X-Ray Scattering of Synthetic Poly(α-amino acid)s in the Solid State. IV. Transition of Poly(γ-methyl D-glutamate) in the β-Form

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ABSTRACT: The temperature dependence of two Bragg reflections was measured for solid poly(γ-methyl D-glutamate) in the β-form in the temperature range from −80 to 120°C. The spacing—temperature curve has a break point in the vicinity of 20°C. From the temperature dependence of integrated intensity, the break point observed is considered to be related to the onset of side-chain motions and to be a transition analogous to the glass transition.
KEY WORDS   X-Ray / Poly(γ-methyl D-glutamate) / β-Form / Transition /

Structures and properties of poly(α-amino acid)s in the solid state have been studied extensively. While most previous efforts have been focussed on the α-helical form, little work has been done with the β-form.

Molecular motions of α-helical poly(α-amino acid)s in the solid state have been accounted for wholly in terms of side-chain motions. It was suggested that poly(γ-benzyl L-glutamate) (PBLG) and poly(γ-methyl L-glutamate) (PMLG), whose side chains are rather flexible, manifest a glass transition at room temperature, due to the onset of the side-chain motions.[1-5] We also obtained the same conclusion from X-ray studies.[6]

The molecular motions of β-forming poly(α-amino acid)s in the solid state have been investigated on poly(S-benzyloxycarbonyl-L-cysteine), poly(S-benzyloxycarbonylethyl-L-cysteine), and poly(S-methoxycarbonylethyl-L-cysteine) using NMR and dielectric methods.[7] All results obtained were interpreted in terms of the rotation of the side chains.

It is, of interest therefore to examine whether a transition related to the onset of the side-chain motions occurs even in the β-form, and what that transition is, if it occurs. The purpose of

this work is to obtain a more detailed understanding about the relation between the structure and the thermal motion of solid poly(α-amino acid) in the β-form.

EXPERIMENTAL

Poly(γ-methyl D-glutamate) (PBDG) used in this work was kindly supplied Ajinomoto Co., Ltd. The film was obtained by casting trifluoro-acetic acid solution of the polymer on a glass plate. The film in the β-form was prepared by allowing it to swell in formic acid at room temperature for two weeks and then annealing it in vacuo at a temperature of 160°C for an hour.[8]

X-ray diffractometric measurements were performed using a Rigaku Denki diffractometer equipped with a scintillation counter and a pulse height analyzer. Cu-Kα radiation at 40 kV and 20 mA was used. A symmetrical reflection (SR) technique and a symmetrical transmission (ST) technique were employed to measure two strong Bragg reflections of (100) and (020).[9] Intensities were counted in the step-scan mode for 40 sec. at intervals of 0.05° in Bragg angle. The peak position was defined as the center of the half-width. Only the relative change in the peak position with temperature was measured. The

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temperature was changed from -80 to $120°C$ and measured by a copper—constantan thermocouple. More detailed account of the procedure has been reported elsewhere.[6]

RESULTS AND DISCUSSION

According to Brown and Trotter,[10] the unit cell of the PMLG in the β-form is an orthogonal lattice with $a=4.70$ A, $b=21$ A, and $c=6.83$ A (fiber axis), containing four residues. In cast film used in this work the pleated sheets of β-chains are preferentially oriented parallel to the plane of the film. Since the diffraction profiles obtained by SR and ST techniques approximately correspond to photographs taken with the beam parallel to the plane of the film and with the beam normal to the film, respectively, the (020) reflection corresponding to the intersheet periodicity was measured by SR technique, and the (100) reflection corresponding to the interchain periodicity by ST technique.

Figure 1 shows a plot of the spacing of the (020) reflection as a function of temperature. As seen in the figure, the spacing-temperature curve has two break points, at 20 and $100°C$, respectively. On the basis of the results of NMR and dielectric measurements of the three derivatives of poly(L-cysteine) with flexible side chains in the β-form, Kamashima[8] suggested that the molecular motions occurring on these poly-
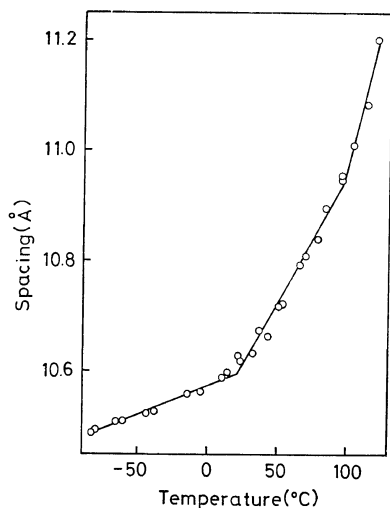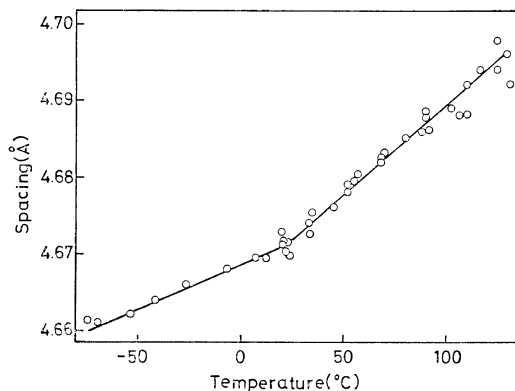

Figure 2. Spacing of the (100) Bragg reflection of PMDG as a function of temperature.

mers were attributed to the rotation of the side chains in a temperature range from -196 to $100°C$. Tsutsumi[11] reported that the NMR second moment of PMLG film which was prepared by allowing it to swell in formic acid decreased markedly at room temperature. This may be interpreted in terms of the onset of the side-chain motions. It is, therefore, probable that the break point at $20°C$ observed in Figure 1 is due to the onset of the side-chain motions.

Figure 2 shows a plot of the spacing of the (100) reflection as a function of temperature. Likewise, the spacing-temperature curve has a break point in the vicinity of $20°C$. It is, therefore, reasonable to assume that the break observed in Figure 2 results from the same origin as that in Figure 1, which was interpreted in terms of the onset of the side-chain motions. Since the (100) reflection corresponds to the spacing in the direction of the intermolecular hydrogen bond, it is evident that the thermal expansion in the direction of the hydrogen bond is affected by the side-chain motions. Similar behavior has also been pointed out in the case of the α-helical PMLG and PBLG by the authors.[12] The linear thermal expansion coefficient in the $\langle 100 \rangle$ direction is one-tenth as large as that in the $\langle 020 \rangle$ direction.

It was found that the intensities of the (020) reflection increased with increasing temperature. An account for this result may require a detailed structure analysis at each temperature, and this procedure is impossible from a practical standpoint. Recently, we found that lateral reflection
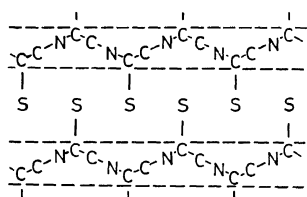

Figure 1. Spacing of the (020) Bragg reflection of PMDG as a function of temperature.

Figure 3. A schematic representation of the β-form orientation projected on the b—c plane.

intensities of α-helical PMLG and PBLG increased with increasing temperature.[6] In order to account for this finding, we assumed two regions differing in electron density: that is, a rigid helical core and a soft side-chain region. Such a "two phase model" has been adopted to account for the results of small-angle X-ray scattering (SAXS) of crystalline polymers. In order to account for the present findings, we have adopted the two phase model on the basis of the following reason.

Figure 3 shows a schematic representation of the β-form orientation projected on the b—c plane. Oxygen and hydrogen atoms of the main chain were not shown for the sake of simplicity. Symbol S represents the side chain. The intersheet distance, 10.6 A, corresponds to the spacing of the (020) reflection. It is assumed that the narrow portion between the two dotted lines separated by 3.70 A is the main-chain region and the rest is the side-chain region. Because the main chain is stabilized by the interchain hydrogen bonds, the main-chain region may be regarded as compact and rigid. On the other hand, the side-chain region is considered to be less compact and soft. This feature describes a typical sandwich structure consisting of two regions differing in electron density, i.e., a "two phase model."

According to the SAXS theory for crystalline polymers,[13] the intensity is proportional to the product of the lattice factor and the square of the structure factor, the latter being related to the electron density difference between the two regions and to their volume fraction. Since the lattice factor and the volume fraction are insensitive to temperature, and the electron density is proportional to mass density, the temperature dependence of the intensity is written as

$$\sqrt{\frac{I(T)}{I(T_0)}} = 1 + \frac{\rho_s \alpha_s - \rho_m \alpha_m}{\Delta\rho_0}(T - T_0) \qquad (1)$$

where ρ_s and ρ_m are the densities of the side chain and the main-chain regions at a reference temperature, T_0, $\Delta\rho_0$ is the difference between the two, and α_s and α_m are thermal expansion coefficient of the side chain and the main-chain regions.

Equation 1 indicates that the square root of the relative intensity is a linear function of temperature with a slope of $(\rho_s\alpha_s - \rho_m\alpha_m)/\Delta\rho_0$. In fact the square root of integrated intensities of the (020) reflection increased linearly with increasing temperature, as shown in Figure 4. The intensity was measured in units of the intensity at 20°C. The intensity—temperature curve has a break point in the vicinity of 20°C. It is evident that this break is related to the one observed in the spacing—temperature curve of Figure 1.

Because the main chain is fairly rigid as compared with the side chain, we may expect the thermal expansion coefficient of the main-chain region, α_m, to be negligibly small at the temperature studied. This assumption will be justified by the difference between the thermal expansion coefficients in the ⟨100⟩ and ⟨020⟩ directions. Therefore, the change in slope indicates that a sudden change in the thermal expansion coefficient of the side-chain region, α_s, occurs at this temperature. A change in slope of this kind observed for crystalline polymers such as polyethylene[14] and polyoxymethy-
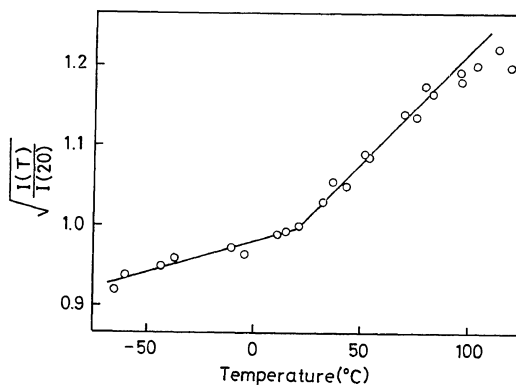

Figure 4. The relative change of the square root of the (020) Bragg reflection intensity of PMDG as a function of temperature.

Table I. Thermal expansion coefficients
of the side-chain region for
PMDG in β-form

	$\alpha_{1s}(T > T_t{}^a),$ $^\circ C^{-1}$	$\alpha_{2s}(T < T_t{}^a),$ $^\circ C^{-1}$
Intensity	5.1×10^{-4}	1.3×10^{-4}
Spacing	7.5×10^{-4}	1.6×10^{-4}

^{a} T_t, transition temperature.

lene[13] provided an evidence for the glass transition in the amorphous surface layers. Therefore, the break observed in this work indicates that a transition analogous to the glass transition takes place in the side-chain region.

From the slope of the square root of the intensity—temperature plot we can estimate the thermal expansion coefficient of the side-chain region, α_s. For this purpose we must know the densities of the main-chain region ρ_m and the side-chain region ρ_s. Assuming that the main-chain region is the sheet having a thickness of 3.70 A, including all backbone atoms, as illustrated in Figure 3, ρ_m and ρ_s are estimated to be 1.567 and 1.320, respectively, from the unit cell dimension. The slope for the (020) reflection gives values of $(\rho_s\alpha_s - \rho_m\alpha_m)/\Delta\rho_0$ of $27 \times 10^{-4}/^\circ C$ and $7 \times 10^{-4}/^\circ C$ above and below 20°C, respectively.

Table I shows the estimated values of the thermal expansion coefficient of the side-chain region; α_{1s} and α_{2s} refer to the ones above and below 20°C, respectively, on the assumption $\alpha_m = 0$. The table also indicates values obtained by the spacing measurements, which were corrected to give the thermal expansion coefficient of the side-chain region rather than of whole unit cell. Taking into account the approximate nature of the analysis made here, we feel that we have obtained a close agreement between values by the X-ray intensity and those by spacing measurements.

CONCLUSION

The spacing—temperature curve of the (100) and (020) reflections of solid PMDG in the β-form has a break point in the vicinity of 20°C, which is related to the onset of the side-chain motions. The temperature dependence of the (020) reflection intensity is interpreted in terms of the side-chain motions. The break point observed seems likely to be a transition analogous to the glass transition.

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