Dilatometric Study on Some Poly(α -amino acid)s

Kunio HIKICHI, Akihiro TSUTSUMI, Shigekazu ISOZAKI,
and Motozo KANEKO

*Department of Polymer Science, Faculty of Science,
Hokkaido University, Sapporo 060, Japan.*

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ABSTRACT: The temperature dependence of the specific volume was measured for poly(γ -benzyl L-glutamate) (PBLG), poly(γ -methyl L-glutamate) (PMLG), and poly(N^{ϵ} -carbobenzyloxy L-lysine) (PCLL) in the range of temperature -35 to 100°C . The specific volume-temperature curve has a break point at 16 , -8 , and 8°C , for PBLG, PMLG, and PCLL, respectively. These break points are related to the onset of side-chain motions. Thermal expansion coefficients and the break point temperatures are discussed in terms of empirical equations proposed for the glass transition phenomenon. An additional break point was found for PBLG and PMLG at higher temperatures.

KEY WORDS Dilatometry / Poly(γ -benzyl L-glutamate) / Poly(γ -methyl L-glutamate) / Poly(N^{ϵ} -carbobenzyloxy L-lysine) / Transition /

Over the past few years, there has been a growing interest in properties of poly(α -amino acid)s in the solid state. Molecular motions of a number of α -helical poly(α -amino acid)s have been investigated in the solid state by means of nuclear magnetic resonance (NMR), dynamic mechanical, and dielectric measurements.¹⁻¹⁶ Poly(γ -benzyl L-glutamate) (PBLG) and poly(γ -methyl L-glutamate) (PMLG) have been found to show mechanical and dielectric relaxations due to side-chain motion.

McKinnon and Tobolsky^{17,18} carried out dilatometric measurements on PBLG, and found a break in the specific volume-temperature curve at about 12°C , where the mechanical and dielectric relaxations begin to appear. They considered that this break is manifestation of the glass transition which is related to the onset of side-chain motion in the noncrystalline "mesomorphic" regions. PMLG and poly(N^{ϵ} -carbobenzyloxy L-lysine) (PCLL) have been reported to have a break point at about 0 and 10°C , respectively.¹⁹

It is believed that the glass transition of amorphous polymers or of the amorphous parts of semicrystalline polymers is related to the onset of the microbrownian motion of polymer backbone chains. Backbone chains of PBLG, PMLG, and PCLL are all known to be rigid α -helices in the solid state. Side-chain motions of vinyl

polymers, for example, poly(methyl methacrylate), are not related to the glass transition. There remains some doubt, therefore, about the observation of the glass transition for these poly(α -amino acid)s. Nevertheless, we suggested from dielectric¹² and X-ray studies²⁰ that PBLG and PMLG manifest a transition analogous to the glass transition which is related to the onset of side-chain motion.

It is of interest, therefore, to examine the specific volume-temperature relations in more detail. The purpose of this work is to undertake dilatometric measurements on some α -helical poly(α -amino acid)s including PBLG, PMLG, and PCLL. The results obtained will be discussed in the light of empirical relations between the glass transition temperature and the thermal expansion coefficient.

EXPERIMENTAL

Polymers used in this work were prepared by polymerization of respective NCA's using triethylamine as an initiator. Specimens for thermal expansion measurements were films cast from solutions of methylene chloride for PBLG and PMLG, and N,N -dimethylformamide for PCLL at room temperature. All of these specimens were dried *in vacuo* and annealed at a temperature of 100°C .

A dilatometer was employed for thermal expansion measurements, using mercury as a filler medium. About two grams of specimens were loaded in the dilatometer and a small amount of mercury then inserted.

For temperatures above room temperature the dilatometer was immersed in an oil-bath regulated at a constant temperature within $\pm 0.1^\circ\text{C}$. For below room temperature the dilatometer was soaked in methanol cooled by liquid nitrogen, the accuracy of temperature being $\pm 1^\circ\text{C}$. All data were obtained by reading the height of mercury in the capillary of the dilatometer during heating, the heating rate being $0.5^\circ\text{C}/\text{min}$.

The absolute value of the specific volume at a temperature of 25°C was determined in aqueous potassium acetate (CH_3COOK) solution. It was found that a mixture of carbon tetrachloride and ethanol is not adequate as a flotation medium in this case, since the density measured in this mixture increases gradually with time probably due to the absorption of CCl_4 . All data were corrected with respect to the value of the specific volume at 25°C .

RESULTS AND DISCUSSION

Figure 1 shows the specific volume as a function of temperature for PBLG, PMLG, and PCLL. As seen in the figure, the specimens all show a break in the specific volume—temperature curve at 16 , -8 , and 8°C for PBLG, PMLG, and PCLL, respectively. These break point temperatures are in approximate agreement with those reported previously.¹⁷⁻¹⁹ Figure 1 also shows another break point at higher temperatures for PBLG and PMLG, which will not be discussed further in the present paper. The results are summarized in Table I, which contains the temperatures of the break point at low temperatures, T_g' the thermal expansion coefficients just below and above T_g' ; α_g and α_1 , and the difference between the two, $\Delta\alpha$.

As mentioned before, these poly(α -amino acid)s with long flexible side chains have been found to exhibit a mechanical and/or dielectric relaxation in the vicinity of the break point.^{4,6-16} A remarkable decrease in line-width of NMR spectra was also observed for these polymers.¹⁻⁵ The relaxation has been interpreted in terms of the

Figure 1. Specific volume as a function of temperature for PBLG, PMLG, and PCLL.

Table I. Data from specific volume—temperature experiments on PBLG, PMLG, and PCLL

	PBLG	PMLG	PCLL
T_g' ($^\circ\text{C}$)	16	-8	8
$v(T_g')$ (cm^3/g)	0.782	0.758	0.783
α_1 ($/^\circ\text{K}$)	6.1×10^{-4}	5.4×10^{-4}	5.4×10^{-4}
α_g ($/^\circ\text{K}$)	2.9×10^{-4}	2.5×10^{-4}	1.1×10^{-4}
$\Delta\alpha$ ($/^\circ\text{K}$)	3.2×10^{-4}	2.9×10^{-4}	4.3×10^{-4}
α_1^s ($/^\circ\text{K}$)	8.1×10^{-4}	8.9×10^{-4}	6.8×10^{-4}
α_g^s ($/^\circ\text{K}$)	3.8×10^{-4}	4.1×10^{-4}	1.4×10^{-4}
$\Delta\alpha^s$ ($/^\circ\text{K}$)	4.3×10^{-4}	4.8×10^{-4}	5.4×10^{-4}
$\Delta\alpha^s T_g'$	0.12	0.13	0.15
$\alpha_1^s T_g'$	0.23	0.24	0.19

onset of side-chain motion.

An interesting feature of the side-chain relaxation in these poly(α -amino acid)s is that the relaxation is governed by the William—Landel—Ferry (WLF) equation,²¹ which is usually applied to the relaxation associated with the glass transition of amorphous polymers. This is in contrast with the fact that the side-chain relaxation of poly(methyl methacrylate) and related polymers²² are governed by the simple Arrhenius

type equation. We, therefore, suggested that a transition which is very analogous to the glass transition occurs in the side-chain regions of these polymers.¹² X-ray studies²⁰ in which the temperature dependence of X-ray intensities and spacings of equatorial Bragg reflections for oriented samples of PBLG and PMLG were examined gave a further evidence to the above-mentioned proposal.

It is of interest to examine this transition from the point of view of change in volume with temperature. Many authors have proposed empirical equations for the glass transition temperature T_g and thermal expansion coefficients. We attempted to apply these equations to the results obtained here.

If we assume that the transition is associated with the side-chain region only, the thermal expansion coefficient of the side-chain region should be used in the application of these equations to the present case. On the assumption that β -carbon belongs to the core region, and that the thermal expansion of the core region, is negligible, Yamashita, *et al.*,²³ estimated the thermal expansion coefficient of the side-chain region (α^s) from that of the specimen as a whole (α). These values are also listed in Table I with the superscript *s* to refer to the side-chain region.

Boyer and Spencer²⁴ proposed an equation which describes the relation between the glass transition temperature and the thermal expansion coefficient, $\alpha_1 T_g = 0.16$. Van Krevelen²⁵ suggested a value of 0.2 instead of 0.16. The last row of the table lists $\alpha_1^s T_g'$ values for three polymers. A very approximate agreement is seen.

Simha and Spencer²⁶ proposed another equation, $\Delta\alpha T_g = 0.11$, which provides a much more adequate description of the glass transition than the Boyer and Spencer equation. Observed value of $\Delta\alpha^s T_g'$ are listed in the penultimate row of the table. Again we have an approximate agreement with the predicted value.

Tobolsky²⁷ and Bueche²⁸ suggested that the difference between thermal expansion coefficients above (α_1) and below (α_g) the glass transition temperature is approximately $5 \times 10^{-4}/^\circ\text{C}$. The third-to-last row of the table lists $\Delta\alpha^s$ values. It is seen that the Tobolsky and Bueche relation holds approximately.

Bearing in mind that the above-mentioned relations are empirical and approximate in nature, the agreement with predicted relations is not unreasonable. It may therefore be concluded that the transition is very analogous to glass transition from the view-point of the temperature dependence of the specific volume as well, although the transition is related to the side-chain motion. The reason why the transition is similar to the glass transition is not known.

In this respect, it should be pointed out that the side chains of these polymers form a "soft" shell of considerable thickness around the helical core, as Flory and Leonard noted.²⁹ Such a structure of the polymers will prevent a direct interaction between the helical core and the side chains that belong to a different helix. Thus, the side-chain region is more or less independent of the helical core region. On the other hand, the side chains of poly(methyl methacrylate) intermingle with the backbone chains and do not form an independent side-chain region. This seems to be an essential difference between the two groups of polymers.

The side-chain region around the helical core is, however, too small to form a single separate phase. We suggested that solids of these poly(α -amino acid)s consist of a single homogeneous crystalline phase (probably with paracrystalline defects).²⁰ The side-chain region and the helix core are more or less regularly arranged in the crystal lattice. It may be possible that the transition is a crystal phase transition of the second order.

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