Dielectric Relaxation of Poly(*n*-butyl acrylate)

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ABSTRACT: Dielectric relaxation of poly(*n*-butyl acrylate) (PBA) was studied over a temperature range from 90 to 300 K. The primary α relaxation was observed around 250 K but the relaxation due to motion of the side ester group as observed for poly(methyl acrylate) (β process) was not observed. Thus the α relaxation was assigned to a merged process where the segmental motions and the rotation of the side group occur cooperatively. A weak secondary (γ) relaxation was observed at 130 K at 1 kHz. The γ relaxation was assigned to motion of the alkyl group of the side chain. Dielectric characteristics such as relaxation strength, effective dipole moment, and Arrhenius plot for the α process were compared with those for poly(butyl methacrylate)s reported.

KEY WORDS Poly(*n*-butyl acrylate) / Dielectric Relaxation / α Relaxation / γ Relaxation / Effective Dipole Moment /

Dielectric properties of poly(alkyl methacrylate) (PAMA) and those of poly(alkyl acrylate) (PAA) are much different.^{1–5} If a PAMA is compared with the corresponding PAA having the same alkyl group, the former exhibits higher glass transition temperature T_g than the latter.¹ The dielectric behavior of PAMA is sensitive to stereoregularity but PAA is not.¹ The differences between PAMA and PAA are believed due to differences in the barrier height for the internal rotation of the backbone chains. Poly(methyl methacrylate) (PMMA) exhibits a strong β relaxation due to rotation of the side group but poly(methyl acrylate) (PMA) exhibits a moderate β relaxation.^{1,2,5} In PAMAs having the ethyl, propyl and higher alkyl groups, the α and β relaxations merge and the β relaxation due to rotation of the side ester group cannot be observed separately.^{1–4} Ishida and Yamafuji reported dielectric data on PAMA and PAA *ca.* 40 years ago and attempted to explain the behavior using a site model.² They explained the dielectric behavior of PAMA qualitatively based on their model. Currently, however, many scientists consider that cooperative intermolecular interactions play important role in segmental motion of bulk polymers.^{6–9} Therefore further analysis based on the intra and intermolecular interactions is needed for interpretation of differences between PAMA and PAA. To discuss differences in the dielectric behavior between PAMA and PAA, we need to compare the dielectric behavior of these homologues having the same side group. Several authors reported the dielectric behavior of poly(*n*-butyl methacrylate) (PBMA),^{2–4} but, as far as we know the dielectric properties of poly(*n*-butyl acrylate) PBA have not been reported. This paper reports the dielectric properties of PBA focusing our attention on the above. Due to intermolecular cooperative effects, temperature dependence of relaxation time for the α process of flexible polymers conforms to the Vogel–Fulcher equation.^{10,11} The cooperative effects should cause anti-parallel or parallel orientation of the neighboring dipoles depending on the in-

termolecular interactions and are reflected on the Kirkwood dipolar correlation factor for the α process.^{12,13} Our objective is to compare the dielectric behavior for PBA and PBMA.

EXPERIMENTAL

Material

PBA was purchased from Aldrich Chemical Company Inc. The sample had very broad distribution of molecular weight. Therefore we carried out fractionation by adding methanol to 1 to 0.1 wt% tetrahydrofuran (THF) solutions. A fraction of high molecular weight was collected. Characterization of the sample was made by GPC equipped with a low angle light scattering detector (Tosoh LS 8000). The weight average molecular weight M_w was 3.80×10^5 and the polydispersity index M_w/M_n was 1.38.

Method

Dielectric measurements were carried out with an RLC bridge (QuadTech Type 1693, Ohio, USA) in the range from 12 Hz to 200 kHz. A dielectric cell designed for measurement of viscous polymer samples was reported previously.¹⁴

RESULTS AND DISCUSSION

Dielectric Behavior of PBA

Figures 1a and 1b show the temperature dependence of the dielectric constant ϵ' and loss factor ϵ'' of PBA, respectively. Strong loss peaks are seen in the range from 230 to 270 K. The glass transition temperature T_g was determined by means of differential scanning calorimetry (DSC) as 218 K at the heating rate of 5 K min^{–1}.¹⁵ Therefore the dielectric loss peak observed in the range 230 to 270 K can be assigned to the primary α process. A small secondary (γ) relaxation appears around 140 K. The peak height of ϵ'' for the γ relaxation is only 0.03,

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Figure 1. Temperature dependence of the dielectric constant ϵ' (a) and logarithm of the loss factor ϵ'' (b).

Figure 2. Arrhenius plots of the α and γ processes.

much smaller than the β relaxations of PMMA or PMA assigned to the rotation of the ester group.^{1,2,5} Thus the γ relaxation of PBA cannot be assigned to overall rotation of the side group. To avoid confusion, we designate the present secondary process as γ relaxation.

The Arrhenius plots of the loss maximum frequencies f_m for the α and γ relaxations are shown in Figure 2. To our surprise the Arrhenius plot for the α process almost conforms to a straight line unlike many amorphous polymers. However the plot is slightly curved. We attempted to fit the plot to the Vogel-Fulcher equation:^{10,11}

$$\log f_m = A - B/(T - T_0) \quad (1)$$

where A , B , and T_0 are adjustable parameters deter-

Figure 3. Frequency dependence of the dielectric loss factor ϵ'' .

mined as 37.0, 4560, and 102, respectively. A for many polymers is 12 to 14, while for the present polymer PBA, A is higher than the ordinary value. Furthermore B of PBA is unusually high. From the Arrhenius plot of PBMA reported by Ishida and Yamafuji,² we obtained $A = 18.5$, $B = 1620$, and $T_0 = 174.5$ for PBMA. Although A and B for PBMA are smaller than those of PBA, A and B of PBMA are still higher than ordinary values. The non-linear Arrhenius plot is a manifestation of the cooperative motion of polymer segments.⁶⁻⁹ The long butyl side group may hinder cooperative motion.

The Arrhenius plot for the γ process is straight. The activation energy for the γ process is 30.8 kJ mol^{-1} .

α Relaxation

Figure 3 shows the frequency dependence of ϵ'' at temperatures where the α process is seen. The height of the loss peak increases with decreasing temperature as observed for ordinary polymers. These ϵ'' curves are approximately superposable. This behavior is much different from the behavior in the α process of poly(*n*-butyl methacrylate) (PBMA) in which the peak height decreases with decreasing temperature and the ϵ'' curve broadens remarkably with decreasing temperature.² The ϵ'' curves for the present PBA were cast to the Havriliak-Negami equation:¹⁶

$$\epsilon' - i\epsilon'' = \frac{\Delta\epsilon}{[1 + (i\omega\tau_0)^\alpha]^\beta} \quad (2)$$

where α and β are parameters determined as 0.57 and 0.36, respectively. For typical amorphous polymers, α and β are 0.8 and 0.5, respectively.¹⁶ The parameters for PBA are relatively small compared with ordinary amorphous polymers such as poly(vinyl acetate) indicating segmental dynamics for polymers having a long flexible side group to differ from polymers having relatively short side groups.

Figure 4. Cole-Cole plots of the α process.

Figure 4 shows representative Cole-Cole diagrams for the α relaxation. From the data at 251 K, the relaxation strength $\Delta\epsilon$ was determined to be 2.85. According to Onsager¹⁷ and Kirkwood¹², $\Delta\epsilon$ is given by (in cgs unit),

$$\Delta\epsilon = \frac{4\pi N g \mu^2}{9k_B T} \frac{\epsilon_R(\epsilon_U + 2)^2}{2\epsilon_R + \epsilon_U} \quad (3)$$

where N is the number of the monomeric units in unit volume; g , the dipolar correlation factor, ϵ_R , the relaxed dielectric constant; and ϵ_U , the unrelaxed dielectric constant. ϵ_R and ϵ_U are given by the Cole-Cole diagram and N is calculated from the density of PBA given by Aldrich Co. as 1.087. From these data $g\mu^2$ ($=\mu_{\text{eff}}^2$) of eq 3 is calculated as $1.952 \times 10^{-59} \text{ C}^2 \text{ m}^2$ ($=1.755 \times 10^{-36} \text{ cgs esu}$) and the effective dipole moment μ_{eff} to be $4.40 \times 10^{-30} \text{ C m}$ ($=1.32 \times 10^{-18} \text{ cgs esu}$, $=1.32 \text{ D}$). If the dipole moment μ of the monomeric unit is taken to be 1.80 D,¹⁸ g becomes 0.54. This indicates that the dipoles of the monomer units tend to orient in the antiparallel direction. For poly(butyl methacrylate) (PBMA) we calculated μ_{eff} to be 1.30 D from the data at 333 K reported by Ishida and Yamafuji.² This value is very close to μ_{eff} of PBA. Therefore, the dipolar correlations of PBA and PBMA are the same.

γ Relaxation

The ϵ'' vs. frequency curve for the γ region was very broad and hence the Cole-Cole plots could not be used for determination of the relaxation strength $\Delta\epsilon$. To determine $\Delta\epsilon$, we used the ϵ'' vs. $1/T$ plots:¹

$$\Delta\epsilon = \left(\frac{2E_a}{\pi R} \right) \int_0^\infty \epsilon'' d \left(\frac{1}{T} \right) \quad (4)$$

where E_a is the activation energy. Figure 5 shows the ϵ'' vs. $1/T$ plots in the γ region. The curve at 100 Hz is extrapolated as indicated by the dashed line and from the area of the curve, $\Delta\epsilon$ is determined to be 0.19. From the Onsager equation,¹⁷ the effective dipole moment for the γ relaxation process was determined to be 0.28 D.

Figure 5. Plots of ϵ'' vs. $1/T$ in the γ relaxation region. Dashed line indicates an estimated curve used to determine the relaxation strength.

The side group has many bonds and thus various degrees of freedom of internal rotation. Hoff *et al.* reported the mechanical measurements on PBMA,¹⁸ and found a weak relaxation around 100 K. They assigned the relaxation to the motion of the butyl groups. Unfortunately, no dielectric data of PBMA in the low temperature range are available. Here we test this possibility for the γ relaxation. To discuss motions of the side group, we label the atoms of the side chain as, $-\text{C}_1\text{O}-\text{O}_1-\text{C}_2-\text{C}_3-\text{C}_4-\text{C}_5$.

Since the dipole moments of normal alkanes are zero, the rotation around the bonds C_2-C_3 or C_3-C_4 is not active in dielectric spectra. Then we calculated the barrier heights for internal rotation around the O_1-C_2 bond based on the MM2 force field.¹⁹ The potential minimum arises at $\pm 80^\circ$ (gauche) and 180° (trans). The difference of the dipole moments for the trans and gauche states was 0.27 D. Although the reliability of this value must be checked, it agrees with the observed effective dipole moment. The barrier height between the gauche and trans sites is 4.6 kJ mol^{-1} and between the two gauche sites, 12 kJ mol^{-1} . These barrier heights are much lower than the observed activation energy (30.8 kJ mol^{-1}) for the γ process. The discrepancy may be attributed to intermolecular interactions. Thus we may assign the γ relaxation to the motion of the butyl group.

CONCLUSION

Dielectric behavior of poly(*n*-butyl acrylate) was examined. Two relaxations α and γ were observed at 250 and 140 K, respectively. The α relaxation can be assigned to a process in which the segmental motion and the rotation of the ester group (β) occur cooperatively. The parameters A and B of the Vogel-Fulcher equation are higher than those of ordinary polymers. The dipolar correlation factor of 0.5 is similar to that of PBMA. The γ relaxation can be assigned to motion of the butyl group around the C-O bond of the ester group.

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