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Ester-Urethane Interchange Reaction

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The ester-urethane interchange reaction has been studied by means of gas chromatography and NMR. The interchange reaction between low-molecular-weight ester and urethane was confirmed by the gas chromatography. Alternating copolyester-urethane was prepared by reacting bis(hydroxyethyl)terephthalate with hexamethylene diisocyanate in anisole. When the polymer is melted at 190°C in the presence of sulfuric acid as a catalyst, the ester-urethane interchange reaction in alternating copolyester-urethane proceeds and causes a more random arrangement of the segments. This was proved by high-resolution nuclear magnetic resonance spectroscopy. An ethylene glycol residue adjacent to terephthalate on both sides, to diisocyanate on both sides, and to terephthalate and diiosyanate could be identified at 4.93, 4.48, and 4.71 ppm respectively in trifluoroacetic acid.

It is well known that condensation copolymers can be obtained by the following three general methods. One method is polycondensation with different kinds of monomer mixtures. The second is a so-called step-by-step polymerization with several kinds of monomer mixtures. Polyurethane elastomers are usually prepared by this method.[1] The third is an interchange reaction with different kinds of homopolymer mixtures. Copolyesters[2] and copolyamides[3] are easily prepared by this method. Usually, copolyester-urethane can be synthesized by the first and second methods. Recently, polyurethane was obtained by the urethane interchange reaction of dimethyl butane-1,4-dicarbamate with glycol;[4] however, no report has appeared describing the synthesis of copolyester-urethane by the interchange reaction. Therefore, this paper will describe the possibility of the synthesis of random copolyester-urethane from alternating copolyester-urethane by the ester-urethane interchange reaction.

The interchange reaction between low-molecular-weight urethane and an ester was studied as a model for the polymer by the aid of gas chromatography. The interchange reaction in polymer may be investigated by the following two methods; (1) an ester-urethane interchange reaction between the homopolyester and homopolyurethane and (2) an ester-urethane interchange reaction in the alternating copolyester-urethane. The melting points of polyethylene terephthalate, polyethylene haxamethylenecarbamate, and alternating copolyester-urethane prepared from hexamethylene diisocyanate and bis(hydroxyethyl)terephthalate are 256, 178, and 179°C respectively. Therefore, the transesterification reaction can be carried out at a lower temperature by using the alternating copolyester-urethane. In this work, the interchange reaction between ester groups and urethane groups in the polymer was studied through a transesterification reaction in the alternating copolyester-urethane, and was confirmed by NMR spectroscopy.

Experimental

Materials. Ethyl benzoate, *n*-butyl benzoate, *n*-butyl *n*-butyrate, and ethyl *n*-butyrate were fractionally distilled twice. *n*-Butyl phenylcarbamate, ethyl phenylcarbamate, ethyl *n*-propylcarbamate, and *n*-butyl propylcarbamate were prepared by reacting the corresponding isocyanates with alcohols. These structures were confirmed by elementary analysis and by a study of their NMR spectra; the gas chromatographs of these compounds showed them to be pure substances.

Interchange Reaction between Low-molecular-weight Urethane and Ester. Interchange reactions were carried out in sealed ampoules at 190°C for 43 hr. The products obtained by the interchange reaction were confirmed by comparing their retention times on gas chromatography with those of authentic samples. The gas chromatography was performed with a Yanagimoto gas chromatograph, model G8, with 15 m*l*/min of helium, using a 1.5-m column containing silicon DC-550 at 200°C.

Interchange Reaction in Molten Copolyester-urethane. Copolyester-urethane was prepared by reacting bis(hydroxyethyl)terephthalate with hexamethylene diisocyanate in anisole. The ester-urethane interchange reaction in the copolyester-urethane was carried out at 190°C in a stream of nitrogen, and new sequence units in the copolyester-urethane were confirmed by a

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[1] For example, H. Suzuki and H. Ono, This Bulletin, **43**, 687 (1970).

[2] W. H. Charch and J. C. Shivers, *Text. Res. J.*, **29**, 538 (1959).

[3] C. W. Ayers, *J. Appl. Chem.*, **4**, 444 (1954).

[4] Y. Miyake, S. Ozaki and Y. Hirata, *J. Polym. Sci., Part A-1*, **7**, 899 (1969).

study of the NMR spectra. The NMR spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz. The solutions containing 15% (w/v) polymers and tetramethylsilane as an external reference in trifluoroacetic acid were run at room temperature.

The viscosity measurements of polymers obtained by interchange reactions were carried out in an Ubbelohde viscometer at 30±0.03°C.

Results and Discussion

Confirmation of Interchange Reaction between Low-molecular-weight Urethane and an Ester. The interchange reaction was carried out in a sealed ampoule at 190°C for 43 hr in the presence of 0.05% sulfuric acid as the catalyst. Figure 1. (A)—(F) shows the results of the gas-chromatographic analysis of reaction mixtures of low-molecular-weight urethane and an ester. The peaks were identified by means of the retention data of pure substances. When the interchange reactions were carried out without sulfuric acid as the catalyst but otherwise under the same conditions as above, no new peak could be observed.

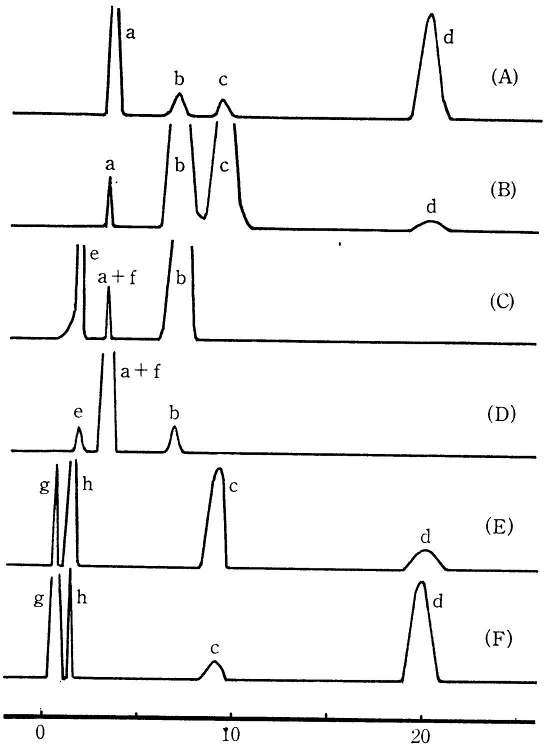


Fig. 1. Gas chromatograms of reaction mixtures. a, Ethyl benzoate; b, *n*-Butyl benzoate; c, Ethyl phenylcarbamate, d, *n*-Butyl phenylcarbamate; e, Ethyl *n*-propylcarbamate; f, *n*-Butyl *n*-propylcarbamate; g, Ethyl *n*-butyrate h, *n*-Butyl *n*-butyrate

There have been a number of reports concerning the thermal dissociation of urethane.[5-7] These reactions can be shown by the following equations:

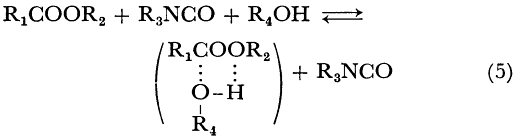
$$\mathrm{RNCO + R'NHCOOR'' \longrightarrow RNHCOOR'' + R'NCO} \quad (1)$$

$$\mathrm{ROH + R'NHCOOR'' \longrightarrow R'NHCOOR + R''OH} \quad (2)$$

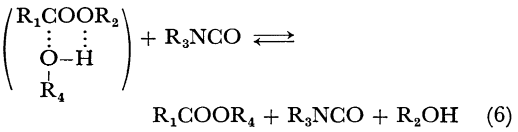
$$\mathrm{RCOOH + R'NHCOOR'' \longrightarrow R'NHCOR + CO_2 + R''OH} \quad (3)$$

It has been reported that ester interchange and interchange reaction between as ester and alcohol proceed easily. Judging from these reports, the first step in an interchange reaction between urethane and ester groups is probably the thermal dissociation of a urethane group, as is shown in Eq. (4). Therefore, the following reaction scheme may hold in the reaction between ester and urethane groups:

$$\mathrm{R_1COOR_2 + R_3NHCOOR_4 \rightleftarrows R_1COOR_2 + R_3NCO + R_4OH} \quad (4)$$



$$\mathrm{R_1COOR_2 + R_3NCO + R_4OH \rightleftarrows \begin{pmatrix} R_1COOR_2 \\ \vdots \quad \vdots \\ O\text{-}H \\ | \\ R_4 \end{pmatrix} + R_3NCO} \quad (5)$$



$$\mathrm{\begin{pmatrix} R_1COOR_2 \\ \vdots \quad \vdots \\ O\text{-}H \\ | \\ R_4 \end{pmatrix} + R_3NCO \rightleftarrows R_1COOR_4 + R_3NCO + R_2OH} \quad (6)$$

$$\mathrm{R_1COOR_4 + R_3NCO + R_2OH \rightleftarrows R_1COOR_4 + R_3NHCOOR_2} \quad (7)$$

Confirmation of Interchange Reaction in Molten Copolyester-urethane. Recently, Miyake[4] synthesized polyurethane by the carbamate exchange reaction shown in the following scheme:

$$\mathrm{CH_3OCONH(CH_2)_4NHCOOCH_3 \xrightarrow[-CH_3OH]{+HO(CH_2)_{\mathit{n}}OH} [(CH_2)_{\mathit{n}}OCONH(CH_2)_4NHCOO]_{\mathit{m}}} \quad (8)$$

The first step in the reaction may be assumed to proceed as is shown in Eq. (4). If the ester-urethane interchange reaction in copolyester-urethane proceeds, random copolyester-urethane may be prepared from the homopolyester and homopolyurethane as is shown in Eq. (9) or from alternating copolyester-urethane as is shown in Eq. (10):

$$(\text{-T-G-})_n + (\text{-I-G-})_m \longrightarrow [\{\text{T-G}\}_p\{\text{I-G}\}_q]_l \quad (9)$$

$$[\{\text{T-G}\}\{\text{I-G}\}]_l \longrightarrow [\{\text{T-G}\}_p\{\text{I-G}\}_q]_l \quad (10)$$

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[5] G. Muller, *Chem. Ber.*, **98**, 1097 (1965).

[6] S. Murahashi and N. Nakanishi, *Gosei Sen-i Kenkyu*, **1**, 333 (1944).

[7] T. Hoshino, T. Mukaiyama and H. Hoshino, This Bulletin, **25**, 396 (1952).

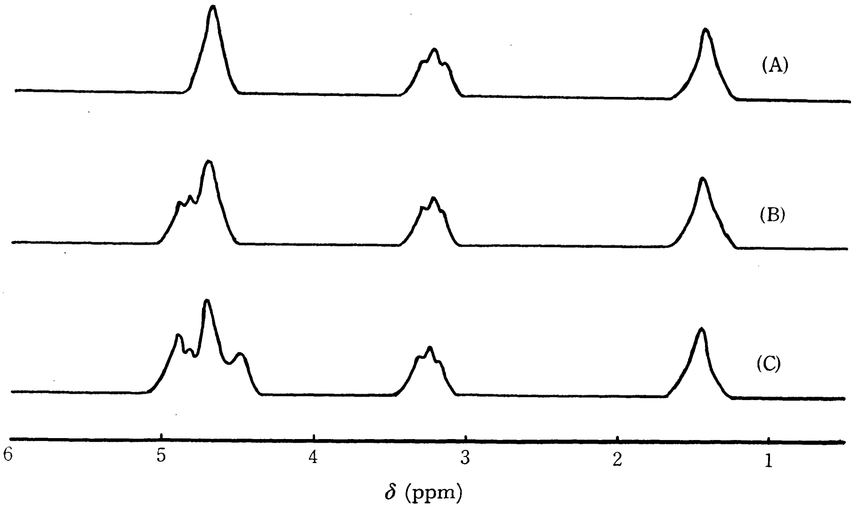
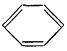


Fig. 2. NMR spectra of copolyester-urethane after interchange reaction. (A): 0 hr, (B): 4 hr, (C): 20 hr

where T=OCCO, G=OCH$_2$CH$_2$O, and I=CO-NH(CH$_2$)$_6$NHCO

The present work has been concerned with the application of nuclear magnetic resonance spectroscopy to the analysis of alternating copolyester-urethane that has been heated for various lengths of time.

In the first step of the reaction, the polymer has the T-G-I unit only. The ethylene glycol residue in the T-G-I unit was confirmed at 4.71 ppm. When the interchange reaction proceeds, new two kinds of ethylene glycol residues (–G–), one of which is adjacent to terephthalate (T) an both sides, T-G-T, and the other of which is adjacent to diisocyanate (I) an both sides, I-G-I, may be produced. The glycol residues could be confirmed at 4.93 and 4.48 ppm respectively by comparing the proton signal of the ethylene groups in polyethylene terephthalate and polyurethane prepared from ethylene glycol and hexamethylene diisocyanate. These assignments of the proton signals were reported in a previous paper.[8] If these three signals are confirmed in molten copolyester-urethane, the thermal interchange reaction between an ester and urethane in the polymer can be confirmed.

The interchange reaction was carried out at 190°C without a catalyst or in the presence of 0.2% sulfuric acid as the catalyst, and the intrinsic viscosities and NMR spectra of the polymers were measured. Figure 2 shows the results of the NMR spectra. When there was no catalyst in the copolymer, the T-G-T and I-G-I signals at 4.93 and 4.48 ppm could not be confirmed after 43 hrs reaction. On the other hand, when there was sulfuric acid as a catalyst in the copolymer, the T-G-T and I-G-I signals could be confirmed. The signal at 4.85 ppm is due to the hydroxyethyl end group produced by molecular scission due to the catalyst. Table 1 shows the proportions of the intensities of the four signals due to T-G-T, I-G-I, T-G-I and hydroxyethyl group, and the intrinsic viscosity.

TABLE 1. MOLAR FRACTION OF THE FOUR STRUCTURAL UNITS AND INTRINSIC VISCOSITY AFTER THE INTERCHANGE REACTION

Reaction time (hr)	T-G-T	I-G-I	T-G-I	Hydroxyethyl group	[η]
0	0.00	0.00	1.00	0.00	0.618
2	0.02	0.00	0.94	0.04	0.379
4	0.08	0.00	0.86	0.06	0.331
6	0.14	0.05	0.75	0.06	0.419
10	0.21	0.10	0.62	0.07	0.466
20	0.27	0.10	0.56	0.07	0.504

The molar fraction of the hydroxyethyl end group is related to the number-average molecular weight. Therefore, the decrease in intrinsic viscosity for the first 4 hours may correspond to the decrease in the number-average molecular weight. Although the molar fraction of the hydroxyethyl group is kept approximately constant after heating for 6 hrs, the intrinsic viscosity gradually increases. Since the number-average molecular weight remains constant, the increase in intrinsic viscosity after 6 hrs may be assumed to correspond to the change in sequence distribution.

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[8] H. Suzuki, H. Ono and T. Hongo, *Makromol. Chem.*, **132**, 309 (1970).