January, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **54**, *73—80 (1981)* 73

Chiral Mesophases of 12-Hydroxyoctadecanoic Acid in Jelly and in the Solid State. II. A New Type of Mesomorphic Solid State

Taro Tachibana,* Tomoko Mori, and Kayako Hori
Department of Chemistry, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112

(Received June 18, 1980)

A new type of chiral solid mesophase was obtained by evaporating the solvents from solutions or jellies of chiral 12-hydroxyoctadecanoic acid (12HOA). The mesomorphic solids exhibited some optical properties characteristic of a helicoidal mesophase: (1) spherulitic or Schlieren texture under a polarizing microscope, (2) reflective circular dichroic band, and (3) induced circular dichroic spectra with a single sign due to achiral molecules added to the solid. From the circular dichroic and X-ray studies, it was concluded that the helicoidal mesophase structure exists locally as small domains with a chiral smectic structure within the mesomorphic solids. Microscopic observation revealed that, upon heating, the transition of the mesomorphic solid to the crystalline solid occurred. This process was studied by differential scanning calorimetry. Formation of a variety of helicoidal systems from chiral molecules such as 12HOA and polypeptides was regarded as a phenomenon characteristic of chiral assemblies of amphiphilic molecules.

In the preceding paper,$^{1)}$ we described a chiral mesomorphic system which occurs in jellies of 12-hydroxyoctadecanoic acid (12HOA) with a solvent such as benzene or carbon tetrachloride. The jellies were shown to be composed of a number of small ordered domains with a supramolecular helicoidal structure such as has been found in the chiral smectic phase. In the course of the investigation, we have found that solids prepared by evaporating the solvents from the jellies showed liquid crystalline textures under a polarizing microscope, and that they exhibited enantiomeric circular dichroism (CD) similar to that observed for the jellies.$^{2)}$ Further, the solids yielded almost the same X-ray diffraction patterns as those of the crystalline powder. These results indicate that much of the original structure of the jelly is retained in the mesomorphic solid: the solid also is composed of a number of small ordered domains with a chiral structure, which is probably a chiral smectic type.

Mesomorphic solids with a chiral structure were first found for a synthetic polypeptide, poly (γ-benzyl L-glutamate) (PBG), by Samulski and Tobolsky.$^{3)}$ They reported that it forms stable solid films with a liquid crystalline local structure when the films are made by casting from solutions. This was evidenced from the X-ray study and the swelling experiment. Tachibana and Oda$^{4)}$ found that solid films prepared from some samples of poly (γ-methyl D(L)-glutamate) (PMG) exhibit iridescent colors due to the selective reflection of circularly polarized light of one sense. Hatano *et al.*$^{5)}$ observed an induced circular dichroism (ICD) for achiral molecules such as pyrene or acridine orange buried in solids of PMG. All these observations were attributed to the presence of the cholesteric (chiral nematic) phase in the solid films of PBG or PMG. The chiral solid mesophases have been hitherto known only for synthetic polypeptides and other biopolymers,$^{6)}$ and their mesomorphic behavior was associated with the structure of polymer molecules. However, the chiral solid mesophase of 12HOA is different from that of the above-mentioned polymers in that the former is made up of a low-molecular-weight compound; it is probably a chiral smectic phase. The present paper will deal with the structure and properties of the newly found mesomorphic solid state.

Experimental

Materials. Crystalline samples of chiral 12HOA used were the same ones as in the preceding paper.$^{1)}$ The solvents used were of reagent grade and further purified by standard methods. The samples of chiral 12HOA in the mesomorphic solid state were (1) apparently amorphous solids obtained by freeze-drying jellies or concentrated solutions, and (2) translucent solid films cast from solutions on quartz plates at room temperature. For freeze-drying, jellies (conc. of 12HOA, 50—100 mmol l^{-1}) were previously frozen at -40 °C in a deep-freezer, and solutions (0.6 mol l^{-1}) in 1-pentanol or 1-hexanol were frozen with liquid nitrogen.

Methods. The apparatus and procedure were essentially the same as those described in the preceding paper.$^{1)}$ The CD of 12HOA in the solids obtained from jellies and from solutions were measured by a Nujol mull method after the solids had been powdered. The Nujol mull was enclosed between two flat quartz plates in the form of a thin layer. The CD spectra were not modified by varying the content of samples in a Nujol mull. The CD of 12HOA in the solid film state was measured on films formed by evaporation of the solvent from the solution on a quartz plate. The linear dichroism contribution to the observed CD signal was eliminated by rotating the sample around the light beam.$^{7)}$ Thermal studies were made by the use of a DSC-2 Perkin-Elmer differential scanning calorimeter. The temperature scale was calibrated using the mp of indium supplied by the Perkin-Elmer Corp. The heat of transition was calibrated using the area under the fusion peak of indium and its known enthalpy of fusion (3.26 kJ mol^{-1}). IR spectral change with temperature was recorded on a JASCO IR-G infrared spectrophotometer with a controlled heating apparatus.

Results and Discussion

Formation of Mesomorphic Solids. Chiral 12HOA dissolves readily in cyclohexane, aromatic solvents, and chlorinated solvents such as carbon tetrachloride, chloroform, dichloromethane, and chlorobenzene, and these solutions set into jellies above a certain concentration. The jellies exhibit the optical properties characteristic of the helicoidal mesophase.$^{1,2)}$ Ap-

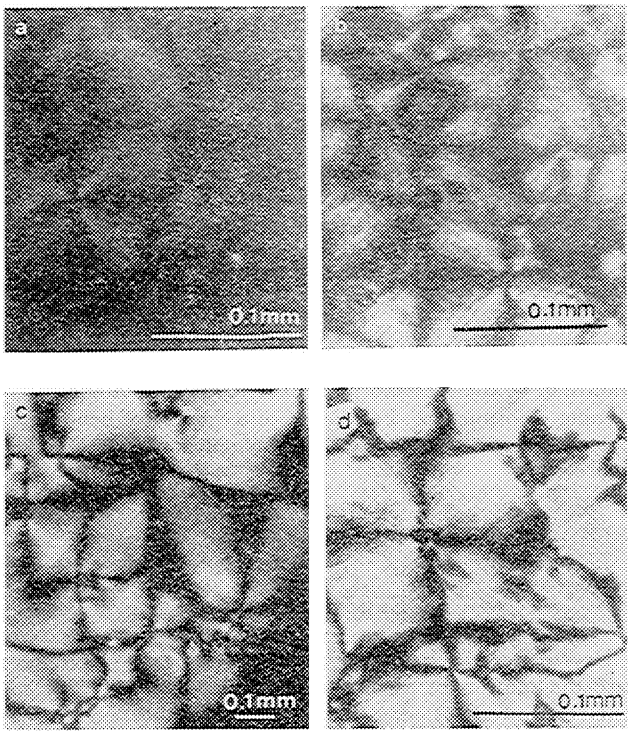

Fig. 1. Typical textures under a polarizing microscope. (a): Spherulitic texture of a CCl_4-jelly ($35.2\ \mathrm{mmol\ l^{-1}}$), (b): spherulitic texture of a solid film made from CCl_4-jelly ($35.2\ \mathrm{mmol\ l^{-1}}$), (c): schlieren texture of a CCl_4-jelly ($318\ \mathrm{mmol\ l^{-1}}$), (d): schlieren texture of a solid film made from CCl_4-jelly ($318\ \mathrm{mmol\ l^{-1}}$).

parently amorphous solids were obtained by freeze-drying the jellies, and solid films were made by casting from the jelly-forming solutions at room temperature. These solids dissolved readily in solvents for the crystalline solid. Visual observation by means of polarizing microscopy showed that these solids displayed, between crossed polarizers, the same spherulitic or Schlieren texture as did the original jellies, irrespective of solvents used, of the supporting material such as quartz, glass, potassium bromide, or calcium fluoride, and of the surface-treatment. The texture was more strikingly observed with the solid films. Figure 1 shows typical examples of the texture. The spherulitic domains in the solid films showed negative birefringence, as did that in the original jellies. These observations demonstrate that the texture in the original jellies was retained, on drying, in the solids, suggesting that the solid formed from the jellies have the same mesomorphic structure as was present in the original jellies.

On the other hand, solutions of chiral 12HOA in normal alcohols with the numbers of carbon atoms from two to seven did not form jellies; but another interesting phenomenon was observed. A drop of each hot concentrated solution of chiral 12HOA in alcohols was placed between two glass plates for microscopic use, allowed to come to room temperature, and continuously observed under a polarizing microscope. At first, there appeared a number of spherulites, but after a short period they were replaced by many needle-like microcrystals. The change from the spherulites to the crystals was faster when the alcohol used was shorter in hydrocarbon chain. Therefore, it was difficult to separate the spherulites from the solution by evaporation or filtration. However, it was possible to keep the spherulites stable for some time by mixing the thick suspension of the spherulites with Nujol immediately after occurrence of the spherulites. Figure 2 presents spherulites of (*R*)-12HOA, which were precipitated from 1-hexanol. The spherulites showed birefringence with an optically negative sign, as observed for spherulitic textures in jellies with other solvents such as benzene or carbon tetrachloride. Apparently amorphous solids from alcoholic solutions of chiral 12HOA were obtained by freeze-drying a 1-pentanol or 1-hexanol solution of chiral 12HOA. As will be described later, this solid also is a mesomorphic state.

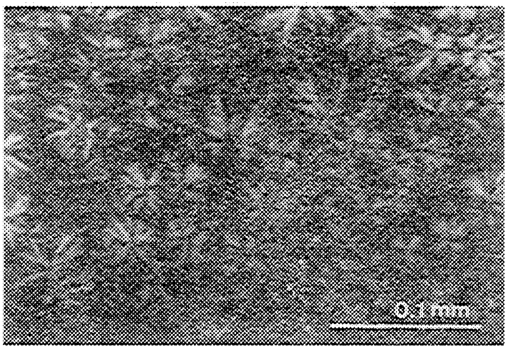

Fig. 2. Spherulites of (*R*)-12HOA in a suspension in 1-hexanol under a polarizing microscope.

Circular Dichroism in the Mesomorphic Solids. As described in the preceding paper, jellies of chiral 12HOA with benzene or carbon tetrachloride exhibit a weak but definite CD band in a range of wavelengths in which they absorb no light; the sign is negative for the (*R*)-enantiomer and positive for the (*S*)-enantiomer. The observed CD has been ascribed to the preferential reflection of circularly polarized light of one sense by the jellies in which there are a number of ordered domains with a supramolecular helicoidal structure. Mesomorphic solids of 12HOA prepared by freeze-drying the jellies also were found to exhibit a definite, but broad CD band around 550 nm with negative sign for the (*R*)-enantiomer and positive sign for the (*S*)-enantiomer, while the crystalline powder of chiral 12HOA in Nujol mull showed no CD peak except that due to the molecular absorption (≈ 200 nm). Figure 3 shows a typical example of the CD spectra of the mesomorphic solids of both enantiomers. Jellies of chiral 12HOA with various solvents exhibited a CD band in a longer wavelength region with an increase in the refractive index of the solvent used. However, mesomorphic solids prepared from the jellies exhibited a CD band in almost the same region of wavelength, 520—580 nm, irrespective of the kind of the solvent used. These data are given in Table 1. From these CD results, it is reasonable to consider that the orginal supramolecular helicoidal structure in jellies (probably a chiral smectic structure) is essentially retained in the mesomorphic solids. Thus, the solids can be regarded as a new type of chiral mesomorphic solid state.

On the other hand, the solid films of chiral 12HOA

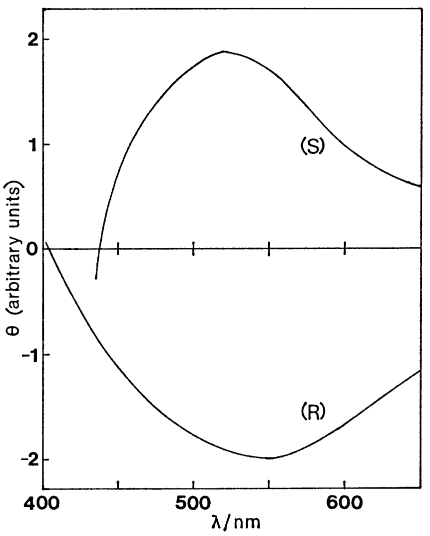

Fig. 3. Enantiomeric CD spectra of the mesomophic solids in Nujol mulls for (*R*)- and (*S*)-12HOA, made from benzene-jellies. The shape of the curve and the location of the peak varied slightly for different samples.

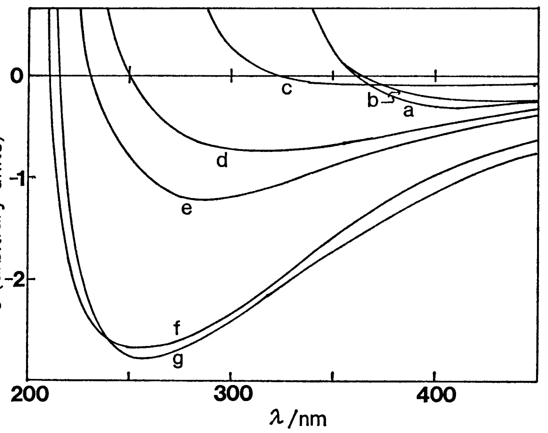

Fig. 4. Changes of CD spectra from a jelly state (128 mmol l^{-1}, with CCl_4) to a solid film state, (a) 5 min, (b) 20 min, (c) 35 min, (d) 40 min, (e) 45 min, (f) 50 min, (g) 80 min after jelly formation.

Table 1. The maximal wavelengths of CD of helicoidal mesophase formed from solutions of (*R*)-12HOA in various solvents

	n_D^{20}	λ_{max}/nm		
		Jellies	Solids	
			Freeze-dried	Films
Cyclohexane	1.426	370	520—580	250
CCl_4	1.460	370	520—580	255
Toluene	1.497	490—530	—	255
Benzene	1.501	480	520—550	260
Chlorobenzene	1.524	530—580	530—590	250

The signs of the CD bands were all negative. Jellies or solids were made with solutions ranging in concentration of (*R*)-12HOA from 50 to 100 mmol l^{-1}. Measurements were all made at room temperature.

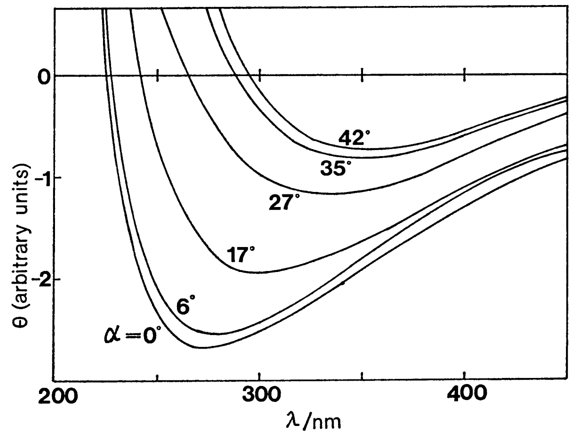

Fig. 5. CD spectra of a solid film for oblique incidence. Here, α denotes the angle between incident beam and normal to the film-supporting plate. Corrections were made for variation of the path length for oblique incidence.

cast from solutions showed a definite CD band around 250—270 nm with a negative sign for the (*R*)-enantiomer and with a positive sign for the (*S*)-enantiomer, irrespective of the solvents used. Since this result required further investigations, the change of the CD spectrum with drying of the jelly was measured on the films of benzene solution on a quartz plate. The CD change occurred gradually with drying; as the solvent evaporated, the CD increased in its intensity after an initial small decrease and shifted its band maximum from 400 to 250 nm. Figure 4 shows various CD spectra intermediate between the jelly spectrum and the solid film spectrum. This result seemed to be related to a special ordering of the molecules due to some orientational effect at an interface with air or a wall effect of film-supporting plate, but not due to the change of the helical pitch in the supramolecular helicoidal structure, since the CD bands of the solids obtained by freeze-drying locate in a longer wavelength region than those of the jellies, as shown in Table 1. In order to investigate this possibility, measurements were made on the variation of the CD spectra with the angle, α, between the incident beam and the normal to the film supporting plate. As shown in Fig. 5, the CD spectrum was found to be remarkably dependent on the angle α; the CD intensity decreased and the CD maximum shifted to a longer wavelength side with increasing α. Such a tendency was not observed for the jellies. One can see a striking similarity between the CD spectra in Fig. 4 and those in Fig. 5. This similarity suggests strongly that the CD change shown in Fig. 4 may be explained by the occurrence of an oriented local order in solid films. This deduction was confirmed by the fact that, when the solid films were detached from the quartz plate and crushed to powder, the CD maximum appeared at a wavelength region near to that observed for the amorphous solids obtained by freeze-drying jellies. The details of the alignment in solid films should be examined by using other methods.

Interestingly, both the jellies of (*R*)-12HOA and the solids from them exhibited a CD band with a negative sign, but suspensions of spherulites of (*R*)-12HOA in alcohols were found to exhibit a positive CD band around 250 nm, regardless of the normal alcohols used. Suspension of (*S*)-12HOA exhibited a negative CD band. Mesomorphic solids from alcohols were obtained by freeze-drying 1-pentanol or 1-hexanol solutions of (*R*)-12HOA, though it was difficult to prepare mesomorphic solid samples by freeze-drying the other alcoholic solutions. The amorphous solids thus obtained exhibited a positive CD band around the same wavelength region as did the suspensions. This CD result indicates that the spherulites in the alcoholic suspensions and the mesomorphic solids from the suspensions have both a supramolecular helicoidal structure, the helical sense of which is opposite to that of a supramolecular helicoidal structure in the mesomorphic solids from the jellies. The chirality of the helicoidal mesophase can be determined by the sign of the reflective CD band; a right-handed (left-handed) helicoidal mesophase reflects right (left) circularly polarized light and transmits left (right) circularly polarized light at the reflective CD band.[8-10] The mesomorphic solids from jellies of (*R*)-12HOA exhibit a negative CD band, and those from alcoholic solutions of (*R*)-12HOA exhibit a positive CD band. This indicates that the circularly polarized light reflected selectively by the solids from jellies is right-handed and that from alcoholic solutions is left-handed. This result leads us to conclude that the screw sense of the supramolecular helicoidal structure in the mesomorphic solids from jellies of (*R*)-12HOA is right-handed and on contrary, that from alcoholic solutions of (*R*)-12HOA is left-handed. Solvent dependence of the chirality of the helicoidal mesophase has already been reported[11] for the cholesteric lyotropic mesophases of polypeptides. The present results show that chiral smectic mesophases of 12HOA also undergo a similar solvent effect.

Induced circular dichroism could be detected for anthracene, which was incorporated into mesomorphic solids from jellies of (*R*)-12HOA. The ICD bands with single negative sign were obtained; these were superimposed on the CD curve of the mesomorphic solids, corresponding to the electronic spectra between 300 and 400 nm. Such ICD characteristics have been reported for jellies of 12HOA,[1,2] and for lyotropic cholesteric liquid crystals of poly(glutamate)[12] and *N*-acyl amino acids,[13] and attributed to a weak interaction between anthracene and the helicoidal systems. The ICD results obtained here also support the assertion that there are helicoidal systems in the mesomorphic solids of 12HOA.

Thermal Behavior. Microscopy with a controlled hot stage showed that, when the solid films were heated, the mesomorphic texture became obscure at about 348 K, followed by the appearance of needle-like microcrystals. Finally the microcrystals melted at 353 K. The microcrystals were stable at room temperature upon cooling and showed no reflective CD bands, indicating the absence of the supramolecular helicoidal structure. This optically observed kinetic behavior was investigated by differential scanning calorimetry (DSC). Figure 6 shows typical thermograms obtained by heating solid samples made from the carbon tetrachloride-jellies from room temperature to 356 K at four different heating rates. Each DSC trace showed two endothermic peaks, designated as I and III, and one exothermic peak, designated as II. The endothermic peak III occurred at 353 K. The peak III corresponds to the fusion of the needle-like microcrystals observed under a microscope, and occurred very close to the melting point (353.6 K) of the crystalline solids precipitated from solution. The endothermic peak I, which began to appear at 348 K at the appropriate heating rate, indicates a phase transition from the mesomorphic solid to a more disordered solid state. This peak did not recur upon reheating a sample cooled to room temperature from the melt, and the second run showed only the peak at 353 K. This result indicated that the mesomorphic solid state is a monotropic modification which occurs only when it separates out from solution.

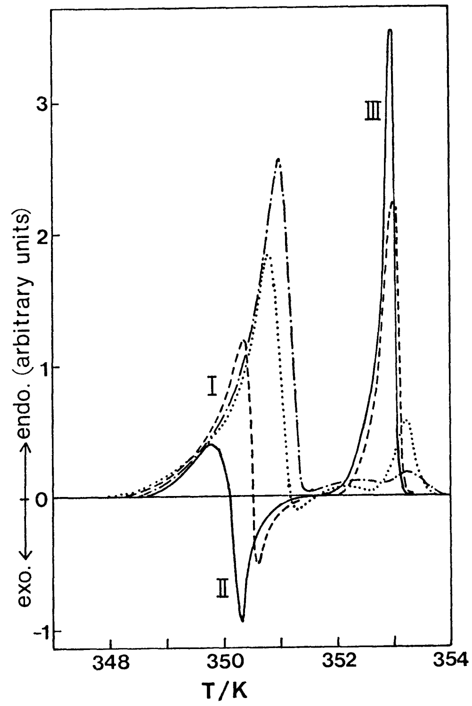

Fig. 6. DSC traces of the mesomorphic solids made from CCl_4-jelly at the various heating rates, ——: 0.31 K min^{-1}, ----: 0.62 K min^{-1}, ······: 1.25 K min, —·—: 2.5 K min^{-1}.

It is noticeable that the endothermic peak I was followed by an exothermic peak II within an extremely narrow temperature range. The combination of the DSC result with the microscopic observations would suggest that, upon heating, the mesomorphic solid state transformed into a more disordered solid state at 348 K with an endothermic process (peak I) and that, immediately after the transformation, crystal formation from the disordered solid state occurred with the exothermic process (peak II).

The thermograms for the mesomorphic solids were greatly dependent upon the heating rate, as shown in Fig. 6; those for crystalline samples of 12HOA, however, did not show such dependence. Therefore, the heating rate dependence of DSC traces for the mesomorphic solids is inherent to the materials and not due to the distortion introduced by machine time constants. The enthalpy change at each phase transition was estimated from the peak-area in the thermograms. Figure 7 represents the heating rate dependence of the enthalpy change, ΔH, corresponding to each peak. At a fast heating rate of 2.5 K min^{-1}, only the two endothermic peaks I and III occurred, and the exothermic peak II disappeared. In this case, crystal formation does not occur and the sum of the two enthalpies of transitions, 53.1 (peak I) and 3.1 (peak III) kJ mol^{-1}, agrees well with the observed value for the enthalpy of fusion of (R)-12HOA crystals, 55.6 kJ mol^{-1}.[14] This result shows that melting can occur directly from the disordered solid state to isotropic liquid at a comparably high rate of heating. On the other hand, as shown in Fig. 7, upon sufficiently slow heating, the enthalpy change at the peak I tends to vanish and, instead of it, the enthalpy changes at the peaks II and III increase. This is taken as evidence that there is a path through which the solid mesophase can transform directly into the crystalline phase. In summarizing these results, the phase transition paths may be represented as in Fig. 8.

The transition from a mesomorphic solid to a more disordered solid state is considered to involve a change in the state of hydrocarbon chains, since it has been reported for long hydrocarbon chain compounds that an order-disorder transition in the organization of hydrocarbon chains occurs prior to the melting of the crystal in bulk.[15] In order to investigate this problem, measurements were made to obtain the temperature dependence of infrared spectra of the mesomorphic solids which had been made as a thin film on a potassium bromide plate. Figure 9 shows a series of bands in the range of 1300—1150 cm^{-1}; these are regarded as the band progression of wagging vibrations of the trans-zigzag methylene chains, as have been assigned for polymethylene chains.[16] On heating, transmission of the background began to decrease at about 348 K, and the progressive bands changed into a broad band at 351 K. At the same time, hydrogen-bonded hydroxyl band (3200 cm^{-1}) and C=O band (1700 cm^{-1}) in the carboxyl group were shifted to the higher wavenumbers. Further heating brought a rapid increase in the transmission of the background at 353 K, the melting point of the crystal separated out from the mesomorphic solid. On the other hand, the infrared spectra of the crystalline solids precipitated from solution were measured by a Nujol mull method and retained the distinct structure of the progressive bands until 352 K, just below the melting point of 353.6 K. These infrared results indicate that "melting" of the hydrocarbon chains occurs in the endothermic process of the mesomorphic solid-a more disordered solid state transition and that the "melting" remains still in the needle-like microcrystals separated out from the disordered solid state, though they showed almost the same melting point as that of the crystalline solids precipitated from solution.

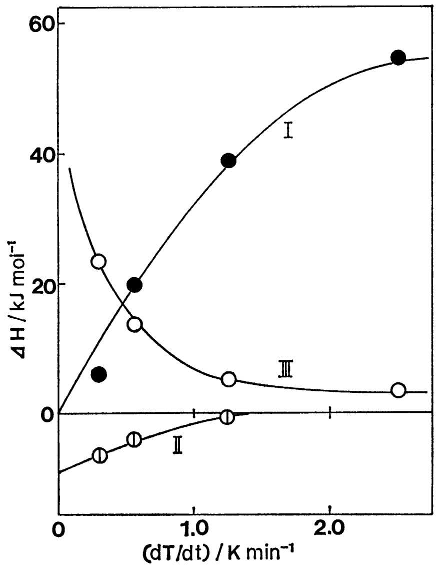

Fig. 7. Heating rate dependence of the enthalpy changes at the phase transitions in the mesomorphic solids made from CCl_4-jellies. Symbols I, II, and III denote the peaks represented in Fig. 6.

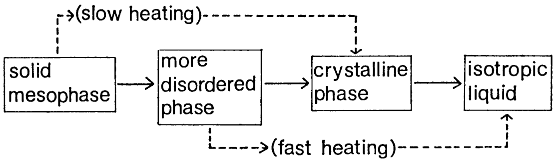

Fig. 8. Phase transitions of the mesomorphic solid by heating.

Moreover, the thermal studies were done for the mesomorphic solids prepared from jellies or solutions with various solvents, since it was shown that the CD spectra of these mesomorphic solids are affected by the particular solvents used. Figure 10 presents the DSC traces obtained at a slow heating rate, 0.31 K min^{-1}, for various samples, showing that the curves

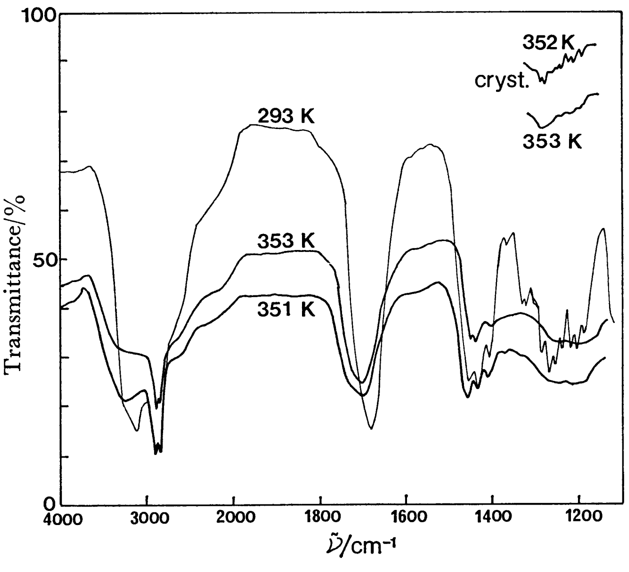

Fig. 9. Temperature dependence of IR spectra of the mesomorphic solid made from CCl_4-jelly. IR spectra of the crystalline solid in a Nujol mull are shown in the same figure.

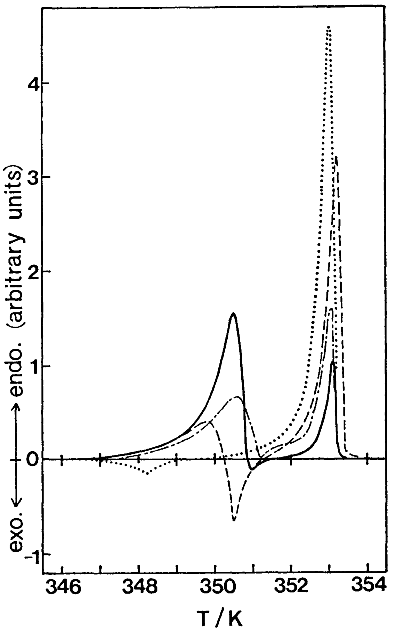

Fig. 10 DSC traces of the mesomorphic solids at a heating rate of 0.31 K min^{-1}.
······: Made from a cyclohexane-jelly, – – –: made from a benzene-jelly, —·—: made from a 1-pentanol suspension, ——: made from a chlorobenzene-jelly.

vary with the solvents used for preparation of the solids. The DSC trace of the solid from the cyclohexane-jelly was missing the endothermic peak I observed for that from the carbon tetrachloride-jelly. The solid from the chlorobenzene-jelly gave a larger endothermic peak I and a smaller endothermic peak III, in comparison with the endothermic peaks I and III, observed for the solid from the carbon tetrachloride-jelly. The DSC curves with an intermediate shape were obtained for the solids from other jellies and alcoholic solutions. In every case, as the heating rate became faster, the endothermic peak I for the transition of the mesophase to a more disordered phase became higher and the endothermic peak III became lower. When the mesomorphic solids are formed by evaporating the solvents from the jellies or the solutions of 12HOA, the degree of organization of the hydrocarbon chains in the smectic domains probably is different, depending on the solvent used. This may explain the difference in the DSC traces and in the CD spectra of the solids prepared by using various solvents.

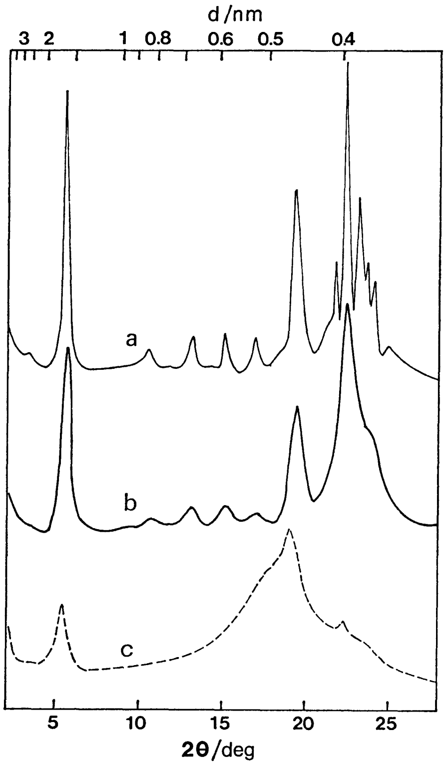

Fig. 11. X-Ray diffraction patterns of (a) powdered crystalline solids, (b) mesomorphic solids from a CCl_4-jelly, (c) jelly (257 mmol l^{-1}, with benzene) (cited from Ref. 1).

X-Ray Diffraction Studies. Figure 11 shows the X-ray diffraction patterns of a powdered sample of the mesomorphic solids and of the crystalline solids, together with that of the benzene-jelly. The mesomorphic solids exhibit the patterns which are very similar to those of the powdered crystalline solids, although each peak in the former is broader than that in the latter. These patterns are composed of comparably sharp peaks corresponding to a long spacing of 4.67 nm (shorter than twice the extended length of 12HOA molecule)[1)] and peaks corresponding to short spacings (below 0.46 nm) associated with the interchain packing. This result indicates that there is little difference in short-range-order structure between the mesomorphic solid and the crystalline solid and that, consequently, the mesomorphic solids are composed of a number of small domains with a lamellar structure similar to that in the crystalline solid, though the organization of the alkyl chains in the lamellar structure in the former is less ordered than that in the crystalline solid. Since the lamellar mesophase is a separate phase from the crystalline phase, as evidenced by the thermal studies, it is concluded that the mesophase has a smectic structure, which often forms lyotropic liquid crystals of amphiphilic molecules.

The X-ray examination was also done for the solid films formed by air-drying the benzene-jellies on a sample plate. The diffraction patterns were almost the same as those of the mesomorphic solids obtained by freeze-drying the jellies, except that the patterns from the solid films were missing the reflection peak corresponding to a short spacing of 0.46 nm. The 0.46 nm peak was recovered for the powdered sample obtained by crushing the solid films which were detached from the plate. Therefore, this effect is considered to be attributable to the same orientation effect as has been found in the CD study of the solid films.

Concluding Remarks. *Helicoidal Order in Micellar and Polymer Systems*: In the present series of papers (I and II), it was described that chiral 12HOA can form lyotropic helicoidal mesophase and solid analogues. This acid and its salt have been found to form helically twisted microfibrils.[17,18)] Here it would

TABLE 2. SIMILARITY OF MODE IN MOLECULAR ASSOCIATION BETWEEN PMDG AND (*R*)-12HOA

State	Aggregated forms	
	PMDG	(*R*)-12HOA
Dil soln	α-Helix	Chiral micelle
Concd soln and amorphous solid	Helicoidal mesophase (chiral nematic)	Helicoidal mesophase (chiral smectic)
Fibrous state	Helically twisted fibrils (right-handed)	Helically twisted fibrils (left-handed)

be useful to call attention to the helicoidal association of polymer molecules of some polypeptides such as PBG or PMG. That is, these polymer molecules can assemble into a variety of helicoidal forms,[3] *i.e.* (1) helicoidal configuration[3] of single molecule (α-helix), (2) helicoidal (chiral nematic) mesophase in solution above a critical concentration, (3) solid films with helicoidal (chiral nematic) local order, and (4) helically twisted microfibrils.[19] Table 2 illustrates the similarities between 12HOA and PMG with regard to the mode of molecular association. Here a micelle of 12HOA corresponds to the α-helix of a PMG molecule, since the former itself also constitutes a chiral system[20] as does the α-helix. Polypeptides are considered to be amphiphilic in nature since they can form stable monomolecular films at an air-water or oil-water interface. Furthermore, it should be pointed out that both polypeptides and 12HOA are capable of forming the inter- or intramolecular hydrogen bonds. Undoubtedly these common properties of both chiral amphiphiles are responsible for the similarities in the formation of helicoidal assemblies. Chiral 12HOA is a small molecule, but these molecules can link with each other to form "a chiral polymer" by intermolecular hydrogen bonding between the hydroxyl groups; as a result, these "polymer molecules" behave like chiral amphiphilic macromolecules such as polypeptides. The polymer-like behavior of chiral 12HOA that forms jellies with solvents, spherulites or microfibrils are well explained by the formation of the hydrogen-bonded polymers.

The similarity between chiral 12HOA and polypeptides led us to infer that there are some other amphiphiles exhibiting a similar behavior. In fact, this has been shown in several reports. Sakamoto *et al.*[13,21] found that optically active *N*-acyl amino acids such as *N*-lauroyl amino acid form cholesteric mesophase in apolar solvents and form chiral aggregates in polar solvents. They ascribed this result to chiral intermolecular hydrogen bonding. Sato and Hatano[22] found that the nonionic surfactant, "Tween 80" (Atlas Powder Co.) induced CD spectra to an achiral dye solubilized into the micellar solutions. They ascribed this result to the formation of a helicoidal mesophase in concentrated aqueous solution of the surfactant. Kunitake *et al.*[23] observed ICD spectra of a hydrophobic azo dye added to synthetic bilayer membranes of chiral dialkylammonium amphiphiles derived from alanine and glutamic acid. This result seems to suggest that the bilayer membranes constitute a chiral mesomorphic system.

The association behavior of bile acids and their salts also is worthy of remark. Several workers[24,25] have reported ICD results for achiral molecules dissolved in aqueous micellar solutions of sodium deoxycholate, suggesting the fomation of chiral micelles. Ramanathan *et al.*[26] observed that deoxycholic acid formed helical microfibrils when its water suspensions were dried on carbon films and that the helical twist was right-handed. The gelation of sodium deoxycholate solutions also has been often investigated, and the role of hydrogen bonding in the molecular association has been discussed.[27,28] These results seem to suggest that the gels of the deoxycholate can form helicoidal mesophases under a suitable condition, but the evidence has not yet been obtained. All the results observed with these chiral amphiphiles indicate that chiral amphiphiles constitute chiral or helicoidal micellar systems throughout the formation of sequences of intermolecular hydrogen bonds.

In general, amphiphilic molecules exhibit a variety of modes of molecular association, such as micelle, mono- and multilayers, bilayer membrane (liposome), smectic phase, and nematic phase. In addition, when amphiphilic molecules have a chiral structure, they are able to take a preferred orientation in the molecular assemblies, leading to occurrence of chiral assemblies. The resulting assemblies have a different structure from that of assemblies of achiral molecules or racemate molecules. This is reflected in the critical micelle concentration of solution[29] or in the compression curve of monolayers at an air-water interface.[30,31]

In a macroscopic scale observable with a microscope, amphiphiles form thin ribbons or microfibrils. This has been investigated most often with soaps and phospholipids. In some cases, these ribbons or fibrils twist helically regardless of whether the amphiphiles are chiral or not. Then, achiral amphiphiles produce both right-handed and left-handed helices in equal numbers, *e.g.* as have been observed for helical microfibrils from calcium tallowate in grease or from alkali-metal soaps. On the other hand, chiral amphiphiles produce a one-handed helix depending on the chirality of the molecule, though the helical sense is influenced by solvent effects.

The morphology of the assemblies of chiral amphiphilic molecules is of biological interest, since helically twisted lamellae or microfibrils are often encountered in biological systems. The present study suggests that these biological materials form helicoidal mesophases. On this connection, it is instructuve to cite a recent review by Bouligand,[6] who collected examples illustrating that biopolymers assemble into cholesteric liquid crystals or into more or less solid analogues, and that certain fibrous and regularly twisted materials can be considered as polymerized cholesterics.

We wish to thank Miss Y. Onishi for her co-operation in the experimental work, Dr. K. Sakamoto of Central Research Laboratories, Ajinomoto Co., Inc., for his valuable comments, Professor M. Hatano of

Tohoku University for valuable information regarding the signs of CD, and Professor M. Nakazaki of Osaka University for the kind advice concerning the definition of the handedness in a helix. We also are indebted to Professor J. Kumanotani of the University of Tokyo, for giving us the opportunity to use a DSC-2 Perkin-Elmer differential scanning calorimeter.

References

1) T. Tachibana, T. Mori, and K. Hori, *Bull. Chem. Soc. Jpn.*, **53**, 1714 (1980).

2) T. Tachibana, T. Mori, and K. Hori, *Nature*, **278**, 578 (1979).

3) F. T. Samulski and A. V. Tobolsky, "Liquid Crystals and Plastic Crystals," ed by G. W. Gray and P. A. Winsor, Ellis Horwood, Chichester (1974), pp. 175—198.

4) T. Tachibana and E. Oda, *Bull. Chem. Soc. Jpn.*, **46**, 2583 (1973).

5) N. Tsuchihashi, H. Nomori, M. Hatano, and S. Mori, *Chem. Lett.*, **1974**, 823.

6) Y. Bouligand, "Mesomorphic Order in Polymers and Polymerization in Liquid Crystalline Media," ed by A. Blumstein, American Chemical Society, Washington, D. C. (1978), pp. 237—247.

7) F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, **99**, 4848 (1977).

8) This was derived for a helical stacking of birefringent layers (see, *e.g.* E. B. Priestley, *RCA Rev.*, **35**, 584 (1974)).

9) H. Kozawaguchi and M. Wada, *Mol. Cryst. Liq. Cryst.*, **45**, 55 (1978).

10) Right- and left-handed helicoids are defined here as they have been usually for the screw sense; that is, this definition of helical sense is consistent with the usual description that a double-helix of DNA is right-handed. The definition of twist and helical sense adopted by Saeva and Olin (*J. Am. Chem. Soc.*, **78**, 2709 (1976)) is in contrast to our definition.

11) H. Toriumi, Y. Kusumi, I. Uematsu, and Y. Uematsu, *Polymer J.*, **11**, 863 (1979) and references cited therein.

12) F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, **95**, 7882 (1973).

13) K. Sakamoto, R. Yoshida, M. Hatano, and T. Tachibana, *J. Am. Chem. Soc.*, **100**, 6898 (1978).

14) Uzu and Sugiura (*J. Colloid Interface Sci.*, **51**, 346 (1975)) reported the enthalpy of fusion of (*R*)-12HOA crystal to be 8.50 kcal mol^{-1} (35.5 kJ mol^{-1}), which seems to be too small when compared with that of octadecanoic acid (57.5 cal $g^{-1}=68.4$ kJ mol^{-1}) (W. S. Singleton, T. L. Ward, and F. G. Dollear, *J. Am. Oil Chem. Soc.*, **27**, 143 (1950)).

15) V. Luzzati, H. Mustacchi, and A. E. Scoulios, *Nature*, **180**, 600 (1957).

16) M. Tasumi, T. Shimanouchi, and T. Miyazawa, *J. Mol. Spectrosc.*, **9**, 261 (1962); R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 85 (1963).

17) T. Tachibana and H. Kambara, *Bull. Chem. Soc. Jpn.*, **42**, 3422 (1968).

18) T. Tachibana, S. Kitazawa, and H. Takeno, *Bull. Chem. Soc. Jpn.*, **43**, 2418 (1970).

19) T. Tachibana and H. Kambara, *Kolloid-Z.*, **219**, 40 (1967).

20) T. Tachibana and K. Kurihara, *Naturwissenschaften*, **63**, 532 (1976).

21) K. Sakamoto and M. Hatano, *Bull. Chem. Soc. Jpn.*, **53**, 339 (1980).

22) A private communication from Professor M. Hatano of Tohoku University.

23) T. Kunitake, N. Nakashima, S. Hayashida, and K. Yonemori, *Chem. Lett.*, **1979**, 1413.

24) J. H. Perrin and M. Wilsey, *J. Chem. Soc., Chem. Commun.*, **1971**, 769.

25) J. Gawronski, *Tetrahedron Lett.*, **1976**, 3845.

26) N. Ramanathan, A. L. Currie, and J. R. Colvin, *Nature*, **190**, 779 (1961).

27) G. Sugihara, T. Ueda, S. Kaneshima, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **50**, 604 (1977).

28) D. G. Oakenfull and L. R. Fisher, *J. Phys. Chem.*, **81**, 1838 (1977).

29) M. Takehara, I. Yoshimura, and R. Yoshida, *J. Am. Oil Chem. Soc.*, **51**, 419 (1974).

30) E. M. Arnett, J. Chao, B. Kinzig, M. Stewart, and O. Thompson, *J. Am. Chem. Soc.*, **100**, 5575 (1978).

31) T. Tachibana, T. Yoshizumi, and K. Hori, *Bull. Chem. Soc. Jpn.*, **52**, 34 (1979).