

## Dynamic Mechanical Behavior of DL Mixtures of Poly( $\gamma$ -benzyl glutamate)

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**ABSTRACT:** The dynamic mechanical properties of mixtures of poly( $\gamma$ -benzyl D-glutamate) and poly( $\gamma$ -benzyl L-glutamate) were studied as functions of frequency, temperature, and the molar ratio of D to L. The results obtained were interpreted in terms of the stacking of benzene rings of the D and L polymers on top of each other. The dependence of the relaxation strength of the dispersion at room temperature on the molar ratio of D to L clearly indicates that stacking of side chains occurs.

**KEY WORDS** Racemic Mixture / Poly( $\gamma$ -benzyl glutamate) / Stacking / Mechanical Properties /

Considerable investigation has been made of the relationship between the structure and properties of  $\alpha$ -helical synthetic poly( $\alpha$ -amino acid)s in the solid state. Studies on mixtures of poly( $\gamma$ -benzyl D-glutamate) (PBDG) and poly( $\gamma$ -benzyl L-glutamate) (PBLG), among others, are very interesting because mixtures of two polymers of opposite screw sense are expected to affect solid state properties.

Infrared and X-ray diffraction studies showed that the solid structure of a racemic mixture of PBDG and PBLG is somewhat different from that of only PBLG.<sup>1-3</sup> The X-ray diffraction pattern of the fiber of the racemic form shows an "extra" meridional reflection of 10.5 Å, which does not appear in the enantiomorphic form. This meridional reflection was interpreted in terms of the stacking of benzene rings of the D and L polymers. Uematsu *et al.* observed this reflection disappears when the sample is heated to some 90°C, and ascribed the disappearance to the disruption of the stacking.<sup>4</sup> The present authors also made X-ray and dielectric measurements on mixtures of the D and L polymers, and discussed the results on the basis of the theory of order-disorder transition.<sup>5,6</sup>

In this paper, we present the results of a dynamic mechanical investigation on mixtures of PBDG and

PBLG and provide further evidence for the stacking of benzene rings.

### EXPERIMENTAL

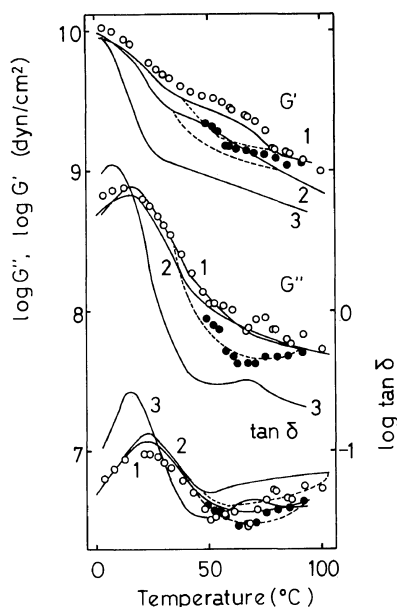
The PBDG and PBLG used in this work were prepared by polymerizing respective NCA's in dioxane with a trace of triethylamine as the initiator. The molecular weights were approximately the same, *i.e.*, 140,000. PBDG and PBLG were dissolved in methylene chloride at three molar ratios of D to L: D:L=1:1, D:L=1:3, and D:L=1:5. The solutions were cast on a glass plate to make films for dynamic measurements. Each film was heated *in vacuo* at 120°C for 24 h to remove any residual solvent, and cooled slowly to room temperature.

The dynamic mechanical measurements were carried out with a forced-oscillation torsion pendulum apparatus over an ultra-low frequency range from 0.003 to 1.0 Hz. Temperature was changed from 0 to 100°C. The details of the apparatus and the procedure are reported elsewhere.<sup>7</sup>

### RESULTS AND DISCUSSION

Figure 1 shows the real and imaginary parts of the complex shear modulus,  $G'$  and  $G''$ , and the loss

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**Figure 1.** Temperature dependence of  $G'$ ,  $G''$ , and  $\tan \delta$  for DL mixtures of PBG and PBLG at a frequency of 0.05 Hz:  $\circ$ , D:L=1:1, heating;  $\bullet$ , D:L=1:1, cooling; 1, D:L=1:3; 2, D:L=1:5; 3, PBLG; solid line, heating; dotted line, cooling.

tangent  $\tan \delta$  at a frequency of 0.05 Hz as a function of temperature for the three mixtures. Previous results for PBLG are also shown in this figure. Data points are omitted for simplicity, except for the (1:1) sample. The value of  $G'$  decreases with increasing temperature for all samples, and is greater for the mixtures than for PBLG. A rather sharp decrease in  $G'$  observed for PBLG at room temperature becomes less apparent with an increase in the molar ratio of D to L. A sudden decrease in  $G'$  was

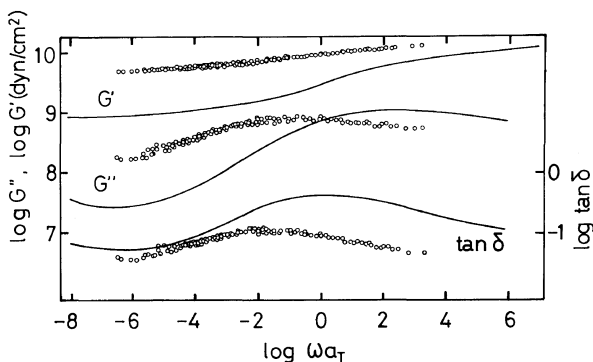
clearly observed in the vicinity of 80°C for the (1:1) sample, and less noticeably for the other mixtures. This is attributed to the disruption of the stacking of benzene rings.<sup>4-6</sup>

Thermal hysteresis was observed for the mixtures;  $G'$  values are greater for heating than for cooling in the temperature range from 50 to 80°C. Such hysteresis behavior was not observed for the enantiomorphic form, and this provides evidence for the phase transition at a temperature of 80°C.

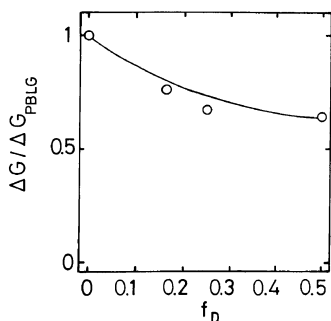
Each sample shows a peak at about 20°C in both the  $G''$ - and  $\tan \delta$ -temperature curves. The peak becomes smaller and shifts to higher temperatures on increasing the molar ratio of D to L.

The complex shear modulus and  $\tan \delta$  were measured for each sample as a function of frequency ranging from 0.003 to 1 Hz at temperature from 0 to 40°C. A frequency dispersion peak was observed in this temperature range. This mechanical dispersion has been interpreted as the motion of the side chain. The frequency dispersion curves at various temperatures could be superposed onto a single master relaxation curve at a temperature of 18.5°C by shifting each curve horizontally along the logarithmic frequency axis. Figure 2 shows the master relaxation curves thus obtained for the (1:1) mixture. The results obtained for PBLG are also included in this figure. It is clear that the dispersion strength of the (1:1) mixture is smaller than that of PBLG.

Figure 3 shows the ratio  $\Delta G/\Delta G_{\text{PBLG}}$  of the relaxation strength of the mixture to that of pure PBLG at 18.5°C as a function of the mole fraction  $f_D$  of the D polymer. The relaxation strength  $\Delta G$  was estimated to be the difference between the  $G'$  values at the low and high frequency limits of the master



**Figure 2.** Master relaxation curve for D:L=1:1 sample. Solid line represents the results for PBLG.



**Figure 3.** Ratio of the relaxation strength of the mixture to that of pure PBLG,  $\Delta G/\Delta G_{PBLG}$ , as a function of the mole fraction of the D polymer  $f_D$ . The solid line represents eq 2.

relaxation curve. It is apparent that  $\Delta G/\Delta G_{PBLG}$  decreases on increasing the mole fraction.

Squire and Elliott<sup>3</sup> reported that the stacking of benzene rings of the D and L polymers is not complete even for the (1 : 1) mixture, in which one L polymer is surrounded on the average by four D polymers. If one polymer chain is hexagonally surrounded by six D polymer chains, benzyl groups of 31 residues out of 43 residues of the L polymer chain which forms a 43 residue-12 turn  $\alpha$ -helix are stacked with the D polymers. Thus, if the mixing of D and L is completely random, the fraction  $F_u$  of unstacked benzene rings is given by,

$$F_u = 1 - (31/43) \cdot 2f_D(1-f_D) \quad (1)$$

If the dispersion observed for DL mixtures can be

associated with the motion of unstacked side chains, the ratio of the relaxation strength of the mixture to pure PBLG is equal to  $F_u$ , and we obtain,

$$\Delta G/\Delta G_{PBLG} = 1 - (31/43) \cdot 2f_D(1-f_D) \quad (2)$$

This relation is shown in Figure 3 by a solid line. The general behavior of the curve is in agreement with the plotted data, indicating that stacked side chains do not contribute to the dispersion at room temperature. Thus, it is concluded that the stacking of benzene rings markedly hinders the motion of side-chains.

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