Chiral Mesophases of 12-Hydroxyoctadecanoic Acid in Jelly and in the Solid State. I. A New Type of Lyotropic Mesophase in Jelly with Organic Solvents

Taro TACHIBANA,* Tomoko MORI, and Kayako HORI*
Department of Chemistry, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112
(Received October 26, 1979)

Thermally reversible jellies of optically active 12-hydroxyoctadecanoic acid (12HOA) with CCl_4 or aromatic solvents form a lyotropic mesophase, which shows enantiomeric circular dichroism (CD) and induced CD due to achiral molecules added to the jellies, indicating that the jellies have a supramolecular helicoidal structure. The X-ray examination revealed that the jellies are composed of a number of small, ordered domains with such a lamellar structure as is observed in the crystalline solid. The supramolecular helicoidal structure was associated with the lamellar structure; as a result, it was suggested that the lyotropic mesophase has a chiral smectic structure and, furthermore, that the mesophase is present in thin, fibrous aggregates of 12HOA molecules within which the jellies are enmeshed.

Optically active 12-hydroxyoctadecanoic acids (12HOA) form thermally reversible jellies with aromatic solvents or carbon tetrachloride, while the racemic 12HOA separates out as crystals from the saturated solution in these solvents. We have recently found that the jellies present images very similar to that of the liquid crystalline phase under a polarizing microscope, and that they exhibit an enantiomeric circular dichroism (CD) in a region of wavelengths where the molecules have no absorption.[1] These hitherto undescribed observations led us to infer that the jellies form a lyotropic mesophase with a supramolecular chiral structure. The best-known example of such mesophases is a cholesteric (chiral nematic) mesophase formed by such synthetic polypeptides as poly(γ-benzyl glutamate) (PBG) in organic solvents.[2] Lyotropic mesophases with a cholesteric structure composed of a low-molecular-weight compound were recently reported for swelling gels of *N*-acylamino acids in aromatic solvents.[3] We found that the jellies of 12HOA were composed of a chiral smectic mesophase structure which exists locally as small domains with randomly-oriented helical axes. This paper will describe a new chiral mesophase, which is different from the cholesteric mesophase of PBG or *N*-acylamino acids.

Experimental

Materials. The crystalline samples of (*R*)-12HOA were purified from commercial products, as has been described previously.[4] The (*S*)-12HOA was prepared by a method described previously from the methyl ester of (*R*)-12HOA.[4] The purities, as estimated from the results of gas chromatography, the melting point, and the specific rotatory power ($[\alpha]_D^{25}$/deg dm^{-1} cm^3 g^{-1} (in pyridine)), of these samples were as follows: (*R*), 99.1%, 353.4 K (lit,[4] 353.6 K), −0.46 (lit,[5] −0.41); (*S*), 97.2%, 352.3 K, +0.44 (lit,[5] +0.3±0.1). The solvents for jelly formation were of a reagent grade and were further purified by the standard method.

Methods. The mesomorphic textures were observed by using an Olympus POM polarizing microscope. The CD spectra were recorded on a JASCO J-20A spectropolarimeter using 1—10 mm thick cells, depending on the concentration (25—120 mmol l^{-1}). The CD were expressed by the molar ellipticity $[\theta]$/deg dm^2 dmol^{-1}. The absorption spectra were measured on a Shimadzu UV-200S spectrophotometer. The X-ray diffraction patterns of jellies were obtained using a Rigaku Rotaflex 2078 diffractometer with Cu $K\alpha$ radiation, with 50 kV and 200 mA. Jellies about 1 mm thick were formed in the opening of an aluminum sample holder and were sandwiched by two poly(ethylene terephthalate) films 7 μm thick. X-Ray diffraction patterns for jellies with benzene were successfully obtained by a transmission method, which was carried out for samples fixed vertically to an incident beam. By this method, the obtained patterns were almost uninfluenced by poly(ethylene terephthalate) films in the range of $2\theta = 1°$—$30°$. However, the transmission method was unsuccessful for jellies with CCl_4 because of the large scattering power of the Cl atoms. In this case, a conventional reflection method was available, but the peaks at low diffraction angles were very much smaller than those for jellies with benzene measured by means of a transmission method, because of the absorption of X-rays due to their long path in a poly(ethylene terephthalate) film cover at a low-angle incidence.

Results and Discussion

Jelly Formation. Chiral 12HOA dissolves readily in aromatic solvents and chlorinated solvents, such as carbon tetrachloride, chloroform, or dichloromethane, at high temperatures. These solutions set to jellies, on cooling, in a reversible way. Jellies with benzene or carbon tetrachloride are almost transparent; therefore, these are used as samples for optical studies. Solutions above 25 mmol l^{-1} in carbon tetrachloride and above 33 mmol l^{-1} in benzene set to jellies at 25 °C. The transition between solution and jelly occurred over a narrow temperature range and showed hysteresis because of the slow rate of the transition. The jellies were thixotropic, indicating that the jelly structure is held by weak bondings.

According to our previous infrared spectroscopic study,[6] the jellies are held by molecular association involving intermolecular hydrogen bonding in which almost all the hydroxyl groups take part; isotropic solutions of chiral 12HOA in carbon tetrachloride exhibited the absorption bands due to the free hydroxyl groups in addition to the absorption bands due to the hydrogen-bonded hydroxyl groups, while the jellies gave only the absorption bands due to the hydrogen-bonded

hydroxyl groups. Furthermore, the infrared spectral results led us to conclude that the hydroxyl groups link the chiral molecules by multiple hydrogen bonding, forming long sequences of hydrogen bonds. Such hydrogen bonding was also found for both the crystalline solids and the built-up multilayers, and it was assumed to exist also in the monolayers at the air-water interface.

When hot solutions of 12HOA were rapidly cooled in an ice-bath, the jellies thus formed were found to scatter a bluish light, which disappeared at room temperature after a short period. This indicates a heterogeneous structure of the jellies; the scattering centers grow to such various sizes that the centers scatter light over a wide range of wavelengths. A bluish scattering light was also observed for the crystalline powder of 12HOA immersed in benzene or carbon tetrachloride. This indicates that the dissolution of crystals of 12HOA into the solvents occurs through the jelly formation.

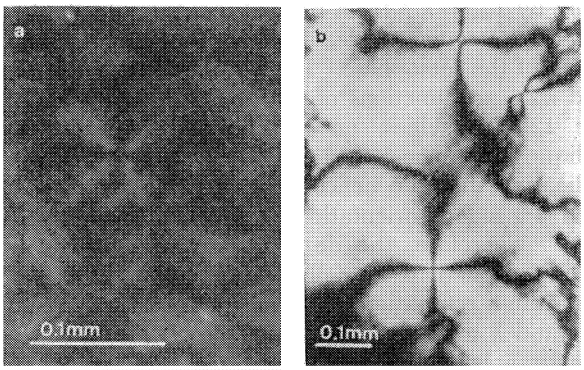

Fig. 1. Microscopic textures of jellies of (*R*)-12HOA–CCl_4 between crossed polarizers.
(a): Spherulitic texture (43 mmol l^{-1}); (b): Schlieren texture (318 mmol l^{-1}).

Microscopic Examination. Hot solutions of (*R*)-12HOA in carbon tetrachloride were placed between two glass plates and cooled to room temperature. The resultant thin films of the jellies were examined by means of a polarizing microscope. The jellies were birefringent; however, the sign of birefringence was not determined because of the difficulty of preparing the oriented single domain samples. The jellies displayed a spherulitic or Schlieren texture between crossed polarizers. The microscopic textures are shown in Fig. 1. The surface treatment of supporting plates had no effect on these textures. There was a general tendency for the spherulitic texture to occur in the jellies prepared by the slow cooling of the solutions of a lower concentration and for the Schlieren texture to occur in the jellies prepared by the rapid cooling of the solutions of a higher concentration. These textures are similar to the patterns observed previously in thermotropic[7] or lyotropic liquid crystals.[8] Thus, the microscopic observation indicates that the jellies have local orders with a mesomorphic structure. Generally, it is difficult to determine from the microscopic texture whether the type of lyotropic mesophase is nematic, smectic, or cholesteric.

The spherulitic domains showed an extinction cross, which was unchanged on the rotation of the stage of the polarizing microscope. The optical sign of the spherulitic domains, as determined by using a sensitive color plate, was negative. A similar spherulite-like phase with optically negative sign has also been observed for the *N*-octadecanoyl-L-glutamic acid–dimethyl phthalate system, which was regarded as a liquid crystalline phase of the cholesteric type.[3]

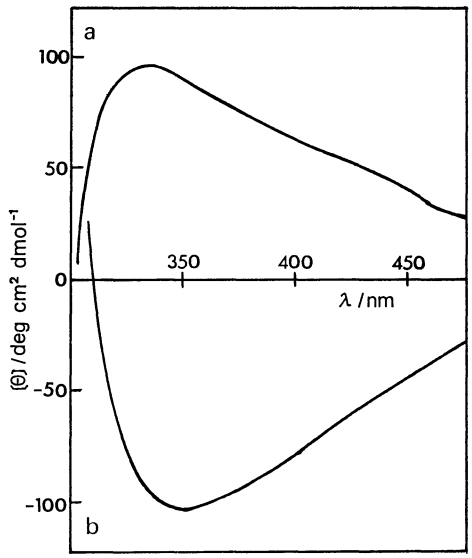

Fig. 2. Enantiomeric CD bands of jellies of 12HOA–CCl_4 at room temp.
(a): (*S*)-12HOA, 25.7 mmol l^{-1}; (b): (*R*)-12HOA, 35.7 mmol l^{-1}.
The location of the CD maximum was insensitive to change of temperature (see Fig. 6).

Circular Dichroic Studies. The jellies exhibited a weak, but definite CD band with a peak around 370 nm, a range of wavelengths in which they absorbed no light. The sign was negative for the *R*-enantiomer and positive for the *S*-enantiomer, irrespective of the solvents used. Figure 2 shows a typical example of the enantiomeric CD bands for jellies of (*R*)- and (*S*)-12HOA with carbon tetrachloride. This enantiomeric relationship was observed quite reproducibly, though the intensities, $[\theta]$, and the locations of the CD maximum, λ_{max}, were rather scattered. This indicates that the CD bands originate from the chirality of the 12HOA molecule. A similar CD spectrum was also observed for jellies with other solvents, such as benzene (λ_{max}: around 480 nm) and toluene (λ_{max}: around 470 nm). Linear dichroism, which is attributable to any strain introduced on jelly formation, was little observed when examination was done by means of the procedure of Tunis-Schneider and Maestre.[9] The observed CD spectrum is thus ascribed to the selective reflection of circularly polarized light in one sence by the chiral jellies. The same optical phenomenon has been observed for cholesteric liquid crystals and explained by assuming a supramolecular helicoidal structure with a twist determined by the chirality of the constituent molecules.[7]

An enantiomeric induced circular dichroism (ICD) could also be observed for some achiral molecules when

they were dissolved in jellies of chiral 12HOA. Figure 3 shows the ICD bands (superimposed on the CD curve of the jelly) and the electronic spectra between 330 and 395 nm for anthracene dissolved in a jelly of (*R*)-12HOA. The ICD bands show a single sign (negative for (*R*)-12HOA and positive for (*S*)-12HOA) and follow the electronic spectral bands closely. Such ICD characteristics have also been observed for lyotropic cholesteric mesophases of PBG[10] and other polypeptides, and more recently for those of *N*-acylamino acids.[3] Figure 4 shows similar ICD results obtained for a cyanine dye, pynacyanole chloride, which was not soluble in carbon tetrachloride, but was solubilizable in solutions or jellies of 12HOA with the same solvent. These ICD results support the assumption that 12HOA jellies are composed of a type of lyotropic chiral mesophase with a supramolecular helicoidal structure.

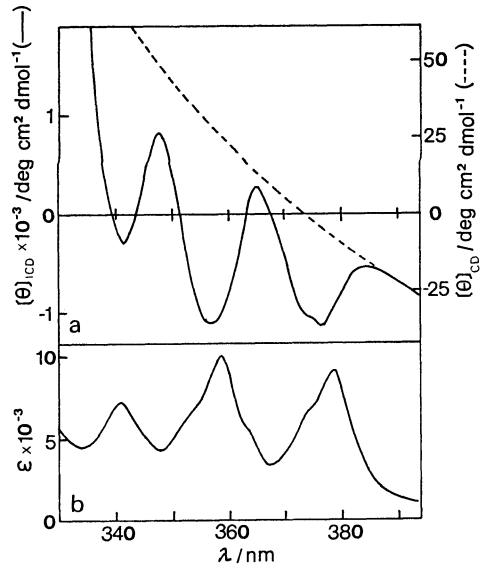

Fig. 3. (a) ICD spectral bands (——) for anthracene (8.8 mmol l^{-1}) superimposed on the CD curve (----) of the jelly of (*R*)-12HOA- CCl_4.
Enantiomeric ICD bands of jellies of (*S*)-12HOA-CCl_4 are omitted from the figure.
(b) Electronic spectra of anthracene.

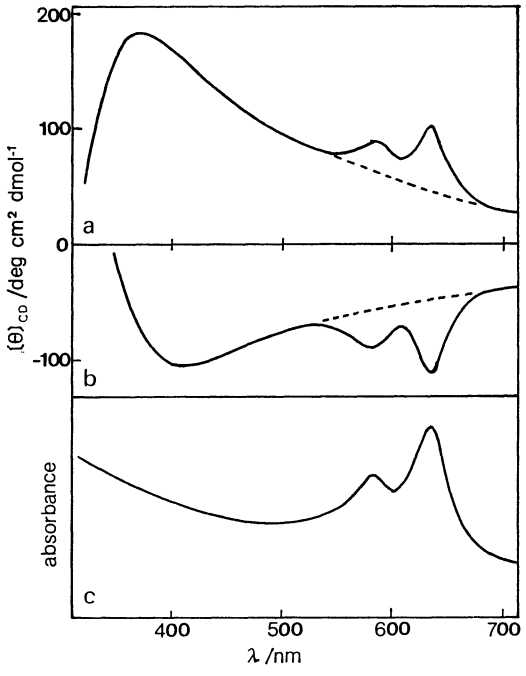

Fig. 4. (a) ICD spectral band for pynacyanole chloride superimposed on the CD band of a jelly of (*S*)-12HOA-CCl_4 (52.7 mmol l^{-1}). (b) Those of a jelly of (*R*)-12HOA-CCl_4 (42.3 mmol l^{-1}). (c) Electronic spectral bands for pynacyanole chloride in the jelly.

The dimensions of the structure may be estimated assuming the model of the helicoidal structure proposed by de Vries.[11] The model postulates only a helical stacking of birefringent layers, regardless of whether or not the helicoidal structure is a cholesteric type. The CD band is due to the selectively reflected light with circular polarization in one sense. In this case, λ_{max} is simply related to the pitch, p, of the supramolecular helix by $\lambda_{max}=\bar{n}.p$ for a normal incidence to the layers in a homeotropic sample, where $\bar{n}$ is an average refractive index of the mesophase. For an oblique incidence, $[\theta]$ and λ_{max} are functions of the angle of incidence. For the 12HOA jellies, no angular dependence for an oblique incidence could be found in $[\theta]$ and λ_{max}, indicating that the helicoidal structures are dispersed, with a random orientation of the helical axes in the jelly. Therefore, the de Vries equation can not be strictly applied to the jellies of 12HOA. However, a very rough estimation of p from the observed values of λ_{max} and $\bar{n}$ may be possible. For example, p was 250 nm for a jelly with carbon tetrachloride with $\lambda_{max}=$ 370 nm and $\bar{n}=1.46$, while p was 320 nm for a jelly with benzene with $\lambda_{max}=480$ nm and $\bar{n}=1.50$. Though λ_{max} appeared in a visible wavelength region, the band ranged within a wide region of wavelengths, so that such an iridescent color as was observed for cholesteric liquid crystals was not exhibited. The CD maximum for a jelly sample containing any additive was found to be shifted to a longer wavelength than that for the original jelly. Since little differences in $\bar{n}$ were found between additive-free and additive-containing jellies with carbon tetrachloride (for example, n_D^{22} is 1.4600 for the former and 1.4603 for a jelly containing 8.8 mmol l^{-1} of anthracene), the shift of λ_{max} is ascribed to an increase in the pitch of the helicoid with the incorporation of additive molecules into the helicoidal structures.

The chirality of the chiral mesophase can be found by determining the handedness of the reflected or transmitted light with circular polarization from the CD band (the pitch band). In the case of jellies of (*R*)-12HOA, the sign of the CD is negative, as is shown in Fig. 2, indicating that right-hand circularly polarized light is selectively reflected by the jelly. Therefore, the screw sense of the molecular helical arrangement is right-handed.[12] That is, the sense of the supramolecular helix is right-handed (P-helicity) for (*R*)-12HOA and left-handed (M-helicity) for (*S*)-12HOA.

The above-mentioned results indicate that there is a striking similarity between jellies of 12HOA and typical cholesteric mesophases. However, there are several differences in CD characteristics between two systems.

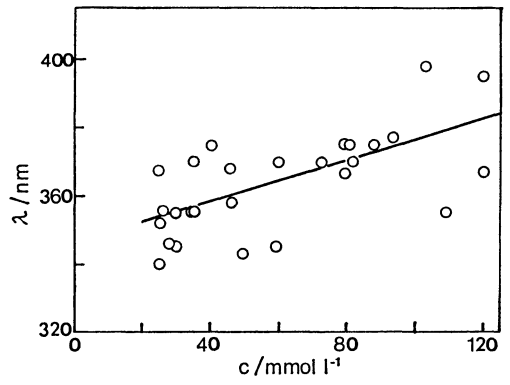

Fig. 5. Concentration dependence of λ_{max} of jellies of (*R*)-12HOA–CCl_4.

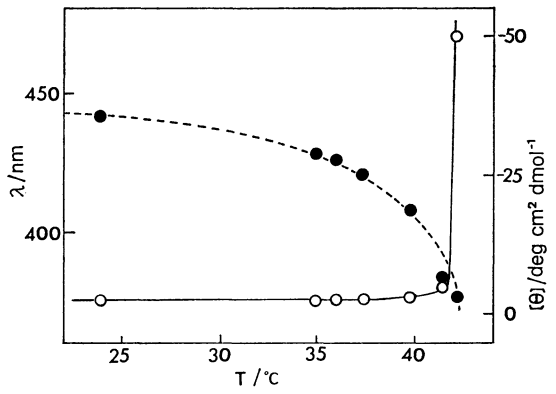

Fig. 6. Temperature dependence of λ_{max} (○) and $[\theta]$ (●) of a jelly of (*R*)-12HOA–CCl_4 jelly (81.7 mmol l^{-1}).
The jelly melted into isotropic soln. at 42 °C.

First, the magnitude of ICD for anthracene is about 2000 deg cm^2 $dmol^{-1}$, which is small compared to the values for thermotropic cholesteric liquid crystals ($\approx 10^6$)[13] and to those for lyotropic cholesteric liquid crystals such as PBG ($\approx 10^4$).[10] Second, the value of λ_{max}, which is related to p, increased slightly with an increase in the concentration of 12HOA, as is shown in Fig. 5. This is quite different from the result observed for the lyotropic cholesteric mesophase of PBG, since Robinson reported[14] that p was proportional to $1/C^2$, where C is the volume fraction of the polymer in the lyotropic cholesteric mesophase. Thirdly, the location of λ_{max} was independent of the temperature in the range from 22 to 41 °C, just below the melting point of the jelly, as is shown in Fig. 6. The temperature independence of λ_{max} is remarkably in contrast with the observations for thermotropic or lyotropic cholesteric mesophases. These facts suggest that the chiral mesophase of 12HOA is different from the chiral nematic phase. Figure 6 shows also that $[\theta]$ decreases rapidly to zero, only when the temperature approaches the melting point of the jelly.

X-Ray Diffraction Studies. Figure 7 shows the X-ray diffraction patterns for jellies with benzene and for a specimen of the crystalline powder of (*R*)-12HOA. The jelly patterns exhibited comparably sharp reflections corresponding to a long spacing of 4.67 nm, together with a wide, diffuse reflection corresponding to a short spacing of 0.46 nm. Similar patterns have often been obtained for lyotropic liquid crystals composed of amphiphilic compounds,[15] in which the values of the long spacing becomes larger with a decrease in the concentration of the solute. However, it was found that, in contrast with such lyotropic liquid crystals, the long spacing obtained for the jellies was almost in accord with that obtained for the crystalline powder, independent of the concentration of 12HOA. Therefore, the jelly pattern obtained is essentially the same as the powder pattern, although the former is, as a whole, broader. This indicates that the jellies are composed of a number of small domains with a lamellar structure similar to that in the crystalline solids, though the diffuse reflection with spacing corresponding to 0.46 nm indicates that the organization of the hydrocarbon chains in the lamellar structure of the small domains in the jellies is less ordered than that in the crystalline solids. The gel patterns are generally known to be similar to the powder patterns, as has been shown, for example, in the case of the aluminum dilaurate–cyclohexane gels.[16]

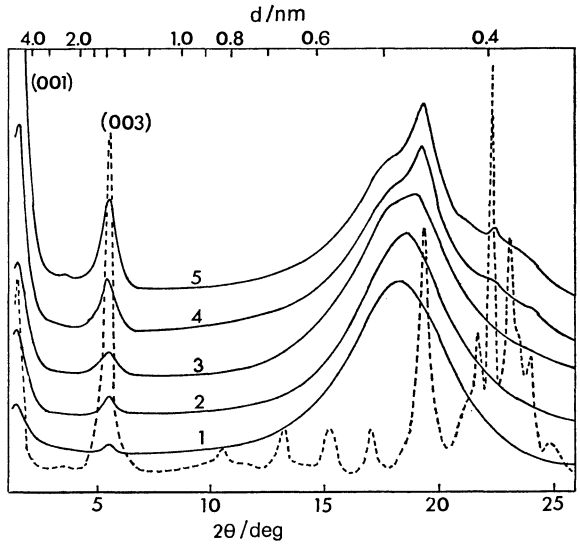

Fig. 7. X-Ray diffraction patterns for jellies of (*R*)-12HOA–benzene (——) and for a specimen of crystalline powder of (*R*)-12HOA (------).
(1) 24.3 mmol l^{-1}, (2) 57.6 mmol l^{-1}, (3) 64.1 mmol l^{-1}, (4) 160 mmol l^{-1}, (5) 257 mmol l^{-1}.

The long spacing, 4.67 nm, is interpreted as the distance between double plane layers of oriented amphiphilic molecules. The extended length of the bimolecule of 12HOA can be inferred from that of octadecanoic acid, which is an analogue of 12HOA. The latter is estimated from the length of the crystallographic c axis, it having been reported to be 4.938 nm for the B-form[17] and 5.07 nm for the C-form.[18] A comparison of these values with 4.67 nm leads us to conclude that, both in small domains in jellies and in crystalline solids, the bimolecules of 12HOA are packed in layers, with the long axis of the molecule tilting at about 21° from normal to the layer plane.

The crystal structure of 12HOA has not been analyzed, because it was not obtained as single crystals of a suitable size. However, a tentative interpretation has been given[6] on the basis of the powder patterns, in combination with the infrared spectral results and the concept of the subcell introduced by Vand.[19] The molecular chains of 12HOA can be closely packed, with a simultaneous formation of hydrogen-bond sequences extending along the b_s axis, in the triclinic subcell, whose dimensions, a_s, b_s, and γ_s, are 0.45 nm, 0.54 nm, and 120°. Assuming the remaining subcell dimensions, c_s, α_s, and β_s, to be 0.26 nm, 70°, and 108°, which are typical values previously reported for triclinic subcells,[20] the short spacings between a_sc_s planes and between b_sc_s planes are calculated to be 0.46 nm and 0.39 nm respectively. These values are consistent with those corresponding to strong reflections observed for the crystalline powder sample, as is shown in Fig. 7.

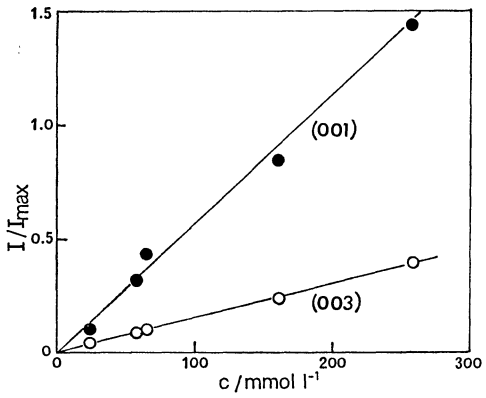

Fig. 8. Concentration dependence of the ratio of the peak height (I) of the (001) or (003) reflection relative to the maximal height (I_{max}) of the reflection corresponding to the short spacings.

The reflection peaks corresponding to the long spacing were found to become greater with an increase in the concentration. For convenience, the ratio of the peak height of the (001) or (003) reflection relative to the maximal height of the wide, diffuse reflection corresponding to a series of short spacings was plotted against the concentration. Figure 8 shows that the ratio is linearly proportional to the concentration, indicating that the lamellar structure becomes more ordered as the concentration is increased. It can also be seen from Fig. 7 that the peak corresponding to a spacing of 0.46 or 0.39 nm, which represents the spacing between a_sc_s planes or between b_sc_s planes respectively, comes to appear on the broad reflection curve with an increase in the concentration. This suggests that a crystalline order develops as the concentration is increased. Similar X-ray results were also obtained for the jellies with carbon tetrachloride by using a reflection method described in the Experimental section.

X-Ray studies were done also for the jellies containing anthracene or pynacyanole chloride, which gave the ICD. On adding the additives, it was found that the reflection peaks corresponding to the long spacing decreased remarkably in intensity without any alternation in the position of the peak, and that the peak of the broad reflection tended to shift slightly to a lower diffraction angle. This fact indicates that the lamellar structure in the jellies becomes less ordered when the additives are included. On the other hand, the CD maximum for the jellies containing any additive shifted to a longer wavelength than that for the additive-free jellies. This shift implies an increase in the helical pitch in supramolecular helicoidal structures, that is, a decrease in the helicoidal order in the jellies. The X-ray studies and the CD results strongly suggest that the supramolecular helicoidal structure exists in the lamellar structure constituting the small domains locally dispersed in the jellies. As has been described previously, the bimolecules of 12HOA in the domains are packed in layers with the long axis of the molecule tilting from normal to the layer. Therefore, one can consider the possibility that tilted chiral amphiphilic molecules of 12HOA in adjacent parallel layers are slightly skewed rather than parallel, so that a helicoidal structure is formed with a helical axis normal to the molecular layers. Such a structure has recently been found[21] in some thermotropic smectic liquid crystals; it is called the twisted smectic C mesophase or the chiral smectic C mesophase. It is thus possible to consider that 12HOA in jellies forms a lyotropic mesophase with a chiral smectic structure, a new kind of mesophase. Further studies are required to establish the details of such a mesophase and to locate the additive molecules which give rise to the ICD by becoming involved into the helicoidal lamellar structure.

Chiral Structure in Jellies. Jellies are composed of a continuous network of molecular aggregates or polymer chains in which the solvent is trapped.[22] The presence of helically twisted fibers in the jellies of 12HOA has been demonstrated by the use of an electron microscope after the removal of the solvent by evaporation.[4] It was then found that fibers were of a uniform thickness of about 10—100 nm and that the pitch of the helical twisting was about 80—1000 nm. There is no doubt that such fibers provide the crystalline domains responsible for the X-ray diffraction, although the fibers enmeshing the jellies may be thinner than the fibers seen by an electron microscope.

A very interesting and relevant question is the relation between the supramolecular helicoidal structure in the chiral mesophase and the macro-helical structure of twisted fibers observed under an electron microscope. With regard to the one enantiomer, the two helices are reversed; in the case of the *R*-enantiomer, the screw sense is right-handed for the chiral mesophase and left-handed for the macro-helix of the fibers. Therefore, the twisting of the fibers itself is not the origin of the CD in the jellies.

When the jellies on the supporting plates are dried, solid films were formed. As will be described in detail in Part 2, the solid films exhibited a CD band and X-ray diffraction patterns similar to those observed in the jellies. Therefore, the molecular arrangement in the solid films is considered to be essentially the same as

that in fibers within the jellies. It may thus be concluded that a chiral smectic structure giving rise to the CD exists in the structure of molecular layers constituting the solid films or the fibers. Such a chiral structure of 12HOA is formed only through the jelly state. It was impossible to obtain the chiral mesophase by heating the crystals or by cooling the isotropic melt.

The optical properties of the chiral smectic mesophase are known to be identical with those of cholesteric mesophases for the normal incidence of light.[23] The same optical properties would be expected to be displayed by the chiral mesophase of 12HOA. However, the fibers of 12HOA are randomly dispersed in the jellies, so that the chiral mesophase in the jellies is present locally as small domains which are dispersed with randomly-oriented helical axes within the jellies. This would explain the broadening and the weak intensity of the observed CD band compared with the effect in planar cholesteric mesophases.

Electron microscopy in our laboratory has shown that large ribbon-like fibers tend to be split into many thinner and helically twisted fibers.[24] This indicates that the double molecular layers of 12HOA are stacked approximately parallel to the direction of the width of the fibers. The helical axis of the chiral smectic structure in the molecular layers is directed to the width of the fibers.

It is also interesting to note that the chiral amphiphilic molecules such as 12HOA form helically organised systems in such different stages as a helical mesophase and helically twisted fibers. A similar relationship has also been seen in the case of synthetic polypeptides; the polymer molecules of the α-helix form a lyotropic cholesteric liquid crystal[2] and helically twisted fibers.[25]

The jellies of chiral 12HOA are a two-phase system, composed of the solvent and the fibers comprising the chiral smectic mesophase. In this point, the jellies of 12HOA are a unique chiral system of matter. This interesting chiral mesophase may provide an asymmetric medium in which any asymmetric reactions can occur.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 254129).

References

1) T. Tachibana, T. Mori, and K. Hori, *Nature*, **278**, 578 (1979).
2) E. 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.
3) K. Sakamoto, R. Yoshida, M. Hatano, and T. Tachibana, *J. Am. Chem. Soc.*, **100**, 6898 (1978).
4) T. Tachibana and H. Kambara, *J. Colloid Interface Sci.*, **28**, 173 (1968); *Bull. Chem. Soc. Jpn.*, **42**, 3422 (1968).
5) K. Serck-Hanssen, *Chem. Ind. (London)*, **1958**, 1554.
6) T. Tachibana, T. Yoshizumi, and K. Hori, *Bull. Chem. Soc. Jpn.*, **52**, 34 (1979).
7) A. Saupe, "Liquid Crystals and Plastic Crystals," ed by G. W. Gray and P. A. Winsor, Ellis Horwood, Chichester (1974), pp. 18—47.
8) F. B. J. Rosevear, *J. Am. Oil Chem. Soc.*, **31**, 628 (1954).
9) M. J. B. Tunis-Schneider and M. F. Maestre, *J. Mol. Biol.*, **52**, 521 (1970).
10) F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, **95**, 7882 (1973).
11) H. de Vries, *Acta Crystallogr.*, **4**, 219 (1951).
12) M. Aihara and H. Inaba, *Opt. Commun.*, **3**, 77 (1971).
13) F. D. Saeva, P. E. Sharpe, and G. R. Olin, *J. Am. Chem. Soc.*, **95**, 7656 (1973).
14) C. Robinson, Tetrahedron, **13**, 219 (1961).
15) F. Husson, H. Mustacchi, and V. Luzzati, *Acta Crystallogr.*, **13**, 668 (1960).
16) S. S. Marsden, Jr., K. J. Mysels, and G. H. Smith, *J. Colloid Sci.*, **2**, 265 (1947).
17) E. von Sydow, *Acta Crystallogr.*, **8**, 557 (1955).
18) V. Malta, G. Celotti, R. Zannetti, and A. F. Martelli, *J. Chem. Soc., B*, **1971**, 548.
19) V. Vand, *Acta Crystallogr.*, **4**, 104 (1951).
20) E. von Sydow, *Ark. Kemi*, **9**, 231 (1956).
21) S. L. Arora, J. L. Fergason, and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **11**, 243 (1970).
22) B. Jirgensons and M. E. Straumanis, "A Short Textbook of Colloid Chemistry," 2nd ed, Pergamon Press, Oxford (1962), Chap. 15.
23) D. W. Berreman, *Mol. Cryst. Liq. Cryst.*, **22**, 175 (1973); O. Parodi, *J. Phys. (Paris), Colloq.*, **36**, Cl-325 (1975); M. Brunet, *ibid.*, Cl-321. The second and third papers show that de Vries' analysis for cholesterics can be applied to chiral smectics C, both theoretically and experimentally respectively.
24) T. Tachibana, S. Kitazawa, and H. Takeno, *Bull. Chem. Soc. Jpn.*, **43**, 2418 (1970).
25) T. Tachibana and H. Kambara, *Kolloid-Z.*, **219**, 40 (1967).