# Molecular motion in poly(amino acid)s:
# 6. Molecular motion in a β-form crystal of poly(γ-methyl-D-glutamate)

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The molecular motion in a β-form crystal of fully annealed poly(γ-methyl-D-glutamate) was investigated by means of an X-ray diffractometer and an infra-red spectrophotometer. The interchain periodicity (chains are bound side by side with intermolecular hydrogen bonds) increases linearly with increasing temperature, indicating ordinary thermal expansion of the lattice. The intersheet periodicty (sided chains pack into sheets) increases linearly up to 150°C and then the slope of the temperature dependence of the periodicty increases owing to the onset of active segmental motion of the side chains.

It is evident from the temperature dependence of the wavenumber of the maximum of the infra-red absorption for NH stretching in the crystal that thermal expansion in the direction of the hydrogen bond is hardly affected by the segmental motion of the side chain.

**Keywords** Poly(γ-methyl-D-glutamate); β-form crystal; hydrogen bond; molecular motion; spacing; NH stretching

## INTRODUCTION

Kajiyama *et al.*[1,2] studied the molecular motion in the α-form crystal of poly(γ-methyl-D-glutamate), PMDG, or poly(γ-methyl-L-glutamate), PMLG, and showed that the α-helical molecules with intramolecular hydrogen bonds started undergoing motion parallel to the molecular axis, i.e. intermolecular slip-motion, at about 140°C and accordion-motion in each helical molecule above 180°C with decreasing hydrogen bonding force.

The β-form crystal of poly(γ-methyl-D-glutamate), in which the molecules form a sheet by intermolecular hydrogen bonds, was prepared by Ichikawa *et al.*,[3] who obtained a drawn fibre containing 70% of the β-form. Kajiyama *et al.*[4] and Nakajima *et al.*[5] obtained a β-form rich film from a solution of PMDG in dichloroacetic acid and a solution of PMDG in trifluoroacetic acid, respectively. Matsushima *et al.*[6] used PMDG annealed at 160°C for 1 h, and observed the segmental motion of the long side chains in the β-form crystal above 20°C by X-ray measurements.

In previous papers[7,8], we found that there was another type of molecular motion different from the thermal molecular vibration in the β-form of poly(amino acid)s such as silk fibre and poly(L-alanine), having short side chains, above about 160°C. Below 160°C, the interchain and intersheet thermal expansions were anisotropic to each other.

In this paper, the molecular motion in the β-form crystal of fully annealed PMDG was investigated by means of an X-ray diffractometer and an infra-red spectrophotometer, and was briefly compared with the molecular motion in crystals of poly(amino acid)s reported in previous papers[7,8].

## EXPERIMENTAL

The β-form of PMDG was prepared by the procedure reported by Nakajima *et al.*[5] The film was obtained by casting from a solution of PMDG in trifluoroacetic acid on a glass plate and was then drawn up to twice its original length. The film in the β-form was prepared by allowing it to swell in formic acid at 50°C for two days and then drying it at 10°C for two days at atmospheric pressure. After drying *in vacuo* at 105°C for one day, in order to anneal the film it was gradually heated up to 180°C and held at this temperature for 1 h. This annealed condition represents a higher temperature and a longer time than that used by Matsushima *et al.*[6]

X-ray measurements were performed on a Rigaku Geigerflex 2028 diffractometer equipped with a scintillation counter and a pulse height analyser, using Cu Kα radiation. The temperature was controlled within an accuracy of ±0.5°C under $N_2$ gas flow.

Infra-red measurements were made on a Jasco A-302 infra-red spectrophotometer equipped with a heating device. The infra-red spectra were measured by the KBr tablets method.

## RESULTS AND DISCUSSION

*Figure 1* shows the infra-red spectrum. There are four absorption bands of the β-form of poly(amino acid) at 1630, 1530, 1260 and 700 $cm^{-1}$. According to Nakajima *et al.*[5] and Brown *et al.*,[9] the unit cell of PMLG was an orthogonal lattice with $a = 4.70$ Å, $b = 21.0$ Å and $c = 6.83$ Å (fibre axis), containing four residues. The spacings for the 100 and 020 reflections correspond to the interchain periodicity (chains are bound by intermolecular hydrogen

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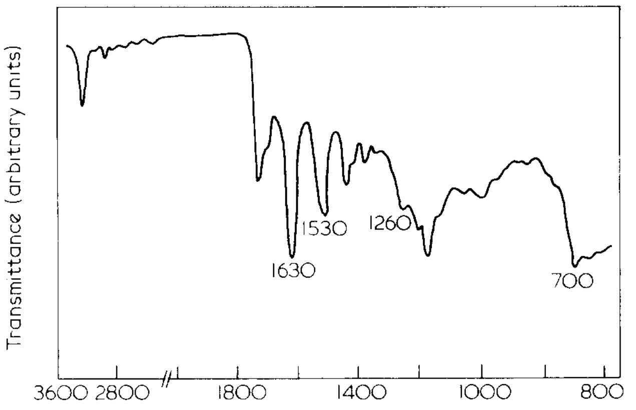

*Figure 1* Infra-red spectrum for the $\beta$-form crystal of PMDG

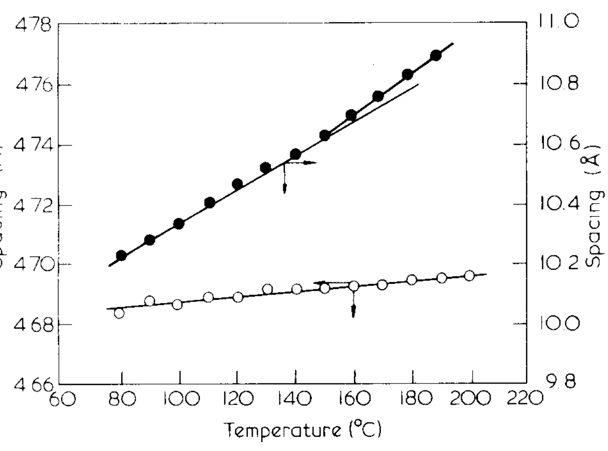

*Figure 2* Temperature dependence of the spacings of 100 and 020 reflections for the $\beta$-form crystal of PMDG: —○—, $d_{100}$; —●—, $d_{020}$

bonds) and the intersheet periodicity (the sided chains pack into sheets), respectively. To elucidate the molecular motion in the sheet and between sheets, the spacings of the 100 and 020 reflections were measured as a function of temperature (*Figure 2*). The spacing for the ⟨100⟩ direction expands linearly. This result indicates ordinary thermal expansion of the lattice. The slope of the temperature dependence of the spacing for the ⟨020⟩ direction increases slightly above 150°C. This increase of slope causes active segmental motion of the side chains independent of the main chain between the sheets above 150°C.

The linear thermal expansion coefficients ($\alpha$) were calculated from the slopes of the lines in *Figure 2*. The values are given in *Table 1* along with the results for PMDG reported by Matsushima *et al.*[6] The thermal expansion is found to be anisotropic. This result agrees with that for silk fibre[7] and poly(L-alanine),[8] and means that the intersheet force is weaker than the intermolecular hydrogen bonding force in the sheets. The $\alpha_{020}$ in this work is smaller than that given by Matsushima *et al.* This is due to the dense packing of side chains between the sheets, because $d_{020}$ decreases from 10.85 to 10.23 Å as shown in *Table 1*, and the dense packing indicates that segmental motion of the side chains was restricted even above 150°C. Consequently it is evident that thermal expansion in the direction of the hydrogen bonds is hardly affected by segmental motion of the side chains, i.e. the $\alpha_{100}$ in this work is smaller than that of Matsushima *et al.*[6]

According to Aoki *et al.*[10] and Matsushima *et al.*[11], when the Laue function is insensitive to temperature, the temperature dependence of the relative intensity is written as

$$[I(T)/I(T_0)]^{1/2} = 1 + (T - T_0)(\alpha_1\rho_1 - \alpha_2\rho_2)/\Delta\rho \qquad (1)$$

where $\rho_1$ and $\rho_2$ are the densities of the two phases in a unit cell, composed of the main chain and the other atomic groups in the molecular sheets respectively, at a reference temperature ($T_0$). $\Delta\rho$ is the difference between the densities of the two phases. $\alpha_1$ and $\alpha_2$ are the thermal expansion coefficients in the two phases. *Figure 3* shows the relative intensity for the 100 and 020 reflections. The relative intensity for the 100 reflection increases linearly in the whole temperature region studied. This linear increase means a constant value of $(\alpha_1\rho_1 - \alpha_2\rho_2)/\Delta\rho$, and corresponds to linear thermal expansion in the ⟨100⟩ direction. The relative intensity for the 020 reflection is constant up to 150°C and then increases. The increase of the relative intensity above 150°C is due to the onset of active segmental motion of the side chains as described above.

*Figure 4* shows the wavenumber of the maximum infrared absorption due to NH stretching as a function of temperature. The wavenumber of the absorption band increases steadily between 80 and 195°C. According to Suzuki *et al.*,[12] the hydrogen atoms in the NH groups in the amorphous phase of PMDG are so easy to deuterate that the undeuterated NH groups are in the crystalline phase. Thus the above result means that the intermolecular hydrogen bonding force in the crystalline phase is

*Table 1* Thermal expansion coefficients and spacings for $\beta$-form crystal of PMDG

| | Thermal expansion coefficient, $\alpha$ (°C$^{-1}$) | | Spacing at 80°C (Å) | |
|---|---|---|---|---|
| | $\alpha_{100}$ | $\alpha_{020}$ | $d_{100}$ | $d_{020}$ |
| This work | $2.1 \times 10^{-5}$ | $5.3 \times 10^{-4}$ | 4.684 | 10.23 |
| Matsushima *et al.* | $5.2 \times 10^{-5}$ | $7.5 \times 10^{-4}$ | 4.686 | 10.85 |

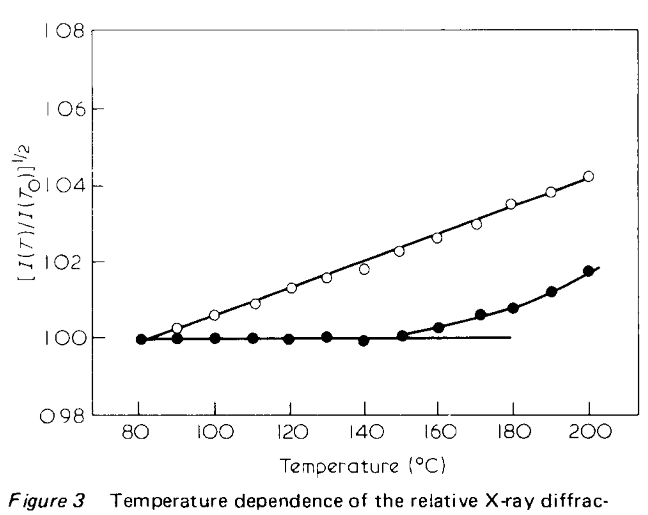

*Figure 3* Temperature dependence of the relative X-ray diffraction intensities of 100 and 020 reflections for the $\beta$-form crystal of PMDG: —○—, $[I(T)_{100}/I(T_0)_{100}]^{1/2}$; —●—, $[I(T)_{020}/I(T_0)_{020}]^{1/2}$

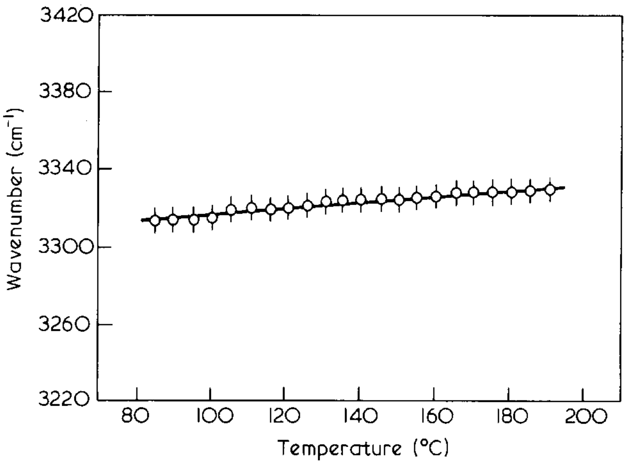

***Figure 4*** Temperature dependence of the wavenumber of the infra-red absorption band of NH stretching for the $\beta$-form crystal of PMDG

not seriously affected by the active segmental motion of the side chains above 150°C.

These results of the molecular motions for the PMDG are different from the cases of silk fibre[7] and poly(L-alanine),[8] and are explained as follows. PMDG is polymerized from only the D type of amino acid, while poly(L-alanine) is polymerized from only the L type of alanine. Thus both configurations of PMDG and poly(L-alanine) have ideally isotactic stereoregularity. As mentioned above, the PMDG was fully annealed, but the poly(L-alanine) was not annealed. Therefore the PMDG chain will fall into a stable and dense packing and vibrate only thermally in the crystal lattice; this is like the case of the highly syndiotactic stereoregularity of poly(vinyl alcohol) as discussed in a previous paper.[13] The poly(L-alanine) will contain much rough molecular packing in the crystalline phase and will move incoherently at high temperature. Silk fibre is constituted by many kinds of amino acids,[14] and the silk fibre used was not annealed. Thus it will have many defects and disordered parts in the crystalline phase, and consequently the silk fibre will also move incoherently at high temperature.

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