Dynamic Mechanical Properties of Poly(α-amino acid)s. I. Side-Chain Dispersions of Poly(γ-benzyl L-glutamate) and Poly(γ-methyl L-glutamate)

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ABSTRACT: Dynamic mechanical measurements for solid films of poly(γ-benzyl L-glutamate) (PBLG) and poly(γ-methyl L-glutamate) (PMLG), which were cast from helicogenic solvents, were carried out with a torsion pendulum apparatus over a frequency range of 1.0 to 0.003 Hz at various temperatures in their side-chain dispersion regions. Master curves for the real and imaginary parts of the complex rigidity and loss tangent were composed by performing suitable translations of the obtained dispersion curves along the logarithmic frequency axis. The shift factor a_T derived from the superposition procedure was satisfactorily represented by the "universal" Williams—Landel—Ferry equation with T_s's chosen as 65 and 57°C for PBLG and PMLG, respectively. The dispersions resemble those associated with glass-transition phenomena in some respects, unlike the side-chain dispersions of amorphous polymers, such as poly(alkyl methacrylate)s. This may suggest that the side chains of these poly(α-amino acid)s are randomly packed surrounding a rigid helical backbone.

KEY WORDS   Poly(γ-benzyl L-glutamate) / Poly(γ-methyl L-glutamate) / Side-Chain Dispersion / Time—Temperature Superposition / WLF-Equation / Free Volume / Relaxation Spectra /

Molecular motions of poly(α-amino acid)s in the solid state have been the subject of several investigations. Sizable mechanical[1-4] and dielectric[5,6] dispersions and a sharp decrease in the NMR second moment with temperature[7-9] were observed near room temperature for poly(γ-benzyl L-glutamate) (PBLG) and poly(γ-methyl L-glutamate) (PMLG), whose side chains are rather flexible. These dispersions have been interpreted in terms of the onset of random motion of the side chain.

McKinnon and Tobolsky[10] suggested that solid films of PBLB cast from solutions contain both paracrystalline and mesomorphic regions; the latter maintains the same relative molecular disposition as in the cholesteric phase of a concentrated solution. They found a change in the thermal expansion coefficient and a rapid decrease in the creep modulus near room temperature for PBLG, and attributed them to side-chain motion in the mesomorphic regions.

Fukuda and his coworkers[11,12] found piezoelectric dispersions in the vicinity of room temperature for PBLG and PMLG, and interpreted the dispersions in terms of side-chain motions of the α-helical molecules in the noncrystalline regions surrounding the crystallites.

X-ray studies have suggested that side chains of PBLG, in particular of the racemic form of poly(γ-benzyl glutamate), adopt a regular definite conformation in the crystalline or paracrystalline state.[13] This would imply that the side chains do not undergo random motion, at least in the crystalline region. NMR data, however, do not indicate the existence of two regions having different mobilities,[8,9] *i.e.*, crystalline (or paracrystalline) and noncrystalline (or mesomorphic) regions. Moreover, very recent results of an X-ray study showed that the transition occurs obviously in the crystalline region and is related to the side-chain motion.[14]

Most of the investigations of relaxation pheno-

mena of poly(α-amino acid)s have been isochronous. In order to discuss the mechanism of the relaxation and the relation with the structure in detail, it is desirable to obtain isothermal data for viscoelastic behavior over a wide range of frequency. In this paper, temperature and frequency dependences of the complex rigidity for PBLG and PMLG in the α-helix conformation are described and discussed in terms of the structure and the motion of side chains.

EXPERIMENTAL

PBLG and PMLG used in the present study were prepared by polymerization of their α-amino acid NCA's in dioxane and methylene chloride, respectively, in the presence of hexamethylenediamine as an initiator.

A concentrated chloroform solution of PBLG was poured onto a glass plate and allowed to evaporate to dryness. The film sample thus obtained was heat-treated at a temperature of 150°C for 21 hr *in vacuo* to eliminate the residual solvent.

A film sample of PMLG was prepared from an intact polymerization solution in the same way as PBLG, and heat-treated *in vacuo* at 95—100°C for six hours. It was comfirmed from IR spectra that the samples are predominantly in the α-helix conformation.

Dynamic mechanical measurements were carried out with a forced-oscillation torsion pendulum apparatus over an ultra-low frequency range of 1.0 to 0.003 Hz. Details of the apparatus and the procedure have been reported elsewhere.[15]

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the real and imaginary parts of the complex rigidity, G' and G'', and the loss tangent tan δ for PBLG at frequencies of 0.1, 0.02, and 0.003 Hz. Results for PMLG at 0.1 and 0.01 Hz are shown in Figure 2. According to previous NMR, dielectric, and mechanical measurements, the dispersions observed near room temperature for both polymers are caused by the onset of side-chain motion which do not involve motions of the backbone segments in the α-helical conformation.[5,8,16]
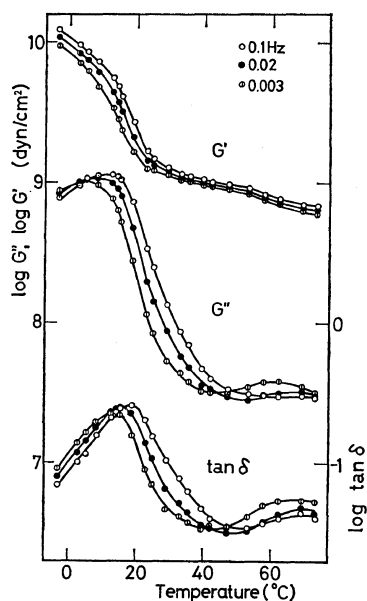
Figures 3 and 4 show the frequency dependence

Figure 1. Real and imaginary parts of the complex rigidity and the loss tangent for PBLG as a function of temperature at frequencies of 0.1 (○), 0.02 (●), and 0.003 Hz (◔).
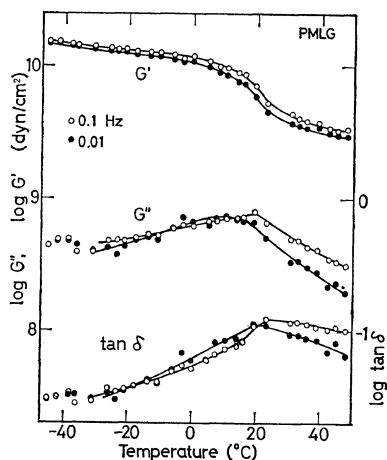

Figure 2. Real and imaginary parts of the complex rigidity and the loss tangent for PMLG as a function of temperature at frequencies of 0.1 (○) and 0.01 Hz (●).

of G', G'', and tan δ for PBLG at various temperatures between -3.0 and 53.0°C and for PMLG between -17.5 and 48.0°C, respectively. The side-chain dispersions are observed fragmentarily on each curve.

The time—temperature superposition principle was applied to the above results. All of the G', G'', and $\tan \delta$ curves could be superposed onto a set of master curves by performing suitable horizontal translations along the logarithmic frequency axis. The time—temperature superposition principle is expressed as follows[17]

$$G'(\omega) = G_0'(\omega a_T)$$
$$G''(\omega) = G_0''(\omega a_T)$$

and

$$\tan \delta(\omega) = \tan \delta_0(\omega a_T)$$

(1)

where the subscript zero refers to a value at a reference temperature T_0, ω is the angular frequency, and a_T is the reduction or so-called shift factor; $\log a_T$ gives the amount of a horizontal translation. The correction factor $\rho_0 T_0/\rho T$ resulting from the change in density and rubber-like character of the elasticity was neglected here.

Figure 5 shows the composite relaxation curves of G', G'', and $\tan \delta$ for PBLG reduced to a temperature of 19°C, composed from the curves
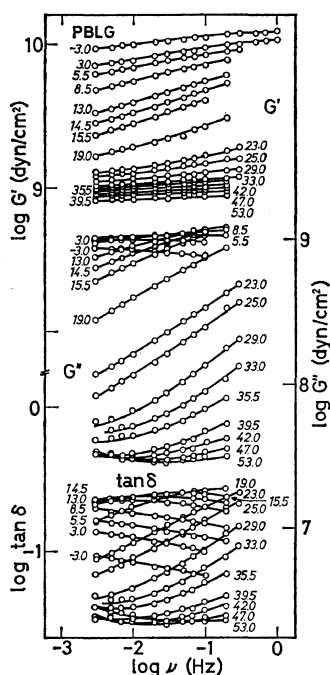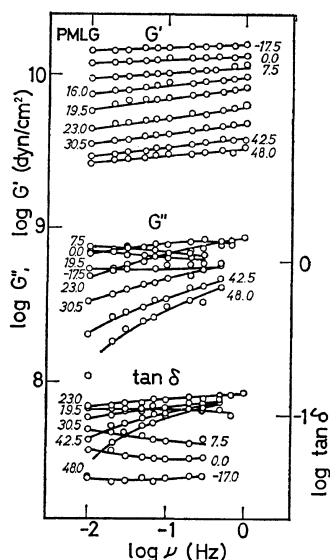

Figure 4. Variation of the real and imaginary parts of the complex rigidity and the loss tangent with frequency for PMLG at temperatures between -17.5 and $48.0°C$. Data at -13.5, -10.5, -6.5, -3.0, 5.0, 10.5, 14.0, 16.0 (except G'), 36.0, and $45.0°C$ are omitted to avoid making the figure too complicated.
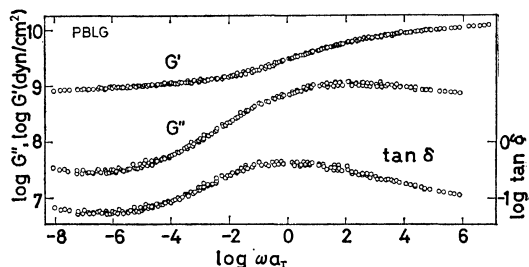

Figure 5. Composite relaxation curves of the real and imaginary parts of the complex rigidity and the loss tangent for PBLG reduced to 19°C.

given in Figure 3. It was not possible to superpose the dispersion curves at temperatures above 53°C, since another dispersion begins to appear above this temperature, as can be seen in Figure 1.

Figure 6 shows composite relaxation curves for PMLG reduced to a temperature of 19.5°C, composed from the curves given in Figure 4. The superposition seems fairly good. In Figure 7 the logarithm of the shift factor $\log a_T$ derived from the superposition procedure is plotted against temperature.
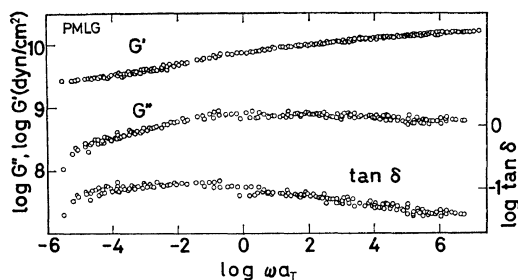

Figure 3. Variation of the real and imaginary parts of the complex rigidity and the loss tangent with frequency for PBLG at temperatures between -3.0 and $53.0°C$.

Figure 6. Composite relaxation curves of the real and imaginary parts of the complex rigidity and the loss tangent for PMLG reduced to 19.5°C.
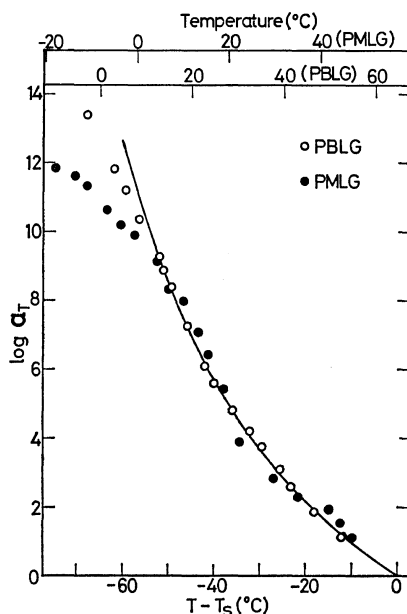

Figure 7. $\log a_T$ plotted against temperature for PBLG (○) and PMLG (●). The solid curve represents the "universal" WLF equation, eq 2. T_s's are chosen as 65.0 and 57.0°C for PBLG and PMLG, respectively.

Side-chain relaxations occurring in poly(alkyl methacrylate)s have been investigated both above and below their glass transition temperaturs.[18-22] On either side of the glass transition temperature the shift factor was found to be represented by the Arrhenius type equation. For the side-chain dispersion of PBLG and PMLG, however, $\log a_T$ does not fit a straight line when plotted against reciprocal absolute temperature, but is well represented by the "universal" Williams—Landel—

Ferry (WLF) equation,[23]

$$\log a_T = -8.86(T - T_s)/(101.6 + T - T_s) , \quad (2)$$

if T_s's are chosen as 65 and 57°C for PBLG and PMLG, respectively, as shown by the solid curve in Figure 7.

A break point on the volume—temperature curve has been observed at 12—17°C[10,24,25] for PBLG and at $-8 - 0°C$[24,26] for PMLG, corresponding to the side-chain dispersions. If we assume these break-point temperatures to be glass transition temperatures T_g, these temperatures are close to those expected from the empirical relation, $T_s - T_g = 50 \pm 5°C$.[23] Deviations from the WLF curve are significant below about 10°C and about 5°C for PBLG and PMLG, respectively, as seen in Figure 7.

Figure 8 shows the transition map for the side-chain dispersion of PBLG, in which the frequencies of the loss maxima are replotted from data in the literature as a function of reciprocal absolute temperature. The slope of the curve becomes steeper as the temperature decreases. The apparent activation energy of the relaxation process increases from 28 kcal/mol (at 60°C) to
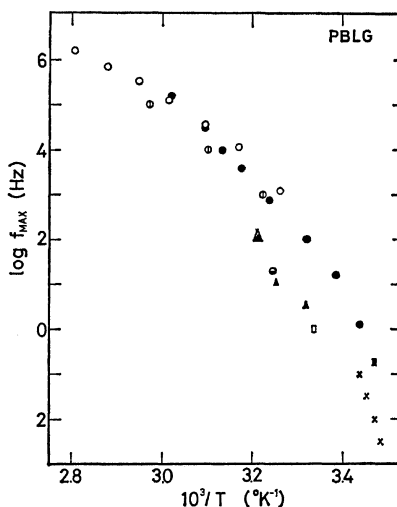

Figure 8. Transition map for the side-chain dispersion of PBLG: from dielctric data of Tsutsumi, et al.[27] (○), Tsutsumi, et al.[28] (⊕), and Hikichi, et al.[5] (●); from dynamic mechanical data of Saba, et al.[1] (■), Hashino, et al.[3] (▲), Ogawa, et al.[29] (◕), Hiltner, et al.[16] (□), Fukuzawa, et al.[30] (△), and the present study (×).

more than 120 kcal/mol upon approaching the temperature of the break point on the volume—temperature curve.

According to the free-volume theory of the glass transition, the dependence of the fractional free volume on temperature is expressed as

$$f = f_g + \alpha_f (T - T_g) \qquad (3)$$

where f_g is the value at the glass transition temperature T_g, and α_f the thermal expansion coefficient of the free volume. α_f is usually taken to be the difference between the thermal expansion coefficients above and below the glass transition temperature, $\Delta\alpha$.

We apply, tentatively, the free-volume theory of the glass transition to the prepresent case, assuming the break-point temperature to be the glass transition as noted before.

The values of $\Delta\alpha$ determined from dilatometric measurement are reported to be $3.2 \times 10^{-4}/°C$ and $2.8 \times 10^{-4}/°C$ for PBLG and PMLG, respectively.[24] These values are somewhat smaller than those expected from the "unversal" WLF-equation (eq 2); $\alpha_f = 4.8 \times 10^{-4}/°C$.

In these polymers, the side chains form a soft shell of considerable thickness, referred to as the side-chain region in this paper, around the rigid helical core, as noted by Flory and Leonard.[31] Such structure of the polymers prevents a direct interaction between the cores or any interaction between the core and the side chains of neighboring molecule. Therefore, the side chains will relax more or less independently of the cores, but will require cooperation with each other.

The $\Delta\alpha$ obtained experimentally is for the sample as a whole. In the present case, we should use $\Delta\alpha$ of the side-chain region. If we assume that the change in the thermal expansion coefficient of the core at the transion temperature is negligible as compared with that of the side-chain region, then the increase in the thermal expansion coefficient of the side-chain region becomes

$$\Delta\alpha_s = \frac{1}{v - v_c(1 - w_s)} \Delta\alpha \qquad (4)$$

where v and v_c are the specific volumes of the sample as a whole and of the core, respectively, and w_s is the weight fraction of the side chains excluding β-carbon, which was assumed to be included in the core region.

Values of $\Delta\alpha_s$ were estimated from the above equation using volumetric data in the literature. In the estimation of v_c, we assumed that the helical core, into which the side chains cannot penetrate, has a radius of 3.9 Å, corresponding approximately to the outside of β-carbon.[32] Values are listed in Table I. Values in the last column of the table are very close to those expected from the WLF equation.

This suggests that the dispersions observed here resemble those associated with glass transition phenomena, although they arise from side-chain motion. A recent X-ray study[14] showed that that PBLG and PMLG consist of a homogeneous crystalline (or paracrystalline) region and that the side-chain motions occur in the crystalline region. Therefore the above results also indicate that the side chains are randomly arranged even in the crystalline region, in accordance with the results of a thermodynamic study by Flory and Leonald.[31]

On the other hand, only minor changes in the thermal expansion coefficients associated with the side chain relaxations of poly(alkyl methacrylate)s[33] and poly(vinyl alkyl ether)s[34] were reported. The side chains of these polymers intermingle with both the other side chains and the backbone segments of neighboring molecules[21]

Table I. Specific volumes and thermal expansion coefficients for PBLG and PMLG

	v, ml/g	v_c, ml/g	w_s	$\Delta\alpha_{obs}$, °C	$\Delta\alpha_s$, °C
PBLG	0.787[a]	0.634	0.689	3.2×10^{-4} [a]	4.3×10^{-4}
	0.783[b]			2.7×10^{-4} [b]	3.6×10^{-4}
PMLG	0.769[a]	0.634	0.524	2.8×10^{-4} [a]	4.8×10^{-4}

[a] Ref 24.
[b] Ref 10. Reexamination of Figure 2 cited in ref 10 leads to a somewhat larger value of $\Delta\alpha_{obs} = 3.2 \times 10^{-4}/°C$. Then $\Delta\alpha_s$ becomes $4.3 \times 10^{-4}/°C$.
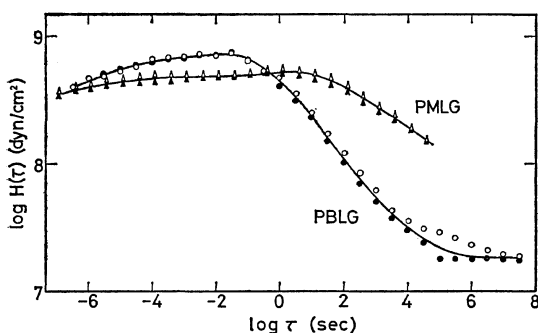
Figure 9. Relaxation spectra for PBLG and PMLG reduced to 20.0°C, calculated using the second approximation method of Williams and Ferry: ◯ and △, from G'; ● and ▲, from G''.

and do not segregate to form a side-chain region, unlike the poly(α-amino acid)s. This seems to be an essential difference between the two groups of polymers.

Figure 9 shows the relaxation spectra at a temperature of 20°C for PBLG and PMLG calculated from the respective composite G' and G'' curves in Figures 5 and 6 using the second approximation method of Williams and Ferry.[35] Values obtained separately from the real and imaginary components of the experimental data are in close agreement for each polymer. The distribution of relaxation times is rather broad. The wedge portion, the longer time region, of the spectrum for PBLG has a negative slope of about 0.3 for about six decades of time. The spectrum for PMLG is much broader. This may be due to an intramolecular interaction between the side chain and the rigid backbone segments.

CONCLUSIONS

The frequency dispersion curves of G', G'', and tan δ for PBLG and PMLG obtained at various temperatures in their side-chain dispersion regions could be closely superposed onto a single set of master curves by applying a horizontal shift along the logarithmic frequency axis. The temperature dependence of the shift factor follows the "universal" WLF-equation. The thermal expansibities of the fractional free volume referred to the side-chain region, on the assumption that the backbone forms a rigid core, are close to those expected from WLF equation.

Such behavior of the dispersion is reminiscent of a glass transition. This may suggest that the side chains are randomly packed surrounding the the helical backbone.

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