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Thermotropic Polypeptides. 6. On Cholesteric Mesophase with Grandjean Texture and its Solidification

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The domain texture was examined for thin cholesteric mesophases (~20 μm) of the thermotropic polypeptides which were placed between glass plates by giving a shear flow under pressure. The optical microscopy shows the Grandjean monodomain texture for these thin mesophases and the electron microscopy (TEM method) clarifies its direct structure, having a regular stack of cholesteric layers lying parallel to the film plane. The easy preparation of the Grandjean texture is characteristic of polypeptide cholesterics and can be attributed to a preferential planar orientation of rigid-rod molecules with their long axes lying parallel to a glass surface. Solid Grandjean cholesteric films could be prepared by quenching the mesophases and retained beautiful cholesteric colors if cholesteric mesophases with small pitches were treated. The color of solid cholesteric which arises in a narrow band region less than 30 nm is insensitive to temperature variation and stable for a long time (beyond years). Some applications

of the optical properties of solid Grandjean cholesteric films are suggested.

INTRODUCTION

As reported in previous papers,[1-5] we originally found that α-helical polypeptides can form themotropic liquid crystals. Thermotropic polypeptides in all cases have long-alkyl side chains. Hence, the flexibility of the side chain is responsible for the occurrence of a thermotropic nature, such that the side chains may play a role of the solvents in familiar lyotropic liquid crystals of polypeptides. This novel liquid crystalline (LC) polymer, having a mesogenic α-helical rod surrounded by flexible side chains, is differentiated from two familiar kinds of thermotropic main-chain and side-chain LC polymers and classified into a third kind of LC polymer.

For these polypeptides, the type of mesophase is cholesteric because of a chirality of the main chain and the details of cholesteric mesophase properties have been presented. Among their remarkable properties is a strong temperature dependence of cholesteric pitch[5] and hence one can prepare the cholesterics with arbitrarily selected pitches larger than 200 nm by changing the mesophase temperature. We have also found that the cholesteric helical structure can be preserved in a solid film by quenching the cholesteric mesophase below the crystal-liquid crystal transition temperature (T_C).[3]

Solid cholesterics are interesting and promising, since they possess extremely strong rotatory power and the ability of selective reflection of circularly polarized light in a narrow band of wavelength. The latter leads to the spectacular color effects. These optical properties of films can be usefully applied to passive optical filtering such as band-pass and notched filters[6,7] or to some recording systems,[8] although the preparation of the Grandjean monodomain texture is required for these applications.

In this study, we examined the cholesteric mesophase texture of thermotropic polypeptides by optical and electron microscopies and from the observations of CD spectra. The experimental data showed that the cholesteric mesophase in this system can be easily prepared with the well-developed Grandjean monodomain and variable pitches. We also found that the polypeptides are proper materials for the above-mentioned applications due to their perfect solidification of the cholesteric mesophase structure.

EXPERIMENTAL

Poly(γ-benzyl L-glutamate-co-γ-dodecyl L-glutamate) with a dodecyl content of 44% and a polymerization degree of 2.5×10^2, as designated by BD-1-44 in a previous paper,[3] was selected as a typical material among thermotropic polypeptides for the present study. The polymer exhibits a cholesteric mesophase above $T_C = 104°C$ and invariably takes up the right-handed α-helical conformation in a temperature range of 25–250°C as detected by IR spectra.[1]

For this material, reciprocal cholesteric pitches I/P (measuring the twisting angle between adjacent pseudonematic layers) are plotted against the temperature in Figure 1. Here, the pitches given by the closed circles correspond to the wavelength of visible light and were determined from a circular dichroic measurement, while those of open circles larger than 1 μm were detected from the optical microscopic observation of retardation lines characteristic of cholesterics. The overall data points fall on a smooth curve which exhibits a remarkable variation of twisting angle at lower temperatures and seems to approach a constant value passing through zero from positive to negative at 220°C. The change of sign indicates the cholesteric sense inversion from the right-hand helix to the left-hand one as described in a previous paper.[5]

Optical microscopic observation of the mesophase texture was made with an Olympus BH-2 polarizing microscope equipped with a Mettler FP82 hot stage. The domain texture was also observed by a transmission electron microscope, TEM, (Philips Model EM420). For this examination, thin microtomed specimens about 10 μm thick were cut perpendicular to the cholesteric film plane in liquid nitrogen and exposed to 100 KV of electron beam without any coating. Circular dichroic spectra were measured by utilizing an automatic recording spectropolarimeter (JASCO Model J-20) in the wavelength range of 300–700 nm.

RESULTS AND DISCUSSION

Thin mesophases with a thickness of 10 to 20 μm were prepared between glasses by spreading them under slight pressure. At that time, the cholesteric twisted structure is gradually formed and its uniformity is attained after 2 or 3 hours, which phenomena have been clarified from the time dependence of circular dichroism due to a

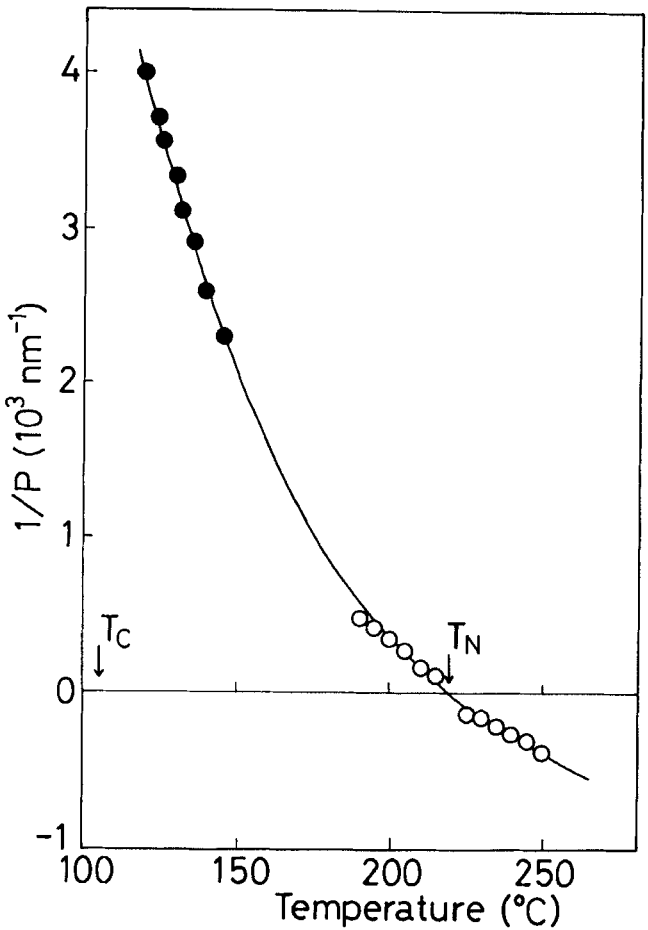

FIGURE 1. The temperature dependence of the inverse pitch 1/P for BD-1-44 measured in the meseophase temperature range above T_C = 104°C. The positive value indicates right hand cholesterics and the helical sense is reversed at T_N of 220°C. The values 1/P given by the closed and open circles were determined from the CD measurement and optical microscopic observation, respectively.

selective reflection.[3] The microscopic texture of such a thin sample is shown in Figure 2a. No appreciable domain texture is observed, implying a regular Grandjean texture in which the cholesteric helical axes lie uniformly perpendicular to the glass surface. The proof for the Grandjean texture can be given by a conoscopic picture which is shown for the present material in Figure 2b. The dark cross typical of monoaxial crystals between crossed polarizers indicates that the optical axis is parallel to the incident light and hence perpendicular

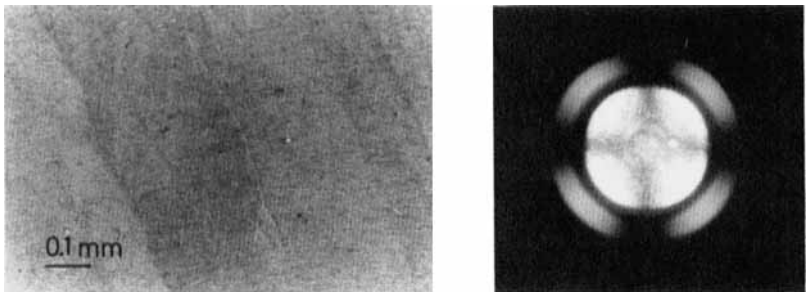

FIGURE 2. (a) Photomicograph of the Grandjean texture of the cholesteric mesophase at 120°C and (b) its conoscopic picture.

to the glass surface. The use of a quarter-wave plate further dictates the opitcally negative crystals. Both are to be expected for Grandjean cholesterics.

When the mesophases are prepared in the temperature range of 110–150°C, they have pitches comparable to the wavelength of the visible light (see Figure 1) and exhibit beautiful iridescent cholesteric colors. The color changes from blue to red with increasing temperature. This color effect can be quantitatively analyzed from the circular dichroism which is caused by a selective reflection of circularly polarized light. Typical CD spectra are shown by solid curves in Figure 3. Fairly sharp spectra are observed having a spectral width of 10 to 30 nm. Since the spectral width $\Delta\lambda$ can be given by the equation $\Delta\lambda = \Delta n\, P$ for Grandjean cholesterics[9] and the observed birefringence, Δn, is around $0.02 \sim 0.03$ as detected by an Abbe refractometer, one can calculate $\Delta\lambda = 6 \sim 9$ nm for the cholesteric of $P = 300$ nm and $\Delta\lambda = 14 \sim 21$ nm for one of $P = 700$ nm. The observed values are only slightly larger than these values, again leading to a uniform Grandjean arrangement.

The direct proof of the Grandjean cholesteric structure is given by the TEM observation for thin microtomed films cut out perpendicularly to the film plane of solid cholesterics. Here, solid cholesterics were prepared by quenching the mesophase into liquid nitrogen. In Figure 4, a typical TEM photograph is shown. It exhibits a set of black and white lines periodically placed. The variation in transmissibility of electron beam from one psuedonematic layer to the other is attributable to an alternative appearance of black and white lines;[10] a black line means less transmissibility of an electron beam and its portion corresponds to the layers with their molecular directors almost

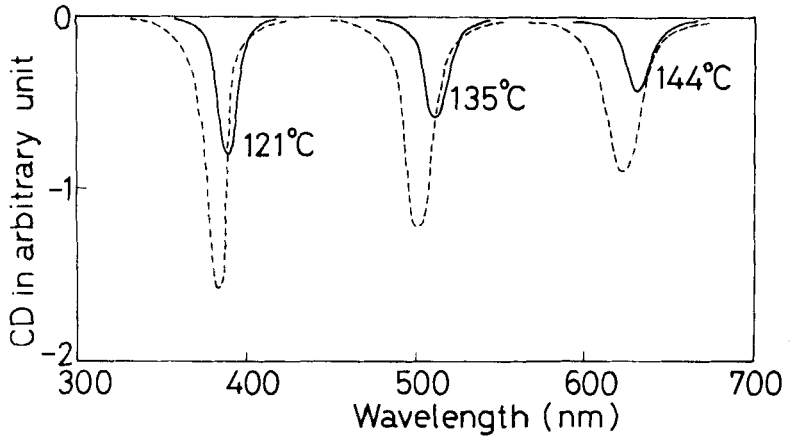

FIGURE 3. The circular dichroic spectra of cholesteric mesophases at different temperatures (solid curves) and their solid cholesterics prepared by quenching the mesophases to room temperature (dashed curves).

parallel to the microtomed film plane while the white portion corresponds to the layers having the directors nearly perpendicular to the plane. The spacing between the white lines or black lines gives a half-pitch, which is in good agreement with that determined by a spectroscopic method. Apart from this argument, it is surprising that Figure 4 exhibits a regular stack of layers lying parallel to the plane

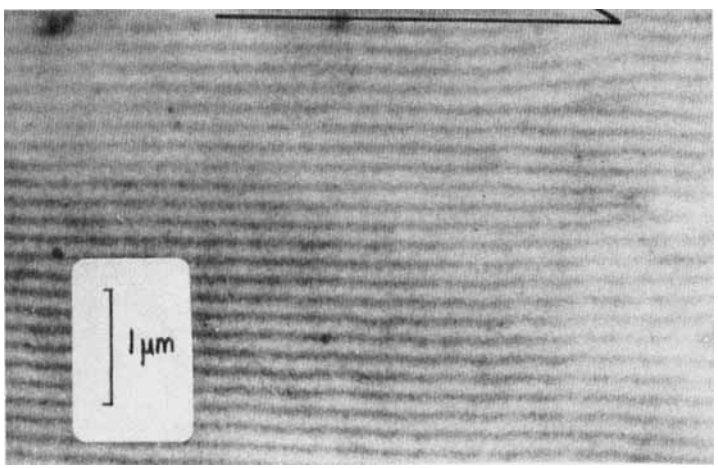

FIGURE 4. The TEM photograph of thin microtomed films (~10 μm) cut perpendicularly to the plane of solid cholesteric film which was prepared by quenching the mesophase at 125°C into liquid nitrogen. The arrow indicates the direction of the plane of solid cholesteric film.

of the cholesteric film. The layers are continuously piled up from one surface of film to another and there are no appreciable defects such as dislocations and disclinations, just confirming the ideal cholesteric Grandjean texture.

An easy preparation of the Grandjean texture in the present polypeptide system is attributed to a preferential planar orientation of rigid-rod molecules with a large axial ratio of about 20. For rigid-rod mesophases it has been argued that the director must be parallel to the surface; condensing many ends of rods at the surface costs a lot of entropy and is therefore unlikely unless there is a strong binding energy for ends at the surface. A suitable treatment of the glass surface (e.g., by rubbing or obliquely evaporating solid materials) might help the development of the Grandjean texture, but it is not necessary in the present system although an ordinary flatness of the glass surface is required to prevent an induction of splay deformation of cholesteric helical axes which leads to a polygonal texture.[11] There is hence no serious condition for the preparation of the Grandjean texture in thermotropic polypeptides. Only some shear flow is needed to get a thin mesophase of less than 20 μm and to promote the parallel alignment of rod molecules to the surface. These conditions suggest that the Grandjean texture can be also prepared by a melt processing method which is one of the important ways of making a commercial polymer film.

In order to utilize the remarkable optical properties, those solid Grandjean cholesterics which can be prepared by quenching the mesophase to a temperature below T_C are useful. The dashed curves of Figure 3 show CD spectra of such solid cholesterics. The data show that their color effects are not seriously changed from those in the mesophase, since there is no essential difference between the spectra with respect to the maximum wavelength, although a substantial increase of intensity is seen for the solid cholesteric. Thus, one can see beautiful iridescent colors on solid films, similar to the mesophase. The insensitivity of colors to temperature characterizes solid cholesterics; as can be seen in Figure 5, only a slight increase of the wavelength of color with temperature is observed within a temperature region below T_C, which is caused only by a thermal expansion of the distance between adjacent pseudonematic layers. The retained colors are arbitrarily selected by changing the temperature of the prior existing mesophase and remain stable for a long time (beyond years). The spectrum width is still so narrow as in the mesophase that nine or ten independent colors are attained within a wavelength region of visible light (refer to Figure 3). We can thus utilize these cholesteric

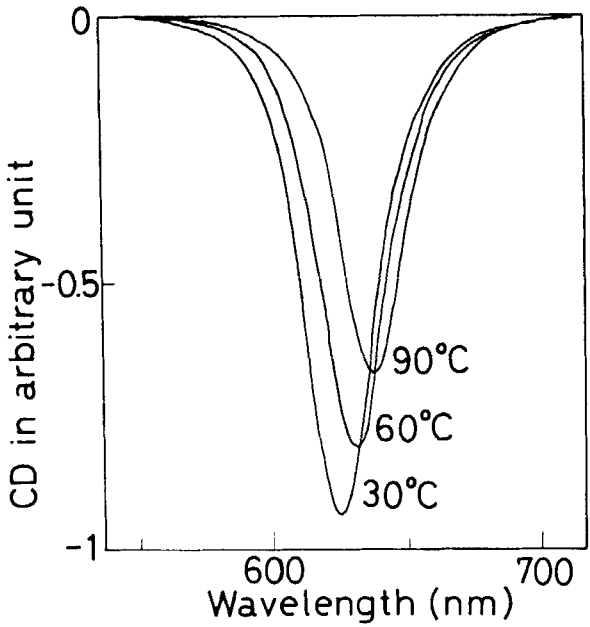

FIGURE 5. Circular dichroic spectra of solid cholesteric film measured at different temperatures below T_C. Here, the solid cholesteric film was prepared by quenching the mesophase at 144°C.

films as notched and band-pass filters, a performance which is based on a selective reflection of the circularly polarized light with the desired wavelength.[7] On the other hand, if one wants to change the color of a solid cholesteric film, heat the film again into the mesophase temperature region above T_C. Then, the pitch or the color changes to get an equilibrium one at a selected mesophase temperature (refer to Figure 1). This can allow us to apply these cholesteric-colored films for some record systems in which for example, the recording may be accomplished by subjecting the films to a focused laser beam (as a heat source).[8] A detailed study of these applications is in progress.

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