

## Lamellar liquid crystal polymerization of sodium oleate/oleic acid/octadiene/water system

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In the lamellar liquid crystallization (LLC) phase of NaOL/OLA/H<sub>2</sub>O system, the small angle X-ray diffraction measurements show that the oleic acid is solubilized in the oil layer at first and then into the amphiphile layer. The octadiene added is also located partly in the oil layer and partly in the amphiphile layer in the LLC. With the addition of octadiene as cross-linking agent, the LLC phase of NaOL/OLA/H<sub>2</sub>O system was polymerized under the initiation of AIBN with the protection of pure nitrogen at 60°C. Most of the double bond absorption of the monomers in IR spectra disappeared after polymerization. The polymerization takes place not only in the middle of the amphiphile layer between the double bonds of NaOL or OLA and those of octadiene, but also in the oil layer of LLC between the double bonds of OLA and those of octadiene. Interlayer spacing measurements on the copolymer proved *d* values decreased by about 1 ~ 2 nm compared with those of the corresponding system before the polymerization, indicating a disruption of the ordered structure by the polymerization. The copolymer still has superior surface activity with the critical micellar concentration (CMC) decreased almost to the half of the value for the system before the polymerization.

**Keywords**      LLC polymerization, oleic acid, sodium oleate, octadiene

### Introduction

Polymerization in surfactant associated systems has become a research area<sup>1</sup> which has received wide attention recently, especially in lamellar liquid crystal (LLC) system.<sup>2-5</sup> Polymerization in lyotropic mesophase was reported first in the open literature by Sardron,<sup>6</sup> who described the *in-situ* photo-polymerization of a liquid-crystalline system based on polystyrene poly(ethylene oxide) block copolymer and acrylic acid.

After the photo-polymerization of the acrylic acid, heterogeneous gels with organized structures were obtained. Also Friberg and coworkers reported the polymerization in a lyotropic liquid crystals of sodium undecenoate and water. They observed a change of structure from hexagonal to lamellar during photo-polymerization.<sup>7</sup> All the work reported are concerned with the polymerization of monomers in LLC matrix but the LLC matrix itself did not take part in the polymerization. In lyotropic liquid crystals, the surfactant molecules are arranged in an organized fashion. If the LLC matrix can take part in the polymerization, it is possible to take advantage of this ordered structure to synthesize polymers with novel molecular architecture and develop a new kind of polymeric surfactant. Many chemists have tried for a long time in order to make the two-dimensional ordered structure of LLC system fixed in the polymers through this way and to achieve the three-dimensional structure by molecular design. But it is still very difficult to make it a reality.

Sodium oleate (NaOL) can form lamellar liquid crystal with water under definite compositions and oleic acid (OLA) can be solubilized into the LLC phase. The main idea in this research is to attempt to keep the LLC structure through the polymerization of the double bonds in the middle of the hydrocarbon chain of NaOL and OLA, which are the main components of the LLC matrix. Since it is very difficult for these double bonds to polymerize themselves, a cross-linking agent, octadiene, has been used as comonomer.

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## Experiment

### Materials

Oleic acid (95%) was purchased from Fisher Scientific (Pittsburgh, PA). Sodium oleate was synthesized from oleic acid and metal sodium by reflux at 50°C until the sodium metal disappeared completely and was followed by washing with pure ethanol at least six times. White powder of sodium oleate was obtained through drying in vacuum oven at 45°C. The final product of sodium oleate is white powder with the carbonyl group absorption in IR spectra shifted from 1711  $\text{cm}^{-1}$  in OLA to 1562  $\text{cm}^{-1}$  in NaOL. 1,7-Octadiene (98%), and 2,2'-azobisisobutylnitrile (AIBN, 98%) were all purchased from Aldrich Chemical Company, Inc. Water was deionized and doubly distilled before use.

### Polymerization

The lamellar liquid crystalline phase of sodium oleate (NaOL), oleic acid (OLA), octadiene, and water was polymerized with the initiation of AIBN by heating at 60°C for 48 h under the protection of the pure nitrogen. The molar ratio of double bonds between octadiene and (NaOL + OLA) was kept from 1:2 to 1:1.

### Infrared spectra

The IR spectra were recorded on a Mattson Galaxy 202 Fourier Transform Infrared Spectrometer after casting the chloroform solutions of the systems before and after polymerization onto  $\text{CaF}_2$  disks and letting the solvent evaporate.

### Determination of lamellar liquid crystalline phase

Samples were prepared with addition of chemicals in the test tube with cap and were mixed on the mixer (Thermolyne, Type 37600) for several minutes, and then, they were placed in a thermostat at  $20 \pm 0.1^\circ\text{C}$  for at least 2 h for phase equilibrium. The lamellar liquid crystalline phase were verified with a polarizing microscope (Olympus Microscope, Model BHA-P) and microphotos were obtained with a Polaroid micro-camera. The boundary of the liquid crystalline phase was confirmed by small-angle X-ray diffraction.

### Surface tension

The surface tension of the aqueous solutions of the NaOL and copolymer was measured by the drop weight method with Fisher Model 21 Surface Tensionmat. The surface tensions of the copolymer aqueous solutions studied decrease quickly with time at the beginning and tend to be a definite value after at least 35 minutes. Thus, the surface tension values of the copolymer were measured after reaching equilibrium, approximately 40 minutes. The same phenomenon was not found in the NaOL aqueous solutions.

### Small-angle X-ray diffraction

Samples were placed in capillary (0.7 mm) after mixing and centrifuging (0.01 mol/L) for 20 min in order to take gas out. The instrument is from Philips Electronic using a Kiessig low-angle camera (Richard Seifert) and an ORDELA detection system with Ni filter and Cu radiation ( $\lambda = 0.542 \text{ nm}$ ), tube voltage 50 kV and tube current 180 mA. Lead stearate with an interlayer spacing value of 4.82 nm was applied as the calibration standard.

## Results and discussion

### Structure of NaOL/OLA/water LLC system

Fig. 1 is the partial phase diagram of the NaOL/OLA/water system. NaOL can form LLC phase with water at a concentration of NaOL from 18% to 40% (wt).

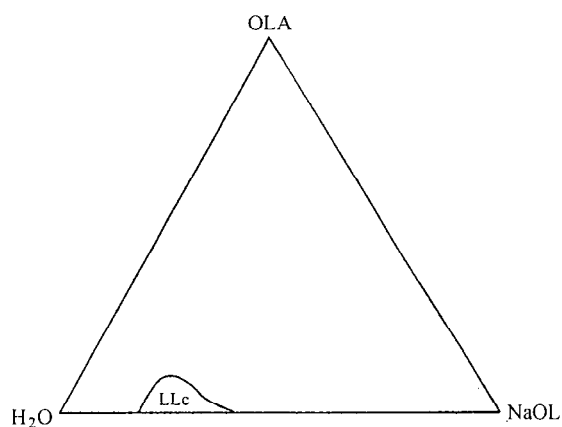
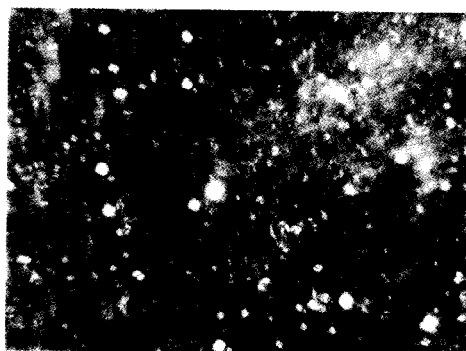


Fig. 1 Partial phase diagram of NaOL/OLA/water system.

OLA can be solubilized into the LLC phase of NaOL/water with the maximum solubility up to 10% (wt) under the weight ratio of water to NaOL equal to 70:20. The textures of the LLC phases of NaOL/water and NaOL/OLA/water systems under microscope with crossed polarizers are given in Fig.2(a) and (b), respectively. The "oily streaks" in Fig.2(a) and the "mosaic" texture as well as the maltese crosses in Fig.2(b) are typical features for lamellar liquid crystals. The bilayer model of NaOL/OLA/water LLC system is shown in Fig.3. Inter-layer spacings,  $d$ , of the LLC phase of NaOL/OLA/water system have been measured and the values of the interlayer spacing without water,  $d_0$ , are obtained through extrapolating the volume ratio ( $R$ ) of water to (NaOL + OLA) to zero (Fig. 4). The  $d_0$  values for different weight ratio of NaOL to OLA are listed in Table 1. It is



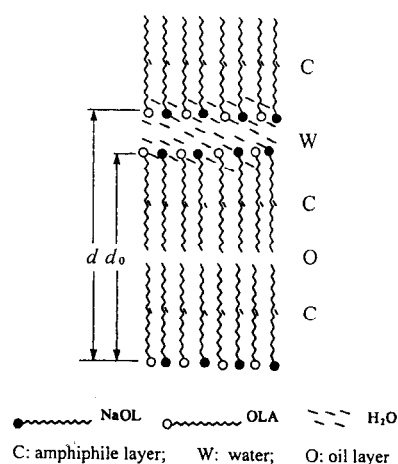
(a)



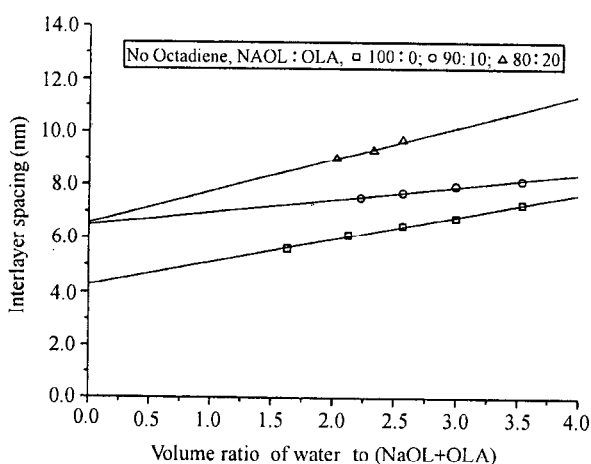
(b)

**Fig. 2** The LLC textures of NaOL(28%)/water(72%) system (a) and NaOL (24%)/OLA (6%)/water (70%) system (b) under polarized microscope.

shown in Table 1 that when the weight ratio of OLA to NaOL increases from zero to 10/90, the  $d_0$  increases greatly from 4.28 nm to 6.5 nm. This result means that the OLA solubilized into the LLC system is located in the oil layer (O in Fig. 3) of lamellar liquid crystal. But when this ratio increases from 10/90 to 20/80, the  $d_0$  values are kept nearly constant, which means that the solubilized oleic acid begins to enter the amphiphile layer (C in Fig.3) of the LLC phase.



**Fig. 3** Illustration of lamellar liquid crystalline structure.

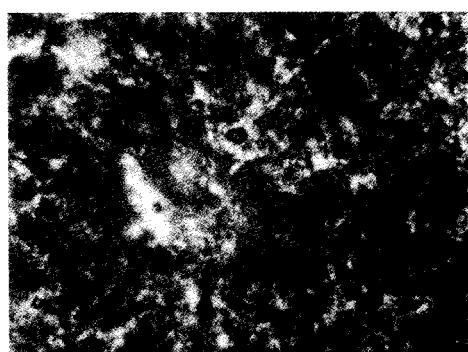


**Fig. 4** Variation of interlayer spacing of LLC with the volume ratio of water to (NaOL + OLA).

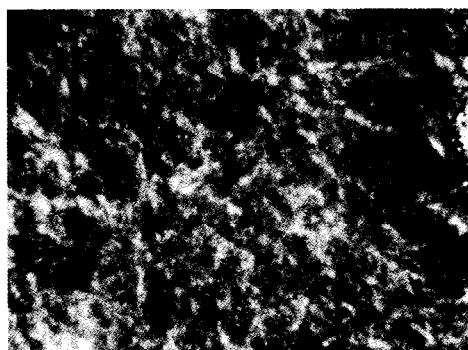
#### Properties of the polymer systems

Fig.5(a) and (b) present the textures under the microscope after the polymerization for the system

NaOL/OLA/octadiene/water and NaOL/octadiene/water, respectively. It can be concluded from these photos that the system after polymerization shows the typical LLC structure. The comparison of the IR spectra on the systems before and after polymerization proves that the double bond absorptions decrease greatly after the polymerization. With the increase of the octadiene added, the double bond absorptions tend to disappear, which means that more and more OLA and NaOL are cross-linked by the more octadiene added.



(a)



(b)

**Fig. 5** The textures after the polymerization. (a): NaOL/OLA/octadiene/water system. (b): NaOL/octadiene/water system.

Fig. 6 gives the relationship between surface tension and concentration for NaOL and the copolymer. The relationship for copolymer exhibits some typical tendency of macromolecules. The critical micellar concentration (CMC) for copolymer is almost the half of the CMC of NaOL aqueous solutions, which is equal to 0.325 g/L.

Both the copolymer and NaOL can decrease the surface tension of water to below 30 mN/m. These results prove that the polymer molecules still keep excellent surface activity.

**Table 1** Interlayer spacing without water ( $d_0$ ) in the NaOL/OLA/water LLC system

Weight ratio of NaOL to OLA	$d_0$ (nm)
100:0	4.28
90:10	6.50
80:20	6.57

Fig. 6 also represents the relationship between surface tension and concentration for the copolymer with different molar ratio of double bonds between NaOL and octadiene. With the increase of the molar ratio of double bonds between NaOL and octadiene in copolymer, the tendency before CMC becomes more characteristics of macromolecules, which results from more complete polymerization of the double bonds in NaOL and OLA by the increase of cross-linking agent in the system.

In order to study the polymerization mechanism, the location of octadiene before polymerization must be made clear although we have already known the location of OLA in the NaOL/OLA/water LLC phase.  $d_0$  values, the interlayer spacing without water, are measured from the change of interlayer spacing with the volume ratio of water to (NaOL + OLA + octadiene) under different double bond molar ratio of octadiene to (NaOL + OLA) and different weight ratio of NaOL to OLA. The relationship between the  $d_0$  value and volume ratio of octadiene to (NaOL + OLA) is referred to Fig. 7. It can be concluded from this relationship that the octadiene added enters the oil layer (O in Fig. 3) at first and then in the amphiphile layer (C in Fig. 3) of LLC phase. At certain compositions, OLA and octadiene will exist partly in the oil layer and partly in the amphiphile layer of LLC phase. Thus, the polymerization will happen in these two places. In the oil layer, the copolymerization happens between the double bonds of octadiene and oleic acid while in the amphiphile layer of LLC phase, the copolymerization happens not only between the double bonds of octadiene and oleic acid but also between those of octadiene and sodium oleate. Definitely the copolymerization between the double bonds in hydrocarbon chains of NaOL or OLA and the double bonds of octadiene will affect the order of the arrangement in LLC phase. That is

why the interlayer spacing values of the systems after polymerization decreased 1.0 ~ 2.0 nm compared with

the corresponding systems before polymerization (Table 2).

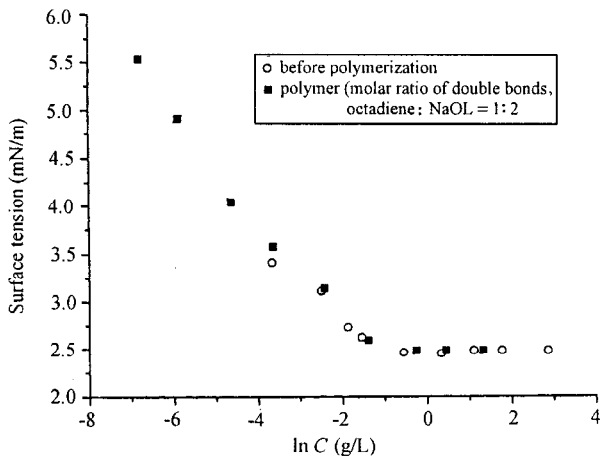


Fig. 6 Variation of surface tension with the  $\ln C$ .

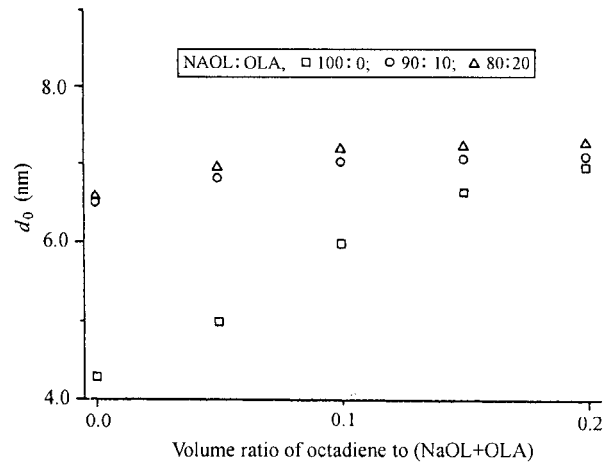


Fig. 7 Relation of interlayer spacing without water ( $d_0$ ) with the volume ratio of octadiene to (NaOL + OLA).

Table 2 Interlayer spacing,  $d$ , in the NaOL/octadiene/water LLC systems before and after polymerization

Compositions (wt%)			$d$ (nm)	
NaOL	water	octadiene	(before)	(after)
22.5	72.1	5.4	8.4	7.15
21.7	69.6	8.7	9.95	7.57

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