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# Thermotropic Polypeptides. 1. Investigation of Cholesteric Mesophase Properties of Poly($\gamma$-methyl D-glutamate-*co*-$\gamma$-hexyl D-glutamate)s

**J. Watanabe,* Y. Fukuda, R. Gehani, and I. Uematsu**

*Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152 Japan. Received April 15, 1983*

ABSTRACT: A series of poly($\gamma$-methyl D-glutamate-*co*-$\gamma$-hexyl D-glutamate)s were prepared with varying hexyl content by an ester exchange method from poly($\gamma$-methyl D-glutamate). Copolymers with intermediate hexyl contents from 30% to 70% indicated different structure and mechanical properties compared to those of the constituent homopolymers by X-ray and viscoelastic measurements. The most predominant property, induced newly in copolymers, is the formation of thermotropic liquid crystals reflecting visible light in the high-temperature range above around 150 °C. The cholesteric pitches were measured by circular dichroism as a function of temperature and hexyl content. The results confirmed the same cholesteric nature as that observed in the lyotropic cholesteric mesophases of polypeptides. The present liquid crystals were easily solidified on cooling, offering films with various colors.

## Introduction

Polymers, whose degree of molecular order either in solution or in melt is intermediate between the perfect long-range order found in crystals and the statistical disorder in liquids, are called lyotropic or thermotropic liquid crystalline polymers. Since these polymers are able to form partially ordered solutions or melts, they are expected to produce fibers with high degrees of molecular orientation and order,[1,2] giving superior mechanical strength, and films with properties useful for photoelectrics.[3] In addition to the development of materials based on this concept, biological implications of liquid crystallinity of many biopolymers and membranes are also attracting a great deal of interest.[4]

Extensive studies have been conducted on lyotropic systems of natural[5,6] and synthetic polypeptides,[7–9] synthetic polymers such as polyamides[10,11] and polyisocyanates,[12,13] and cellulose derivatives.[14–16] More recently, thermotropic liquid crystalline polymers have been synthesized. The synthesis of these polymers can be achieved by using suitable mesogenic monomers, which are able to build up a liquid crystalline phase. There are two possible ways of obtaining the thermotropic polymers with liquid crystalline properties: (1) side-chain liquid crystalline polymers with mesogenic groups attached to a polymer backbone;[17–19] (2) main-chain liquid crystalline polymers with mesogenic groups incorporated into a polymer backbone.[20–28] In principle, thermotropic liquid crystals in these polymers could be achieved by decoupling the motions of the mesogenic units from the motions of polymer segments by introducing flexible spacers. Up to the present time, many types of liquid crystalline phases (smectic, nematic, and cholesteric phases) have been obtained, mainly depending on the nature of mesogenic unit.

The study of thermotropic liquid crystals has been directed to synthetic polypeptides. In their lyotropic liquid crystalline state,[7] the rigid $\alpha$-helix forces a parallel orientation of the chains, the chirality of main chain imports a twist to the parallel arrangement, and the solvent allows the mesogenic main chains to migrate and form the equilibrium cholesteric arrangement. By analogy with the above mentioned liquid crystalline polymers, the role of solvent would be replaced by the flexible long side chains. Thus, it is possible that thermotropic liquid crystals may be induced in the polypeptides with long flexible side chains. This approach, however, failed for homopolymers of hexyl glutamate and octyl glutamate.

Recently, it was found that the poly($\gamma$-benzyl L-glutamate-*co*-$\gamma$-methyl L-glutamate)s with intermediate benzyl contents showed different structures and properties

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Table I
Mechanical Transition Temperature and Maximum tan δ at Loss Peak

| copolymer | intrinsic viscosity, dL/g | β-transition | | α-transition | |
|---|---|---|---|---|---|
| | | temp, °C | tan δ at peak | temp, °C | tan δ at peak |
| H-0 | 0.95 | 0 | 0.06 | 185 | 0.12 |
| H-12 | 0.92 | 8 | 0.10 | 180 | 0.10 |
| H-33 | 0.92 | 16 | 0.15 | 125<br>180[a] | 0.26<br>~0.7 |
| H-50 | 0.90 | 8 | 0.21 | 110<br>165[a] | 0.45<br>~0.7 |
| H-58 | 0.89 | 6 | 0.22 | 100<br>150[a] | 0.34<br>~0.6 |
| H-71 | 0.92 | −2 | 0.23 | 75<br>130[a] | 0.41<br>~0.6 |
| H-90 | 0.85 | −23 | 0.30 | 105 | 0.06 |
| H-100 | 0.83 | −35 | 0.28 | 110 | 0.06 |

[a] Since these transitions showed broad loss peaks, the temperature corresponding to the minimum value of the modulus is regarded as the transition temperature.

from those of each homopolymer.[29-31] In further experiments with other copolyglutamates,[29] it was found by accident that the intermediate copolymers with two kinds of side chains fairly different in length form thermotropic liquid crystals in the temperature range above 150 °C.[32] In this paper, we confirm the formation of thermotropic cholesteric liquid crystals in copolypeptides of poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamate)s and describe their structural properties.

## Experimental Section

**Materials.** A series of poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamate) (PMHDG) samples with different hexyl contents were synthesized by ester exchange reaction[30,33] between poly(γ-methyl D-glutamate) (PMDG, $M_v$ = 100000) and hexyl alcohol. The reaction was carried out in 1,2-dichloroethane using *p*-toluenesulfonic acid as a catalyst at 60 °C. After conducting the reaction for over 12 h, the reaction mixture was poured into excess methanol. The copolymer separated as fibers. It was washed several times with water and methanol to remove reactants and dried. Copolymers of various hexyl contents were obtained by changing the PMDG to catalyst ratio, keeping other factors constant.

The copolymer composition was examined by high-resolution NMR spectroscopy in trifluoroacetic acid; the molar percent hexyl content in the PMHDG copolymers was determined by comparing areas of the signals from the terminal hexyl groups of hexyl ester residues with those from the methyl groups of methyl ester residues, in the side chains. The samples were designated by the letter H followed by the molar percent hexyl content. The intrinsic viscosities were obtained in solutions of dichloroacetic acid. As noted in column 2 of Table I, they ranged from 0.95 of PMDG to 0.83 of poly(γ-hexyl D-glutamate) (PHDG), offering the viscosity-average molecular weight of about 100000.[34]

The solid films for all measurements were prepared by casting the solutions in chloroform on a glass plate. After the solvent evaporated, films were immersed in methanol for 1 day in order to remove residual traces of solvent, and then dried in vacuo for several days.

**Measurements.** Wide-angle X-ray patterns were recorded with a flat-plate camera using a Rigaku Denki X-ray generator with Ni-filtered Cu Kα radiation. Reflection intensity profiles were measured from X-ray photographs by using a microphotometer. The samples for this experiment were sealed in a glass capillary tube and heated at the desired temperature by a heater which could be maintained to within ±1 °C. Dynamic mechanical measurements in the temperature range from −50 to 200 °C were made at a frequency of 110 Hz with a Rheovibron viscoelastometer Model DDV-II (Toyo Baldwin Co., Ltd.). Circular dichroic spectra were obtained by using a JASCO automatic recording spectropolarimeter Model J-20, in the wavelength range from 300 to 700 nm. IR spectra were measured with a JASCO model DS-701G spectrometer. Densities of films were determined by flotation in aqueous KBr solutions.

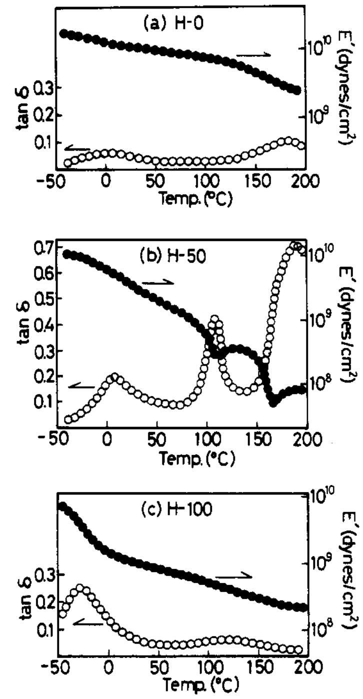

Figure 1. Temperature dependence of tan δ and $E'$ measured at 110 Hz: (a) H-0 (PMDG), (b) H-50, (c) H-100 (PHDG).

## Results and Discussion

### A. Variation of Mechanical Properties and Structure of Copolymers with Their Hexyl Content.

The transition temperatures for the entire series of copolymers were studied by using the viscoelastic measurements. In Figure 1a–c are shown viscoelastic data measured in the temperature range from −50 to 200 °C for H-0 (PMDG), H-50, and H-100 (PHDG), respectively.

The homopolymers generally show two loss peaks in this temperature range as observed for PMDG and PHDG in Figure 1a,c. A lower temperature peak is observed around room temperature and associated with the rotational motion of side chains. This motion has also been detected by broad-line NMR[35,36] and dielectric measurements.[37,38] PMDG and PHDG gave loss peaks at 0 and −35 °C, respectively. The higher temperature transition is due to the motion of the main chain, indicated by X-ray diffraction studies of oriented specimens.[39,40] In these X-ray studies, the layer line reflections disappeared in the temperature range where the loss peak was observed, the equatorial ones remaining sharp. As in poly(tetrafluoroethylene),[41] the main-chain motion could be assigned to the librational and translational motion with respect to the long axis of the chain, since it should offer no disorder for the lateral packing of chains projected on a plane perpendicular to their long axes. Mechanical loss peaks due to this motion were observed at 185 and 110 °C for PMDG and PHDG, respectively. Similar properties indicating two peaks were observed for copolymers H-12 and H-90.

On the other hand, the copolymers with intermediate contents showed three transitions as typically observed for H-50 as shown in Figure 1b. The transition around 8 °C can be attributed to side-chain motion, but two high-temperature transitions at 110 and 165 °C cannot be compared to those of the homopolymers. Their mechanical losses are remarkably larger than those of the homopolymers, and are also accompanied with the abrupt decrease in Young's modulus. For all specimens, transition temperatures at the loss peak maximum are summarized with loss peak

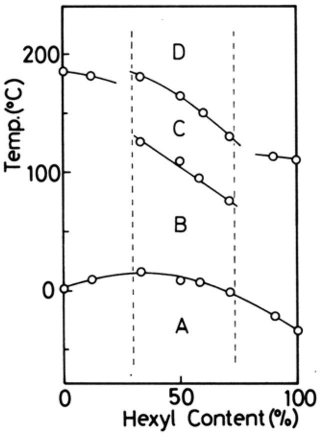

**Figure 2.** Variation of transition temperatures as a function of molar percent hexyl content. For copolymers with intermediate contents from 30% to 70%, four regions divided by three transitions are labeled A, B, C, and D in order of increasing temperature.

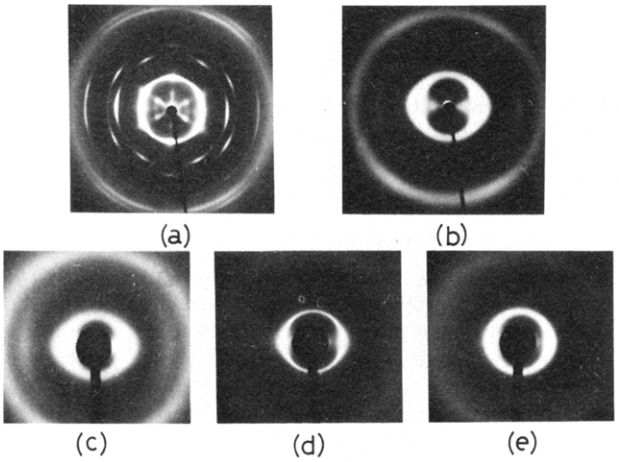

**Figure 3.** Wide-angle X-ray patterns: (a) H-90 at room temperature, (b) H-50 at room temperature, (c) H-50 at 75 °C, (d) H-50 at 130 °C, (e) H-50 at 170 °C. The sample to film distance was 10 cm for a and b and was 9 cm for the others.

heights in Table I and plotted against the hexyl content in Figure 2. These results indicate that a novel characteristic is induced for copolymers with hexyl contents ranging from 30% to 70%.

X-ray data also confirmed that there is an intermediate region of composition in which copolymers show different packing structure from those observed for the two homopolymers. Typical X-ray patterns are shown for H-90 and H-50 in parts a and b of Figure 3, respectively. As seen in Figure 3a, copolymers with hexyl contents below 30% and above 70% indicated a high crystallinity similar to PMDG and PHDG crystals in which α-helical molecules are packed in a hexagonal lattice with dimensions $a = b = 11.96$ Å and $c = 27$ Å, and $a = b = 15.5$ Å and $c = 27$ Å, respectively. In contrast, fairly poor patterns consisting of a few broad reflections were observed for the copolymers with intermediate hexyl contents (see Figure 3b). A packing difficulty for these copolymers can be understood to be caused by the statistical disorder in their side-chain structure. Over the entire range of composition the observed densities change almost linearly from 1.29 g/mL of PMDG to 1.05 g/mL of PHDG, but the spacings of first equatorial reflections fell on the two disconnected solid and dashed lines indicated in Figure 4. The densities require that the solid lines in the regions near homopolymers be attributed to hexagonal packing of α-helices, while the α-helices in copolymers with intermediate contents assume a tetragonal packing as represented by the dashed line. The structural change from hexagonal to tetragonal packing seems to be abrupt around 70% and 30% hexyl contents. The copolymerization, thus, affects not only the crystallinity but also the type of molecular packing.

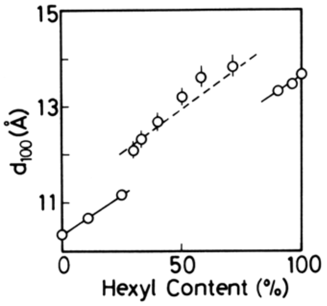

**Figure 4.** Variation of spacing of the first equatorial reflection ($d_{100}$) as a function of molar percent hexyl content. The solid and dashed lines indicate the variation of spacings expected when the α-helices are packed into hexagonal and tetragonal packings, respectively.

Such dissimilarity in property and structure between homopolymers and intermediate copolymers has been also observed for poly(γ-benzyl L-glutamate-*co*-γ-methyl L-glutamate)s[30,31] and other copoly(γ-*n*-alkyl L-glutamate)s[29] and will be discussed in detail in another article. Here, we confine the discussion to the thermotropic liquid crystals induced in PMHDG with intermediate hexyl contents.

**B. Mechanical Properties and Structure of Intermediate Copolymers.** The three mechanical transitions observed in copolymers with intermediate contents are conveniently indexed $\beta$, $\alpha_1$, and $\alpha_2$ in the order of increasing temperature. As shown in Figure 2, the β-transition temperature becomes maximum around 30% hexyl content so that, interestingly, copolymers show a higher β-transition temperature than that of each homopolymer, which was also observed in other copolymeric systems.[29] The other two transition temperatures, $\alpha_1$ and $\alpha_2$, decreased with the increase of hexyl content. Three smooth lines joining each transition temperature divide the temperature range from −50 to 200 °C into four regions, A, B, C, and D, as illustrated in Figure 2.

IR spectra over the temperature range from 20 to 180 °C have shown no significant change in wavelength and no abrupt decrease of relative intensity with respect to amides A (N–H stretching mode) and V (out of peptide plane mode) characteristic of α-helical conformation. Accordingly, it seems to be unlikely that the stabilization of α-helices is lowered by copolymerization. In region A below the β-transition temperature, the side chains are in a glassy state and probably only the local motion of methyl groups at the end of side chains may be allowed.[35,42] At the β-transition temperature, the entire side chains attain a rotational motion activated at a frequency of 110 Hz. On further elevation of temperature, the side chains have greater amplitude of motion and, at the same time, some extent of librational and translational motions are induced in the main chains as mentioned above. The existence of two regions of C and D, unlike in homopolymers, strongly suggests that there are two kinds of motion with respect to α-helical main chains.

The average Young's moduli observed in the four regions are cited and compared with those of several kinds of homopolymers in Table II. In region A, similar values on the order of $10^{10}$ dyn/cm$^2$ can be seen for all specimens. The values in region B depend on the side-chain length

Table II
Young's Moduli (dyn/cm$^2$) for Homopolymers with Various Side Chains and Copolymers of H-33, H-50, and H-58

| | region A | region B | region C | region D |
|---|---|---|---|---|
| poly($\gamma$-methyl glutamate) | $3 \times 10^{10}$ | $9 \times 10^{9}$ | $2 \times 10^{9}$ | |
| poly($\gamma$-propyl glutamate) | $2 \times 10^{10}$ | $6 \times 10^{9}$ | $8 \times 10^{8}$ | |
| poly($\gamma$-hexyl glutamate) | $1 \times 10^{10}$ | $8 \times 10^{8}$ | $3 \times 10^{8}$ | |
| poly($\gamma$-benzyl glutamate) | $2 \times 10^{10}$ | $\sim 1 \times 10^{9}$ | $\sim 1 \times 10^{9}$ | |
| H-33 | $2 \times 10^{10}$ | $\sim 2 \times 10^{9}$ | $3 \times 10^{8}$ | $5 \times 10^{7}$ |
| H-50 | $2 \times 10^{10}$ | $\sim 2 \times 10^{9}$ | $3 \times 10^{8}$ | $5 \times 10^{7}$ |
| H-58 | $2 \times 10^{10}$ | $\sim 2 \times 10^{9}$ | $2.5 \times 10^{8}$ | $5 \times 10^{7}$ |

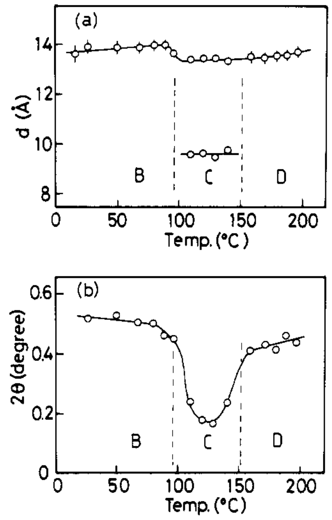

**Figure 5.** Temperature dependence of (a) spacings of the equatorial reflections and (b) integral width of 100 reflection for H-50.

and the kind of side chain; an increasing length of the side chain decreases the modulus and a bulkiness of the side chain increases it. This is reasonable because the $\beta$-transition is due to the side-chain motion. The Young's moduli in regions C and D of the copolymers are on the order of $10^8$ and $10^7$ dyn/cm$^2$, respectively. The values in region D are fairly lower than the values observed finally in homopolymers, while those in region C are comparable. It is evident that a new type of molecular motion of $\alpha$-helices has been induced in region D of the copolymers.

In Figure 5 is shown the temperature dependence of spacing and integral width of the equatorial reflections for H-50 over three regions of B, C, and D. This figure also indicates that there is an appreciable change in the packing structure from one region to another. Typical photographs for the B, C, and D regions, taken at 75, 130, and 170 °C, are shown in Figure 3, parts c, d, and e, respectively. As found in these figures, the poor pattern for region B was transformed in region C to a pattern with three sharp equatorial reflections. These reflections with spacings of 13.1, 9.25, and 6.54 Å, can be well explained by a tetragonal packing. Such an improvement in the lateral packing may be generated by the averaging of packing disorder as a result of the librational and translational motion of the main chain along its long axis.[39,43] In region D, the pattern becomes poor again, leaving a few broad reflections. In this case, the dynamic disorder is likely to be in contrast to the statistical disorder in regions A and B. The motion of the $\alpha$-helical main chain, to give rise to this kind of disorder in lateral packing, should be of a type containing some extent of librational and translational motion around the short axis as well as around the long axis, so that the material may be in a liquid crystalline state.

**C. Thermotropic Liquid Crystals in Region D.** In region D, as suggested from the low modulus on the order of $10^7$ dyn/cm$^2$, the specimens flow between glass plates under the slight stress. The thin samples of H-50 and H-58 thus spread between glass showed iridescent colors changing from blue to red, depending on the applied temperatures. Circular dichroism (CD) was measured for bright blue H-50 at 173 °C as presented by a dashed curve in Figure 6. The large CD band around 430 nm indicates that the color is due to selective reflection of circularly polarized light, which is a unique characteristic of a cholesteric helical structure.[44,45] The CD effect, together with the flowing of the specimen, thus confirms that a thermotropic liquid crystal has formed in region D.

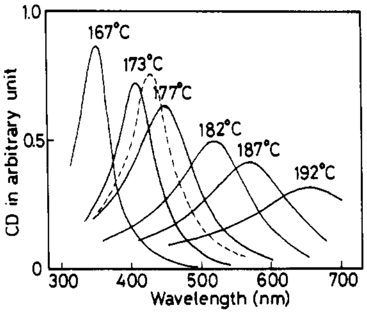

**Figure 6.** Circular dichroism (CD) of H-50 specimens. Dashed CD curve was measured at 173 °C, while solid curves were obtained for films quenched after being heated for 2 h at the temperature noted above each curve.

Since the positive CD band indicates that the left circularly polarized light was reflected, the sense of the cholesteric helix is left handed for the D molecule.[46,47] Naturally, the L molecule showed CD with the opposite sign. The pitch, $P$, of the cholesteric helical structure can be estimated from the equation $\lambda_m = nP \sin \theta$,[44] where $\lambda_m$ is the wavelength corresponding to maximum reflectivity, $n$ the average refractive index (approximately 1.4 for these copolymers[48]), and $\theta$ the angle between the incident light and the cholesteric plane. Rigid $\alpha$-helical chains tend to lie parallel to the film surface with the decreasing sample thickness.[49] In sufficiently thin films, accordingly, a cholesteric helical structure can be formed with its helical axis perpendicular to the film surface. The CD measurements reported here were performed for samples with a thickness around 10 $\mu$m and the pitches were estimated below by using $\lambda_m = nP$ with $\theta = 90°$.

In the present system with rigid $\alpha$-helices embedded in a matrix (sea) of side chains, high viscosity is presumed for the liquid crystalline phase, creating difficulty in reorganizing the chains from a parallel arrangement in the crystal to a twisted one in the cholesteric liquid crystal. Figure 7 shows the heating-time dependence of the peak height and half-width in the CD curves of H-50 measured at 180 °C. The increase of height and the decrease of width correspond to an increase in the ratio of liquid crystalline phase to crystalline phase and a narrowing of the distribution of pitch, respectively.[45] Initially, both parameters change remarkably with time and then level off after around 2 h. These results indicate that heat treatment for at least 2 h is necessary for the complete formation of cholesteric liquid crystals. This time period

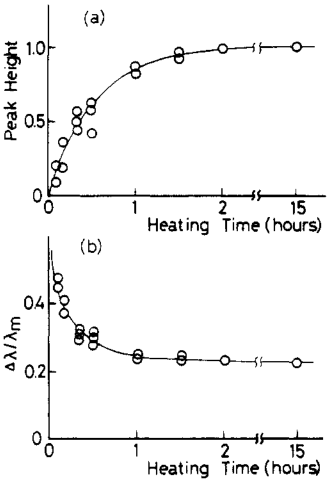

**Figure 7.** Heating-time dependence of (a) peak height and (b) half-width of CD curves measured at 180 °C for H-50.

is extremely long in comparison with less than a few minutes required in thermotropic main-chain polymers based on 4,4′-dihydroxybiphenyl.[50]

The high viscosity of the liquid crystalline phase also suggests that the cholesteric structure would be retained in the solid film on cooling. In fact, the films with various colors could be easily prepared by quenching the liquid crystals. In Figure 6, the circular dichroism of the colored film quenched from 173 °C is compared with that (dashed curve) measured at that temperature. The pitch slightly decreased on quenching, but no other significant change was observed. Here, it should be emphasized that the colored specimens are no more in the liquid crystalline state below the $\alpha_2$ transition temperature. In this temperature range from 20 to 150 °C for H-50, no distinct color change was observed, even when the temperature was changed very slowly. The change of $\lambda_m$, reversibly observed on heating and cooling, was less than 5%. This change can be accounted for only by the thermal expansion (or shrinkage) of molecular distance, the coefficient of which was estimated as $3.2 \times 10^{-4}$ °C$^{-1}$ from the temperature dependence of specific volume.

Hereafter, the temperature dependence of pitch in the liquid crystalline state was examined for films which were quenched to room temperature after being heated for 2 h in region D under an atmosphere of nitrogen. This method is very useful because the decomposition, which might occur in the heated specimen during measurements, can be avoided. However, one must take into account that the actual pitch in a liquid crystal is larger by about 5% than that of quenched film as mentioned above. The heating-temperature dependence of CD for quenched H-50 films is shown in Figure 6. $\lambda_m$ changed through the entire range of visible wavelengths from blue to red in a temperature interval of 30 °C. The change of $\lambda_m$ (i.e., pitch) is obviously attributed to that of the twist angle between layers, since all the quenched films have the same planar distance between chains and accordingly the same layer thickness. The twist angles were estimated to range from 1° to 2°, with the assumption that the layer thickness may correspond to the spacing of the 100 reflection of the tetragonal lattice (13.2 Å for H-50 and 13.6 Å for H-58). In Figure 8, the reciprocals of the pitiches are plotted against heating temperature for H-50 and H-58. A clear trend can be seen such that the reciprocal of the pitch decreases linearly with increasing temperature. Furthermore, the comparison of data for H-50 and H-58 leads to a second conclusion that the pitch increases with increase of the hexyl content. The other copolymers of H-33 and H-71 also flowed in region D, but they indicated no color. Probably, the pitches for these specimens may be beyond the region of visible wavelengths.

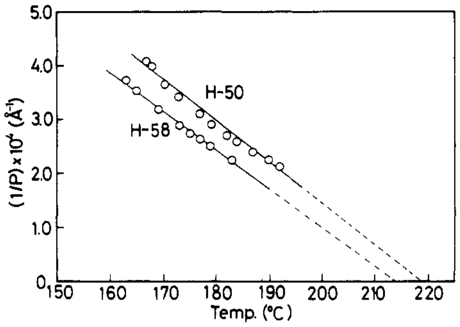

**Figure 8.** Heating temperature dependence of the reciprocal of the cholesteric pitch for quenched films of H-50 and H-58.

It should be noticed that the transition to cholesteric liquid crystals was also detected by the measurement of DSC and specific volume. Both data indicated that the transition is approximately first order. The markedly small values, about 0.04 cal/(residue·°C) and 0.005 mL/g, were estimated for the changes of entropy and specific volume, respectively. This may be reasonable since no conformational change of the main chain has taken place during the transition.

**D. Similarity in Liquid Crystalline Behavior between Thermotropic and Lyotropic Liquid Crystals.** Di Marzio[51] pointed out that solvent molecules in lyotropic liquid crystalline systems could be replaced by flexible segments. This idea seems to be consistent with that of de Gennes[52] in which the polymers exhibiting thermotropic mesophase might be prepared by incorporating a rigid and a flexible segment in the repeating unit. Many thermotropic liquid crystalline main-chain polymers,[21-28] based on these ideas, have been produced after the first example of polyesters by Roviello and Sirigu.[20]

In the same way, it is likely that the thermotropic liquid crystals of polypeptides may be attained by attaching long flexible side chains to the rigid $\alpha$-helical main chains. However, homopolymers with simply long side chains have never thus far exhibited thermotropic liquid crystals, as already mentioned. On the other hand, our previous experience[29] has also indicated that the copolyglutamates consisting of methyl and ethyl ester residues and those consisting of methyl and butyl ester residues afforded no liquid crystals. Thus, an appreciable difference in length of the side chain, probably a difference of 5 or more methylene units, is necessary for thermotropic liquid crystals of copolymers. This assumes that the longer side chain sticking out of the region of shorter side chains may play the role of a solvent in the lyotropic liquid crystals. Under this assumption, we can point out some similarities in the structural properties between thermotropic and lyotropic liquid crystals.

For lyotropic liquid crystals of polypeptides,[8] the relationship between twisting power expressed by the reciprocal of half-pitch ($2/P$) and temperature has been experimentally determined to be

$$2/P = A(1 - T/T_n)$$

where $A$ is a proportionality factor and $T_n$ is the absolute nematic temperature. The inversion of cholesteric sense at $T_n$ is a typical phenomenon for lyotropic systems.[8,9] The data of Figure 8 can also be described by this equation since $1/P$ decreases linearly with temperature, although the inversion of sense was not observed in the present temperature range. The concentration dependence of the twisting power, on the other hand, was theoretically treated by Kimura et al.,[53] in which the factor $A$ of the equation was shown to be a function which increased with polymer concentration. For lyotropic systems having polymer concentration around 20%, the values of $A$ have ranged from $3.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ Å$^{-1}$ depending on solvent,[8,53] while liquid crystals of H-50 and H-58 exhibited fairly large values of $7.4 \times 10^{-3}$ and $7.1 \times 10^{-3}$ Å$^{-1}$, respectively. If the hexyl residues sticking out of side-chain region of methyl residues are regarded as solvents, the present liquid crystal corresponds to a higher polymer concentration of around 80%. The large values of $A$ are thus qualitatively consistent with the theoretical predication. Comparison of H-50 and H-58 further indicates that the pitch varies inversely with the hypothetical concentration. This trend is also consistent with that observed experimentally for lyotropic systems.[8]

## Concluding Remarks

The poly($\gamma$-methyl D-glutamate-*co*-$\gamma$-hexyl D-glutamate)s with intermediate hexyl contents from 30% to 70% exhibited thermotropic cholesteric liquid crystals. The transition temperatures to the liquid crystalline phase, ranging from 130 to 180 °C, decreased with increasing hexyl content. It should be noticed that no transition to the isotropic phase was observed up to the temperature of decomposition (around 250 °C). The cholesteric pitch increased with increasing temperature and hexyl content. This cholesteric nature can be explained in the same manner as in lyotropic liquid crystals, if the terminal alkyl chains in longer side chains of hexyl residues are regarded as solvents. These polymers having mesogenic rods surrounded by the flexible side chains, together with the cellulose derivatives,[54] should be classified to a third type of thermotropic liquid crystalline polymer.

This study suggests the possibility of varying the properties of liquid crystals by controlling the kind of side chains; the combination of two side chains with remarkably different length may offer a low transition temperature to the liquid crystalline phase, and the attachment of long flexible side chains may produce a low viscosity to facilitate the development of cholesteric structure. Studies on this point are now in progress.

The liquid crystals reported here have such a high viscosity that the cholesteric structure is easily preserved in the solid films by quenching—the cholesteric colors of films have remained unchanged for periods of up to 1 year. This ability to conserve the structure of the cholesteric mesophase is a significant step in the preparation of composite materials having a biaxial orientation of chains as proposed by Krigbaum et al.[55] In addition, preparation of polymeric films of the various colors without need for added dyes suggests industrial utilizations for these novel materials.

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