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A novel transition in the lyotropic cholesteric mesophase induced by the helix sense inversion of α-helical poly(β-phenethyl L-aspartate)

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Poly(β-phenethyl L-aspartate) was found to exhibit a thermally-induced helix–helix transition between the low temperature (right-handed) and the high temperature (left-handed) forms in the lyotropic cholesteric solution. The transition takes place sharply and reversibly at around 90°C, the birefringent character of the cholesteric mesophase being maintained throughout the transition range. The cholesteric helical sense, as well as the cholesteric pitch, were determined as a function of temperature. The results suggest that the inversion of the α-helical screw sense triggers a reversal of the cholesteric macro-helix.

Poly(aspartic acid ester)s are known to form an α-helix in either a right- or left-handed screw sense depending on the chemical constitution of the side chain group [1–5]. The stability of these helices varies with the solvent as well as temperature. Sasaki *et al.* [2], have reported that the right-handed α-helix of poly(β-phenethyl L-aspartate) (PPLA) transforms into a left-handed form in a solid film at elevated temperatures (130–140°C). Such a transition in the solid film was found to occur irreversibly. Toriumi *et al.* [3], also observed a helix–helix transition from right-handed to left-handed in dilute chloroform solution by addition of a small amount of dichloroacetic acid.

In our recent studies [5], PPLA was found to transform from the right-handed to the left-handed α-helix in tetrachloroethane with increase in temperature. The transition takes place in the isotropic dilute solution as well as in the liquid crystalline state at around 90°C. In this communication, we wish to present some further evidence of the helix sense inversion, with emphasis on the associated transition in the cholesteric structure.

PPLA was prepared by a standard *N*-carboxy L-amino acid anhydride (NCA) method using triethylamine as an initiator in chloroform. The intrinsic viscosity in dichloroacetic acid was determined at 25°C: $[\eta] = 0{\cdot}5\,\mathrm{dL/g}$. Differential scanning calorimetric (DSC) measurements were carried out with a Perkin–Elmer DSC Model II. Circular dichroism (CD) spectra and optical rotatory dispersion (ORD) curves were recorded with a Jasco J-20 spectrometer. The cholesteric microscopic texture was observed by using an Olympus polarizing microscope. In the CD, ORD and optical microscopic measurements, temperatures were regulated by using a Mettler FP 82 hot stage.

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[DSC]—A cholesteric liquid crystalline solution was prepared by dissolving PPLA in tetrachloroethane, the concentration being 24 wt%. Figure 1 shows the DSC heating and cooling curves which were recorded at a scanning rate of 10°C min^{-1}. The transition was first order and reversibly observed on heating and cooling cycles. The transition takes place at around 90°C, although some supercooling occurs on cooling. For a solid film, the corresponding transition was observed at 130°C, as has been previously reported [4]. An isotropic solution containing 10 wt.% of PPLA also exhibited a broad transition peak at around 90°C on the DSC thermograms. The enthalpy change (ΔH) measured was about 1·7 kJ mol^{-1} per repeat unit of PPLA for the liquid crystalline solution as well as for the solid film.

[CD and ORD]—Circular dichroism studies should provide direct evidence for the helix–helix transition under consideration. Shown in figure 2 are the spectra taken at temperatures below and above the DSC transition. The CD spectrum for the n–π^* absorption (around 225 nm) changes its sign from negative to positive at this transition temperature. The profiles of the curve resemble each other, although the signs are opposite. These observations indicate that the right-handed α-helix transforms to the left-handed on heating. Essentially, the same behaviour was detected for a solid film and an isotropic solution. In the latter system, the transition has also been confirmed by the ORD method where the sign of the b_0 value of the Moffit–Yang plot has been adopted as a measure of the screw sense of α-helices [5].

[Optical microscopy]—Under optical microscopy, the birefringent cholesteric texture, with characteristic striation lines, can invariably be observed in the temperature range from 10°C to 93°C. The cholesteric pitches (P) were obtained by measuring the spacing between striation lines, which corresponds to half a pitch. In figure 3 the pitches thus obtained are plotted against temperature. Initially, the pitch increases with temperature and diverges first at around $T_n = 25$°C. Then the value of P decreases monotonically up to 85°C. Over a narrow temperature span from 85°C to 89°C, the pitch again increases somewhat and decreases after the second divergence at $T_n = 89$°C. Accordingly, the temperature dependence of the pitch exhibits certain characteristics in each of the three regions—regions I ($T < 25$°C), II ($25°\mathrm{C} < T < 89°\mathrm{C}$) and III ($T > 89$°C)—separated by two T_ns. This somewhat unusual behaviour was observed reversibly on heating and cooling cycles. At temperatures above 93°C, the pitch lines become practically indistinguishable by optical microscopic observation.

To ascertain the helical sense of the cholesterics, the optical rotation (Θ) was measured as a function of wavelength (λ). Here, the measurement was performed for the cholesterics with the polygonal domain texture to eliminate the effect of birefringence

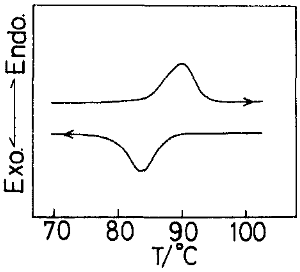

Figure 1. DSC thermograms obtained from a cholesteric liquid crystalline solution at a concentration of 24 wt%.

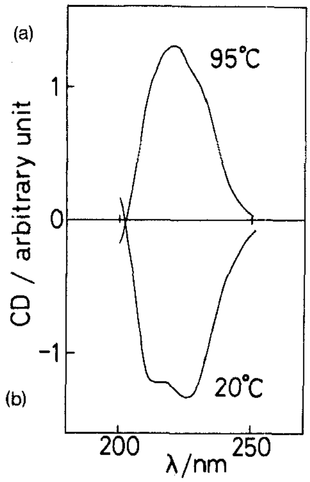

Figure 2. CD spectra observed for a cholesteric solution: (*a*) at 95°C; (*b*) at 20°C.

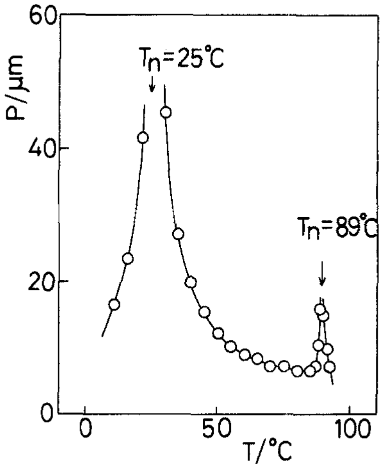

Figure 3. Variation of the cholesteric pitch (P) with temperature.

due to a uniaxial orientation. The de Vries relation [6] has been examined in the wavelength region from 550 to 700 nm in figure 4, where the Θ versus $1/\lambda^2$ plots are shown for temperatures 15°C, 70°C and 95°C, respectively, chosen from the aforementioned characteristic regions. In each plot, the linearity between optical rotation and $1/\lambda^2$ was satisfied. The sign of the slopes changes from positive to negative on going from region I to II, and again comes back to a positive value in region III. Accordingly, the sense of the cholesteric macro-helix is right-handed in regions I and III, whereas it is left-handed in the intermediate region II.

In consideration of the helical screw sense, reciprocal values of the pitch ($1/P$), which are proportional to the twisting angle of molecules, are plotted against temperature in figure 5. Here, the positive and negative values correspond to the right-handed and left-handed macro-helices, respectively. As shown in this plot, variation of $1/P$ with temperature is continuous between regions I (right-handed) and II (left-handed). In these two regions, the screw sense of the α-helical polypeptide backbone remains

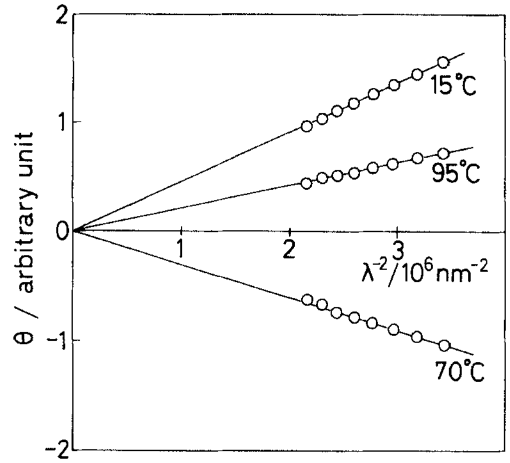

Figure 4. Plots of optical rotation (Θ) versus $1/\lambda^2$ for a cholesteric solution at 15°C, 70°C and 95°C.

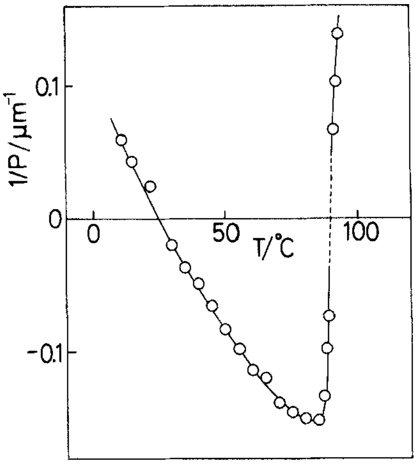

Figure 5. Variation of the reciprocal pitch ($1/P$) with temperature.

unaltered. This type of helical inversion has often been encountered for both lyotropic and thermotropic cholesterics composed of right-handed α-helical L-polypeptides [7, 8]. Experimental analyses [7, 9] and statistical theories [10] have been reported to explain the mechanism. In contrast, the cholesteric sense inversion between regions II and III occurs abruptly within a very narrow temperature range around 90°C. This novel transition is undoubtedly induced by the inversion of the α-helix sense of the polypeptide backbone.

In this paper, we have presented an interesting example in which an L-polypeptide assumes both the right-handed and left-handed helical conformations capable of forming cholesteric liquid crystals. The helix–helix transition takes place sharply and reversibly at around 90°C, the birefringent character of the mesophase being maintained throughout the transition range. These observations exclude a transition via a state such as random coil, which should result in an optically isotropic phase. A similar conclusion has been drawn from ^{2}H NMR observations [5]. We have proposed a mechanism in which unwinding and rewinding of the α-helix take place while the orientational order of the molecular axis is maintainted in the nematic environment under a magnetic field. Finally, it may be interesting to note that the inversion of the α-helix screw sense accompanies a reversal of the cholesteric macro-helix sense. More detailed studies regarding the mechanism of the transition are in progress and will be reported elsewhere.

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