Notes

Secondary Transitions in Poly(γ-benzyl-L-glutamate) and in Poly(γ-benzyl-DL-glutamate)

J. V. Koleske and R. D. Lundberg

Union Carbide Corporation, Chemicals and Plastics, South Charleston, West Virginia 25303.

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Although the dynamic shear behavior of poly(γ-benzyl-L-glutamate), PγB-L-G, dried from chloroform solution and the proton magnetic resonance of the same polymer in a pressure formed pellet have been described,[1,2] it appears that no dynamic mechanical measurements have been made with compression molded PγB-L-G or with poly(γ-benzyl-DL-glutamate), PγB-DL-G. Because of a similarity in the secondary transition temperatures obtained by nmr and low-frequency torsion pendulum measurements[3] and since the method of specimen preparation appears to affect the transitions apparent in these polypeptides, it appears worthwhile to report our investigations.

Experimental Section

Dynamic mechanical measurements were made by means of a freely oscillating, recording torsion pendulum that operates at about 1 cps.[4,5] Values of the glass transition temperature, T_g, were taken from the loss component, G'', of the complex shear modulus unless otherwise noted. PγB-L-G with a molecular weight of 3.5×10^5 (Lot. No. G-79) and PγB-DL-G with a molecular weight of 3×10^4 (Lot No. 6774) were obtained from Pilot Chemicals, Inc.

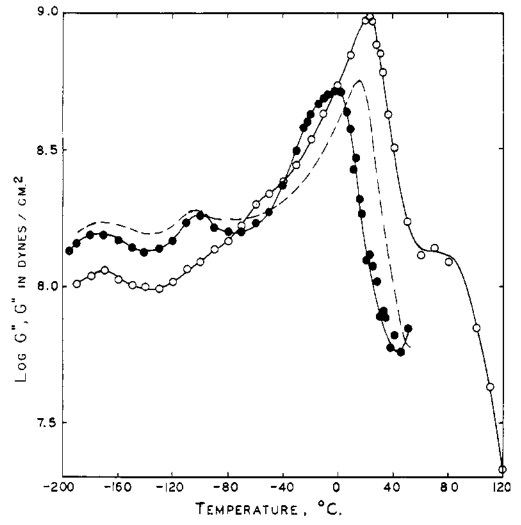

Figure 1. Loss component of the complex shear modulus, G'', for poly(γ-benzyl-L-glutamate) as a function of temperature: ○, compression molded; ●, cast from chloroform and aged 48 hr *in vacuo* at 30°; — — —, same as ● but also aged 34 months at 25°.

Translucent plaques of both PγB-L-G and PγB-DL-G can be formed by merely applying pressure to either polymer at room temperature. This factor implied that the T_g of the polymers could be near room temperature. Since the integrity of the specimens so molded by pressure alone was not complete enough for our use, plaques were molded under pressure at 60°. When prepared in this manner, translucent specimens with excellent integrity were obtained. For comparison purposes, films of the polymers were prepared by evaporation from chloroform solution.

Results and Discussion

The loss component of the complex shear modulus, G'', for PγB-L-G is shown in Figure 1. When dried to constant weight (48 hr in a vacuum oven at 30°) from chloroform solution, this polymer has a T_g of about 0° (0.9 cps) with secondary transitions occurring at −100 and −175°. The earlier cited work[1] which was done with films cast from chloroform listed transitions at 15° (0.18 cps) and −130° with the possibility of another relaxation occurring below −173°. The molded specimen studied with the torsion pendulum had a T_g of 25° (1.8 cps) and only a single definite low temperature relaxation peak at −170°. The magnetic resonance data[2] on molded polymer are in good agreement with these values.

Figure 2 is a plot of G'' as a function of temperature for PγB-DL-G. When dried from chloroform as above, the polymer has a T_g of 5° (2.0 cps) and when compression molded at 15° (2.0 cps). The transition temperatures are summarized in Table I. No low-temperature relaxation was apparent in the PγB-DL-G. In fact, the

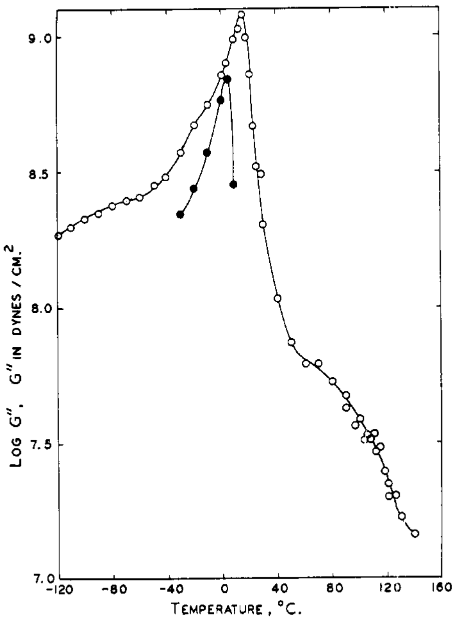

Figure 2. Loss component of the complex shear modulus, G'', for poly(γ-benzyl-DL-glutamate) as a function of temperature: ○, compression molded; ●, cast from chloroform.

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(2) J. A. E. Kail, J. A. Sauer, and A. E. Woodward, *J. Phys. Chem.*, **66**, 1292 (1962).

(3) J. A. Faucher, J. V. Koleske, E. R. Santee, J. J. Stratta, and C. W. Wilson, *J. Appl. Phys.*, **37**, (11), 3962 (1966).

(4) L. E. Nielsen, *Rev. Sci. Instr.*, **22**, 690 (1951).

(5) J. V. Koleske and J. A. Faucher, *J. Chem. Educ.*, **43**, 254 (1966).

TABLE I
SECONDARY TRANSITIONS FOR POLY-(γ-BENZYLGLUTAMATES)

	L form		DL form	
	Compression molded	Cast from chloroform	Compression molded	Cast from chloroform
T_g, °C (frequency, cps)				
Vacuum dried 48 hr, 30°	25 (1.8)	0 (0.9)	15 (2.0)	5 (2.0)
Aged 34 months, 25°		15 (0.9)		
Low-temperature relaxations, °C				
Vacuum dried 48 hr, 30°	−170	−100, −175		
Aged 34 months, 25°		−105, −170		
High-temperature relaxation, °C	90		113	
T_g, °C obtained from other studies				
a		12–15		
b		15		
c	~27			

[a] Reference 6; films cast from chloroform and heated *in vacuo* at 100°. [b] Reference 1; films cast from chloroform. [c] Reference 2; molded polymer sample.

polymer was very brittle at low temperatures (< −120°) and samples broke repeatedly below this temperature under even the slight strain imposed by the torsion pendulum. This was equally true for the film cast from chloroform. Since the T_g of the DL polymer is some 10° lower than the L form, it would be expected that the DL form would be capable of absorbing slightly more energy near 0° and thus should be the tougher of the two polymers. However, this is not the case. The apparent brittleness of the DL form at low temperatures (< −120°) may be due to the apparent absence of a low-temperature relaxation maximum. The T_g of the L form has been associated with side chain motion for these helical structures.[6] It appears likely that the low-temperature relaxation (−170°) is also associated with side chain motion or rotation. On this basis, the possible absence of a low-temperature relaxation and the resulting brittleness of the DL form can be rationalized as arising from steric hindrance of the side chains. In the case of the L form, steric interactions would appear to be less likely.

Table I also provides a comparison of values for the T_g of PγB-L-G obtained in other studies with those of the present work. The T_g values obtained for cast films are significantly lower in all cases than for the compression molded samples. However, this comparison should be made with some caution since some of the transition values have been obtained by different techniques. The lower T_g for cast films when compared to values for molded samples can be attributed to either, or even both, of two causes. First, plasticization by residual chloroform may lower T_g for the cast materials. Second, differences in conformation which depend on whether the film is cast from solution or compression molded may result. The relaxation mechanism that occurs at about −100° also could be due to the second possibility.

To test the possibility of plasticization by residual solvent, the sample of PγB-L-G used was aged 34 months at ambient conditions (25°) and then rerun. The data are shown in Figure 1 as a dashed curve. In this case the glass transition temperature was 15°, which is in good agreement with other investigators[1,6] who worked with films cast from chloroform solution but who used more stringent drying conditions. However, this value is still 10° lower than was obtained with the compression molded samples. In addition, the −100° relaxation is again apparent, but is somewhat diminished in character. A chlorine analysis of this aged film indicated the presence of about 0.4% chlorine. Even if all of this chlorine were due to residual solvent, such a small amount of chloroform (~0.1%) would not be expected to cause a 10° decrease in T_g. However, its presence does suggest that the data obtained with the sample that had been aged only 2 days in a vacuum oven contained a higher percentage of chloroform which would account for the 0° temperature first obtained. Since the −100° relaxation is apparent in both the freshly cast sample and in the aged sample, one would suspect that there could be a difference in either the conformation of the polymer chains or the paracrystalline or mesomorphic (see below) content which is caused by casting the polymer from chloroform. Of course, this must remain a speculation from these data, but the evidence does point in this direction.

The sample of PγB-DL-G cast from chloroform was not examined after extended aging. In view of the above work with cast films of PγB-L-G, the 5° T_g value for PγB-DL-G could be somewhat low. To study the effect of quenching, a molded specimen of PγB-DL-G was heated to about 170° and then quenched to 0°. The T_g of this quenched sample was 13° which is in good agreement with the value for the room temperature annealed specimen (error limit is ±2°).

As noted in Table I, a high-temperature relaxation above T_g exists. Figure 3 describes the mechanical loss behavior of the compression molded specimens of the two polypeptides. The T_g occurs at 30° for PγB-L-G and at 20° for PγB-DL-G in this plot, which is somewhat higher than shown by G'', but this is expected. The magnitude of the mechanical loss at T_g is markedly greater for PγB-DL-G than for PγB-L-G. Since T_g is usually related to the amorphous portion of a crystalline polymer, the larger energy absorption at T_g suggests that the DL form is noticeably less crystalline in nature than is the L form. This factor could be also related to the brittleness of the DL form and, of course, to the mesomorphic or paracrystalline content. Of greater interest is the fact that a new peak or relaxation is ap-

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(6) A. J. McKinnon and A. V. Tobolsky, *J. Phys. Chem.*, **70**, 1453 (1966).

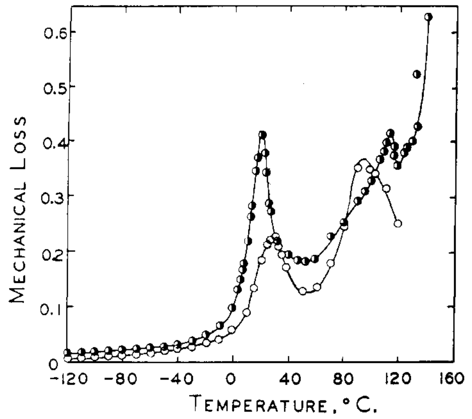

Figure 3. Mechanical loss-temperature spectrum for (○) poly(γ-benzyl-L-glutamate) and for (◑) poly(γ-benzyl-DL-glutamate).

parent in each of the curves above the glass transition temperature. In Figures 1 and 2 a shoulder and rather marked decrease in G'' occurs near this temperature. Such behavior is somewhat reminiscent of a melting point in polymers. However, the polypeptides gave no evidence of a melting point when examined by the usual methods (loss of birefringence or visual observation) near these transition temperatures. Above these temperatures the polymers appear to be quite leathery, but not very strong for they tear quite easily. It has been suggested[6] that films of PγB-L-G contain both paracrystalline and mesomorphic regions. It is possible that the relaxation observed near 90° for PγB-L-G is indicative of a change from a mesomorphic phase to a paracrystalline phase. Likewise, the relaxation at about 115° for PγB-DL-G may be related to such a phase change.

To determine whether these apparent transitions were accompanied by changes in infrared absorption, such data were obtained at three different temperatures with films of PγB-L-G which had been deposited from chloroform solution on salt plates. Selected portions of these curves are shown in Figure 4. The remainder of the ir curves were essentially independent of temperature. While there are some minor changes in these spectra with temperature, they do not suggest any significant conformational change over the temperature range of interest.

Conclusions

It would appear that the differences in T_g found in our work and the cited work[1] cannot be attributed to molecular weight differences since all polymers used should have been above the asymptotic value required for constancy of properties. We conclude the following on the basis of these studies.

(a) The method of sample preparation for these systems can be an important factor affecting mechanical loss results. The possibility that a small amount of solvent is tenaciously held by the polypeptide and therefore plasticizes the polymer and/or causes a structural change appears consistent with the results.

(b) A significant difference exists in mechanical loss measurements for the DL polymer compared with the L polypeptide. The DL polymer examined in these studies appeared significantly more brittle than the L form suggesting the absence of a low-temperature peak in the former material.

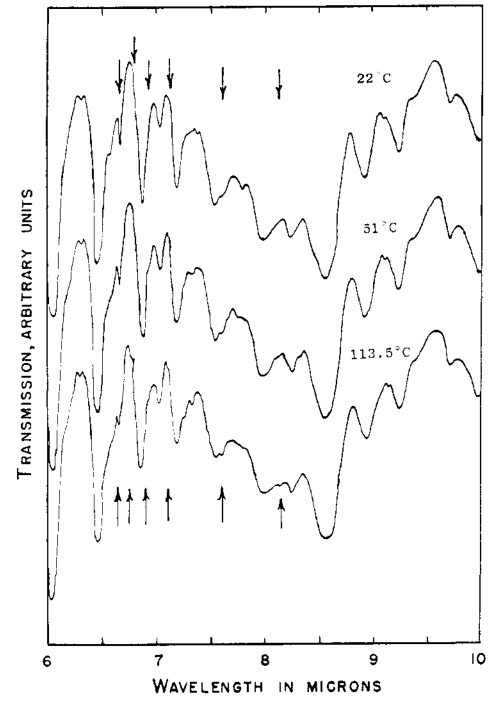

Figure 4. Portions of infrared spectra that show real differences for poly(γ-benzyl-L-glutamate).

(c) In both L and DL forms, a high-temperature secondary transition at 90–115° occurs.

Polymer Entanglement Spacings Estimated from Integration of the Loss Compliance

James F. Sanders and John D. Ferry

Department of Chemistry, University of Wisconsin, Madison, Wisconsin. *Received April 24, 1969*

There are two common measures of the average molecular weight between entanglements in an amorphous polymer of high molecular weight:[1-3] M_C, the critical molecular weight for influence of entanglements on steady-flow viscosity, and M_e, the effective network strand molecular weight calculated from the magnitude of a viscoelastic modulus or compliance. They are not related in a simple manner. Although M_C can be obtained with reasonable precision from the dependence of viscosity on molecular weight and several alternative sources, there has been no reliable method for obtaining M_e. Its estimation from the plateau level of a relaxation modulus, storage modulus, creep compliance or storage compliance involves an arbitrary choice. Calculation from the maximum in the loss compliance[4] involves application of a theory which describes the

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(1) F. Bueche, "Physical Properties of Polymers," Interscience Publishers, New York, N. Y., 1962, p 79.

(2) G. C. Berry and T. G Fox, *Advan. Polym. Sci.*, **5**, 261 (1967).

(3) R. S. Porter and J. F. Johnson, *Rheol. Acta*, **7**, 332 (1968).

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