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Studies of the Structure of Polyurethane Elastomers. I. The Number-average MW Determination of the Hard-segment in the Poly(Ether)Urethane Elastomer by Means of Perchloric Acid Depolymerization

Hajime Suzuki and Hiroshi Ono

Katata Research Institute, Toyobo Co., Ltd., Honkatata, Otsu

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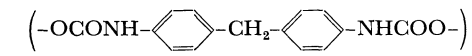
Urea segment which is called a hard-segment in the poly(ether)urethane elastomer (PEUE) consisting of a polyether segment,urethane segment,and urea segment was isolated by means of perchloric acid depolymerization. The number-average molecular weight (MW) of the urea segment obtained by the above method was determined by elemental analysis and by volumetric analysis. By comparing the analytical results with the results calculated for a random polymerization, the number-average MW of the hard-segment was found to deviate from that expected from the equal reactivity of the two isocyanate groups in 4,4′-diphenyl methane diisocyanate (MDI). Therefore, an apparent reactivity ratio of two isocyanate groups in MDI (A) can be calculated from the number-average MW of the hard-segment isolated by means of perchloric acid depolymerization.

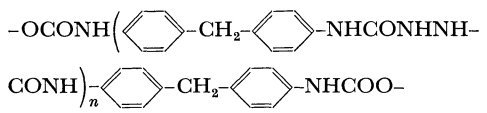
There have been a number of reports concerning the determination of randomness[1] and copolymer compositions[2] by means of the high-resolution NMR, but the determination of the sequence length of the hard-segment in PEUE has not been successful, mainly because of the complication of the spectra of poly (ether) urethane elastomers. Therefore, we have studied the isolation of three segments by means of the difference in the cleavage rate of three segments in a typical PEUE prepared from MDI, polyoxytetramethylene glycol (PTG), and hydrazine (HD). Although the structure of the PEUE can not be written in one formula, it may be expressed by the following three segments:

polyether segment, $(-CH_2CH_2CH_2CH_2O-)_n$

urethane segment,



urea segment,



By determining the MW of the urea segment, we were able to show the blockiness in the PEUE, and also the apparent reactivity ratio of two isocyanate groups in MDI. These studies will be very useful for the elucidation of the relationship between the structure and the physical properties of the elastomers.

Experimental

Materials. The PEUE's used in this work were synthesized by the prepolymer method. The prepolymer was prepared by reacting 0.02 mol (20 g) of PTG (MW, *ca.*, 1000) with MDI (0.03—0.07 mol, as in Table 1) in 60 m*l* of *N*,*N*-dimethyl acetamide at 30°C for 3 hr. The completeness of the prepolymer reaction was ascertained by the *n*-dibutylamine titration method reported by Otey *et al.*,[3] and the PEUE's were prepared from the prepolymer and HD as a chain extender. The molar ratios of the various monomers in the polymers prepared in this way are listed in Table 1.

Poly(ether)urethane (PEU) was synthesized by reacting PTG (MW, *ca.* 1000) with the equivalent mole of MDI as polyether and urethane segment models.

Depolymerization of PEUE. The depolymerization was carried out by placing the PEUE (5 g) in perchloric acid (60%, 60 m*l*) for 24 hr at room temperature, and by then treating it at 70°C for 40 hr in a water bath. An excess of water was added to the mixture to precipitate the perchlorate of the amine end group of the urea segment. The salt was collected by filtration, and then washed with water and dried.

The completeness and the selectivity of depolymerization reaction were ascertained by the following procedure. A mixture of 5 g of model compounds of PEU and 2 g of the urea segment obtained by the above depolymerization was depolymerized by perchloric acid (60%, 60 m*l*) under the same conditions as in the depolymerization of PEUE. After the depolymerization of this mixture,

1) R. Yamadera and M. Murano, *J. Polym. Sci., Part A-1*, **5**, 2259, (1967).

2) T. Harada and N. Ueda, *Kobunshi Kagaku*, **22**, 685 (1965).

3) F. H. Otey, Bornnie L. Zagoren and C. L. Mehltretter, *J. Appl. Polym. Sci.*, **8**, 1985 (1964).

Table 1. Preparation and elementary analysis of the hard-segments of PEUE's

No.	Prepolymer MDI (mol)	Prepolymer PTG (mol)	Chain extender HD (mol)	[Urea]/[Urethane]	Found (%) C	Found (%) H	Found (%) N	Found (%) Cl	Calcd (%) C	Calcd (%) H	Calcd (%) N
1	0.030	0.020	0.010	1/2	53.60	4.33	14.59	7.18	53.85	4.58	14.67
2	0.035	0.020	0.015	1.5/2	54.41	4.17	14.85	6.81	54.36	4.60	14.94
3	0.040	0.020	0.020	2/2	55.23	4.60	15.32	6.33	55.03	4.62	15.29
4	0.050	0.020	0.030	3/2	56.72	4.72	16.21	5.18	56.64	4.69	16.12
5	0.060	0.020	0.040	4/2	57.22	4.65	16.40	4.75	57.23	4.71	16.43
6	0.070	0.020	0.050	5/2	57.87	4.78	16.79	4.22	57.96	4.74	16.81

the weight loss was measured, and the change in the MW of the urea segment was measured by the titration method.

MW Determination of the Hard-segment. The MW of the hard-segment was determined by elemental analysis and by titration. In the elemental analysis the MW was calculated directly from the chlorine content.

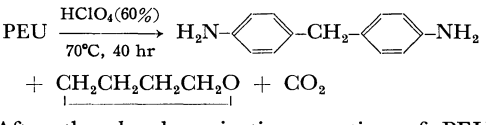
In the titration method, about 30 mg of the hard-segment obtained by the above method was immersed in 10 m*l* of a N/100 aqueous solution of NaOH and titrated by a N/100 aqueous solution of HCl, using methyl orange as the indicator. The MW of the hard-segment was calculated by the following equation:

$$\text{MW of hard-segment} = \frac{2\{\text{Weight of hard-segment (mg)} - 100.5 \times (T_B - T_S)(\text{m}l) \times 1/100 \times F\}}{(T_B - T_S)(\text{m}l) \times 1/100 \times F}$$

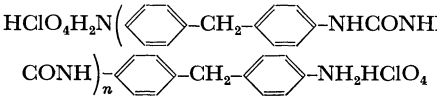
where F is a factor of an aqueous solution of HCl and where T_S and T_B are the volume of an N/100 aqueous solution of HCl required for the titration of the sample and the blank solution respectively.

Results and Discussion

Depolymerization Reaction. A previous paper[4] has described how THF is formed quantitatively in the reaction of PTG and perchloric acid. After the reaction of PEU and perchloric acid, an aqueous solution of sodium hydroxide was added to the reaction mixture until the pH value reached 9; 4,4′-diaminodiphenylmethane (mp, 93—94°C) was thus obtained. From these findings, the reaction of PEU and perchloric acid may be assumed to proceed as follows:



After the depolymerization reaction of PEUE under the conditions described above, precipitates were obtained by adding an excess of water to the reaction mixture. The IR absorption spectrum of the precipitate is shown in Fig. 1. A comparison of the IR absorption spectra of the precipitate (B) and of PEUE (A) shows that the 2900 cm^{-1} region due to the methylene group and the 1700 cm^{-1} region due to the urethane group disappeared in B. The IR absorption spectrum of the precipitate washed with an aqueous solution of sodium hydroxide is shown in C of Fig. 1. The comparison of the IR absorption spectra of C and B in Fig. 1 shows that the absorption at 1100 cm^{-1} can not be seen in C, but this absorption C was again coincident with the IR absorption spectrum of B after this precipitate had been washed with perchloric acid; therefore, the absorption in the 1100 cm^{-1} region in B may be due to the perchlorate of amine. On the other hand, the absorption in the 1100 cm^{-1} region in A is due to the ether segment in PTG. From the above results, the precipitate obtained by the perchloric acid depolymerization can be written by the following formula:



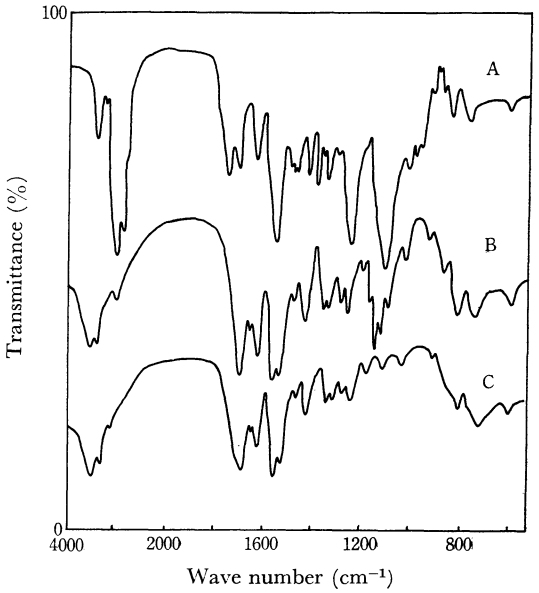


Fig. 1. IR spectra of PEUE and hard-segment. A: PEUE, B: urea segment with the perchlorate of the amine endgroups, C: urea segment with amine endgroups

4) H. Suzuki and H. Ono, *Kogyo Kagaku Zasshi*, **72**, 1593 (1969).

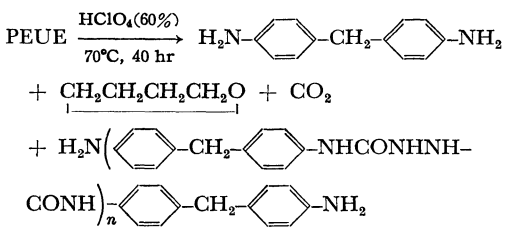
The results of the elementary analysis of the above hard-segments of the PEUE's are given in Table 1. The calculated values shown in Table 1 were obtained from the analytical results of the chlorine.

To ascertain the recovery of the hard-segment from PEUE, the mixture of PEU and the hard-segment obtained by the above experiment was depolymerized by perchloric acid under the same conditions as above. In this experiment, the recovery and the MW of the hard-segment were measured. Table 2 shows these results.

Table 2. Recovery and MW of hard-segment

Recovery (wt%)	MW before re-depolymerization	MW after re-depolymerization
99.7	782	779
99.2	828	808
99.5	931	945
99.7	1213	1215
98.3	1333	1315
99.0	1573	1575

From these results, the reaction of PEUE with perchloric acid can be assumed to proceed as follows:



Since 4,4′-diaminodiphenylmethane, which came from the urethane segment, was soluble in perchloric acid, while the hard-segment was insoluble, it could be separated by precipitation.

Table 3. MW of hard-segment

No.	[Urea]/[Urethane] molar ratio	MW of Hard-segment: Titration method	MW of Hard-segment: Elemental analysis method	MW of Hard-segment: Calcd value
1	1/2	782	789	621
2	1.5/2	828	842	691.5
3	2/2	931	921	762
4	3/2	1213	1172	903
5	4/2	1333	1295	1044
6	5/2	1573	1482	1185

Table 3 shows the number-average MW of the hard-segment. The calculated values in Table 3 were obtained in a manner to be shown later.

MW of the Hard-segment. The reactivity between MDI and alcohols has been reported on by many authors.[5,6] Naito and Tanaka[7] have shown the equal reactivity of two isocyanate groups in MDI for the reactions with low-molecular-weight alcohols. Moreover, Ferstandig and Scherrer[8] reported that the reactivity ratio ($A=K_2/K_1$) of two isocyanates in MDI was about 0.33. Although there has been no report concerning the reactivity between the polymer diol and MDI, we assumed an equal reactivity of the isocyanate group in MDI in the prepolymer reaction and in the chain-extender reaction.

The PEUE composition is given by:

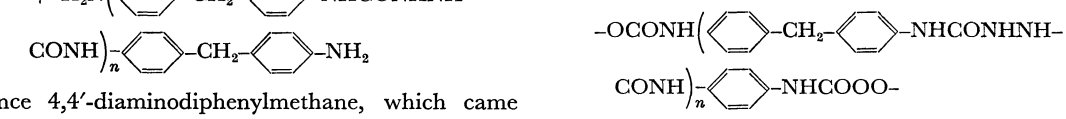
$$C = E + H \tag{1}$$

where C, E, and H are the numbers of moles of MDI, PTG, and HD respectively. After the prepolymerization, the concentration ratio of the three structural units could be obtained by a probability calculation, as is shown in Table 4.

Table 4. Concentration ratio of three structural units after prepolymerization

Structural unit	Concentration ratio
$CH_2\left(\bigcirc\text{-NHCOO-}\right)_2$	$P_{E\text{-}I\text{-}E}=E^2/C^2$
$CH_2\left(\bigcirc\text{-NCO}\right)_2$	$P_{H\text{-}I\text{-}H}=(C-E)^2/C^2$
OCN-⬡-CH-⬡-NHCOO-	$P_{H\text{-}I\text{-}H}=1-\{E^2+(C-E)^2\}/C^2$

After the prepolymerization, the prepolymer was polymerized by HD to give the following structure:



The probability to produce a sequence of $n=1$ is given by:

$$\frac{1/2[1-\{E^2+(C-E)^2\}/C^2]}{(C-E)^2/C^2+1/2[1-\{E^2+(C-E)^2\}/C^2]}=E/C \tag{2}$$

and the probability for $n=2$ is given by:

$$\frac{(C-E)^2/C^2}{(C-E)^2/C^2+1/2[1-\{E^2+(C-E)^2\}/C^2]}\times E/C = \{(C-E)/C\}\times E/C \tag{3}$$

Generally, the probability for $n=m$ is given by:

$$\{(C-E)/C\}^{m-1}\times E/C \tag{4}$$

and the sum of the hard-segment is given by the

5) M. E. Bailey, V. Kriss and R. G. Spaunburgh, *Ind. Eng. Chem.*, **48**, 794 (1956).

6) J. Burkus and C. F. Echert, *J. Amer. Chem. Soc.*, **80**, 5948 (1958).

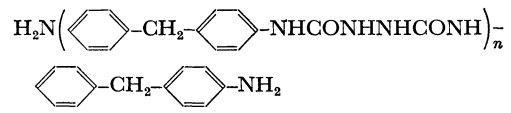
7) K. Naito and M. Tanaka, Preprints for 19th Annual Meeting of the Chemical Society of Japan, Hiyoshi (1963), p. 76.

8) L. L. Ferstandig and R. A. Scherrer, *J. Amer. Chem. Soc.*, **81**, 4838 (1959).

following equation:

$$\sum_{n=1}^{\infty}\{(C-E)/C\}^{n-1}\times E/C = 1 \qquad (5)$$

The hard-segment obtained by the perchloric acid depolymerization of the PEUE has the following structure:



The MW for $n=1$ is 480, and that of the repeating unit is 282, so the number-average MW of the hard-segment is calculated as:

$$\sum_{n=1}^{\infty}\{480+282(n-1)\}\{(C-E)/C\}^{n-1}E/C = 480 + 282(C-E)/E \qquad (6)$$

In the case of the random polymerization, the MW of the hard-segment may be calculated from the monomer content by means of Eq. (6).

The contents of the urea linkage and the urethane linkage in PEUE do not depend on the way of polymerization, as is shown in Table 5.

Table 5. Concentration ratio of each linkage in PEUE

Linkage	Concentration ratio
[NHCONH]	$(C-E)/C=H/C$
[NHCOO]	E/C
[NHCONH]/[NHCOO]	$(C-E)/E=H/E$

A plot of [NHCONH]/[NHCOO] *versus* the absorbance ratio at 1680 cm^{-1} and 1740 cm^{-1} gives a straight line, as is shown in Fig. 2. As may be seen from Fig. 2, the [Urea]/[Urethane] ratio in PEUE is obtained by the IR measurement, and by inserting the above result into Eq. (6), the MW of the hard-segment can be determined. The results are shown in Table 3. These results show that the distribution of the monomer unit deviates from that expected from the equal reactivity of the two isocyanate groups in MDI.

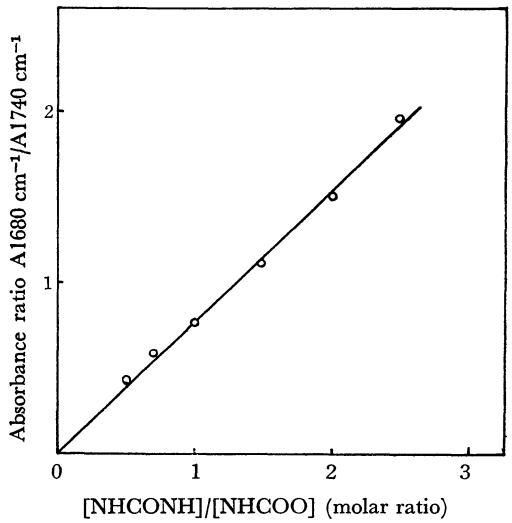


Fig. 2. Absorbance ratio at 1680 cm^{-1} and 1740 cm^{-1} of PEUE.

Apparent Reactivity Ratio of Two Isocyanate Groups in MDI. In the case of the random polymerization, the distribution of monomers in PEUE may be decided by the reactivity ratio of the two isocyanate groups in MDI. The apparent reactivity ratio of the two isocyanate groups is calculated from the MW of the hard-segment in the following way.

In the prepolymerization, the following reaction scheme may hold:

$$\text{OCN–I–NCO} + \text{HO–E–OH} \xrightarrow{k_{11}} \text{HO–E–OCONH–I–NCO} \qquad (7)$$

$$\text{OCN–I–NHCOO–} + \text{HO–E–OH} \xrightarrow{k_{21}} \text{HO–E–OCONH–I–NHCOO–} \qquad (8)$$

$$\text{OCN–I–NCO} + \text{HO–E–OCONH–} \xrightarrow{k_{12}} \text{OCN–I–NHCOO–E–OCONH–} \qquad (9)$$

$$\text{OCN–I–NHCOO} + \text{HO–E–OCONH} \xrightarrow{k_{22}} \text{–OCONH–I–NHCOO–} \qquad (10)$$

where OCN–I–NCO and HO–E–OH denote MDI and PTG respectively and where k denotes a rate constant. Assuming that $k_{11}=k_{12}=k_1$ and that $k_{21}=k_{22}=k_2$, the reactivity ratio of the two isocyanate groups in MDI is given by:

$$A = k_2/k_1$$

Thus, the rate of the reaction may be expressed by the following equations:

$$d[I_1]/dt = -2k_1[I_1][E] \qquad (11)$$

$$d[I_2]/dt = k_1[I_1][E] - k_2[I_2][E] \qquad (12)$$

$$d[E]/dt = -k_1[I_1][E] - k_2[I_2][E] \qquad (13)$$

where $[I_1]$, $[I_2]$, and $[E]$ are the concentrations of isocyanate in MDI, in OCN–I–NHCOO–, and in PTG respectively. From Eqs. (11) and (12),

$$d[I_2]/d[I_1] = (k_2/2k_1)\cdot[I_2]/[I_1] - 1/2 \qquad (14)$$

In the case of $A \neq 2$, the integration of Eq. (14) from time 0 to T, which is the time for the prepolymer reaction, gives the following result:

$$1/(1-A/2)\ln\frac{(1-A/2)[I_2]_T/[I_1]_T+1/2}{(1-A/2)[I_2]_0/[I_1]_0+1/2} = -\ln[I_1]_T/[I_1]_0 \qquad (15)$$

These are also the following relations:

$$[I_1]_0 = 2\times 1 \qquad [I_1]_T = 2\times P_{\text{H-I-H}}$$

$$[I_2]_0 = 0 \qquad [I_2]_T = P_{\text{H-I-E}}$$

By inserting the above relations into Eq. (15), we obtained:

$$2/(2-A)\log\{1-(1-A/2)P_{H\text{-}I\text{-}E}/P_{H\text{-}I\text{-}H}\} = \log(1/P_{H\text{-}I\text{-}H}) \quad (16)$$

Similarly, for $A=2$ we obtained:

$$P_{H\text{-}I\text{-}E}/P_{H\text{-}I\text{-}H} = \ln(1/P_{H\text{-}I\text{-}H}) \quad (17)$$

The values of $P_{H\text{-}I\text{-}E}$, $P_{H\text{-}I\text{-}H}$, and $P_{E\text{-}I\text{-}E}$ are determined by the following known procedure. Inserting the experimental results in Table 3 into Eq. (18), the average sequence length (L_{nH}) of the hard-segment of PEUE is calculated:

$$\overline{L_{nH}} = (\overline{MW}-198)/282 \quad (18)$$

Since the molar fractions of a hard-segment and a soft-segment in PEUE correspond to those of HD and PTG in PEUE respectively, the following equations may be obtained.

$$[\text{Urea}] = [\text{HD}] = P_{H\text{-}I\text{-}H} + \frac{1}{2}P_{H\text{-}I\text{-}E} \quad (19)$$

$$[\text{Urethane}] = [\text{PTG}] = P_{E\text{-}I\text{-}E} + \frac{1}{2}P_{H\text{-}I\text{-}E} \quad (20)$$

The following equation can also be written:

$$P_{H\text{-}I\text{-}H} + P_{E\text{-}I\text{-}E} + P_{E\text{-}I\text{-}H} = 1 \quad (21)$$

Therefore, the number-average sequence length of the hard-segment is given by:

$$\overline{L_{nH}} = \frac{P_{H\text{-}I\text{-}H}+\frac{1}{2}P_{H\text{-}I\text{-}E}}{\frac{1}{2}P_{H\text{-}I\text{-}E}} \quad (22)$$

By inserting the experimental results derived from Table 3 into Eqs. (16) and (17), the reactivity ratio, A, may be calculated. Table 6 shows the reactivity ratio calculated by using an electronic computer.

Table 6. Reactivity ratio of two isocyanate groups in MDI

No.	[Urea]/[Urethane]	$P_{H\text{-}I\text{-}H}$	$P_{H\text{-}I\text{-}E}$	A
1	1/2	0.172	0.322	1.86
2	1.5/2	0.237	0.384	1.68
3	2/2	0.307	0.386	1.79
4	3/2	0.433	0.334	2.40
5	4/2	0.501	0.332	2.25
6	5/2	0.568	0.292	2.69

These calculated apparent reactivity ratios of the two isocyanate groups in MDI (A) are obtained on the assumption of a homogeneous reaction in the prepolymer and chain-extender reactions. It is also necessary to consider the cases of $K_{11} \neq k_{12}$ and $K_{21} \neq k_{22}$. Therefore, thses results deviate from the results obtained by many previous authors.[7,8]

The composition analysis of PEUE's by NMR will become increasingly important since it often provides a direct, simple fingerprint of the various structures.

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