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Thermotropic Polypeptides. 3. Investigation of Cholesteric Mesophase Properties of Poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamates) by Circular Dichroic Measurements

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ABSTRACT: A series of poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamates) were synthesized with various dodecyl contents, and the thermotropic mesophase properties of the cholesterics were investigated. The mesophase arose in copolymers with dodecyl content >30%. Its temperature region ranged above a definite temperature, T_2, which decreased from 115 to 50 °C with increasing dodecyl content. The cholesteric pitches corresponding to the visible wavelength, as determined from the CD spectrum, were observed for mesophases in copolymers with dodecyl content of 30–60% and in the temperature region 100–160 °C. In this limited observation of pitches, the pitch increased with temperature for a given copolymer or with dodecyl content at a given temperature. Each dependence appeared to be independent of the degree of polymerization. The present liquid crystal was characterized by having a high viscosity. The formation of a cholesteric twisted configuration or the transformation of one configuration to another, hence, proceeded with a fairly long response time, and some structural characteristics of the cholesterics were able to be extracted from the observation of CD spectra through these slowly proceeding events. The high viscosity also enabled the perfect solidification of the cholesteric structure or its related optical properties by chilling the cholesteric mesophase below T_2.

Introduction

Paper 1 of this series[1] reported the first observation of thermotropic liquid crystals on α-helical poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamates). In that paper, it was deduced that the thermotropic liquid crystalline nature can be induced for copolymers with intermediate hexyl contents of 30–70% and that an appreciable difference in the length of the side chains, probably a difference of five or more methylene units, is necessary for producing the thermotropic nature in copolymers. Paper 2[2] also indicated that even in homopolymers of L-glutamates, the thermotropic nature appears if *n*-alkyl groups longer than decyl are attached to the side chain. In both cases, the long flexible side chains are responsible for the occurrence of thermotropic liquid crystals such that they may play the role of solvent in familiar lyotropic liquid crystals. These novel liquid crystalline (LC) polymers, having a mesogenic α-helical rod surrounded by flexible side chains, should be differentiated from two familiar kinds of thermotropic LC polymers—the so-called main-chain LC polymers[3,4] and the side-chain LC polymers[5,6]—and classified into a third kind of LC polymer together with cellulose and isocyanate derivatives,[7-10] as illustrated in Figure 1.

The type of liquid crystal formed in a polypeptide system is cholesteric because of the chilarity of the main chain. Cholesteric liquid crystals are especially interesting and promising. Among their most important properties are their extremely strong rotatory power and their selective reflection of circularly polarized light in a narrow band of wavelength.[11] The latter leads to spectacular color effects, the wavelength, λ_m, of the color being related to the pitch, P, of the cholesteric helix and the refractive index, n, according to the relation

$$\lambda_m = nP \sin \theta \quad (1)$$

This equation also represents the dependence of λ_m on the angle θ between the plane of the cholesteric layer and the direction of the incident light. For light perpendicular to the plane of a thin sample and with molecules lying parallel to a planar surface, the relation is $\lambda_m = nP$. Tilting the plane of the sample to the incident light causes a blue shift of λ_m.[12] In general, the pitch is sensitive to changes in temperature or pressure for both lyotropic and thermotropic cholesteric liquid crystals. Such a sensitivity has been extensively examined by experimental and theoretical analyses to establish what essential physical force causes the twisted configuration of the cholesteric structure.[13-15] With respect to application, the sensitivity has also promised the use of cholesteric liquid crystals in electrooptical displays and temperature indicators.[15,16]

Apart from their optical properties, cholesteric LC polymers are of special interest in the search for materials having superior mechanical properties. The uniaxial alignment characteristic of the nematic phase is useful for the production of high-modulus fibers,[17] since the resulting distribution of molecules about the fiber axis can be very narrow. On the other hand, a biaxial orientation characteristic of the cholesteric phase is ideal for polymeric films.[18] A thin cholesteric layer exhibiting a Grandjean texture (or a planar texture) would have all of the molecular axes uniformly distributed in the plane of the film. If this structure can be retained during solidification, the resulting film, similar to an "angle-ply" laminate, would have optimum mechanical properties when tested along any arbitrarily selected direction in the film plane. This

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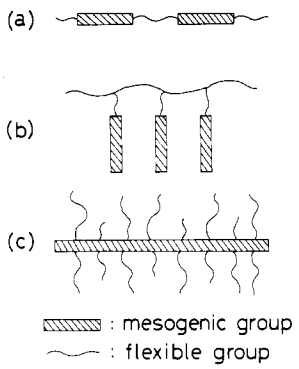
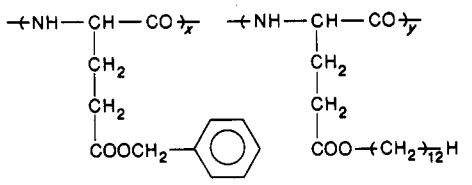


Figure 1. Classification of liquid crystalline (LC) polymers: (a) main-chain LC polymer; (b) side-chain LC polymer; (c) rigid-rod LC polymer.

concept has been realized through the deformation of solid cholesterics of polypeptide films due to stretching[19] and has led to our interest in investigating the cholesteric mesophase.[20,21]

In this paper, we will treat thermotropic cholesteric liquid crystals of poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamates) having the following chemical structure:



The homopolymer of benzyl glutamate is one of the most familiar polypeptides, the structure and properties of which have been extensively studied. It can be easily prepared with various degrees of polymerization by a conventional NCA method and is characterized by a high stability of the α-helical conformation and a high solubility in various solvents. On the other hand, α-helical poly(γ-dodecyl L-glutamate) composed of another comonomer can also adopt the stable α-helical conformation and form thermotropic liquid crystals in the temperature region above 50 °C.[2] As judged from the induction of the thermotropic nature due to the copolymerization,[1] one can assume that the present copolymers exhibit the thermotropic liquid crystalline phase over a wide composition range and over a wide temperature range. The detailed study of cholesteric mesophase properties of polypeptides will be described mainly through circular dichroic measurements.

Experimental Section

Materials. Poly(γ-benzyl L-glutamate) (PBLG) as a starting polymer for ester interchange reaction was synthesized by a conventional NCA method. The polymerization of NCA was carried out in dioxane with triethylamine as an initiator. Five kinds of PBLG, having different viscosity-average molecular weights, were prepared by changing the ratio of initiator to NCA.

A series of poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamates) were prepared by ester interchange reaction, which was performed at 60 °C for 1 g of PBLG and 25 mL of dodecyl alcohol dissolved in 50 mL of 1,2-dichloroethane with 1.5 g of *p*-toluenesulfonic acid as a catalyst. After an arbitrary reaction time, the polymers were isolated by precipitation upon pouring the solution into methanol. Then they were twice purified by fractional precipitation from solution in chloroform–methanol mixed solvent and dried under vacuum at 100 °C. The copolymer composition, as determined by ^{1}H NMR spectroscopy, was adjusted by changing the reaction time; reaction times of 10–60 h produced copolymers with dodecyl contents from 20% to 90%.

The polymers are designated by the letters BD followed by a number specifying the degree of polymerization of the starting PBLG; the degrees of polymerization of BD-1, BD-2, BD-3, BD-4, and BD-5 are 2.5×10^2, 3.3×10^2, 7.8×10^2, 1.1×10^3, and 1.5×10^3, respectively. The copolymer composition is expressed by an additional succeeding number indicating the molar percent of dodecyl content.

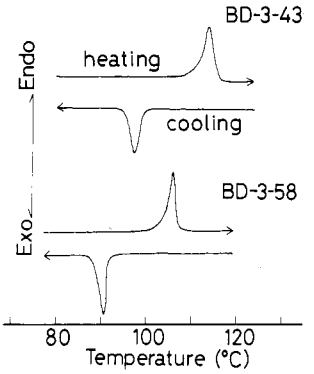


Figure 2. DSC thermograms of BD-3-43 and BD-3-58, exhibiting first-order transitions from crystal to liquid crystal.

All of the films examined here were prepared by casting the solutions in chloroform. IR spectra and X-ray patterns indicated that all polymers assume a right-handed α-helical conformation in this experimental temperature range.

Methods. DSC measurements were performed with a Perkin-Elmer DSC-II calorimeter. The samples were examined at a scanning rate of 10 °C/min. The selective reflectance of circularly polarized light was detected by circular dichroism (CD) using a Jasco Model J-20 automatic recording spectrometer in the wavelength range 250–700 nm. The selective reflection in the additional wavelength range 700–1500 nm was followed by measuring the transmission with a Model 330 Hitachi spectrometer. In these experiments, the specimens were heated at the desired temperature by a heater that can be maintained to within 1 °C and then spread between glasses. The resultant film was less than 100 μm thick. The maximum wavelength of reflectance, λ_m, was related to the optical pitch, nP, by $\lambda_m = nP$ as noted in the Introduction. The thickness of each pseudonematic layer in the mesophase was determined from X-ray photographs taken with Ni-filtered Cu Kα radiation, on the assumption that it corresponds to the spacing of the most inner reflection on the equator.[1,2] Photomicrographs with an original magnification of 100× were taken with an Olympus BH-2 photo attachment with a Mettler FP 80.

Results and Discussion

A. Phase Diagram. Transformation of crystal to liquid crystal in the polypeptide system appears as a first-order transition, which can be detected by DSC thermograms.[1,2] It can be further followed by X-ray and dynamic mechanical methods.[1,2] In the X-ray method, one observes that the crystal pattern is replaced by a pattern displaying only diffuse halos at the transition temperature. Simultaneously, the mechanical method exhibits an abrupt drop of storage modulus, showing the liquid-like nature of the material.

In this study, the transition behavior was detected by DSC thermograms. A representative example is shown for BD-3-43 and BD-3-58 in Figure 2. The transition, appearing as a clear peak, is reproducible on heating and cooling. Transition temperatures, T_2, of BD-3 copolymers based on heating data are listed in the second column of Table I and plotted against the dodecyl content in Figure 3. The phase diagram thus obtained indicates that the thermotropic liquid crystalline phases are induced for copolymers with dodecyl content >30%. The transition temperature is around 115 °C for copolymers with dodecyl content of 30–40%, gradually decreases with increasing dodecyl content, and finally reaches 50 °C for poly(γ-dodecyl L-glutamate) (PDoDLG). The markedly small values

Table I
Characteristics of BD-3 Copolymers

polymer	T_2, °C	ΔS, cal/(mol K)	nP,[a] nm	D,[a] Å
BD-3-33	102	0.17	360	~16
BD-3-43	114	0.19	430	~16.5
BD-3-50	115	0.20	530	~17
BD-3-58	107	0.13	735	~17.5
BD-3-66	101	0.17		~17.5
BD-3-84	77	0.14		~18
BD-3-100	50	0.40		~18.5

[a] At 125 °C.

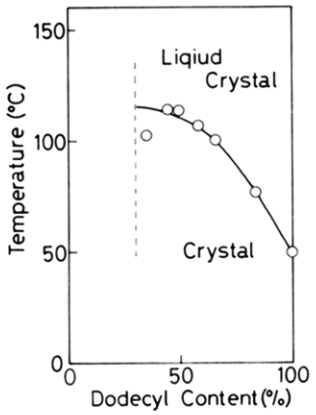


Figure 3. Phase diagram of the BD-3 copolymer system based on DSC heating data.

of transition entropy of 0.1–0.2 cal (mol of residue)$^{-1}$ K^{-1} are estimated in the third column of Table I. Such small values may be reasonable since no conformational change of the main chain has been included in this transition. Similar phase behavior was observed for other systems with different degrees of polymerization except that the increase in degree of polymerization caused a slight increase of the transition temperature.

B. Formation of Cholesteric Helical Structure. The specimen flows when it is heated above T_2 and so is easily spread between glasses by adding a slight stress. The present material in liquid crystal, thus, is like a liquid in mechanical aspects. The expected cholesteric structure in this system, however, would not be uniformly made immediately after the material enters into the liquid crystalline phase, since the material initially has a parallel arrangement of α-helices in the crystal and the cholesterics require the α-helices with high axial ratio to migrate into a twisted configuration.

The formation of the cholesteric twisted configuration was isothermally detected through the change of the CD spectrum. Figure 4 indicates the time dependence of the CD spectrum for BD-1-37 maintained at 120 °C. Here, the time was measured instantaneously after the material was set on a hot stage and spread between glasses so as to have a thickness of around 50 μm. Initially, the CD spectrum appeared with a fairly large width. The width gradually decreased and simultaneously the maximum intensity increased with time. No appreciable change was observed after around 2 h, indicating that a duration beyond this is necessary for the perfect formation of cholesterics in this material. This duration is considerably longer than that (less than a second) in the low molar mass systems. The latter process was observed for polymers with a higher degree of polymerization, and no development of cholesteric structure was detected in BD-5, which has the highest degree of polymerization. The trend is reasonable since the rate of development is limited by the viscosity of the material, which absolutely increases with

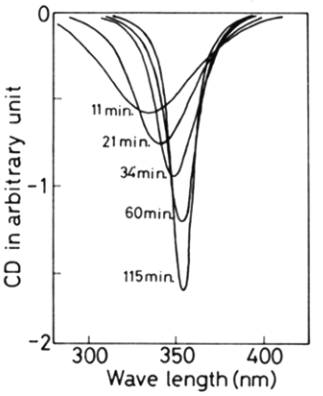


Figure 4. Variation of CD spectrum with time exhibiting the development of cholesteric twisted configuration in the mesophase of BD-1-37 at 120 °C, where the time in minutes was measured immediately after the material was set on a hot stage and spread between glasses. The thickness of the material is around 50 μm.

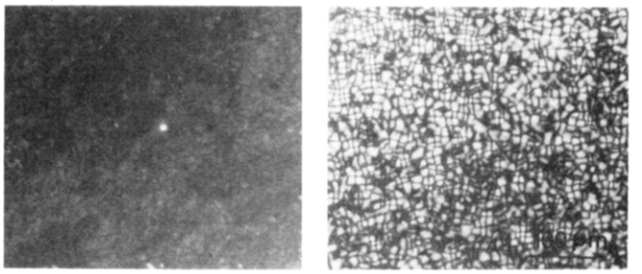


Figure 5. Optical photomicrographs, taken with crossed polarizers, for the cholesteric mesophases of BD-1-37: (a) the planar texture for the mesophase developed at 120 °C; (b) the peculiar texture of the mesophase with a polydomain structure arising on a jump of the mesophase temperature from 148 to 138 °C (see text).

increasing length of α-helical rod.

One can further notice from Figure 4 that the area of the CD band has not been seriously altered over time. The decreasing width and increasing intensity with time thus exhibit a process in which twisted structures with a short correlation length and with a wide distribution of pitches are formed over the whole area immediately after the specimen was set and then coalesce gradually into the final uniform cholesteric structure. Figure 4 also indicates that the CD spectrum initially appears with a maximum wavelength shorter than the equilibrium one. In other words, the spectrum undergoes a gradual red shift to reach the equilibrium wavelength. The shift is small but significant. Possibly, the averaged twisted angle between the neighboring layers may depend somewhat on the correlation length of the cholesteric helical structure; the cholesteric structure composed of fewer layers may have a larger twisted angle.

The CD curve finally obtained at equilibrium is very sharp, and its half-width ($\Delta\lambda$ = 14 nm) approximates to that ($\Delta\lambda$ = 7 nm) theoretically expected from the equation[12,22]

$$\Delta\lambda = \lambda_m \Delta n / n \qquad (2)$$

where the birefringence Δn = 0.026 and n = 1.4 estimated for poly(γ-benzyl glutamate)[23] were adopted. The resultant cholesteric twisted structure is thus seen to be nearly ideal. The color due to the selective reflection is a deep blue and the microscopic photograph shown in Figure 5a exhibits a planar texture, both providing the well-developed cholesteric structure.

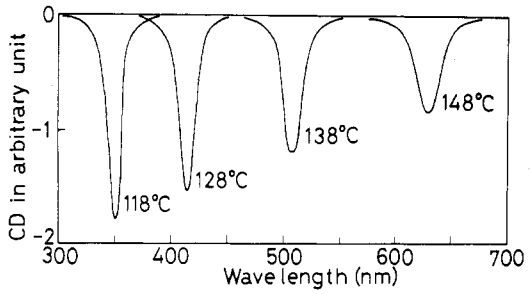


Figure 6. Equilibrium CD spectra observed for the cholesteric mesophases of BD-1-37 at 118, 128, 138, and 148 °C.

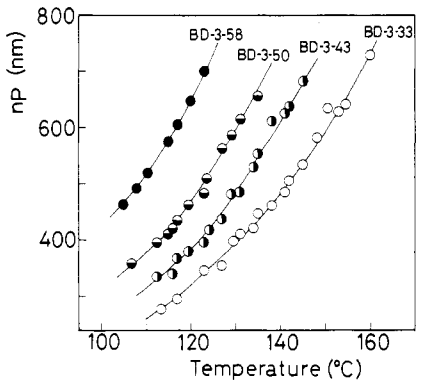


Figure 7. Temperature dependence of the optical pitch, nP, for the cholesteric mesophases of BD-3 copolymers: (○) BD-3-33; (◑) BD-3-43; (◒) BD-3-50; (●) BD-3-58.

C. Variation of Equilibrium Pitches with Physical Factors. Figure 6 indicates typical equilibrium CD bands observed for the mesophases of BD-1-37 polymers at four different temperatures. The negative CD band indicates that the cholesteric helical sense is a right-handed one. The maximum wavelength and so the optical pitch substantially increase with temperature so that λ_m passes through the visible wavelength region in a temperature span of 40 °C. This increase exceeds to a great extent the thermal expansion of the molecular spacing, D, with the expansion factor ($d \ln D/dT$) on the order of 10^{-4} °C^{-1} and so is attributed mainly to a decrease of twisted angle. Such a strong temperature dependence of pitch seems to be characteristic of thermotropic liquid crystals in polypeptides.[1,24] Peak height decreases with temperature, and half-width ($\Delta\lambda$) increases with increasing λ_m. The latter effect is to be predicted from eq 2.

Figure 7 illustrates the temperature dependence of the optical pitch, nP, for four BD-3 copolymers. As found in this figure, the pitches corresponding to the visible wavelength can be attained in copolymers with 30–60% dodecyl content. In every copolymer, the pitch increases with temperature, and its temperature dependence appears to be independent of dodecyl content, at least in this limited composition range. Below we will describe how physical factors such as temperature, copolymer composition, and degree of polymerization affect the cholesteric pitch.

Temperature Effect. The temperature dependence of the cholesteric pitch has been examined on lyotropic systems of polypeptides[25-30] and cellulose derivatives[31] and can be expressed by the empirical equation[28-31]

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

The parameter b is a constant factor for a given polymer–solvent concentration. The compensation temperature, T_N, is defined as the temperature at which the cholesteric pitch is infinite and so the molecular arrangement

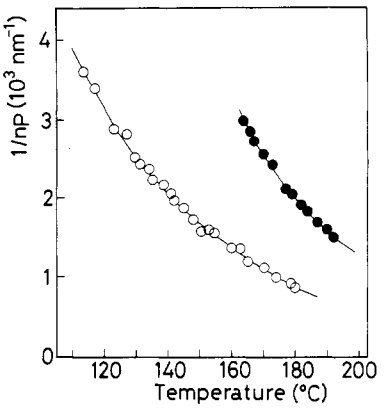


Figure 8. Temperature dependence of the inverse optical pitch ($1/nP$): (○) BD-3-33; (●) poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamate) with 50% hexyl content (see text).

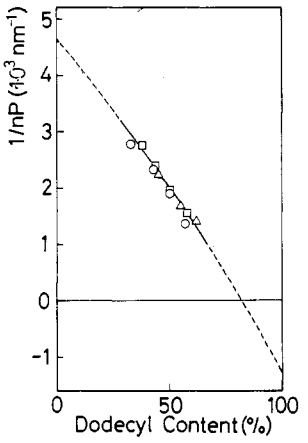


Figure 9. Variation of the inverse optical pitch ($1/nP$), as measured at 125 °C, with dodecyl content: (□) BD-1 copolymers; (○) BD-3 copolymers; (△) BD-4 copolymers.

resembles that in a nematic phase. The equation has satisfactorily rationalized the linear relationship between $1/P$ and T and the thermally induced inversion of sense of the cholesteric helix observed so far for lyotropic mesophases of polypeptides.[28-30,32]

The first paper of this series[1] reported that eq 3 also predicts a linear relationship of $1/nP$ and T over a limited range of pitch (or temperature) for the thermotropic poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamate) system. In the present study, however, we noticed that it is not satisfactory when the temperature dependence is examined for the wide range of nP from 250 to 1500 nm. Results appear in Figure 8, where the relationship of $1/nP$ and T has been presented for BD-3-33. The data, linked by a smooth curve, significantly deviate from the linear relation. In the same figure, there can be also seen a similar deviation for the data of poly(γ-methyl D-glutamate-*co*-γ-hexyl D-glutamate) with 50% hexyl content previously reported in the first paper.[1] Looking at the curves, at lower temperature the remarkable variation of $1/nP$ is observed with temperature whereas at higher temperature, the curve indicates less variation and seems to approach to $1/nP = 0$ (untwisting of the helical pitch). The same trend can be seen in other copolymers, and, hence, the linear relation expressed by eq 3 is unlikely for thermotropic systems, suggesting a different situation between lyotropic and thermotropic systems. More recently, Watanabe et al. have found that pitches with values larger than 5 nm can be determined by the current microscopic observation of striation lines. By adding these data, the detailed description of the temperature depen-

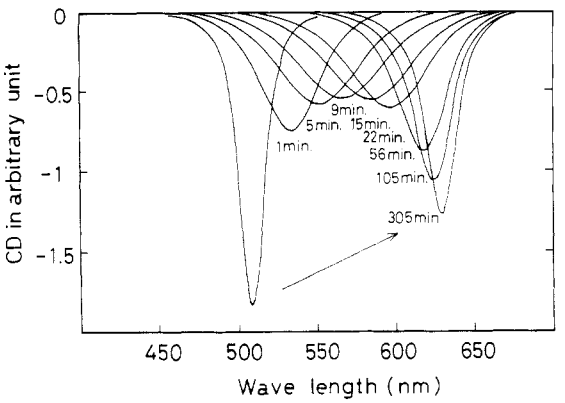


Figure 10. Time dependence of the CD spectrum observed when the temperature of the cholesteric mesophase of BD-1-37 is quickly raised from 138 to 148 °C.

dence of pitch will be given in a succeeding paper.[33]

Composition Effect. In Figure 9, the inverse optical pitches collected at 125 °C are plotted against the copolymer composition. The range of composition accessible to experiment is limited to 30–60%, but the data, which fall on a smooth curve, show a clear trend. It can be deduced that the inverse pitch decreases (or the pitch increases) substantially with dodecyl content. This increase of pitch, again, is attributed mainly to a decrease of twisted angle, since it exceeds greatly the increase of layer thickness as found in a comparison of the fourth and fifth columns of Table I.

If the trend is assumed to extend over the remainder of the range, an extrapolated intercept gives a tentative value of nP = 210 nm for PBLG, which would allow an approximation for the cholesteric pitches of other copolymeric systems derived from PBLG. On the other hand, another intercept interestingly offers a negative optical pitch of around −800 nm for PDoDLG. Although only a rough evaluation can be made here, this strongly suggests that the compensation of pitch and the inversion of helical sense may be induced on increasing the dodecyl content. If this is the case, the same phenomena should be observed as a function of temperature for a given copolymer similarly as in the lyotropic system.[28-30,34] This point will be also clarified by the detailed examination of temperature dependence of pitch.[33]

Effect of Degree of Polymerization. Different variations of pitch with degree of polymerization have been reported in lyotropic systems: constant,[35] decreasing,[36] and increasing.[37] In this case, the influence on the pitch–temperature or pitch–composition relation is negligibly small. An example can be seen in Figure 9, where the pitches for the BD-1, BD-3, and BD-4 copolymers fall on the same curve within experimental error.

D. Configurational Change of Cholesterics Due to Temperature Jump and Its Response Time. As described in section B, the rate at which the specimen assumes a twisted configuration is very slow. In a similar vein, if we cause an instantaneous change in the temperature of a cholesteric liquid crystal, a twisted configuration will transform to a new one with a slow rate process.

A typical example of this transformation is shown in Figure 10, which illustrates the time dependence of the CD spectrum attained for BD-1-37 when the temperature is quickly raised from 138 to 148 °C. Over time, a fairly smooth transformation takes place, exhibiting the following phenomena. In the initial stage, the spectrum width becomes broader and the maximum intensity decreases with time. In the final stage, the reverse tendency is observed,

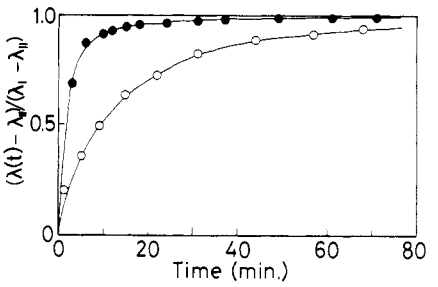


Figure 11. Time dependence of the maximum wavelength of the CD spectrum observed on transformation of the cholesteric twisted configuration due to temperature stimuli: (○) based on the data of Figure 10; (●) based on the data of Figure 13.

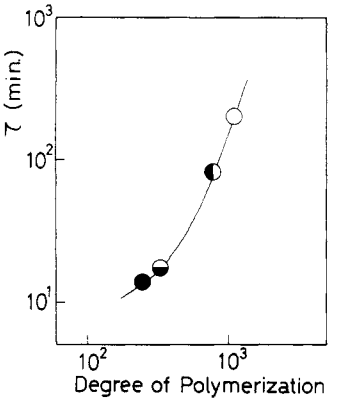


Figure 12. Variation of response time for the transformation of the cholesteric twisted configuration due to temperature stimuli with the degree of polymerization. Here the response times have been elucidated by using BD-1-37 (●), BD-2-42 (◒), BD-3-43 (◐), and BD-4-45 (○) and by applying a temperature jump from 130 to 140 °C.

leading to a final spectrum with the original features of intensity and width. Throughout this time, λ_m, which initially has a value of 510 nm, shifts gradually to the red and reaches the equilibrium value of 630 nm at 148 °C. The time dependence of λ_m is shown by the open circles in Figure 11.

The response time constant can be defined by the equation[38]

$$(\lambda(t) - \lambda_{II})/(\lambda_I - \lambda_{II}) = \exp[-(t/\tau)^{\beta}] \qquad (4)$$

where λ_I is the equilibrium wavelength of maximum reflectance, λ_{II} the initial wavelength, $\lambda(t)$ the wavelength at t (=time), τ the response time constant indicating a measure of the time taken for the transformation, and β a parameter showing the distribution of response time. According to this equation, the time constant was estimated to be around 14 min, having β = 0.7 for the data of Figure 11. Figure 12 compares time constants obtained for specimens with different degrees of polymerization and with a similar dodecyl content of around 40%. The τ are relatively large and increase with degree of polymerization. This directly indicates that the rate of transformation is markedly limited by the high viscosity of the material, which just characterizes the present polymeric liquid crystals.

It is worth noting that such a smooth transformation can be observed only on heating. Upon a jump to lower temperature, the shape of the spectrum is remarkably deformed as can be seen in Figure 13, where the temperature was quickly lowered from 148 to 138 °C. The final spectrum is also observed with the anomalous shape; the anomaly did not disappear even in the spectrum observed after 24 h. In this final spectrum, λ_m of the main peak can

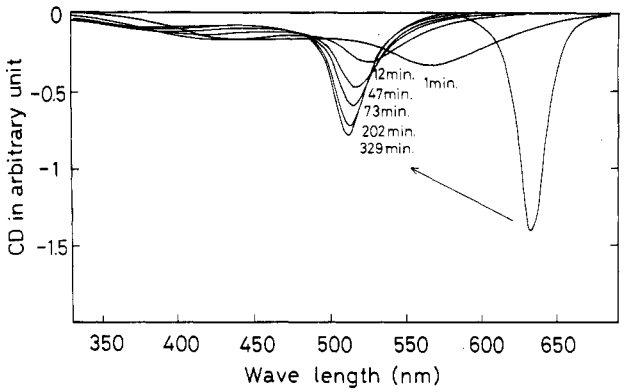


Figure 13. Time dependence of the CD spectrum observed when the temperature of the cholesteric mesophase of BD-1-37 is quickly lowered from 148 to 138 °C.

be observed at the expected equilibrium position of around 510 nm, but only one-third of its intensity is recovered. Compensating this reduction, another broad peak appears in the region of shorter wavelength around 400 nm. Together with this anomaly in the shape of the spectrum, the shift of maximum wavelength appears to be different. As far as the main peak is concerned, there can be seen a more remarkable time dependence of λ_m than that on heating (see the curve denoted by filled circles in Figure 11). The response time constant is around 1.5 min, which is only one-tenth of that on heating. Furthermore, it should be noted that a quick cooling dramatically alters the microscopic texture. As seen in Figure 5b, the original planar texture disappears and changes to a peculiar one with a set of small (5–10 μm) domains. Each domain is separated from others by a square network of dark lines, which is most easily seen in crossed polarizers. This situation is also in contrast with that observed on heating in which the initial planar texture has been maintained. Hence, the difference in texture may be related to the anomalous appearance of the CD spectrum.

Considering the structural characteristics of cholesterics, the process of transformation can be separated, hypothetically at least, into two steps. One involves a change of twist angle between adjacent pseudonematic layers. The other involves a change of macroscopic helical order. In low molar mass systems, the two would take place simultaneously. In the present system with a high viscosity, however, the order in which these two processes occur would be important since the kinetic factor is significant. With these thoughts in mind, we can picture that on heating, the two processes proceed in somewhat cooperative fashion whereas on cooling one process occurs preferentially to the other, leaving some distortion in the resultant cholesteric structure. At the present time, it is far from obvious why the mechanism of transformation should be different on heating and cooling or what kind of distortion is left on cooling. The examination is in progress.

E. Solidification of Cholesteric Liquid Crystals. From the long response time, it is certain that the materials will retain the macroscopic twisted structure of the liquid crystalline phase or its optical properties when they are chilled quickly below the transition temperature, T_2. Figure 14 compares the CD spectra of unchilled and chilled materials. As expected, there is no essential difference between the spectra with respect to the maximum wavelength and width, and only a substantial increase of intensity can be observed for the chilled material. The latter may reflect the temperature effect in which the CD peak height increases with decreasing temperature as has been observed in Figure 6.

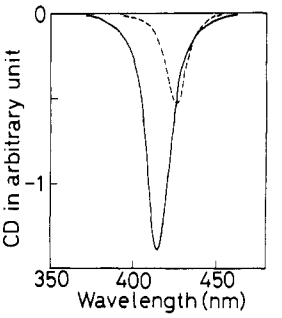


Figure 14. Comparison of CD spectra of unchilled and chilled BD-1-37. The dashed and solid curves indicate the CD spectra for the cholesteric mesophase at 130 °C and for the solid cholesteric prepared by a quick cooling of this mesophase to 20 °C, respectively.

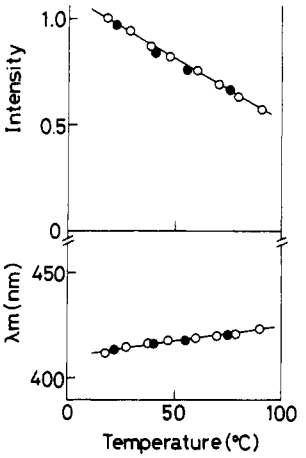


Figure 15. Temperature dependence of intensity and maximum wavelength of the CD spectrum for the solid cholesteric of BD-1-37 which was prepared by a quick cooling of the mesophase from 128 to 20 °C: (○) heating data; (●) cooling data.

For the chilled specimen, the temperature dependence of the maximum wavelength is negligibly small (see Figure 15), although the intensity is reduced with the increasing temperature as a result of the temperature effect mentioned above. With increasing temperature from 20 to 90 °C, λ_m increases only by 10 nm. This slight increase of λ_m can be explained by the thermal expansion of the distance between neighboring pseudonematic layers.[1] Hence, the twist angle remains constant in this temperature range below T_2, which is in contrast to the situation in the mesophase, where the twist angle substantially varies with temperature. We, thus, conclude that the chilling procedure causes solidification of cholesterics without altering the twisted configurational order previously existing in the mesophase. If the mesophase temperature is arbitrarily selected, chilled films can be prepared having desired colors from blue to red, and this color effect remains unchanged as long as the material is retained within a temperature region below T_2.

Concluding Remarks

Poly(γ-benzyl L-glutamate-*co*-γ-dodecyl L-glutamates) with dodecyl contents above 30% exhibited thermotropic cholesteric liquid crystals. Transition temperatures to the liquid crystalline phase decreased from 115 to 50 °C with increasing dodecyl content. The resultant cholesteric structure was well ordered and the cholesteric pitch was precisely determined by the CD spectrum. Cholesteric phases with pitches corresponding to the visible wavelength were attained in copolymers with 30–60% dodecyl content in the temperature region 100–160 °C. In this

limited range of pitch, the cholesteric pitch consistently increased with temperature for a given copolymer or with dodecyl content at a given temperature, although observation of pitches over further wide ranges is still necessary for the best understanding of both dependences. The length of the helical rod had no significant effect on cholesteric pitch.

The liquid crystal in the present polymers is like a liquid in all mechanical aspects similar to low molar mass systems, and it is only differentiated from the latter by a considerably higher viscosity. The high viscosity can be understood from the fact that the kinetic unit in the mesophase is an α-helical rod with a high axial ratio. The response time for transformation from one helical configuration to another on external physical stimuli thus can be easily envisaged to be very long. The present study examining the effect of temperature stimuli, in fact, indicated that even for the polymer with the lowest degree of polymerization of 2.5×10^2, the response time is around 15 min, which is remarkably longer than that (less than a second) in the low molar mass system. Owing to this long response time, we were able to detect the structural change during the transformation and illustrated some interesting structural characteristics of cholesterics through the observation of CD spectra.

Regarding the application of liquid crystals, the present system is not adequate for applications such as thermal indicators, pressure indicators, and radiation sensors, which need a short response time. In a sense, however, the long response time provides a method to control the structure of the polymer by solidification of the mesophase structure and thus create materials with interesting structures and optical properties, leading to another kind of application. Especially, the color effect of solid cholesterics is useful for the passive optical filtering such as low-cost band-pass and notched filters[39,40] or for recording systems.[41] Several advantages of using the present polymers for these applications are given below: (1) The scattering color due to the cholesteric structure is perfectly retained in the solid state by chilling the mesophase below T_2. (2) The retained color is varied through the entire visible spectral region and adjusted to requirement if the mesophase temperature is arbitrarily selected. (3) The selective reflectance responsible for the color effect occurs in a narrow region of wavelength so that eight or nine independent colors can be attained within the visible wavelength region. (4) A certain color retained is changed to another by heating the material at the desired temperature above T_2 and again chilling it below T_2. (5) The polymer is molded in a liquid crystalline phase, which enables easy preparation of materials with desired shape and size.

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