Molecular Motion in Amorphous Polyurethane

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ABSTRACT: The dependence of the molecular motion of polyurethane on the length of methylene chain in the monomer unit and on the molecular weight has been studied by the broad line nuclear magnetic resonance, NMR, dynamic loss modulus, E'' , wide angle X-ray scattering, and the density.

The second moment, $\langle \Delta H^2 \rangle$, at the rigid state increases with an increasing number of methylene groups.

The degree of narrowing of $\langle \Delta H^2 \rangle$ for the secondary dispersion increases with increasing numbers of methylene groups. This agrees with the theoretical prediction based on the local mode motion of the main chain. The force constant of the local mode motion of the polymethylene chain thus estimated is 3.0×10^{-13} erg. The dispersion of the dynamic loss modulus at about -135°C corresponds to the above secondary dispersion of $\langle \Delta H^2 \rangle$.

The primary dispersion temperature decreases with decreasing molecular weight.

KEY WORDS Molecular Motion / Amorphous Polyurethane / Broad-Line NMR / Dynamic Loss Modulus / Wide-Angle X-ray Scattering / Density / Force Constant / Polymethylene Chain /

Jacobs and Jenckel¹ have studied the effects of the number of methylene groups in the monomer unit and crystallinity on the molecular motion of crystalline polyurethane, $\text{[COO(CH}_2)_m\text{OOCNH(CH}_2)_6\text{NH]}_n$, by dynamic mechanical measurements.

Shibata² has studied the molecular motion of the above sample of a low degree of crystallinity by the broad-line NMR, and pointed out that the high value of the second moment, $\langle \Delta H^2 \rangle$, near the melting point can be attributed to the hydrogen bonds of urethane groups in the amorphous part.

In previous papers^{3,4}, some preliminary results were reported on the molecular motion of polyurethane. In this paper, the dependence of the molecular motion of amorphous polyurethane, $\text{[NH-}\langle\bigcirc\rangle\text{-CH}_2\text{-}\langle\bigcirc\rangle\text{-NHCOO(CH}_2)_n\text{OOC]}_p$, on the length of methylene chain in the monomer unit and on the molecular weight have been studied by the broad line NMR, the dynamic loss modulus, the wide angle X-ray scattering and the density.

EXPERIMENTAL

Four samples of polyurethane $\text{[NH-}\langle\bigcirc\rangle\text{-CH}_2\text{-}\langle\bigcirc\rangle\text{-NHCOO(CH}_2)_n\text{OOC]}_p$, $n=2, 4, 5$ and 9 were prepared by polycondensation⁵ of methylene bisphenyl-isocyanate(MDI) with ethylene glycol(EG), butylene glycol(BG), pentamethylene glycol(PG) and nonamethylene glycol(NG). The structural formulas of these samples are shown in Table I. The polyurethane polymers were dissolved in dimethylformamide at 100°C and poured into ice water. The wide angle X-ray scattering patterns of the samples show only an amorphous halo (Figure 1).

The sample powder dried in vacuum at 70°C was sealed into a glass tube, and the tube was placed in the sample holder of the broad-line NMR spectrometer. The NMR apparatus used is a commercial model (Nippon Denshi Kogyo Co., Ltd., Tokyo) equipped with autodyne detector and an electromagnet of homogeneous, constant magnetic field. The first derivatives of the NMR adsorption signal were recorded at a magnetic field corresponding to 25 MHz. The

Table I.

Structural formula of the sample	R-value ^a	$\bar{M}_n$
EG—MDI $\text{[-NH-}\langle\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NHCOO(CH}_2\text{)}_2\text{OOC-}]_p$	1.0	—
EG—MDI $\text{[-NH-}\langle\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NHCOO(CH}_2\text{)}_4\text{OOC-}]_p$	1.0	—
PG—MDI $\text{[-NH-}\langle\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NHCOO(CH}_2\text{)}_6\text{OOC-}]_p$	1.0 0.6 0.3	4600 1400 980
NG—MDI $\text{[-NH-}\langle\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NHCOO(CH}_2\text{)}_8\text{OOC-}]_p$	0.664	—

^a Ratio of the number of isocyanate to that of hydroxyl group used for the synthesis.

Figure 1. X-ray patterns for EG—MDI, BG—MDI, PG—MDI and NG—MDI.

temperature was controlled by a heating coil in air, liquid N₂ or a Dry Ice—acetone mixture in Dewar vessel.

The dynamic loss modulus, E'' , was measured with a forced stretching vibration⁶ by 10 Hz from liquid N₂ temperature up to about 100°C. The samples were heat pressed, quenched in ice water and cut into strips (20×1×1.5 mm).

The wide angle X-ray scattering was measured with Debye—Sherrer camera using Ni-filtered

Cu-K_α radiation.

The density was measured by the flotation method in the mixture of *n*-heptane and carbon tetrachloride at 15°C.

RESULTS AND DISCUSSION

Figure 2 shows the first derivatives of the NMR adsorption signal for PG—MDI. Every line shows only one component, which suggests that

Figure 2. Halves of the first derivatives of the NMR adsorption signal for PG-MDI: H_1 , radio frequency magnetic field; H_0 , main magnetic field.

Figure 3. Temperature dependence of the second moment for polyurethane: $\circ$, EG-MDI; $\times$, BG-MDI; $\triangle$, PG-MDI; $\circ$, NG-MDI.

sample has no crystalline region.

Figure 3 shows the plots of the $\langle \Delta H^2 \rangle$ against temperature for EG-MDI, BG-MDI, PG-MDI and NG-MDI. The narrowing corresponding to the secondary dispersion of the $\langle \Delta H^2 \rangle$ is observed at -30°C beside the primary one which is seen above 50°C and the degree of the narrowing increases with increasing number of methylene groups. The $\langle \Delta H^2 \rangle$ at the secondary dispersion temperature region increases

with increasing number of methylene group. The observed $\langle \Delta H^2 \rangle$ is obtained as the sum of the intermolecular $\langle \Delta H^2 \rangle$ and the intramolecular $\langle \Delta H^2 \rangle$. In this case, since the density decreases with increasing number of methylene groups as shown in Figure 4, it is reasonable to consider that the intermolecular $\langle \Delta H^2 \rangle$ decreases as the number of methylene groups increase. While the intramolecular $\langle \Delta H^2 \rangle$ increases generally with increasing number of methylene groups in which the interproton distance is the shortest for a polymer molecule. Therefore, the above result may be explained by the increase of the intramolecular $\langle \Delta H^2 \rangle$ rather than by the decrease of the intermolecular $\langle \Delta H^2 \rangle$.

Figure 4. Plot of the density vs. the number of methylene group in the structural unit of polyurethane.

Figure 5. Molecular weight dependence of the second moment for PG-MDI: $\times$, $\bar{M}_n=4600$; $\triangle$, $\bar{M}_n=1400$; $\circ$, $\bar{M}_n=980$.

As shown in Figure 5, three plots for PG—MDI having different R -values fall on single curve in the secondary narrowing reaction, where R -value means the ratio of the number of diisocyanate groups to that of hydroxyl groups used for the synthesis. The molecular weight increases with increasing R -value as shown in Table I. Therefore, when the monomer unit has a soft segment such as $-\text{O}(\text{CH}_2)_n\text{O}-$, the secondary narrowing appears independent of the molecular weight. Dependence of the narrowing on the length of the methylene chain in the monomer unit is clearly seen in Figure 6, which is a replot

Figure 6. Plots of $\langle \Delta H^2 \rangle_l / \langle \Delta H^2 \rangle_r$ vs. temperature for polyurethane; $\circ$, EG—MDI; $\times$, BG—MDI; $\triangle$, PG—MDI; $\diamond$, NG—MDI.

Figure 7. Plot of S vs. X .

of Figure 3. In the figure, $\langle \Delta H^2 \rangle_l$ and $\langle \Delta H^2 \rangle_r$ denote the second moments at the temperature where the secondary dispersion appears and that at the rigid state, respectively. Figure 7 shows the plot of the slopes of the dotted lines in Figure 6 against X , which is the ratio of the number of protons in the methylene group in the soft segment, *e.g.*, $-\text{O}(\text{CH}_2)_n\text{O}-$, to that of all protons in the monomer unit of the polyurethane molecule. As shown in Figure 7, S is almost proportional to X . This result agrees with the following theoretical consideration based on the assumption that the secondary dispersion is mainly caused by the local mode motion of the methylene groups⁷.

$$\frac{\langle \Delta H^2 \rangle_l}{\langle \Delta H^2 \rangle_r} = 1 - ST \quad (1)$$

$$S = \frac{6kX}{\sqrt{4f_1g_1}} \quad (2)$$

For eq 2 f_1 and g_1 are the intra and intermolecular force constants, T the absolute temperature and k Boltzmann's constant. The force constant of local mode motion, $\sqrt{4f_1g_1}$, of polyurethane calculated from the slope of solid line in Figure 6 is about 3.0×10^{-13} erg. The force constant of polyethylene estimated by Okano⁷ is about 1.3×10^{-13} erg. The larger value for polyurethane may be due to the effects of the inter and intramolecular hydrogen bonding. This may be supported by the observation made for Nylon-66⁸, which has NH groups in the monomer unit; the value of S for Nylon-66 is shown by a triangle in the same figure and it falls on the line for polyurethane.

Figure 8 shows the temperature dependence of the dynamic loss modulus, E'' , for BG—MDI and PG—MDI at 10 Hz. By using an activation energy of 10 kcal/mol, which is obtained for the local mode motion of polymethylene chain calculated from the slope of the dispersion map of the polyamide⁹, the temperature at which the secondary dispersion appears in the E'' for BG—MDI and PG—MDI is predicted as -125°C . As shown in the figure, the dispersion appears at -135°C which is very close to the above predicted temperature. Therefore, it is very likely that the dispersion at -135°C corresponds to the local mode motion. According to Dammont and Kwei¹⁰, a dispersion at low temperature

Figure 8. Temperature dependence of the dynamic loss modulus, E'' , for polyurethane: $\circ$, BG—MDI; $\times$, PG—MDI.

Figure 9. Molecular weight dependence of the dynamic loss modulus, E'' , for PG—MDI: $\times$, $\bar{M}_n=4600$; $\triangle$, $\bar{M}_n=1400$; $\circ$, $\bar{M}_n=980$.

was observed for Epoxy resin cured with diamine having more than four methylene groups. Shatzki¹¹ has attributed it to the crank-shaft motion among the four methylene groups. In the present samples, the secondary dispersion of the $\langle \Delta H^2 \rangle$, however, was observed even for the

sample having two methylene groups in the monomer unit. This may be attributed to the fact that the monomer unit contains $-\text{C}-\text{O}-\text{C}-$ bond, which is more flexible than $-\text{C}-\text{C}-$ bond.

The dispersion at -50°C is due to the adsorption of water because it disappeared in the sample dried *in vacuo* for six days, and that at 60°C is the primary one corresponding to motional narrowing at about 70°C in Figure 3. Figure 9 shows the dependence of the primary dispersion temperature on the molecular weight. It is evident that the dispersion temperature decreases with decreasing molecular weight, and that each temperature corresponds to the primary narrowing temperature of the $\langle \Delta H^2 \rangle$ (Figure 5).

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