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Relaxation Spectroscopy of the Dielectric β-Relaxation in Poly(*n*-alkyl methacrylate)s by Absorption-Current Measurements. II. Dielectric Relaxation Spectrum for Isotactic Poly(methyl methacrylate)

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ABSTRACT: The time dependence of an absorption current in isotactic poly(methyl methacrylate) (PMMA) was measured from 10 to 600 s after the application of a step voltage at temperatures ranging from -54.0 to $-95.5^{\circ}\mathrm{C}$ in order to determine the dielectric relaxation spectrum for the β-process separated from that for the α-process. The data on the absorption current in the glassy state thus obtained were converted to those on the frequency dependence of loss permittivity using the Hamon approximation. The results were reduced to a master curve by the method of reduced variables. The shape of the β-relaxation spectrum determined from the master curve is the same as that for atactic PMMA in the glassy state, but both activation energy and relaxation strength are about 1/2.5 times as large as those for atactic PMMA. The activation energy obtained from the temperature dependence of the shift factor is *ca.* 8 kcal mol^{-1}. The value of the activation energy and the shape of relaxation spectrum thus obtained for the dielectric β-relaxation are found to be the same as those for the mechanical β-relaxation obtained from creep compliances of isotactic PMMA in the glassy state.

KEY WORDS Relaxation Spectroscopy / Dielectric β-Relaxation / Poly(*n*-alkyl methacrylate) / Isotactic Poly(methyl methacrylate) / Absorption Current / Dielectric Relaxation Spectrum / Loss Permittivity / Side-Chain Motion / Glassy State /

In a previous paper,[1] some of the characteristic features of the dielectric β-relaxation in a series of atactic poly(*n*-alkyl methacrylate)s were investigated by means of absorption current measurement. The results obtained are summarized as follows: (1) loss permittivity in the very low frequency region obtained from time dependence of absorption current by Hamon approximation[2] can be analyzed by the method of reduced variables[3]; (2) the shape of the dielectric relaxation spectrum for the β-process is independent of side-chain length; (3) the activation energy for the β-process is *ca.* 19 kcal mol^{-1} irrespective of the side-chain length; (4) the relaxation strength is proportional to the dipolar density in the sample.

One of the present authors has pointed out[4] that in the glassy state the shape of the mechanical retardation spectrum for the β-process in isotactic poly(methyl methacrylate) (PMMA) determined by creep measurement is the same as in atactic PMMA, while the activation energy and retardation strength for the former are much smaller than those for the latter. This fact implies that the shape of the mechanical retardation spectrum for the β-process in the glassy state is not affected by the difference in main-chain conformation.

On the basis of these results, in the present paper, we investigated the dielectric β-relaxation in isotactic PMMA by the same method as used previously for atactic PMMA so as to clarify the effects of the difference in main-chain conformation on the characteristics of the dielectric β-relaxation in the glassy state. Furthermore, we compared the characteristic features of the dielectric β-process with those of the

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mechanical process in isotactic PMMA to find the correlation between the two relaxations caused by the same molecular motion.

SAMPLE PREPARATION, EXPERIMENTAL CONDITIONS, AND PRELIMINARY EXPERIMENTS

Isotactic PMMA was made by the anionic polymerization of purified monomers in toluene at 0°C with butyllithium as the catalyst. The isotacticity of the polymer estimated by the triad analysis of an NMR spectrum was close to 100%.*[1] Though not determined, the molecular weight of the sample seemed rather low, since the temperature dependence of loss permittivity gave an α-peak at a rather low temperature as will be shown below.

A film for making the dielectric measurement was cast from a benzene solution on a glass plate and dried at room temperature in vacuum for several days. The dried film was amorphous and *ca.* 0.37 mm thick. The current produced by the application of a step voltage was measured with a vibrating-reed electrometer, TR-84M, made by Takeda Riken Industry Co. The step voltage was supplied by a series of dry cells. The method used for measuring the time dependence of the absorption current at various temperatures was the same as described in the previous paper.[1]

The electric-field dependence of absorption current was first investigated up to 5200 V cm^{-1} at several temperatures. A typical result is shown in Figure 1. All the data on the absorption current given in the later section were measured at 2600 V cm^{-1}. Therefore, the linear relation between current and electric field was secured. Charging currents were measured from 10 to 600 s after the application of the step voltage at temperatures ranging from −54.0 to −95.5°C. On the basis of the results obtained in the previous paper,[1] the charging current was regarded as the absorption current.

For the sake of comparison, the temperature dependence of loss permittivity at 0.1, 1, and 10 Hz was measured with an ultra-low-frequency bridge, TR-4, made by Ando Electric Company from *ca.* −100 to *ca.* 60°C. Variation in loss permittivity with temperature throughout the α- and β-relaxation regions is shown in Figure 2. The two relaxations overlap with each other rather appreciably at these frequencies. This situation is similar to that found for the atactic poly(*n*-butyl methacrylate) reported in the previous paper.[1] The glass transition temperature for the sample is considered to be about 20°C. The temperatures mentioned above for measuring absorption current due to the β-process were chosen on the basis of the results shown in Figure 2. Though the lowering of T_g handicaps the study of the β-relaxation, measurement of absorption current at these temperatures afforded a dielectric relaxation spectrum for the β-process as will be shown below.

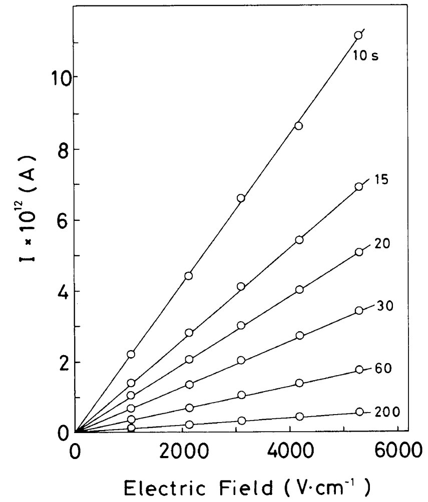

Figure 1. Electric-field dependence of absorption current in isotactic PMMA at −61°C: the numbers indicated are observation times in seconds.

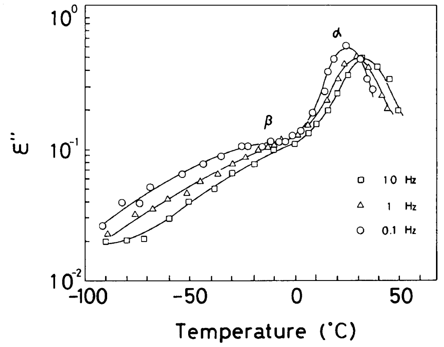

Figure 2. Temperature dependence of loss permittivity of isotactic PMMA at 0.1, 1, and 10 Hz.

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*[1] This polymer was supplied through the courtesy of Professor J. Sohma of Hokkaido University, Japan.

The temperature was controlled by liquid nitrogen and dry ice, and measured by a copper-constantan thermocouple placed near the sample. Fluctuations in temperature during each measurement were kept within ±0.5°C. All measurements were carried out from lower to higher temperatures.

RESULTS AND DISCUSSION

Absorption-Current Measurements

The time dependence of the absorption current at various temperatures is shown in Figure 3. All the data can be approximately represented by a power function of time, $I(t)=At^{-n}$, where I is the absorption current at time t and A and n are constants depending on temperature. The values of n satisfy the condition $0.3<n<1.2$. Consequently the well-known Hamon approximation[2] can be used to calculate the loss permittivity ε'' at very low angular frequency ω from the data on absorption current at time t as

$$\varepsilon''(\omega)=I(t)/\omega C_0 V \qquad (1)$$

$$\omega t=0.63 \qquad (2)$$

where C_0 is the capacitance of electrodes without the medium and V is the applied step voltage.

Loss Permittivity Calculated from Absorption Current and the Method of Reduced Variables

Figure 4 illustrates the frequency dependence of loss permittivity thus obtained at the temperatures indicated. In this range of temperature, the β-process can be observed rather clearly, but at higher temperatures it merges with the α-relaxation appearing at lower frequencies. The master curve for loss permittivity reduced to −54°C was constructed only by the horizontal shift as shown in Figure 5. The shift factor associated with this operation is plotted against the reciprocal absolute temperature in Figure 6. In constructing the master curve, several points which appreciably feathered off were omitted.

The activation energy estimated from the slope of the straight line in Figure 6 is *ca.* 8 kcal mol^{-1}. This value is in good agreement with that obtained from the data on loss permittivity measured at higher frequencies and higher temperatures.[5] Furthermore, it should be noted that this value is in excellent agreement with that determined from the shift factor for the creep compliance associated with the β-process in isotactic PMMA.[4]

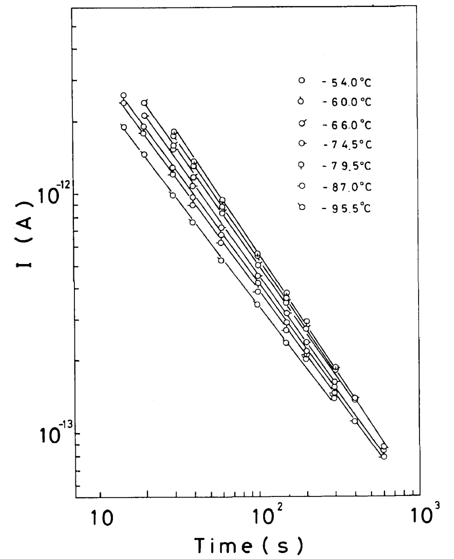

Figure 3. Time dependence of absorption current in isotactic PMMA at the temperatures indicated.

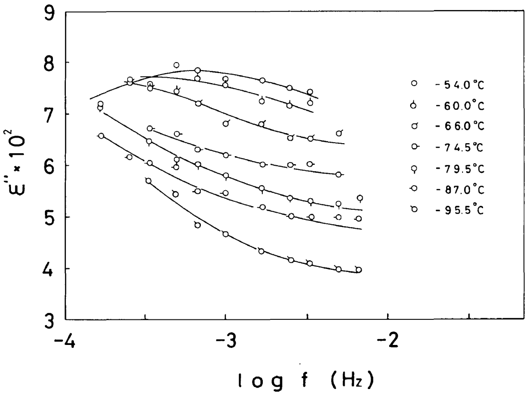

Figure 4. Frequency dependence of loss permittivity of isotactic PMMA calculated from absorption current at the temperatures indicated.

The results mentioned above suggest that no lateral shift factor due to the temperature dependence of relaxation strength of the β-process is necessary for the time-temperature reduction of the data on loss permittivity. The justification for this is as follows. The temperature dependence of the relaxation strength can be estimated from the data reported by Shindo *et al.*[5] at higher temperatures. By assuming that the temperature coefficient, *ca.* 2.5×10^{-3} K^{-1}, estimated from their data ranging

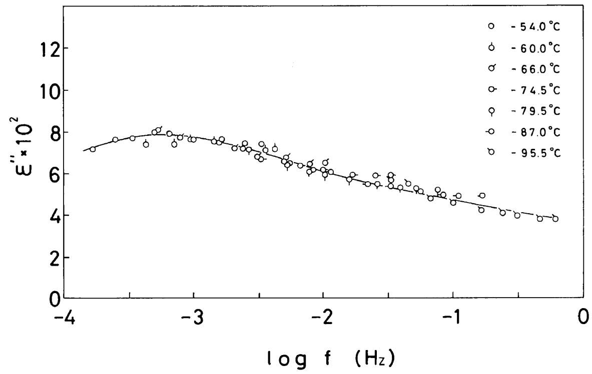

Figure 5. Master curve for loss permittivity in the β-relaxation region of isotactic PMMA reduced to $-54.0°\mathrm{C}$: loss permittivity was calculated from absorption currrent but not corrected for temperature variation in relaxation strength.

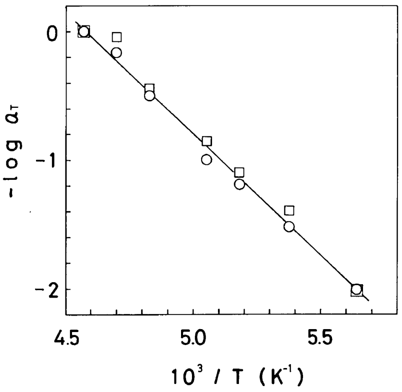

Figure 6. Horizontal shift factor for the dielectric β-relaxation in isotactic PMMA reduced to $-54.0°\mathrm{C}$ and plotted against reciprocal absolute temperature: open circles, for the data not corrected for temperature variation of relaxation strength; open squares, for the data corrected for it.

from *ca.* 40 to *ca.* 20°C could be used for correcting the data given in Figure 4, the master curve and shift factor for the corrected data were determined and are shown in Figures 7 and 6.

As shown in Figure 7, the corrected master curve is almost the same as the uncorrected one represented by the solid curve. As shown in Figure 6, the values of the shift factor for the corrected data are also almost the same as those for the uncorrected data. These results are very similar to those found in the case of atactic PMMA.[1] It is worthwhile to mention that the lateral shift factor cannot be neglected in the case of mechanical relaxation.[4,6]

In Figure 8, the shift factor for the β-process drawn through the loss peak shown in Figure 4 is plotted against the reciprocal absolute temperature. This is the relaxation map for the dielectric β-process in isotactic PMMA. The peak position of loss permittivity at 0.1 Hz given in Figure 2 is also shown. The agreement between the results from dynamic and transient measurements is satisfactory.

The peak positions for the α-process given in Figure 2 are also plotted in Figure 8 for comparison. For atactic PMMA, we observed that above about 10°C the relaxation spectrum became sharper with the increase in temperature.[1] In regard to the present sample of isotactic PMMA, no corresponding critical temperature was determined, since the α- and β-relaxations were not separated from each other as distinctly as in the case of the atactic PMMA.

Dielectric Relaxation Spectrum

The non-normalized dielectric relaxation spectrum, L_e, is approximately determined from loss permittivity by

$$L_e(\ln \tau)=\frac{\pi}{2}\varepsilon''(\ln \tau)\bigg|_{\omega=1/\tau} \tag{3}$$

L_e corresponds to the mechanical retardation spectrum.[3] The shape and intensity of the spectrum for the isotactic sample obtained by eq 3 are compared with those previously reported[1] for the atactic sample in Figure 9. The shapes of these spectra are quite similar to each other, but the intensity of the

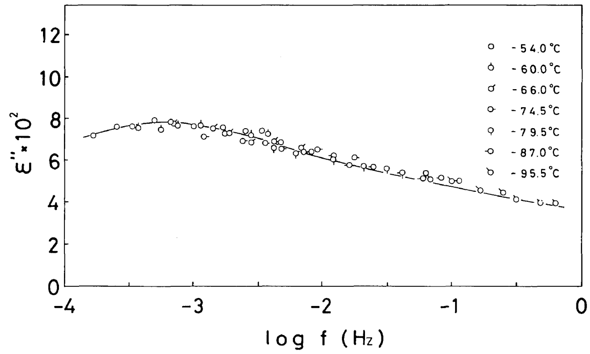

Figure 7. Loss permittivity master curve for the dielectric β-relaxation in isotactic PMMA obtained from the data corrected for temperature variation of relaxation strength (circles with or without a pip) compared with that obtained from the data not corrected for this variation (solid curve): both master curves are reduced to -54.0°C.

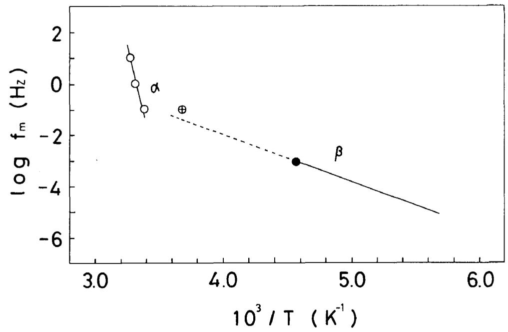

Figure 8. Relaxation map for the dielectric β- and α-relaxations in isotactic PMMA: solid line, for the shift factor obtained from the reduction of loss permittivity in the β-region calculated from absorption current; dashed line, for the extension of the solid line; filled circle, for the loss-permittivity peak for the β-relaxation obtained from the data on absorption current; crossed circle, for the loss-permittivity peak for the β-relaxation found in temperature dependence at 0.1 Hz; open circles, for the loss-permittivity peaks for the α-relaxation found in temperature dependence at 0.1, 1, and 10 Hz.

spectrum for the atactic sample is about 2.5 times as large as that for the isotactic sample. This situation is quite similar to that in case of the mechanical retardation spectra for atactic and isotactic samples of PMMA.[4]

The fact that the shape of the relaxation spectrum is independent of the difference in the main-chain conformation suggests that the mode of molecular motion responsible for the β-process is independent of it. The decrease in activation energy in the case of isotactic PMMA should be due to the decrease in

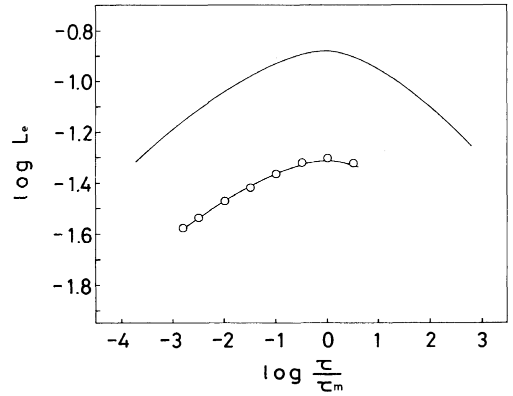

Figure 9. Comparison between the dielectric relaxation spectrum for the β-process in isotactic PMMA (open circles) and that in atactic PMMA (solid curve) in the glassy state: both spectra are plotted against $\log \tau/\tau_m$, where τ_m is the relaxation time for the maximum of the spectrum.

viscous resistance or a barrier to the molecular motion. Actually, according to the potential contour map made by Tanaka and Ishida,[7] two stable sites for the side chain separated by a potential barrier consistent with the activation energy obtained in the present study seem to exist in isotactic PMMA.

The decrease in relaxation strength cannot be attributed to the difference in dipolar density, because the density of isotactic PMMA is larger than that of atactic one. If the two-site model discussed in the previous paper is applicable to the present case, the decrease in relaxation strength may be due

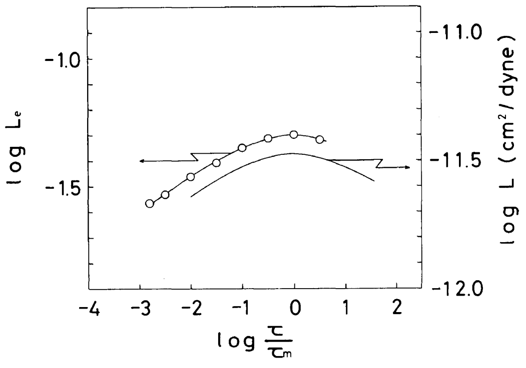

Figure 10. Comparison between the dielectric relaxation spectrum (open circles) and the mechanical retardation spectrum (solid curve) for the β-process in isotactic PMMA in the glassy state: both spectra are plotted against log τ/τ_m, where τ_m is the relaxation or retardation time for the maximum of the spectrum.

to the decrease in the rotation angle of the dipole in the side chain associated with the transition between the two sites.

Furthermore, the shape of the dielectric relaxation spectrum for the β-process in isotactic PMMA is quite similar to that of the mechanical retardation spectrum as shown in Figure 10. The glass transition temperature of the sample used for the mechanical study was *ca.* 45°C.[4] Consequently, the activation energy and the shape of relaxation spectrum for the dielectric β-relaxation in the glassy state are the same as those for the mechanical β-retardation, irrespective of the glass transition temperature. This fact and the results shown in Figure 9 indicate that the shape of the relaxation spectrum for the β-process in the glassy state is independent of the glass transition temperature.

The similarity in the shape of relaxation or retardation spectrum between the dielectric and mechanical relaxations has been found also for the β-relaxations in several atactic poly(*n*-alkyl methacrylate)s in the glassy state.[8] These facts are in striking contrast with the α-relaxation associated with the micro-Brownian motion of the main chain in several amorphous polymers, in which the shape of the dielectric spectrum is very different from that of a mechanical spectrum.[9,10] Though the reason for this difference is still not clear, the facts presented here seem very useful for studying the β-relaxation in poly(*n*-alkyl methacrylate)s.

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