Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Liquid Crystals Composed of N-Acylamino Acids

Kazutami Sakamoto [a]

[a] Contribution from Central Research Laboratories, Ajinomoto Co., Inc., Suzuki-cho, Kawasaki-ku, Kawasaki, Kanagawa, 210, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Kazutami Sakamoto (1980): Liquid Crystals Composed of N-Acylamino Acids, Molecular Crystals and Liquid Crystals, 59:1-2, 59-72

To link to this article: http://dx.doi.org/10.1080/00268948008073498

Mol. Cryst. Liq. Cryst., 1980, Vol. 59, pp. 59–72
0026-8941/80/5901–0059$04.50/0

Printed in the U.S.A.

Liquid Crystals Composed of N-Acylamino Acids

II. Influence of Crystalline Structure of N-Acyl-L-Glutamic Acid on the Formation of Liquid Crystals.

KAZUTAMI SAKAMOTO

Contribution from Central Research Laboratories, Ajinomoto Co., Inc., Suzuki-cho, Kawasaki-ku, Kawasaki. Kanagawa, 210, Japan.

(*Received January 3, 1979; in final form September 20, 1979*)

Optical active N-acyl-L-glutamic acid (L-AGA) exists in two forms distinguishable by differential thermal analysis, infra-red spectroscopy, and X-ray diffraction. The X-ray diffraction patterns suggest that one form is more ordered than the other. As both forms have the same chemical structure and are interchangeable, implying that these are the polymorphic L-AGA, we denote the disordered form L-AGA-A (A: amorphous) and the other more ordered form L-AGA-C (C: crystalline). Data obtained by several methods imply that L-AGA-A is likely to have a parallel order along the long molecular axis with random spaces between the layers. On the other hand, L-AGA-C has a rigid crystalline structure.

A new type of cholesteric liquid crystal was obtained by suspending L-LGA-A in specific organic solvents. L-AGA-C did not form any liquid crystalline phases when suspended in the same organic solvents which resulted in liquid crystals from L-AGA-A. The results strongly imply that the particular crystalline structural features are needed to form suspended cholesteric liquid crystalline phases in organic solvents.

INTRODUCTION

Recently, we have found that the optical active N-lauroyl-L-glutamic acid (L-LGA) forms a new type of lyotropic liquid crystal in some organic solvents.[1] This new liquid crystal, which seems to be a suspension of the swelled L-LGA powder, has been shown to exhibit typical properties of a cholesteric liquid crystal as demonstrated by birefringence of polarized light, circular dichroism (CD) band due to the helical structure, and induced CD bands ascribed to the achiral molecules intercalating in the liquid crystalline phase. Although numerous lyotropic cholesteric liquid crystals are composed of chiral polymers and, to our best knowledge, the L-LGA-organic solvent

systems are the first example of lyotropic cholesteric liquid crystals composed of non-polymer chiral compounds.

In this paper, we describe the conditions necessary to form new lyotropic liquid crystals composed of L-AGA and organic solvents. Attention is focused on the structural feature of L-AGA in the solid states.

EXPERIMENTAL

L-LGA was prepared according to a previously described method.[2] All solvents were the highest grade commercially available and were used without further purification.

A Nikon PH-10 polarizing microscope was used to detect the formation of liquid crystalline phases. X-ray diffraction patterns were obtained at 25°C for the powdered samples using a Rigakudenki X-ray diffractometer: Cu-Kα; 30 KV, 15 mA; Ni-filter; scattering slit; 1°/min. Differential thermal analysis (DTA) was performed on Rigakudenki Thermoflex #8022 and infra-red (IR) spectra were measured on a Hitachi Perkin-Elmer 225 spectrometer by the KBr disc method. ^{1}H NMR relaxation time T_1 was measured at 20 MHz with a Bruker Minispec P-20 pulse spectrometer, using the 180°-τ-90° pulse train at a repetition rate of 20 sec. For the scanning electron microscopic analysis, an appropriate amount of L-LGA powder, which was placed on an aluminum support covered with adhesive tape, was coated *in vacuo* with gold. In the case of suspended liquid crystals of L-LGA-A benzene system, benzene was evaporated beforehand under reduced pressure and the residual L-LGA-A was then subjected to analysis. Scanning electron micrographs (SEM) of the gold coated samples were taken with a Hitachi S-430 Scanning electron microscope. Approximate SEM magnification were x400 for Figure 3b) and x2500 for Figures 3a), and 11.

RESULTS AND DISCUSSION

Crystalline structure of L-AGA

L-LGA was prepared from L-glutamic acid and a fatty acid chloride in the presence of base, washed by petroleum ether to remove the contaminating fatty acid. Residual L-AGA in petroleum ether formed a gel. After evaporating the petroleum ether from the gel, the L-AGA powder (L-AGA-A) formed a liquid crystal when suspended in various aromatic solvents. On the other hand, L-AGA crystal (L-AGA-C) obtained from methanol solution did not swell, and therefore, did not form a liquid crystal in the same aromatic solvents which were effective in preparing liquid crystals from the L-AGA-A

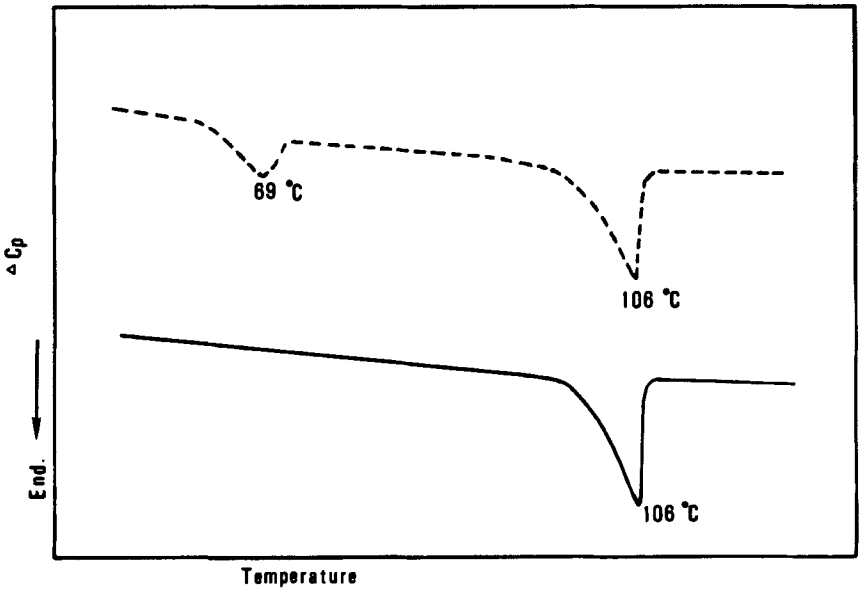

FIGURE 1 DTA diagram of L-LGA: solid line; L-LGA-A, broken line; L-LGA-C.

powder. L-AGA-A and L-AGA-C were shown to be identical by elemental analysis and by neutralization equivalence,[3] and had approximately the same melting temperatures of 101–104°C. Differential thermal analysis (DTA) of N-lauroyl-L-glumatic acid-A (L-AGA-A) showed a single endothermic peak at 106°C, whereas L-LGA-C showed two endothermic peak at 69°C and 106°C (Figure 1). Furthermore, when L-LGA-C was heated above 106°C and thereafter cooled to room temperature, the endothermic peak at 69°C disappeared and only the peak at 106°C remained in the DTA curve. Thus, L-LGA should have two polymorphic structures and the transition between these occurs at 69°C. Similar polymorphism was found for N-stearoyl-L-glumatic acid (L-SGA). The DTA curves of of L-SGA powders are shown in Figure 2. Polymorphic transition from L-SGA-C to L-SGA-A occurred at 92°C, and both melted at 115°C.

A marked difference of crystalline structure was revealed in the SEM of L-LGA-C and L-LGA-A (Figure 3). L-AGA-C showed a typical pattern of crystalline solid, on the other hand, L-AGA-A appeared to have a less crystalline structure.

The X-ray diffraction patterns of L-AGA are shown in Figures 4 and 5. Amorphous powder of L-AGA, L-LGA-A and L-SGA-A, showed broad peaks around the diffraction angle of 22 degrees ($d \simeq 4$ Å) (Figures 4 and 5). Thus, L-AGA-A must have a rather amorphous structure. The long alkyl

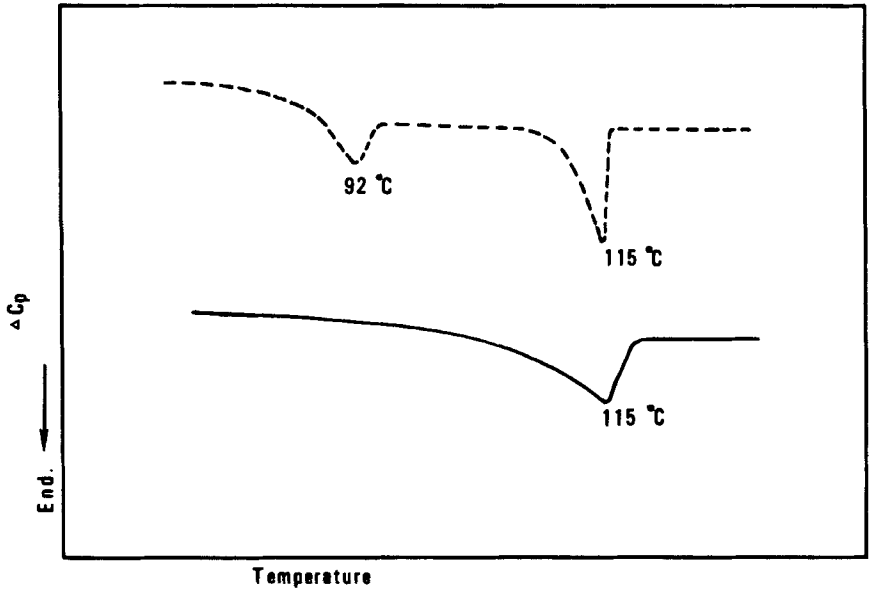

FIGURE 2 DTA diagram of L-SGA: solid line; L-SGA-A, broken line; L-SGA-C.

chains in the acyl moiety may stack parallel to the molecular long axes with the random spacing along the axes. This type of molecular packing is then similar to those characteristics of nematic liquid crystals.

On the contrary, the X-ray diffraction patterns of L-AGA-C, L-LGA-C and L-SGA-C, have sharp peaks not only around 22 degrees ($d \simeq 4$ A) but also around 7 degrees ($d \simeq 12$ Å) (Figures 4 and 5). Since the X-ray diffraction profiles of L-AGA-C are similar to the sodium salts of fatty acids,[4] L-AGA-C may have a rigid crystalline structure. The infra-red (IR) absorption spectra, especially the absorption bands due to the carbonyl groups, provided other evidence showing the difference between L-AGA-A and L-AGA-C. The difference was more prominent for L-SGA than for L-LGA. Thus, L-SGA-C showed *three* absorption bands at 1,535, 1,620, and 1,710 cm^{-1} due to carbonyl groups (Figure 6a), but L-SGA-A showed more complicated absorption bands in this region (Figure 6b). Both of the carbonyl bands for L-SGA-C, namely 1,620 and 1,710 cm^{-1}, appeared to be split into two peaks in the case of L-SGA-A. This result may suggest that the orientation of carbonyl group in L-SGA-C is fixed in a single conformation. On the contrary, there may be two orientations for each carbonyl group in L-SGA-A. Similar IR spectral differences between L-LGA-A and L-LGA-C were observed in powdered L-LGA-A. L-LGA, however, was difficult to crystal-

FIGURE 3 Scanning electron micrographs of a) L-LGA-A, b) L-LGA-C.

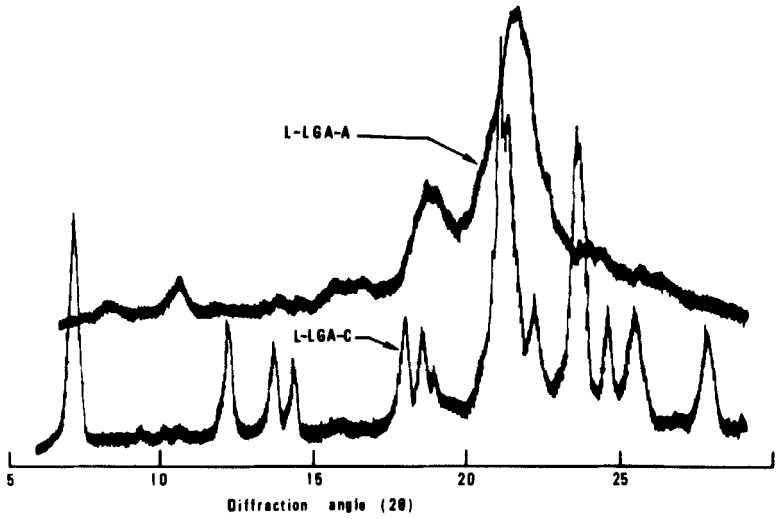

FIGURE 4 X-ray diffraction patterns of L-LGA at 25°C.

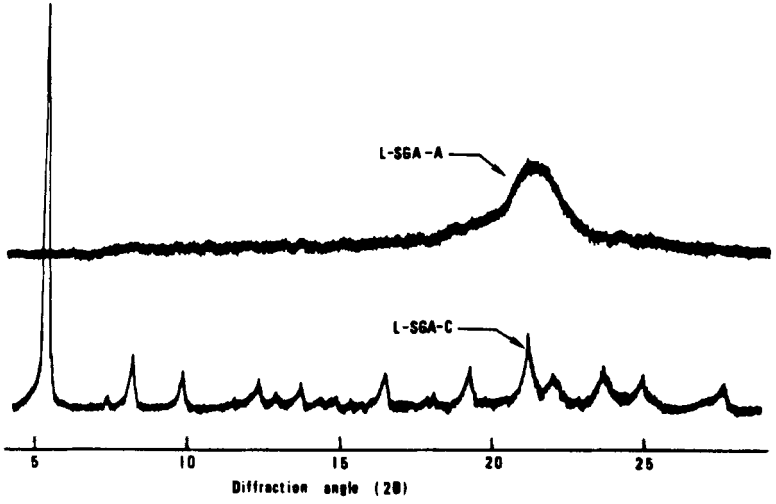

FIGURE 5 X-ray diffraction patterns of L-SGA at 25°C.

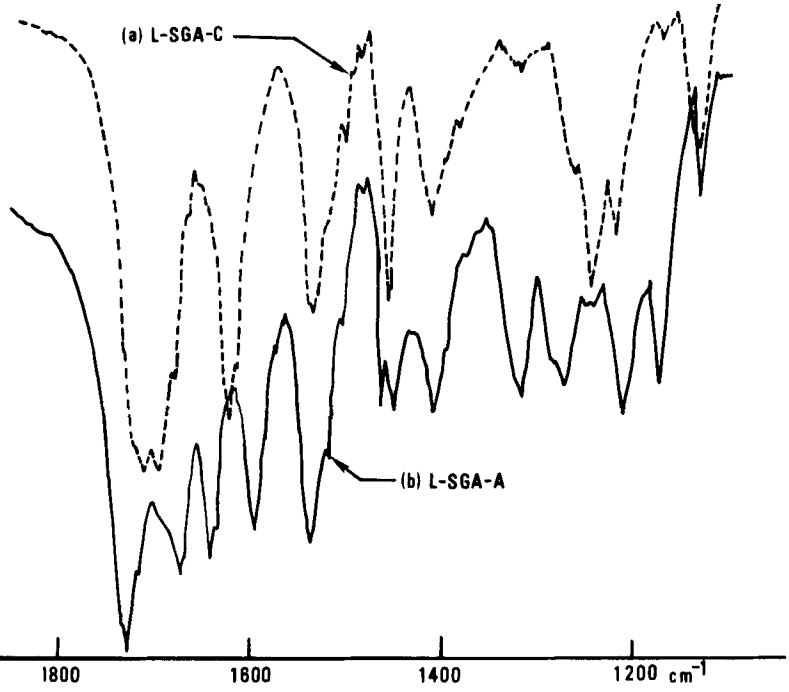

FIGURE 6 IR absorption spectra of a) L-SGA-C and b) L-SGA-A in KBr disk, at 25°C.

lize completely and "L-LGA-C" therefore contained some disordered "L-LGA-A", as characterized by the IR spectrum (Figure 7).

L-AGA shows polymorphic form, one is rather amorphous (L-AGA-A) and the other one is a rather crystalline (L-AGA-C). Both forms are stable at room temperature and can easily be distinguished either by X-ray diffraction or IR absorption spectra.

Formation of liquid crystals

The apparent crystalline shape of L-LGA-A through the polarizing microscope was quite different for the dry powder and for the suspended powder in various solvents such as benzene, toluene, chlorobenzene and n-hexane (Figures 8a,b). Since the suspended L-LGA-A shows birefringence and texture typical for liquid crystals, we denote this new type of liquid crystalline phase as a suspended liquid crystal.

L-AGA-C, on the other hand, did not form liquid crystals, possibly because its crystalline lattice may prevent the organic solvents from penetrating into the crystal interior.

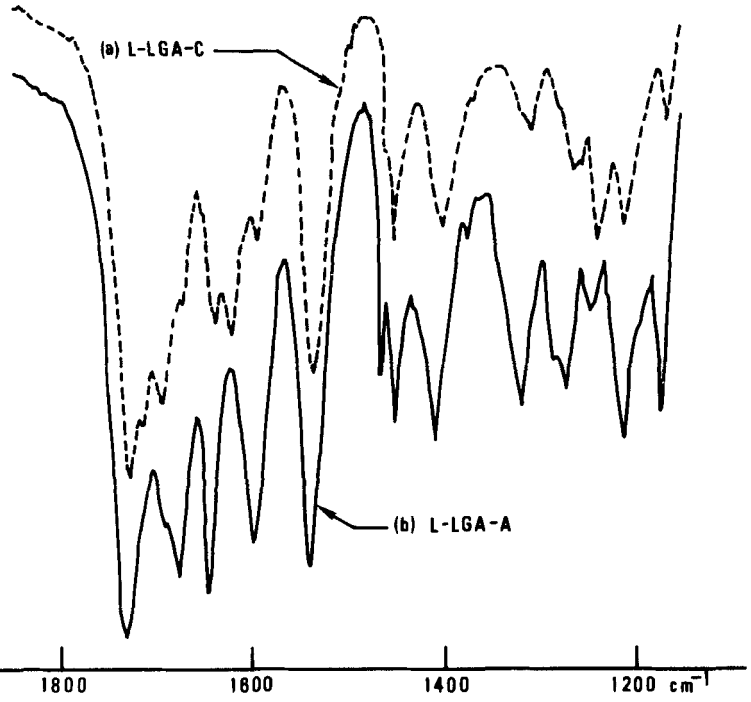

FIGURE 7 IR absorption spectra of a) L-LGA-C and b) L-LGA-A in KBr disk at 25°C.

When an inhomogeneous L-LGA-C-benzene mixture was heated above 80°C, L-LGA-C crystals dissolved completely in benzene. On cooling this solution to room temperature, a gel showing birefringence was obtained. As this gel turned by shaking to the same suspended liquid crystals as the L-LGA-A benzene system, the different capabilities to form suspended liquid crystalline phase of L-LGA-A and L-LGA-C should be attributed to the lattice structural difference which may be lost by dissolving in solvents.

Suspended liquid crystals of L-LGA-A in benzene dissolved also at about 80°C, which is the phase transition temperature from liquid crystal to isotropic phase. This phase transition was demonstrated by measuring spin lattice structural difference which may be lost by dissolving in solvents. (Figure 9). T_1 values therefore changed discontinuously at about 80°C. This phenomenon is frequently observed in liquid crystal-isotropic phase transition. Similar phenomena was observed for the L-LGA-A-toluene system (Figure 9).

The formation of liquid crystals of L-AGA-A depends also on the nature of solvents. The appropriate solvents should swell L-LGA-A but should not

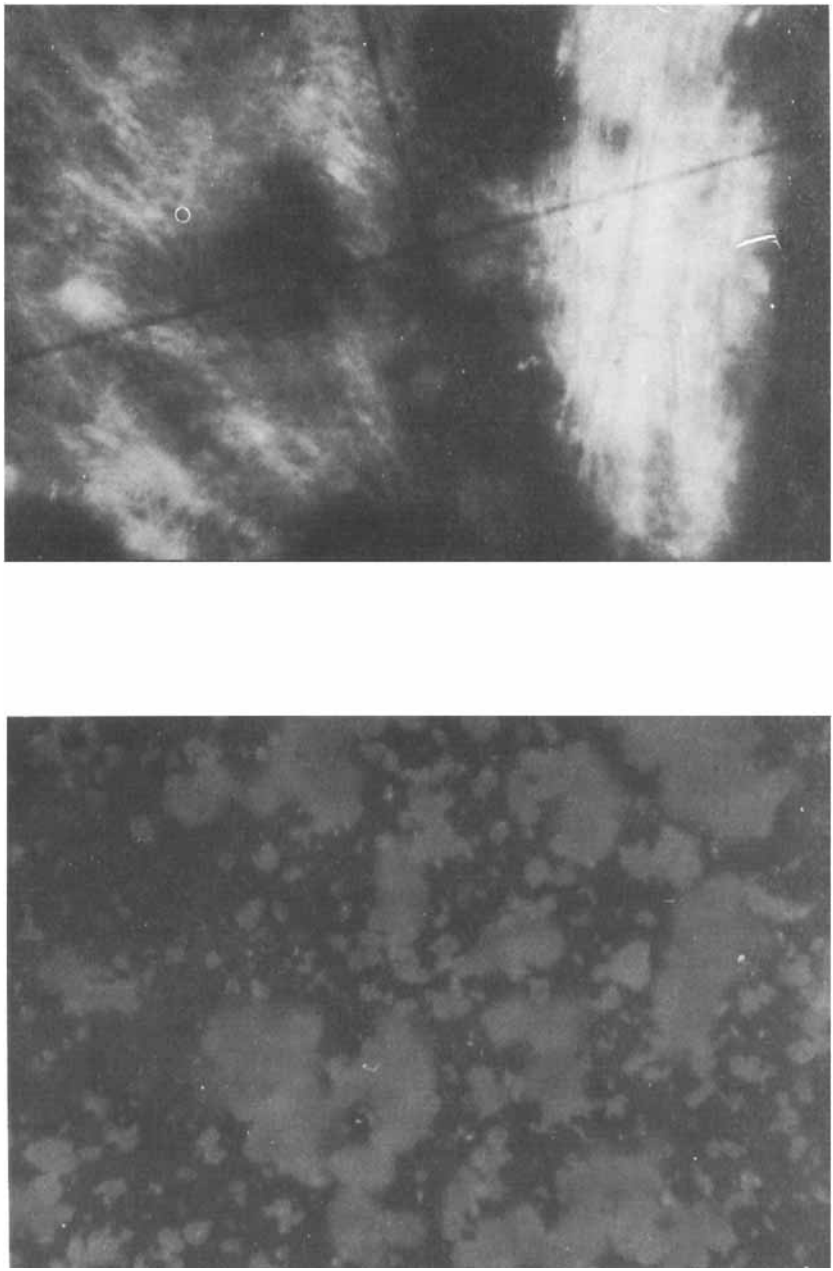

FIGURE 8 Polarized micrographs of a) suspended liquid crystal of L-LGA-A and benzene and b) L-LGA-A (powder), X 100.

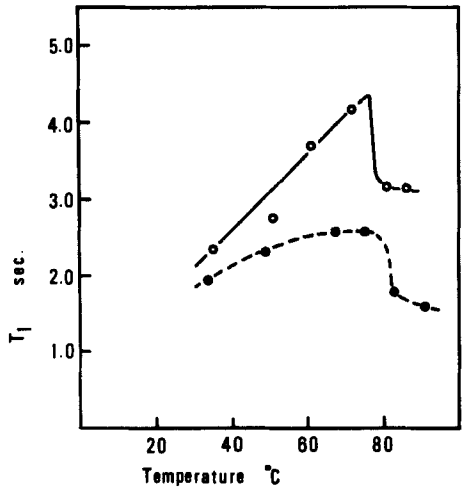

FIGURE 9 Temperature dependence of spin lattice relaxation time (T_1) for the suspended liquid crystals of L-LGA-A at 20 MHz. Solid line; 20 wt % in benzene; broken line; 20 wt % in toluene.

dissolve it. Therefore, when L-AGA was dissolved in such solvents as methanol or ethanol, no formation of liquid crystals could be detected (Table I).[1]

The structural features of liquid crystals

The X-ray diffraction patterns of L-LGA-A in benzene, which forms liquid crystals, and L-LGA-C in benzene, which forms a precipitate, were examined (Figure 10). Surface of the samples on plates was covered with a cellophane film in order to prevent the evaporation of benzene. As both L-LGA-A and L-LGA-C in benzene show their respective spectral profiles found for powder states (Figure 4), the molecular orientation of L-LGA is therefore not appreciably changed even in the swelled liquid crystalline particles of L-LGA-A. Similar results were obtained in the cases of L-LGA-A in toluene and xylene, and of the L-SGA-A in benzene. Judging from these results, it appears that L-LGA-A molecules stack along their long alkyl chains without regular spacing along the molecular axes both in the dry powder and in the suspended liquid crystals.

The suspended liquid crystals of L-LGA-A show some of the characteristics of cholesteric liquid crystals as follows:[1]

1) The CD bands, whose maximal wavelength depended on the variation of temperature or solvent compositions;

TABLE I

Liquid crystal formation in L-LGA-A-solvent systems[a]

Solvent	Refractive index of solvent $n_D^{20.0}$	Appearance	Existence of liquid crystals[b]	Color of transmitted light[c]
Benzene	1.5014	Suspension	+	Violet
Toluene	1.4964	Suspension	+	Violet
Chlorobenzene	1.5248	Suspension	+	Yellow
Methyliodide	1.5293	Suspension	+	Colorless
Chloroform	1.4464	Suspension	+	Colorless
n-Hexane	1.3754	Suspension	+	Colorless
Acetone	1.3589[d]	Solution	−	Colorless
Ethyl alcohol	1.3624[e]	Solution	−	Colorless
Methyl alcohol	1.3312[f]	Solution	−	Colorless
Water	1.3330	Gelationus	−	Colorless

[a] L-LGA-A (0.1 g) and solvent (2 ml) are mixed, respectively.
[b] Observation of birefringence under a polarizing microscope.
[c] The color was observed at room temperature.
[d] 19.4°C.
[e] 18.4°C.
[f] 14.5°C.

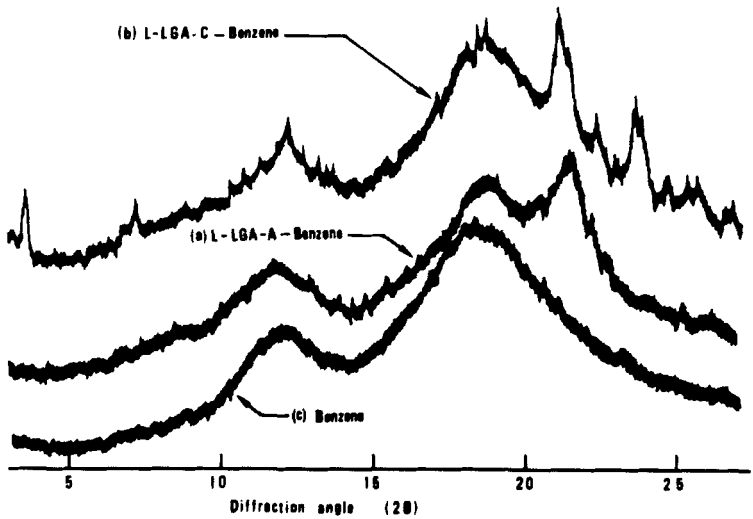

FIGURE 10 X-ray diffraction patterns of L-LGA-benzene system at 25°C. a) L-LGA-A-benzene covered with cellophane. b) L-LGA-C-benzene covered with cellophane. c) Benzene, covered with cellophane.

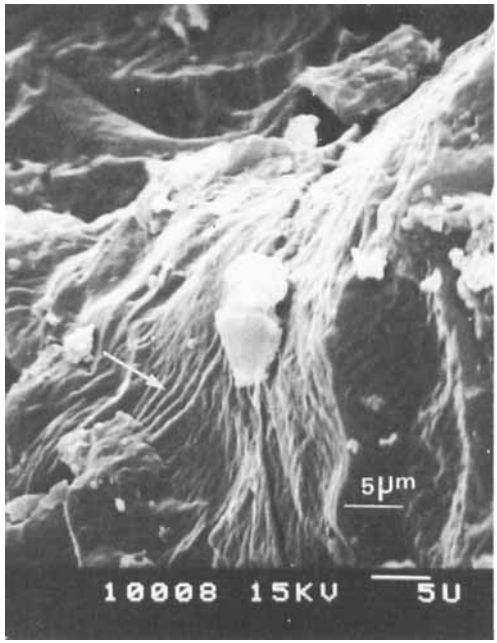

FIGURE 11 Scanning electron micrograph of L-LGA-A obtained by evaporation of benzene from the suspended liquid crystals of the L-LGA-A-benzene.

2) The induced circular dichroism[7] with a single sign for the achiral molecules intercalated into the systems.

With the scanning electron micrographs the layer structures are evident (Figure 11) for the L-LGA-A by evaporation of benzene from the suspended liquid crystals of L-LGA-benzene. This micrograph may confirm the layered cholesteric structure[8] for the L-LGA-A-benzene system. The twisted mode of the L-LGA-A-benzene may be caused by the penetration of benzene into layers, which releases the interlayer interaction of L-LGA-A.

Acknowledgments

The author wishes to express his appreciation for the encouragement and discussions of Professor M. Hatano of Tohoku University and Professor T. Tachibana of Ochanomizu University.

References

1. K. Sakamoto, R. Yoshida, M. Hatano, and T. Tachibana, *J. Am. Chem. Soc.*, **100**, 1898, (1978).
2. M. Takehara, I. Yoshimura, K. Takizawa, and R. Yoshida, *J. Am. Oil Chem. Soc.*, **49**, 157, (1972).

3. M. Takehara, H. Moriyuki, I. Yoshimura, and R. Yoshida, *J. Am. Chem. Soc.*, **50**, 227. (1973).
4. R. H. Ferguson, F. B. Rosevear, and R. C. Stillman, *Ind. Eng. Chem.*, **35**, 1005, (1943).
5. R. H. Ferguson, *Oil and Soap*, **21**, 6, (1944).
6. K. Ogino, *Kogyokagaku-zasshi*, **67**, 1032, (1964).
7. F. D. Saeva, and J. J. Wysocki, *J. Am. Chem. Soc.*, **93**, 5928, (1971).
8. J. Voss, and B. Voss, *Z. Naturforsch.*, **31a**, 1661, (1976).