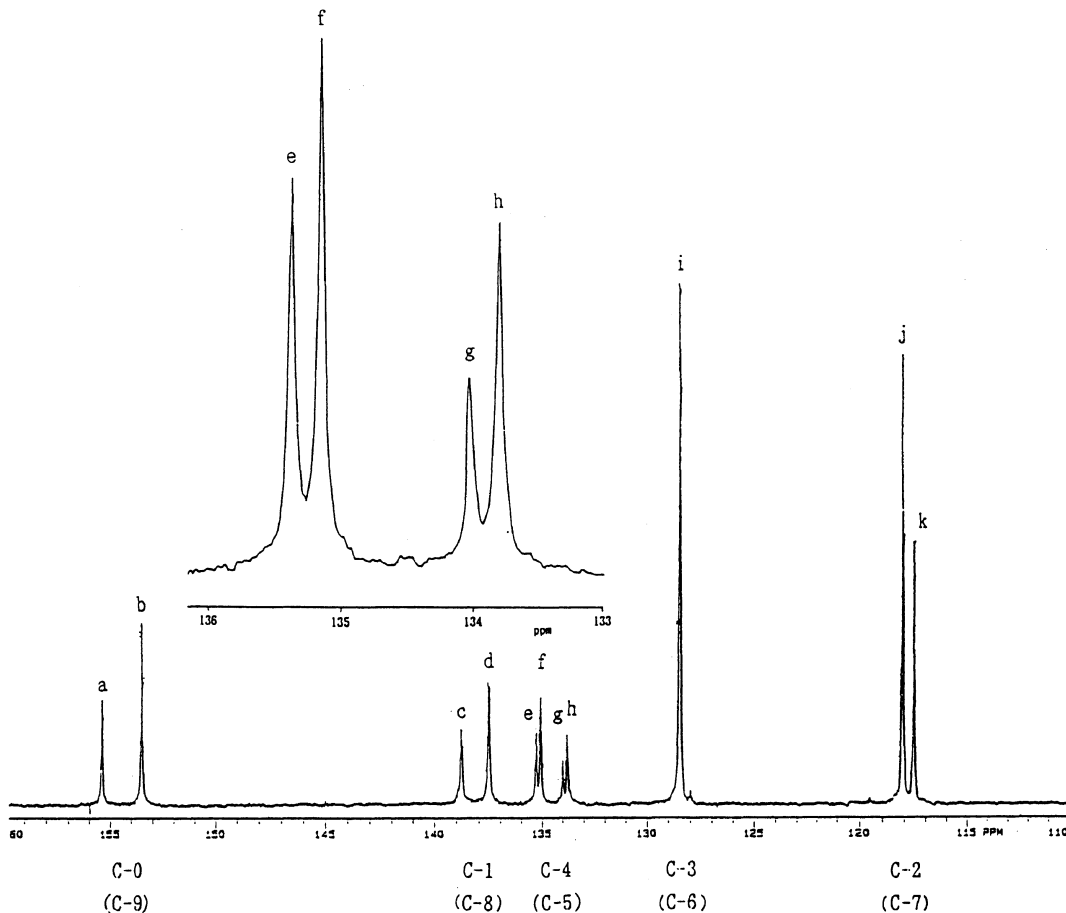


Figure 2. 2D INADEQUATE spectrum of MUT (urethane model compound from MDI). The connectivity of $l(\text{CH}_2)\text{-}f(\text{C-4})\text{-}i(\text{C-3})\text{-}j(\text{C-2})\text{-}d(\text{C-1})$ can be observed.

assigned according to the empirical rule. In the case of models using PHI (PUT, PUA), the signal due to C-1 carbon (located at about 140 ppm) can be distinguished from that of C-4 carbon (~121 ppm) easily. However, the signals of C-1 carbon in MUT and MUA are located close to those of C-4 carbon. The signals of C-1 and C-4 carbons were thus

assigned by 2D INADEQUATE spectra. Figure 2 shows the 2D INADEQUATE spectrum of MUT. The signal d (at about 137 ppm) is due to C-1 carbon of MUT, and signal f (at about 135 ppm) is due to C-4 carbon of MUT. The signals of MUA are assigned in the same way. The signals at about 139 ppm and 134 ppm ((c) and (g)) are due to C-1 and

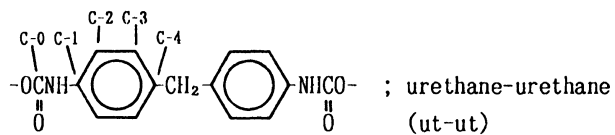
Sequence Distribution of Segmented Polyurethane-Urea



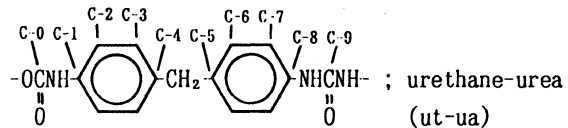
The assignment of the lines

Sequence

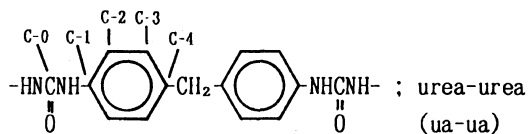
C-0	C-1	C-2	C-3	C-4
(C-9)	(C-8)	(C-7)	(C-6)	(C-5)



b	d	j	i	f
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b	d	j	i	e
a	c	k	i	h



a	c	k	i	g
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Figure 3. ¹³C NMR spectrum of SPU (110—160 ppm). The region of C-4 carbons (133—136 ppm) is expanded.

C-4 carbons, respectively. The positions of the signals of urethane models are slightly different from those of the corresponding carbons in urea models.

The ^{13}C NMR spectrum of SPU is shown in Figure 3. The signals of C-1, C-2, and C-4 carbons split into two or four lines. It is considered that this splitting depends on whether the isocyanate groups of MDI are turned into the urea bonding or the urethane bonding. The peaks a, c, g, h, i, and k are located close to the signals of MUA (urea model) and the peaks b, d, e, f, i, and j to the signals of the MUT (urethane model). The bonding ratio of urea/urethane is estimated from the ratio of these signal intensities. We can calculate the initial molar ratio of MDI/PTMG from the bonding ratio of urea/urethane.

C-1 and C-4 signals split into four lines in the spectrum of SPU. The splitting of C-4 signals is more obvious. The splitting is due to differences of substituents of the other side of diphenylmethane. These signals reveal the sequences of linkages (urethane-urethane (ut-ut), urethane-urea (ut-ua) and urea-urea (ua-ua)). C-9—C-5 are identical to C-0—C-4, respectively in ut-ut and ua-ua sequences because of the symmetric structure. Ut-ua sequence is a junction of polyurethane and polyurea blocks. The signal intensities of lines e and h are almost equal. Though there is no exact data for the assignment of the two lines (e and h), it is not critical for our discussion on sequence lengths. The chemical shifts of these lines are listed in Table II.

Quantitative Analysis

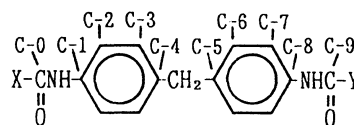
T_1 s and NOEs of carbonyl and aromatic carbons of SPU were measured before quantitative analysis and are listed in Table III. T_1 s of carbonyl and quaternary carbons are 1.3 to 2.9 s and those of protonated carbons are 0.3 to 0.4 s. We took 30 s between pulses for quantitative measurements. The NOEs were about 1.6 and 2.6 for quaternary and

Table II. ^{13}C NMR chemical shifts (ppm from TMS) of SPU

Sequences	C-0 (C-9)	C-1 (C-8)	C-2 (C-7)	C-3 (C-6)	C-4 (C-5)
ut-ut	153.6	137.6	118.0	128.5	135.1
ut-ua		137.5			135.6
		138.8			133.7
ua-ua	155.4	138.7	117.5	128.5	134.0

Solvent, *N,N*-dimethyl acetamide/DMSO- d_6 (ca. 90:10); concentration, 25 wt%; temperature, 50°C.

Sequences



	X	Y
ut-ut urethane-urethane	RO-	-OR
ut-ua, urethane-urea	RO-	-NHR
ua-ua urea-urea	RNH-	-NHR

C-9—C-5 are identical to C-0—C-4 in symmetric structure.

Table III. T_1 's and NOE's of carbonyl and aromatic carbons in SPU^a

Nuclei	T_1 's		NOE ^b	
	Urethane	Urea	Urethane	Urea
Carbonyl	2.3	2.9	1.6	1.6
C-1	2.1	1.9	1.6	1.5
C-2	0.38	0.33	2.6	2.6
C-3	(0.37)	(0.37)	(2.5)	(2.5)
C-4				
ut-ut	1.6	—	1.7	—
ut-ua	1.7	1.4	1.7	1.7
ua-ua	—	1.3	—	1.6

^a Solvent, *N,N*-dimethyl acetamide/DMSO- d_6 (ca. 90:10); concentration, 25 wt%; temperature, 50°C. Since the lines of C-3 in urethane and urea sequences did not split clearly, their T_1 and NOE could not be measured separately.

^b $\text{NOE} = I_{\text{com}}/I_{\text{non}}$, where I_{com} and I_{non} are signal intensities measured by the ^1H -complete decoupling mode and NOE-free mode, respectively.

protonated carbons, respectively. Since the NOEs are not the same even among quaternary carbons, the relative signal areas were measured from spectra taken by the gated de-

Table IV. Initial feed ratios of MDI/PTMG, molar fractions of three structural units (P_{TT} , P_{TA} , P_{AA}), urethane-urea ratio, mean sequence lengths ($\bar{L}_n(\text{ut})$, $\bar{L}_n(\text{ua})$), blockness ($\langle B \rangle$), and reactivity ratio of isocyanate groups in MDI (A)

MDI/PTMG		Molar fraction			Urethane	Sequence length		Blockness	Reactivity ratio
Feed	Observed	P_{TT}	P_{TA}	P_{AA}	Urea	$\bar{L}_n(\text{ut})$	$\bar{L}_n(\text{ua})$	$\langle B \rangle$	A
1.50	1.50	0.43	0.47	0.10	2.00	2.84	1.44	1.05	0.90
1.60	1.57	0.38	0.51	0.11	1.74	2.49	1.43	1.05	0.89
1.65	1.64	0.36	0.50	0.14	1.56	2.43	1.55	1.06	0.88
1.70	1.67	0.34	0.52	0.14	1.50	2.29	1.56	1.08	0.83
1.90	1.89	0.26	0.55	0.19	1.15	1.97	1.69	1.10	0.78

coupling method of the NOE free mode.

Let P_{TT} , P_{TA} , and P_{AA} represent the molar fractions of urethane-urethane (ut-ut), urethane-urea (ut-ua), and urea-urea (ua-ua) linkages, respectively.

$$P_{TT} + P_{TA} + P_{AA} = 1 \quad (1)$$

P_{TT} , P_{TA} , and P_{AA} can be calculated from the relative intensities of C-4 signals. The urethane/urea ratio and feed ratio of MDI/PTMG are calculated from P_{TT} , P_{TA} , and P_{AA} easily.

urethane/urea

$$= (2 \times P_{TT} + P_{TA}) / (2 \times P_{AA} + P_{TA}) \quad (2)$$

MDI/PTMG = (urethane + urea) / (urethane)

$$= 2 / (2 \times P_{TT} + P_{TA}) \quad (3)$$

In the case of the SPU in Figure 3,

$$P_{TT} = 0.38, \quad P_{TA} = 0.51, \quad \text{and} \quad P_{AA} = 0.11.$$

$$\text{urethane/urea} = 1.74$$

$$\text{MDI/PTMG} = 1.57$$

Several SPUs of different feed ratios of MDI/PTMG were also analyzed and the results are given in Table IV.

The Mean Sequence Lengths of Polyurethane and Polyurea Blocks

The mean sequence lengths of polyurethane and polyurea blocks can be written as eq 4, 5

$$\bar{L}_n(\text{urethane}) = (2 \times P_{TT} + P_{TA}) / P_{TA} \quad (4)$$

$$\bar{L}_n(\text{urea}) = (2 \times P_{AA} + P_{TA}) / P_{TA} \quad (5)$$

The mean length of the polyurethane sequence was about 2.49 and that of the polyurea sequence was about 1.43. The results of the other samples are given in Table IV. The polyurea sequence lengths are close to those expected from Bernoullian statistics.

Kimura *et al.*^{4,5} estimated the polyurea sequence length as about 4 by the X-ray diffraction under stress. This seems too long, taking into account that the MDI/PTMG ratio of the SPU they studied was 2. The polyurea sequence observed by X-ray diffraction might be the crystalline region in the polyurea sequences.

The polyurea sequence length estimated by Suzuki *et al.*⁶ was also about 4 (MDI/PTMG = 2). Although they concluded that the deviation from random copolymer was caused by non-homogeneous reaction, short polyurea sequences might be lost in the recovery.

If the reactivity of the isocyanate group in MDI did not change when the other side of the isocyanate group had reacted with amine, the content of the polyurea sequences in which the number of the monomer units is "n" can be calculated as follows using Bernoullian statistics.

The probability of a polyurea block having n monomer units in its sequence ($P(L(\text{urea})_n)$)

Table V. Probability of urethane or urea linkages belonging to the urethane or urea block whose sequence length is "n"

Sequence length "n"	Urethane			Urea		
	$P(L(ut)_n)$	$n \times P(L(ut)_n)$	$P(ut)_n$	$P(L(ua)_n)$	$n \times P(L(ua)_n)$	$P(ua)_n$
1	0.40	0.40	0.16	0.70	0.70	0.49
2	0.24	0.48	0.19	0.21	0.42	0.29
3	0.14	0.42	0.17	0.06	0.18	0.13
4	0.86	0.36	0.14	0.02	0.08	0.06
5	0.051	0.25	0.10	} 0.01	0.05	0.03
6	0.031	0.18	0.07			
7	0.018	0.14	0.06			
8	0.011	0.08	0.03			
≥ 9	0.2	0.18	0.07			

The probability was calculated assuming the reactivity ratio of the isocyanate groups in MDI (A) = 1 (Bernoulli statistics).

Mean sequence lengths in this SPU, $\bar{L}_n(ut) = 2.49$, $\bar{L}_n(ua) = 1.43$. $P(L(ut)_n)$, $P(L(ua)_n)$, molar fraction of urethane or urea block which sequence length is "n". $n \times P(L(ut)_n)$, $n \times P(L(ua)_n)$, contribution to the mean sequence length.

$P(ut)_n$, $P(ua)_n$, probability of urethane or urea linkage belonging to sequence length "n".

is given by

$$P(L(\text{urea})_n) = \frac{(2 \times P_{AA})^{n-1} \times P_{TA}}{(2 \times P_{AA} + P_{TA})^n} \quad (6)$$

When $P_{AA} = 0.11$ and $P_{TA} = 0.51$, each sequence length is estimated as shown in Table V. The content of the polyurea sequence having longer than 3 monomer units is only 3% in urea linkages. SPU can be redrawn schematically from the conventional scheme according to Table V as in Figure 4b. The mean length of polyurea sequences is much shorter than that in conventional scheme of SPU in Figure 4a. The concept of the hard and soft segments might be reconsidered from this result.

If the hard segment is only composed of longer polyurea sequences in this elastomer, the hard segment content in SPU might be very low. If the short urea components do not contribute to the hard segment and belong to the soft segments, the length between the crosslinking points might be very long. However, the mean urea sequence length ($\bar{L}_n(\text{urea})$) defined here is the sequence length of $[-\text{CONH}-\phi-\text{CH}_2-\phi-\text{NHCONHCH}_2\text{CH}_2-\text{NH}-]_n$, (ϕ , phenylene) then "n = 1" means the $-\text{CON}-\phi-\text{CH}_2-\phi-\text{NHCONHCH}_2\text{CH}_2\text{NH}-$

$\text{CONH}-\phi-\text{CH}_2-\phi-\text{NHCO}-$ sequence containing two urea linkages. The sequence of $n = 2$ contains 4 urea linkages. So, these short urea components may also contribute to the hard segment.

Blockness of SPU

The blockness of SPU $\langle B \rangle$ is defined as follows⁶

$$\langle B \rangle = \frac{1}{\bar{L}_n(\text{urethane})} + \frac{1}{\bar{L}_n(\text{urea})} \quad (7)$$

The $\langle B \rangle$ value changes according to the blockness of the copolymer.

$0 < \langle B \rangle < 1$; block

($\langle B \rangle = 0$; homopolymer blend)

$\langle B \rangle = 1$; random

$1 < \langle B \rangle \leq 2$; alternating

The $\langle B \rangle$ values of SPUs are also given in Table IV. They are almost independent of the feed ratio of MDI and PTMG. The value of $\langle B \rangle$ is about 1.05 which means that these SPUs are almost random copolymers and have little alternating tendency. Blockness increased slightly with increasing urea content, but the reason

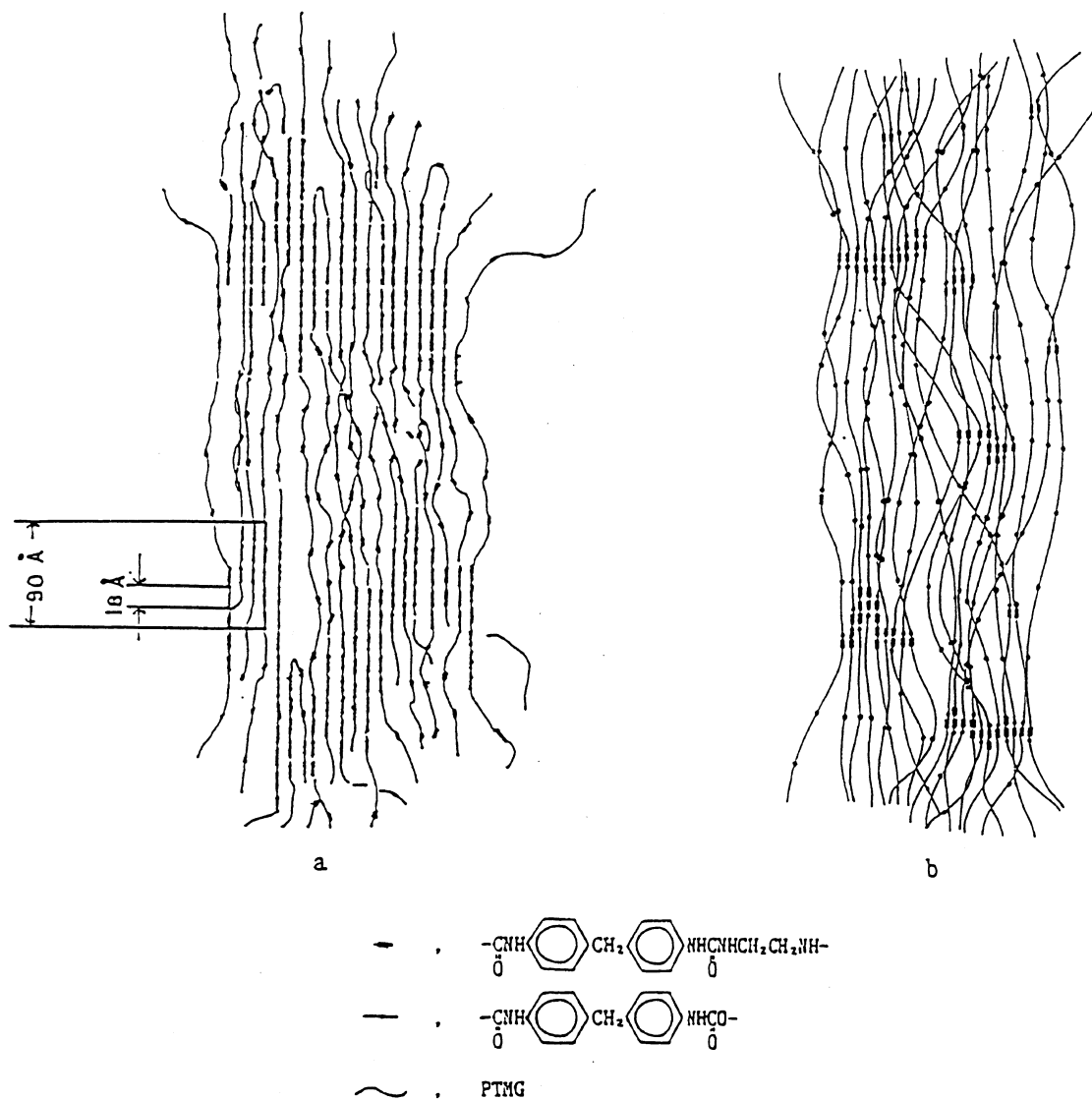


Figure 4. Schematic illustration of stretched and heat set SPU. a, model proposed by Kimura *et al.*⁴; b, reformed model according to the results of ¹³C NMR spectroscopy. The sequences are distributed assuming the Bernoullian model as shown in Table IV.

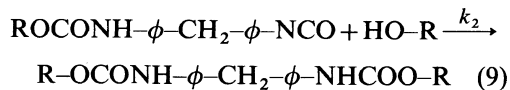
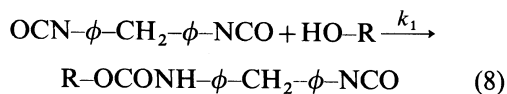
for this is not clear at present.

Reactivity Ratio of Isocyanate Groups of MDI

The reactivity ratio of isocyanate groups of MDI is defined as follows according to Suzuki *et al.*⁶

In the prepolymerization, the following ele-

mental reactions occur.



The reactivity ratio of the two isocyanate groups (A) in MDI is given by

$$A \equiv k_2/k_1 \quad (10)$$

The kinetic equations are as follows.

$$d[I]_f/dt = -2k_1[I]_f[OH] \quad (11)$$

$$d[I]_e/dt = (k_1[I]_f - k_2[I]_e)[OH] \quad (12)$$

where $[I]_f$, $[I]_e$, and $[OH]$ are the concentrations of the isocyanate group in free MDI, the isocyanate group in the end of polymer, and the hydroxyl group in PTMG, respectively.

The integration of eq. 11 and 12 from time 0 to T gives eq. 13 ($A \neq 2$).

$$\begin{aligned} & \frac{1}{1-A/2} \ln \frac{(1-A/2)([I]_e/[I]_f)_T + 1/2}{(1-A/2)([I]_e/[I]_f)_0 + 1/2} \\ &= -\ln \frac{([I]_f)_T}{([I]_f)_0} \end{aligned} \quad (13)$$

Where the boundary conditions are as follows. Time T is the finishing time of stage 1 in Figure 1.

$$([I]_f)_0 = 2: ([I]_f)_T = 2P_{AA}$$

$$([I]_e)_0 = 0: ([I]_e)_T = P_{TA}$$

Thus, then we obtain

$$\ln P_{AA} = \{2/(A-2)\} \ln \{1 - (A-2) \times P_{TA}/2P_{AA}\} \quad (14)$$

In the case of $A = 2$

$$\ln P_{AA} = -P_{TA}/P_{AA} \quad (15)$$

P_{AA} and P_{TA} are obtained from ^{13}C NMR spectra and the reactivity ratios (A) are calculated by the least squares method and listed in Table IV.

The values of A ranged from 0.78 to 0.9 for various feed ratio. The reactivity of isocyanate group in MDI decreased slightly when the other side of isocyanate group reacted to form an urethane linkage.

According to Ferstandig and Scherrer,¹⁰ the reaction rate constant of the first isocyanate in MDI is 3.2 times as large as that of the second

isocyanate for the reaction with ethanol at 30°C. This rate constant ratio (k'_1/k_2) is not the same as the reactivity ratio we define here. As two isocyanate groups are contained in a free MDI,

$$k'_1/k_2 = 2 \times k_1/k_2 = 2 \times (1/A) \quad (16)$$

Therefore the reactivity ratio of isocyanate groups: A (defined by eq. 10) is 1/1.6. Ferstandig and Scherrer also reported that the activation energies of the first and second isocyanate reactions (E_{a1} , E_{a2}) are 7.2 and 9.4 kcal mol⁻¹, respectively. The reactivity ratio (A) at 60°C can be calculated from these activation energies.

The reactivity ratio at temperature T_1 ($A(T_1)$) can be written as

$$A(T_1) = C \exp\{-(E_{a2} - E_{a1})/RT_1\} \quad (17)$$

where C , the constant for this temperature range; R , gas constant. When temperature changes to T_2 , $A(T_2)$ is represented as

$$A(T_2) = A(T_1) \exp\{(E_{a2} - E_{a1})(1/T_1 - 1/T_2)/R\} \quad (18)$$

For $E_{a2} - E_{a1} = 2.2$ kcal mol⁻¹, $R = 1.9872$ cal deg⁻¹ mol⁻¹, $A(T_1) = 1/1.6$, $T_1 = 303.15$ K, $T_2 = 333.15$ K and thus

$$A(T_2) \approx 0.87$$

This agrees well with that obtained from the sequence lengths of SPUs. This means that the reaction mechanism of MDI with PTMG is possibly the same as with ethanol. It is reasonable that the mean sequence length of hard segment is short.

CONCLUSIONS

1) The mean sequence lengths of urethane and urea in SPU can be determined from ^{13}C NMR spectra. The mean sequence lengths of urethane and urea in SPU are shorter than those observed by other authors using X-ray diffraction or other methods. It was found that SPUs are almost random or slightly alternative

copolymers from the view point of the sequences of urethane and urea linkages.

2) The reactivity of an isocyanate group in MDI decreases slightly when the other isocyanate group in MDI has reacted. Decrease in the reactivity of isocyanate group in MDI observed here agrees with the results of Ferstandig and Scherrer¹⁰ (estimated from the reaction with ethanol).

3) The hard segment observed by other authors using X-ray diffraction or other methods might be the longer fraction of polyurea sequences. Short polyurea sequences might also contribute to the network system of SPU.

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