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Thermotropic Cholesteric Mesophases in Copoly(γ-*n*-Alkyl L-Glutamate)s

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SUMMARY

Thermotropic cholesteric mesophases were found for three types of α-helical copoly(γ-*n*-alkyl L-glutamate)s; the combination of the *n*-alkyl groups was methyl–hexyl, methyl–octyl, and propyl–octyl. Cholesteric colors due to the selective reflection were observed in the temperature range from 110 to 190°C for the films with copolymer compositions of about 50/50 in mol%. These thermotropically mesomorphic copolymers had disordered structures in the molecular packing as inferred from the x-ray diffraction patterns. The cholesteric sense was right-handed, since the negative circular dichroism associated with the cholesteric pitch was observed for all the mesomorphic films. The temperature dependence of the pitch was discussed in comparison with that of lyotropic liquid crystals of these polymers.

INTRODUCTION

Structures of solid polypeptides are generally ordered in the two-dimensional packing of α-helical chains, but somewhat disordered with respect to the rotation about the helical axis and the translation along the axis. Such a structure may be a nematic mesophase due to static disorder, but not the liquid crystalline state like low molecular weight liquid crystals.

Studies on thermotropically mesomorphic polymers which exhibit liquid crystalline state by virtue of dynamic chain mobility have remarkably increased recently. They have usually been classified into two categories. One is comb-like polymers which have mesogenic side chains attached to the main chain (FINKELMANN et al. 1978). The other type of polymer has rigid mesogenic units in the main chain, for example, copolyesters (JACKSON and KUHFUSS 1976, KRIGBAUM et al. 1980, LENZ and JIN 1981, OBER et al. 1982), polyisocyanate (AHARONI 1979), hydroxypropylcellulose (SHIMAMURA et al. 1981), acetoxypropylcellulose (TSENG et al. 1980), azoxy and azo type polyesters (IIMURA et al. 1981), and so on.

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The α-helical polypeptides such as poly(γ-benzyl L-glutamate) have been shown to form lyotropic cholesteric (Ch) liquid crystals in concentrated solutions (ROBINSON 1961, 1966, DUPRE and SAMULSKI 1979, TORIUMI et al. 1980). Such a twisted structure has often remained as a static mesophase in the solid film (WATANABE et al. 1977). However, thermotropic Ch mesophase has not been found so far for polypeptides. DiMarzio (1960) pointed out in his calculation that solvent molecules in lyotropic systems could be replaced by flexible polymers. This may be achieved by attaching long side chains to the α-helical main chain. For this purpose, we synthesized a series of copoly(γ-*n*-alkyl L-glutamate)s having long side chains, and examined the thermotropic liquid crystalline behavior.

EXPERIMENTAL

Three types of copoly(γ-*n*-alkyl L-glutamate)s with the combination of methyl(M)–hexyl(H), methyl–octyl(O), and propyl(P)–octyl were prepared by alcoholysis of poly(γ-methyl L-glutamate) (Ajicoat A-2000, Ajinomoto Co. Inc., Jpn., molecular weight = 117,000) in ethylene dichloride using *p*-toluenesulfonic acid as the catalyst at 60°C. The copolymers were recovered by precipitating with methanol and dried *in vacuo*. The copolymer composition was determined from the NMR spectra, some of which are shown in Fig. 1. In the sample notation, for example, of methyl–hexyl copolymers (MH series), the number following to MH denotes the mol% of the longer side chain, that is, the hexyl residue content. The determination of composition by the NMR spectra was verified from the reasonable relation between the composition and the density which was measured by the flotation method in aqueous KBr solution at 25°C (Fig. 2).

Thin solid films were prepared by casting the solution in either chloroform, ethylene dichloride, or DMF. The thermotropic mesophase was detected initially by the iridescent Ch color which appeared by clipping these films between two glass plates and annealing at 110–190°C. The circular dichroism (CD) due to the selective reflection was measured at room temperature in the quenched state for these films with a Jasco J-20 spectropolarimeter. Since the CD spectra were not changed by the rotation of the film in its plane, the effect of the birefringence might be insignificant. The optical rotatory dispersion (ORD) was measured by a Shimazu QV-50 spectrometer at various wavelengths.

The molecular conformation was the right-handed α-helix in all the copolymer films, as judged from the ORD spectra and the characteristic amide frequencies in the infrared absorption (for example, see FRASER and MACRAE 1973).

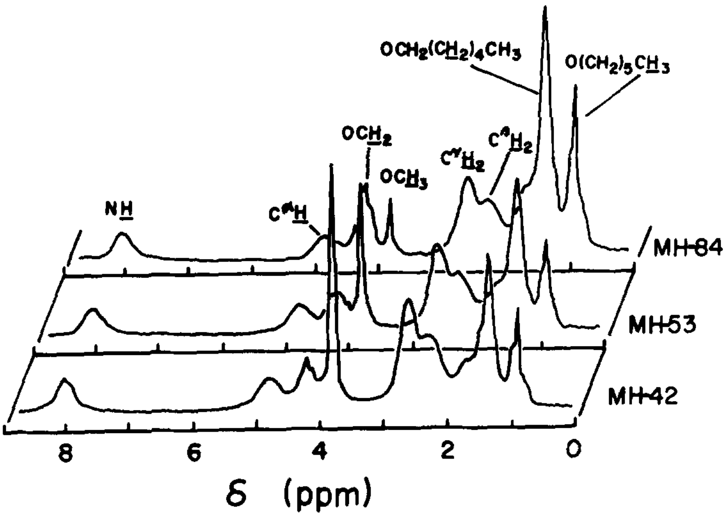

Fig. 1. NMR spectra of copoly(methyl, hexyl L-glutamate)s with hexyl residue content of 42, 53, and 84 mol%.

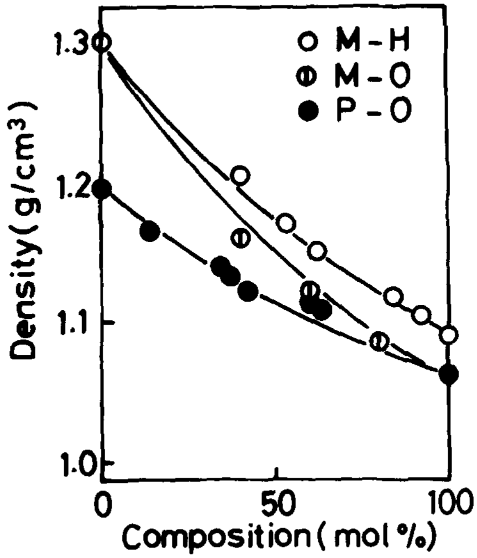

Fig. 2. Plots of density of MH, MO, and PO copolymers. Composition denotes the mol% content of the residue with the longer side chain.

RESULTS AND DISCUSSION

Only the films of MH, MO, and PO series with the copolymer composition of about 50/50 in mol% showed the iridescent Ch colors when they were annealed at suitable temperatures. The color was considered to be due to the selective reflection from the Ch twisted structure (DE VRIES 1951, ROBINSON 1961, 1966).

Fig. 3 shows ORD and CD spectra measured for the MH-53 film annealed at 166°C, which reflected a blue color. This optical property is characteristic of the right-handed twisted structure. All the other colored films exhibited also the negative CD band. The peak position, λ_m, of the CD band is plotted vs. the annealing temperature in Fig. 4.

The range of the annealing temperature to produce the Ch color is limited within an interval of about 30°C for each sample, and it is lower for the copolymer which has the larger amount of long side chains and therefore the lower density (Fig. 2). This fact suggests that chain mobility has something to do with the formation of the mesophase.

By annealing, the samples were spread up to a thickness of about 0.05 mm between glass plates as they had melted. No latent heat, however, was observed by differential scanning calorimetry. Therefore, the system may become gradually into the liquid crystalline state in which the α-helical chains assume the dynamic mobility. The λ_m position was independent of the type of casting solvent. For the initial 1 h in the annealing process, the CD band shifted toward long wavelength and became sharp. The annealing time of 2 h was generally enough for the equilibrium. The λ_m position was reversible with regard to the change of the annealing temperature, although it required about 2 h for the complete reversibility. This is the reason why the CD spectra could be measured at room temperature for the annealed films. Sharpening of the CD band in the annealing process may correspond to the ordering in the Ch pitches. The red shift of λ_m implies that the Ch helical axis tends to be perpendicular to the film surface. The λ_m is generally given by

$$\lambda_m = 2\ n\ s\ \sin\theta \qquad (1)$$

where n is the refractive index, s is half the pitch corresponding to the spacing between retardation lines as observed for lyotropic Ch liquid crystals, and θ is the angle which the incident light makes with the molecular layers of the Ch structure.

For sufficiently annealed films, the angle θ may be assumed to be equal to 90° from the fact of the red shift of λ_m. This type of orientation has been also approved for thin specimens of polypeptide liquid

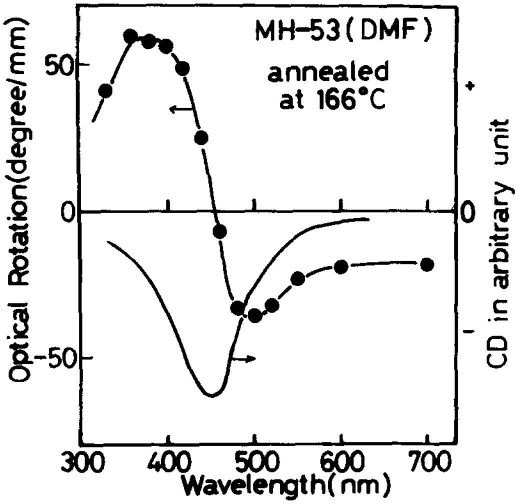

Fig. 3. ORD and CD spectra of a MH-53 film annealed at 166°C.

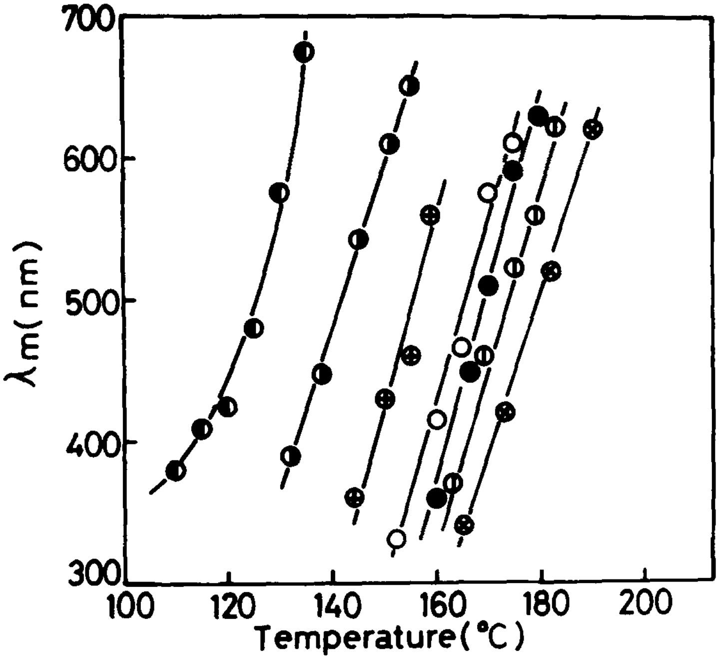

Fig. 4. Plots of λ_m vs. temperature.
◐: MO-80, ◑: PO-63, ⊕: PO-60, o: MO-60,
⦶: MH-58, ●: MH-53, ⊗: MH-50.

crystals. By assuming n = 1.47 (WATANABE et al. 1977) and θ = 90°, values of $1/S$ (proportional to the twist angle) were calculated from λ_m, and are plotted in Fig. 5. For lyotropic liquid crystals of polypeptides, the relation between $1/S$ and temperature has been experimentally obtained as

$$\frac{1}{S} = b\ (1 - \frac{T}{T_N}) \qquad (2)$$

where b is a proportional factor and T_N is the nematic temperature. For lyotropic systems, the inversion of the Ch sense with increasing temperature has been observed (TORIUMI et al. 1979). For the present thermotropic system, the twisting power $1/S$ could be described by equation (2) as shown in Fig. 5, but the sense inversion was not observed. At such high temperatures, the structure may approach the nematic structure owing to the translational and librational motion of the α-helical chains.

Recently, the concentration dependence of the twisting power was theoretically treated by KIMURA et al. (1982), in which the factor b in equation (2) was shown to be a function which increases with the concentration. The b values have been determined to be about 1 μm^{-1} for lyotropic liquid crystals of polypeptides, while it is 60–80 for the present thermotropic system. Since the side chains are considered to play a role as solvent

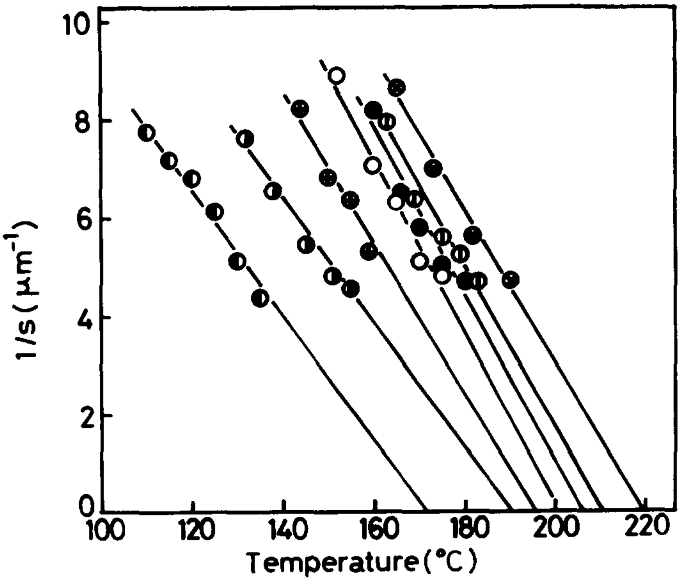

Fig. 5. Plots of $1/S$ vs. temperature. Symbols are the same as in Fig. 4.

molecules, the thermotropic systems may correspond to the highly concentrated solution. The large *b* values are thus qualitatively consistent with the theoretical prediction.

The crystallinity of the mesomorphic copolymers was extremely low as judged from the x-ray diffaction pattern, in which only one broad reflection was observed. The spacing of such an intensity maximum corresponds to the distance between neighboring molecular layers. The expected values of the spacing can be easily calculated from the density and the average molecular weight of the copolymer residues, as ROBINSON (1961) made for lyotropic liquid crystals of polypeptides. If the molecular packing is hexagonal, the spacing will fall on the H line in Fig. 6 in the case of MH copolymers, and if tetragonal, onto the T line. The methyl and the hexyl homopolymers take the well-defined hexagonal packing (SASAKI et al. 1979). The spacings observed for the mesomorphic copolymers were found to be plotted above those lines. Such abnormal spacings, however, decreased thermoreversibly to the value of the tetragonal case by increasing temperature up to the range of the mesophase formation. Therefore, the molecular packing in the mesophase at higher temperature is tetragonal, although it is not clear at room temperature.

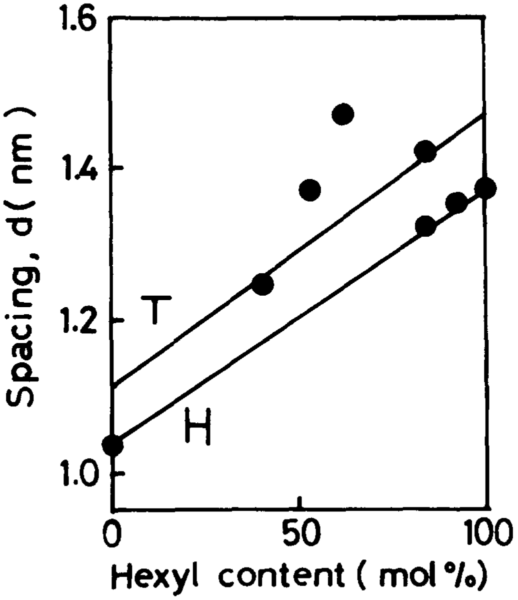

Fig. 6. Plot of x-ray reflection spacings for MH series copolymers. See text.

Similar behavior was observed for MO and PO series in the dependence of x-ray reflection spacings upon the copolymer composition and temperature. The low crystallinity of the mesomorphic copolymers may be an essential point with regard to the chain mobility.

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