Dynamic Mechanical Properties of Poly(α -amino acid)s. III. Poly(γ -alkyl L-glutamate)s

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ABSTRACT: Dynamic mechanical measurements on a series of poly(γ -alkyl L-glutamate)s in the solid state were carried out over a frequency range from 0.005 to 1.0 Hz at various temperatures covering the side-chain dispersion region in order to examine the effects of the side-chain length. Frequency dispersion curves of real and imaginary parts of complex shear modulus and loss tangent at various temperatures could be superposed on a set of master curves by performing a horizontal shift along the logarithmic frequency axis and the additional vertical shift along the logarithmic modulus axis, if necessary, for three polymers of poly(γ -octyl L-glutamate), poly(γ -heptyl L-glutamate), and poly(γ -hexyl L-glutamate). A unique set of horizontal and vertical shift factors could not be found for poly(γ -butyl L-glutamate), poly(γ -amyl L-glutamate), and poly(γ -ethyl L-glutamate). The temperature dependence of the horizontal shift factor is represented by the WLF equation with the conventional parameters. The distribution of the relaxation times was found to become sharper with an increase in the side-chain length. These results are discussed in terms of a two-phase model consisting of the rigid α -helical backbone embedded in the flexible side-chain region.

KEY WORDS Poly(γ -alkyl L-glutamate) / Mechanical Dispersion / Side-Chain Motion / Relaxation Spectra / Two-Phase Model / Side-Chain Length /

Mechanical and dielectric dispersions due to side-chain motions have been reported to occur in the solid state for α -helical poly(α -amino acid)s having long side chains. These side-chain dispersions exhibit the characteristics of glass-transition phenomena.¹⁻⁶ The backbone chains of α -helical poly(α -amino acid)s cannot interact directly with each other, since the long side chains surrounding the α -helical backbone chain prevent the direct interaction between backbone chains. Therefore, the solid state properties of the poly(α -amino acid)s largely depend on the nature of the side chain.

In previous papers,^{6,7} we explained these properties in terms of the coaxial-two phase model, consisting of the rigid α -helical backbone and the flexible side chains surrounding it. The coaxial two-phase model is comparable with the sandwich two-

phase model for conventional semicrystalline polymers. The increase in the side-chain length of α -helical poly(α -amino acid)s may be regarded as the decrease in the degree of crystallinity of the semicrystalline polymer. From this point of view, the dielectric behaviors of poly(γ -alkyl L-glutamate)s with varying side-chain lengths were previously investigated as a function of side-chain length, and the results were interpreted in terms of the two-phase model.⁶

In this paper, dynamic mechanical properties are described as a function of side-chain length for a series of poly(γ -alkyl L-glutamate)s (PALG): poly(γ -ethyl L-glutamate) (PELG), poly(γ -propyl L-glutamate) (PPLG), poly(γ -butyl L-glutamate) (PBtLG), poly(γ -amyl L-glutamate) (PAmLG), poly(γ -hexyl L-glutamate) (PHxLG), poly(γ -heptyl L-glutamate) (PHpLG), and poly(γ -octyl L-glutamate) (POcLG). The results obtained are discussed in terms of the two-phase model.

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EXPERIMENTAL

PALGs were prepared by an ester exchange reaction of poly(γ -methyl L-glutamate) (Ajicoat A-2000) with alkyl alcohols: ethyl, propyl, butyl, amyl, heptyl, and octyl alcohols.

The degree of substitution was checked by the NMR spectra of the resulting polymers. For five polymers of PELG, PPLG, PBtLG, PHxLG, and POcLG, the degree of substitution was more than 99%. It was about 97% for PAmLG and PHpLG.

Films of PALGs were cast on a glass plate at room temperature from concentrated chloroform solution, except for PPLG. PPLG formed gel in chloroform even near the boiling temperature at a concentration of a few percent. Thus the film of PPLG was cast from an acetone solution. All films were dried *in vacuo* for a week, and then annealed at a temperature of 160°C for one day. The IR absorption spectra of thin films of these polymers all showed a peak of amide V at 615–620 cm^{-1} , indicating the α -helical conformation of the backbone chain.

Dynamic mechanical measurements were carried out with torsional pendulum apparatus in a mode of forced oscillation. The details of the apparatus and the procedures are described elsewhere.⁸ The measurements were made over a frequency range from 0.005 to 1.0 Hz at temperatures between -80 and 20°C.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the real part of the complex shear modulus G' and the loss tangent $\tan\delta$ at a frequency of 0.1 Hz for PALGs. The numbers in the figure represent the number of carbon atoms in the alkyl group of the side chain. The data of PPLG for which the casting solvent was different from the others are indicated by a broken line without data points. A $\tan\delta$ peak is clearly observed for each polymer in a temperature range from -60 to -20°C. According to previous work, the peak may be reasonably attributed to the onset of side-chain motion.⁹⁻¹³ The peak moves to lower temperatures with an increase in the side-chain length. These results are in agreement with the results of other authors.¹⁰⁻¹² However, these results contrast greatly with those obtained for poly(alkyl methacrylate)s for which the temperature of the

Figure 1. Temperature dependence of G' and $\tan\delta$ for PALGs at a frequency of 0.1 Hz: $\circ$, PELG; $\times$, PBtLG; $\triangle$, PAmLG; $\bullet$, PHxLG; $\circ$, PHpLG; and $\blacktriangle$, POcLG. Dotted line shows data for PPLG. The numbers represent the number of carbon atoms in the side-chain alkyl group.

Figure 3. Composite relaxation curves of G' , G'' , and $\tan\delta$ for PHpLG reduced to -54°C .

side-chain dispersion is independent of the side-chain length.¹⁴⁻¹⁶ The peak intensity of the dispersion increases with an increase in the side-chain length except for PPLG. The deviation from the systematic change of the dispersion temperature can be also observed for PPLG and POcLG. The explanation of these deviations will be postponed in future.

Figure 2 shows the frequency dependence of G' , G'' , and $\tan\delta$ for PHpLG at various temperatures between -70.0 and -11.0°C . The superposition of data onto a single set of master relaxation curves was possible by performing a horizontal shift of the curves along the logarithmic frequency axis. The composite relaxation curves of G' , G'' , and $\tan\delta$, reduced to a temperature of -54°C are shown in Figure 3.

Figure 4 shows the frequency dependence of G' , G'' , and $\tan\delta$ for POcLG at various temperatures between -78.0 and -16.5°C . In this case the composite of the master curves of G' and G'' required not only the horizontal shift along the logarithmic frequency axis but also the vertical shift along the logarithmic modulus axis at higher temperatures. The vertical shift is relatively large and in a direction opposite to the usual shift expected from changes in the density and rubber-like character of the elasticity. On the other hand, the loss tangent curves could be superposed by only the same horizontal shift as those of G' and G'' curves. The composite relaxation curves of G' , G'' , and $\tan\delta$ for POcLG reduced to a temperature of -55°C are shown in Figure 5.

Figure 6 shows the frequency dependence of G' , G'' , and $\tan\delta$ for PHcLG at various temperatures between -70.0 and -13.5°C . The superposition was achieved neither by just the horizontal shift nor by a combination of the horizontal and vertical

Figure 4. Frequency dependence of G' , G'' , and $\tan\delta$ for POcLG at various temperatures. The figures at both sides of curves represent temperature in $^\circ\text{C}$.

Figure 5. Composite relaxation curves of G' , G'' , and $\tan\delta$ for POcLG reduced to -55°C .

Figure 6. Frequency dependence of G' , G'' , and $\tan\delta$ for PHxLG at various temperatures. The figures at both sides of curves represent temperature in $^\circ\text{C}$.

shifts by the same amount for both G' and G'' curves. The slight increase in the magnitude of $\tan\delta$ peak with an increase in temperature suggests that different amounts of the vertical shift for G' and G'' curves are needed for the superposition. Without theoretical reasoning regarding the different amounts of vertical shift for G' and G'' curves, we attempted the following tentative procedure in order to construct the master curves: only the

Figure 7. Composite relaxation curves of G' , G'' , and $\tan\delta$ for PHxLG reduced to -57°C .

Figure 8. Temperature dependence of the horizontal shift factor a_T : Δ , PHxLG; $\times$, PHpLG; and $\circ$, POcLG. Solid curve represents the WLF equation.

horizontal shift was performed so as to superpose the G'' curves and both the vertical and horizontal shifts were applied for the superposition of the G' curve. The superposition of $\tan\delta$ curves was achieved by the horizontal shift and the additional vertical shift by the same amount as that for G' curves but in the opposite direction. Figure 7 shows the composite relaxation curves of G' , G'' , and $\tan\delta$ reduced by this procedure to a temperature of -57.0°C .

Figure 8 shows the temperature dependence of the horizontal shift factor a_T for PHxLG, PHpLG, and POcLG. The solid curve in this figure represents the universal WLF equation.¹⁷ The reference temperature T_s for each polymer was chosen to give the best fit to data. The reference temperatures are -13.5 , -21.5 , and -23.0°C for PHxLG, PHpLG, and POcLG, respectively, indicating that T_s decreases with the increase in the side-chain length.

Figure 9 shows the vertical shift factor of G' as a function of temperature. The vertical shift is needed above -57 and -50°C for PHxLG and POcLG, respectively. The necessity of the vertical shift to superpose the frequency dispersion curves for PHxLG and POcLG reminds us of the vertical shift reported for crystalline polymers, for which the vertical shift should be related to the change in the degree of crystallinity with temperature (premelting) or to the change in the orientation of crystallites in the amorphous matrix. A possible explanation for PHxLG and POcLG can be made in terms of the motion of the backbone chain.¹⁸

The relaxation spectra for PHxLG, PHpLG, and POcLG were calculated from the master relaxation curves of G' and G'' by the approximation method of Williams and Ferry.¹⁹ The spectra at a temperature of -57°C are shown in Figure 10. A good

Figure 9. Temperature dependence of the vertical shift factor; ●, PHxLG; ⊙, PHpLG; and ○, POcLG.

Figure 10. Relaxation spectra at -57°C for PHxLG (Δ), PHpLG ($\circ$), and POcLG ($\square$). Closed and open symbols represent data calculated from G' and G'' , respectively. Dotted line shows spectrum for poly(γ -methyl L-glutamate).

agreement between both the results calculated from real and imaginary parts of a reduced complex shear modulus indicate the plausibility of the composite relaxation curves thus obtained.

Values of the negative slope at longer relaxation times of the spectra for PHpLG and POcLG are about $1/3$. The spectrum of PHxLG has a negative slope of about $1/4$. The figure also shows the spectrum of poly(γ -methyl L-glutamate) by a dotted line, which has a negative slope of about $1/6$. These results indicate that the spectrum becomes sharper with an increase in the side-chain length, and that the value of the slope approaches $1/2$, the theoretical value for the Rouse chain.

Figures 11, 12, and 13 show the frequency dependence of G' , G'' , and $\tan\delta$ for PAmLG in the temperature range from -70.0 to -7.5°C , for PBtLG in the range from -62.5 to 2.5°C , and for PELG in the range from -57.0 to 22.0°C , respectively. For PPLG, the data of the frequency dispersion were not collected. For PAmLG, PBtLG, and PELG, the superposition of the dispersion curves was not achieved by a unique set of horizontal and vertical shift factors. It is of interest to note that the slope of the frequency dispersion curve at lower frequencies becomes smaller in going from PAmLG to PELG. These results together with the results of relaxation spectra for POcLG, PHpLG, and PHxLG indicate that the distribution of the relaxation times becomes broader with the decrease in the side-chain length.

Figure 11. Frequency dependence of G' , G'' , and $\tan\delta$ for PAmLG at various temperatures. The figures at both sides of curves represent temperature in $^{\circ}\text{C}$.

Figure 13. Frequency dependence of G' , G'' , and $\tan\delta$ for PELG at various temperatures. The figures at both sides of curves represent temperature in $^{\circ}\text{C}$.

Figure 12. Frequency dependence of G' , G'' , and $\tan\delta$ for PBtLG at various temperatures. The figures at both sides of curves represent temperature in $^{\circ}\text{C}$.

It has been generally accepted for semicrystalline polymers that an increase in the degree of crystallinity causes a broadening of the distribution of the relaxation times.²⁰⁻²² As already mentioned, the increase in the side-chain length for PALG is regarded as the decrease in the degree of crystallinity for semicrystalline polymers from the view-point of the two-phase model. Thus, the results obtained here suggest that the two-phase model is adequate for describing the properties of PALG. The broad spectrum of semicrystalline polymers is supposed to be due to the hindrance of crystallites to segmental motions. In the present case, the rigid α -helical backbone will hinder side-chain motions. It is likely that this hindrance diminishes with an increase in the side-chain length. Thus, the relaxation spectrum, becomes sharper and the reference temperature decreases in going from PELG to POcLG.

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