BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 687—689 (1970)

Studies of the Structure of Polyurethane Elastomers. II. The Determination of the Blockiness of Poly(Ether)Urethane Elastomes

Hajime Suzuki and Hiroshi Ono

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

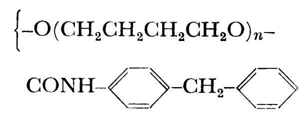
(Received August 18, 1969)

Two types of poly(ether)urethane elastomers (PEUE), which had the same composition ratio but different degrees of blockiness, were synthesized by the reaction of 4,4′-diphenyl methane diisocyanate (MDI), polyoxytetramethylene glycol (PTG), and hydrazine (HD) or ethylenediamine (EDA) by means of the prepolymer method. The degree of blockiness of the PEUE thus synthesized by the reaction of MDI, PTG, and HD was determined by measuring the molecular weight of a hard segment (urea segment), itself obtained by perchloric acid depolymerization. The values of the blockiness of PEUE which had been synthesized by the prepolymer method without any solvent or in a solvent by means of a prepolymer reaction were about 0.4 and 0.7 respectively. The degree of the blockiness of the PEUE prepared from MDI, PTG, and HD, as measured by the above method, corresponded to the infrared absorbance ratio of the PEUE synthesized by the reaction of MDI, PTG, and EDA at 1740 cm^{-1} and 1720 cm^{-1}. From these results two infrared absorbances, at 1740 cm^{-1} and 1720 cm^{-1}, were assigned to the urethane linkage in a soft segment and at the end of an urea segment respectively.

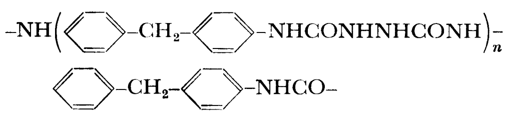
The determination of the blockiness of PEUE would be very helpful in elucidating the relationship between the structure and the physical properties of the elastomer, but previous attempts to determine the blockiness of PEUE were not successful. Therefore, we have attempted to determine the blockiness by the perchloric acid depolymerization method and by means of infrared spectroscopy.

Although the structure of the PEUE synthesized from MDI, PTG, and HD can not be written in one formula, it may be expressed by the following two segments:

soft segment (poly(ether)urethane segment):



hard segment (urea segment):



By expressing PEUE by means of the above two segments, the blockiness of PEUE may be determined in the same way as with a vinyl copolymer or a stereoregular polymer.[1,2]

It was thought that the hard segment was composed of a paracrystalline state,[3] and that the soft segment was composed of a liquid-like state; therefore, the infrared absorbance due to an urethane linkage in the soft segment or at the end of the hard segment was assumed to be assignable to two different absorbances.

Experimental

Materials. The PEUE used in this work had been synthesized by the prepolymer method. The prepolymer was prepared by reacting various molar ratios of PTG (MW, *ca.* 1500) and MDI without any solvent at 75°C for 1 hr and the PEUE was prepared from the prepolymer and HD or EDA as a chain extender in *N,N*-dimethylacetamide (DMAC) at 7°C. Between the prepolymer reaction and the chain-extender reaction,

Table 1. Preparation of PEUE, number average molecular weight and sequence length of hard segment synthesized from MDI, PTG and HD

No.	Prepolymer MDI (mol)	Prepolymer PTG (mol)	MDI (mol)	Chain extender HD or EDA (mol)	$\overline{MW}$	$\overline{L_{nH}}$
1	0.040	0.02	0.000	0.02	1659	5.18
2	0.038	0.02	0.002	0.02	1681	5.26
3	0.034	0.02	0.006	0.02	1960	6.25
4	0.030	0.02	0.010	0.02	2366	7.69
5	0.026	0.02	0.014	0.02	3331	11.1

---

[1] R. L. Miller, L. E. Nielsen, *J. Polym. Sci.*, **46**, 303 (1960).

[2] H. J. Harwood and W. M. Ritchey, *ibid.*, **2B**, 601 (1964); **3B**, 419 (1965).

[3] R. Bonart, *J. Macromol. Sci-Phys.*, **B2 (1)**, 115 (1968).

MDI was added to make the molar ratio [Urea]/[Urethane] = 1.

The various molar ratios of the monomers in the prepolymers prepared in this work are listed in Table 1.

The PEUEs which were synthesized in a solvent by means of the prepolymer reaction were described in a previous paper.[4]

MW Determination of the Hard Segment. The hard segment of PEUE prepared from MDI, PTG, and HD was obtained by the perchloric acid depolymerization method described in our previous communication;[4] it was examined by the titration method, and the number-average molecular weight (MW) of the hard segment was calculated by means of the following equation:

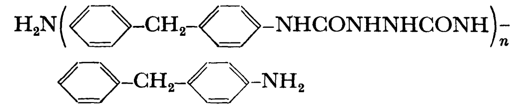
$$\overline{\mathrm{MW}} = \frac{2\{W(\mathrm{mg}) - 100.5 \times (T_B - T_S)(\mathrm{m}l) \times 1/100 \times F\}}{(T_B - T_S)(\mathrm{m}l) \times 1/100 \times F}$$

where W is the weight of the hard segment, F is a factor of an aqueous solution of HCl, and T_B and T_S are the volumes of an N/100 aqueous solution of HCl required for the titration of the blank and the sample solutions respectively.

Infrared Spectra Measurement. The infrared spectra of PEUE prepared from MDI, PTG, and EDA were obtained with a Hitachi EPI-S2-type infrared spectrophotometer, using thin films cast on glass from the DMAC solution of PEUE. The samples were heat-treated at 100°C for 10 min in order to evaporate the solvent.

Results and Discussion

The structure of the hard segment of PEUE prepared from MDI, PTG, and HD can be written as follows:



Therefore, the average sequence length of a hard segment can be calculated by the following equation:

$$\overline{L_{nH}} = (\overline{\mathrm{MW}} - 198)/282 \tag{1}$$

Table 1 shows the number-average molecular weight and the sequence length of the hard segment, both values having been measured by the perchloric acid depolymerization method.

If the number-average sequence length of the hard segment is determined to be as is shown in Table 1, one can determine the blockiness of PEUE by the following known procedure.[1,5] If P_{H-I-H}, P_{H-I-E}, and P_{E-I-E} show the molar fraction of each segment in PEUE, Eq. (2) can be evolved:

$$P_{H-I-H} + P_{H-I-E} + P_{E-I-E} = 1 \tag{2}$$

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

$$[\mathrm{Urea}] = [\mathrm{HD}] = P_{H-I-H} + \frac{1}{2}P_{H-I-E} \tag{3}$$

$$[\mathrm{Urethane}] = [\mathrm{PTG}] = P_{E-I-E} + \frac{1}{2}P_{H-I-E} \tag{4}$$

The number-average sequence length of the $(\overline{L_{nH}})$ hard segment can be determined by inserting the number-average MW of the hard segment into Eq. (5):

$$\overline{L_{nH}} = (\mathrm{MW} - 198)/282 \tag{5}$$

The values of P_{H-I-H}, P_{H-I-E}, and P_{E-I-E} are calculated by means of Eqs. (6) and (9). If one could inspect the units along the soft-segment-hard-segment chain in PEUE from one end to the other, the probability of finding a soft segment unit next to a hard segment unit would be:

$$P_{HE} = \frac{\frac{1}{2}P_{H-I-E}}{P_{H-I-H} + \frac{1}{2}P_{H-I-E}} \tag{6}$$

Similarly, a hard segment unit exists next to a soft segment unit with a probability of:

$$P_{EH} = \frac{\frac{1}{2}P_{H-I-E}}{P_{E-I-E} + \frac{1}{2}P_{H-I-E}} \tag{7}$$

The degree of blockiness is defined by:

$$B = P_{HE} + P_{EH} \tag{8}$$

If $B < 1$, these units tend to cluster in blocks of each unit, and finally $B = 0$ in a homopolymer mixture, whereas if $B > 1$, the sequence length becomes shorter, and $B = 2$ in an alternative copolymer.

The number-average sequence length of the $\overline{L_{nH}}$ hard segment and the $\overline{L_{nE}}$ soft segment are given by:

$$\overline{L_{nH}} = 1/P_{HE} \tag{9}$$

$$\overline{L_{nE}} = 1/P_{EH} \tag{10}$$

Table 2 shows the values of the blockiness (B) of the PEUEs listed in Table 1; these values were calculated by means of Eqs. (1)—(10). The value of the blockiness (B) of the PEUEs prepared in DMAC by means of a prepolymer reaction are shown in Table 3. Sample 1 in Table 2 has the same composition ratio as sample 3 in Table 3, but the blockiness of sample 1 in Table 2 is greater than that of sample 3 in Table 3. When there is no solvent in the prepolymer reaction, the reaction between PTG and MDI occurs through the solvation of MDI into PTG: the reaction rate of MDI with PTG may then shows the effects of viscosity and agitation. Therefore, the greater

---

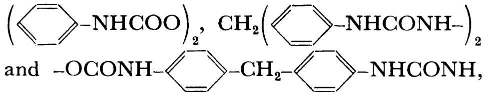
[4] H. Suzuki, H. Ono, This Bulletin, **43**, 682 (1970).

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

TABLE 2. MOLAR FRACTION OF THE THREE STRUCTURAL UNITS AND DEGREE OF THE BLOCKINESS OF PEUE SYNTHESIZED WITHOUT SOLVENT AT PREPOLYMER

No.	P_{H-I-H}*	P_{E-I-E}*	P_{H-I-E}*	P_{EH}	P_{HE}	B
1	0.403	0.403	0.194	0.193	0.193	0.386
2	0.405	0.405	0.190	0.189	0.189	0.379
3	0.418	0.418	0.164	0.164	0.164	0.328
4	0.434	0.434	0.132	0.133	0.133	0.267
5	0.452	0.452	0.096	0.092	0.092	0.185

* P_{E-I-E}, P_{H-I-H} and P_{H-I-E} represent the molar fractions of the following structures; CH_2–



respectively.

TABLE 3. MOLAR FRACTION OF THE THREE STRUCTURAL UNITS AND DEGREE OF THE BLOCKINESS OF PEUE SYNTHESIZED IN SOLVEN AT PREPOLYMER

No.	P_{H-I-H}	P_{E-I-E}	P_{H-I-E}	P_{EH}	P_{HE}	B
1	0.172	0.506	0.322	0.241	0.483	0.724
2	0.237	0.379	0.384	0.337	0.448	0.785
3	0.307	0.307	0.386	0.385	0.385	0.770
4	0.433	0 233	0.334	0.418	0.278	0 696
5	0.501	0.167	0.332	0.499	0.249	0.748
6	0.568	0.140	0.292	0.512	0.205	0.717

blockiness of sample 1 in Table 2 in comparison with sample 3 in Table 3 may be due to the heterogeneity of agitation in the prepolymer reaction. On the other hand, the prepolymer reaction in DMAC is a homogeneous reaction; therefore, the difference in the blockiness of sample 3 in Table 3 and the expected blockiness from a random reaction may be small.

The infrared spectra between 1800 cm^{-1} and 1700 cm^{-1} of the PEUE prepared from MDI, PTG, and EDA in Table 1 are shown in Fig. 1.

There have been no reports concerning the two peaks due to urethane linkage, but these peaks are assumed to be assignable to the urethane linkage for two different states, such as the para-crystalline part of a hard segment[3] and a liquid-like state of a soft segment. Figure 2 shows the relationship between the absorbance ratio at 1740 cm^{-1} and 1720 cm^{-1} and the degree of blockiness of PEUE.

From the above results, the absorptions at 1740 cm^{-1} and 1720 cm^{-1} may be assigned to the C=O stretching vibration of urethane linkage in a soft segment without any hydrogen bond and to that of the urethane linkage at the end of the hard segment with a hydrogen bond for the para-crystalline state.

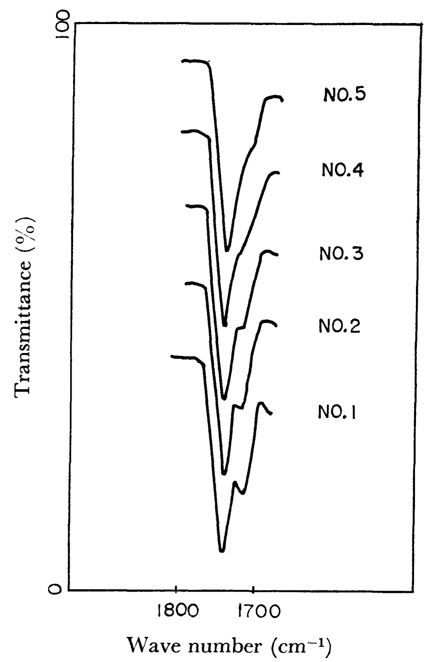


Fig. 1. Infrared spectra of PEUE synthesized from MDI, PTG and EDA in the region 1800—1700 cm^{-1}.

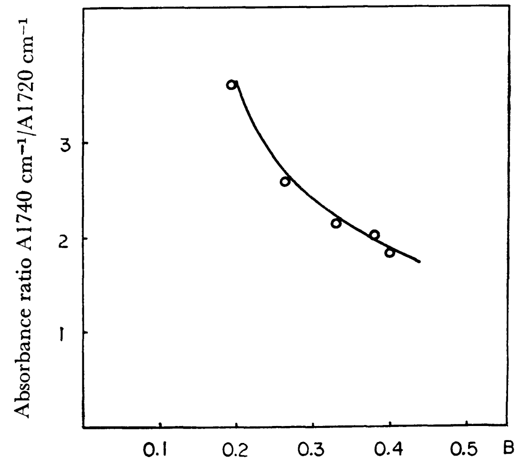


Fig. 2. Relationship between the absorbance ratio at 1740 cm^{-1} and 1720 cm^{-1} and the degree of blockiness.

We should like to express our gratitude to Drs. Yasushi Nishimura and Reizo Yamadera for his helpful discussion and the inspection of this paper. We also wish to express our gratitude to Director Dr. Eiichi Nagai of this institute for permission to publish this paper.