

NOTES

**Thermotropic Polypeptides. VII. Temperature Dependence of Cholesteric Pitches in Poly[( $\gamma$ -benzyl L-glutamate)-*co*-( $\gamma$ -dodecyl L-glutamate)s]**

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In this series of study,<sup>1-7</sup> we examined the thermotropic liquid crystalline nature of  $\alpha$ -helical polypeptides. The type of liquid crystal formed is cholesteric because of the chirality of constituent macromolecules and several cholesteric properties are given. One of the most interesting properties among them is the strong temperature dependence of cholesteric pitches.

In a paper 5 of this series,<sup>5</sup> its details are reported by treating the representative material, poly[( $\gamma$ -benzyl L-glutamate)-*co*-( $\gamma$ -dodecyl L-glutamate)] (PBD<sub>o</sub>LG) with the dodecyl content of 58% which offers the cholesteric mesophase in a temperature region above 104°C. For this materials, the cholesteric pitch ( $P$ ) is comparable to the wavelength of visible light in an initial mesophase temperature region of 100 to 130°C, increases substantially with rising temperature, and then diverges at  $T_N$  (=195°C or 468 K) indicating that the cholesteric mesophase is converted to the nematic one. As temperature is raised further, the cholesteric mesophase again appears and pitches decrease gradually. The cholesteric sense inversion from right-handed helix to left-handed one is clarified to be responsible for this curious phenomenon<sup>5</sup> as has been already reported in the lyotropic polypeptide

system by Uematsu and Uematsu.<sup>8</sup> The temperature dependence of pitches can be described by two empirical equations

$$1/P = (1/P_0)(T_N - T)/(T - T_C) \quad (1)$$

$$1/P = (1/P_0)\{(T_N/T)^\beta - 1\} \quad (2)$$

where the constants  $1/P_0$  and  $T_C$  in the eq 1, and  $1/P_0$  and  $\beta$  in the eq 2 are estimated as  $2.4 \times 10^{-3} \text{ nm}^{-1}$ , 319 K,  $9.7 \times 10^{-4} \text{ nm}^{-1}$ , and 7.3, respectively.

In this study to obtain more detailed information on the temperature dependence of pitches, the examination was extended to the thermotropic cholesteric mesophases of several PBD<sub>o</sub>LG polymers with a wide variety of dodecyl contents. As a result, the similar temperature dependence as mentioned above was observed for all materials and found to be well described by the eq 1. Constants included in the equation were determined and their dependence on dodecyl content is shown.

## EXPERIMENTAL

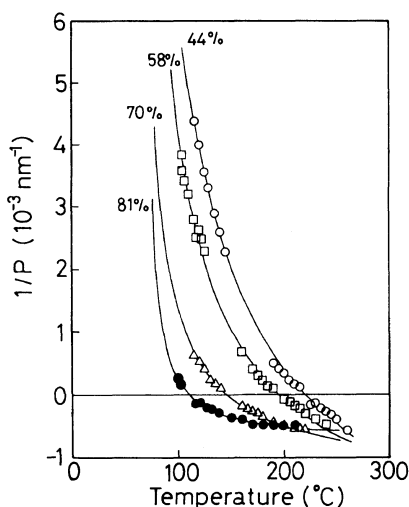
A series of PBD<sub>o</sub>LG with various dodecyl contents were prepared by ester interchange reaction between poly( $\gamma$ -benzyl L-glutamate) (DP=250) and dodecyl alcohol described

elsewhere.<sup>3</sup> The mesophase arose in copolymers with dodecyl content more than 30% and its temperature ranged above a definite temperature,  $T_2$ , which decreased from 115°C to 50°C with increasing dodecyl content of 30% to 100%.<sup>3</sup> All the polymers underwent no appreciable decomposition below 250°C in an atmosphere of nitrogen and invariably took up the right-handed  $\alpha$ -helical conformation in the applied temperature region from 25°C to 250°C.

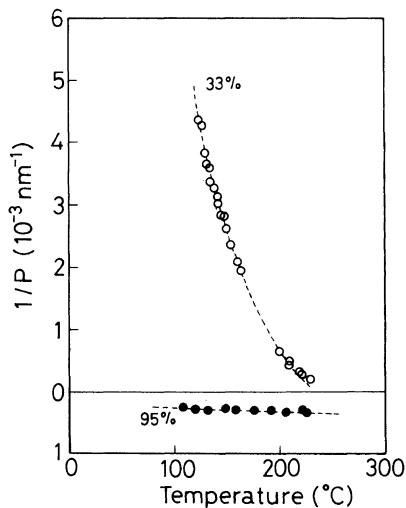
The cholesteric pitches were determined by circular dichroism (CD) using a JASCO automatic recording spectrometer (J-20) and by microscopic observation of striation lines with an Olympus BH-2 polarizing microscope. The helical sense of cholesterics was clarified from the sign of the CD and optical rotational dispersion curves by using J-20. The details of these methods are described in previous papers.<sup>3,5</sup>

## RESULTS AND DISCUSSION

Figures 1 and 2 show the temperature dependence of the reciprocal cholesteric pitches,  $1/P$ , which are proportional to the twist angle between the adjacent pseudo-nematic layers. Here the data points of  $1/P$  ranging from  $2 \times 10^{-3} \text{ nm}^{-1}$  to  $5 \times 10^{-3} \text{ nm}^{-1}$  were obtained from the circular dichroism while ones less than  $1 \times 10^{-3} \text{ nm}^{-1}$  were determined by the microscopic observation. The positive and negative values correspond to the right-handed and left-handed cholesteric helices, respectively, and the zero value at  $T_N$  indicates the compensation of twist. All of the materials employed here which have the dodecyl contents of 33, 44, 58, 70, 81, 95%, show the similar temperature dependence of the reciprocal pitches. As common features, the reciprocal pitches undergo a remarkable variation in the temperature region below  $T_N$  and approach a constant value at higher temperature region after passing through zero at  $T_N$ —the former trend can be typically observed for PBDOLG



**Figure 1.** Variation of the reciprocal pitches with temperature for the cholesteric mesophases of PBDOLG with various dodecyl contents of 44% (○), 58% (□), 70% (△), and 81% (●). The solid curves are based on the calculations according to the eq 1.



**Figure 2.** Variation of the reciprocal pitches with temperature for the cholesteric mesophases of PBDOLG with 33% (○) and 95% (●) dodecyl contents. The dashed curves are arbitrarily drawn to satisfy the data points.

with 33% dodecyl content and the latter seen for PBDOLG with 95% dodecyl content (see Figure 2). In addition, the cholesteric sense inversion commonly occurs from right-handed helix to left-handed one on heating. Figures 1

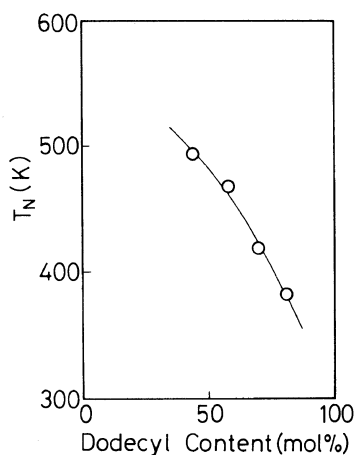


Figure 3. Dependence of  $T_N$  on dodecyl content.

Table I. Experimental parameters,  $1/P_0$ ,  $T_N$ , and  $T_C$ , in eq 2

Sample	$1/P_0/\text{nm}^{-1}$	$T_N/\text{K}$	$T_C/\text{K}$
PBDoLG-44 <sup>a</sup>	$3.3 \times 10^{-3}$	493	309
PBDoLG-58	$2.4 \times 10^{-3}$	468	319
PBDoLG-70	$1.3 \times 10^{-3}$	418	329
PBDoLG-81	$7.5 \times 10^{-4}$	383	340

<sup>a</sup> The number shows the dodecyl content.

and 2 also show an obvious effect of dodecyl content on  $T_N$ . As listed in Table I and illustrated in Figure 3,  $T_N$  decreases consistently with the increasing dodecyl content.

The eq 1 and eq 2 were applied to reproduce the observed temperature variation of reciprocal pitches. The result exhibited that well fitting is obtained by using the eq 1 as represented by the solid curves in Figure 1 while the eq 2 can not reproduce the overall trend. This means that the temperature variation of reciprocal pitches can be approximated by the hyperbolic curve where the reciprocal pitch diverges at  $T = T_C$  on cooling and approaches  $-1/P_0$  on heating. Constants  $T_C$  and  $1/P_0$  determined by curve fitting are listed in Table I and also plotted against dodecyl content in Figure 4. Systematic variation of  $T_C$  and  $1/P_0$  with the dodecyl content is observed in such a

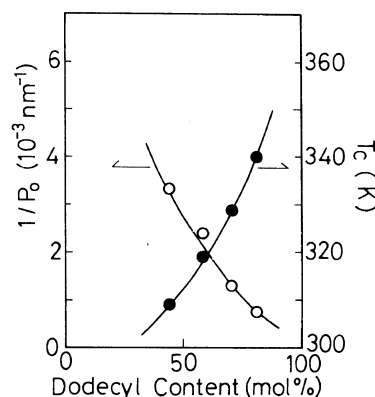


Figure 4. Dependence of the constants  $1/P_0$  and  $T_C$  included in the eq 2 on dodecyl content.

way that the constant  $1/P_0$  decreases with the increase of dodecyl content while  $T_C$  increases.

The results obtained here lead to a conclusion that the temperature dependence of twist angle in thermotropic cholesteric mesophases of polypeptides can be expressed by the eq 1 with the common features as following.

- (1) For the L-enantiomers, the sense inversion of cholesteric helix occurs from right-handed to left-handed one on heating.
- (2) For the right-handed helical cholesterics, the twist angle remarkable decreases with temperature. In contrast, it increases gradually with temperature for the left-handed one.

Such a kind of temperature dependence is exceptional<sup>9,10</sup> and the explanation for this should be directed to the structural characteristics of polypeptide. On this point, the recent paper<sup>11</sup> by Yamagishi *et al.* is very interesting in which the second example of this type of temperature dependence is reported in the thermotropic mesophase of cellulose derivative, since both polymers have the same structural characteristics in two following aspects. First, they are composed of rigid main chain which contains the asymmetric carbons and assumes the helical conformation. Second,

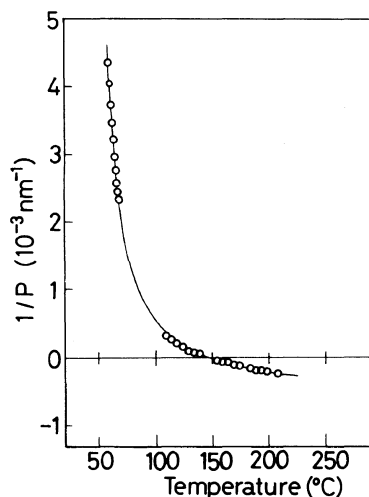
they have flexible side chains protruding from the helical main chain. These, characteristics of biopolymers, cannot be seen for other kinds of cholesteric materials<sup>9,10</sup> and so are attributable to the anomalous temperature dependence of cholesteric pitch.

There is no doubt that the cholesteric twist results directly from the asymmetric carbons of the main chain where the driving force of twist is the dispersion force as presented by Goossens.<sup>12</sup> In these specific systems, however, the twist would be also forced by the side chains. The side chains assume the helical arrangement depending on the helical conformation of main chain, product the screw-like van der Waals surface on the exterior of main-chain backbone, and cause the twist by their steric interaction.<sup>13,14</sup> Both independently affect not only the magnitude but also the sense of helicity. In such a case, the temperature dependence of the pitch appears complicated and as one of the possibilities, the thermally-induced sense inversion can be expected if the twists occur with the opposite sense to each other. Theoretical guidance for this has been already given by Kimura *et al.*, by assuming the intermolecular force as the sum of a repulsion of hard core with shape of twisted rod and of a dispersion force of Goossens type.<sup>14</sup> In addition, it is very significant that the theoretical equation can reproduce the experimental eq 1.<sup>15</sup> The corresponding parameters between them will be discussed in a relation to the structural characteristics of constituent molecules in another article.<sup>16</sup>

Finally, it is interesting to compare the temperature dependences of cholesteric pitch between thermotropic and lyotropic systems of polypeptide. As previously reported by Uematsu and Uematsu,<sup>8</sup> the temperature dependence of pitch in the lyotropic system is given by the empirical equation

$$1/P = a(1 - T/T_N) \quad (3)$$

Comparing the eq 1 and eq 3, one notices that



**Figure 5.** Variation of the reciprocal pitches with temperature for the cholesteric mesophase in the lyotropic system of PBDOLG (with 33% dodecyl content)—benzyl alcohol. The concentration of polymer is 57% in weight fraction. The solid curve is based on the calculation according to the eq 1 with the parameters  $1/P_0 = 6.25 \times 10^{-4} \text{ nm}^{-1}$ ,  $T_N = 418 \text{ K}$ , and  $T_C = 320 \text{ K}$ .

the eq 2 can be rewritten in the same form as the eq 3 at temperatures in which  $T/T_N \approx 1$ ; in practice, the observation of pitches in the lyotropic system has been performed only in the limited temperature region near  $T_N$  because of the low boiling temperature of used solvents. This suggests that the eq 2 would be also applied for the lyotropic system if the observation is made over the wide temperature region. To give an evidence for this, we examined the lyotropic system in which the present material, PBDOLG with the dodecyl content of 33%, was dissolved in benzyl alcohol. Figure 5 shows its temperature dependence of reciprocal pitch observed in the temperature region of 30 to 200°C. Obviously, the data points fall on the curve expected by the eq 1 rather than the eq 3. The more detailed examination is now proceeding on this point.

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