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**Polymeric Surfactants Based on Oleic Acid— Lamellar Liquid Crystal Polymerization of Sodium Oleate/Water/Hexadecane/4-Allyl-1, 6-Heptadiene-4-ol System And Sodium Oleate/ Water/ Hexadecane/Pentaerythritol Triacrylate System**

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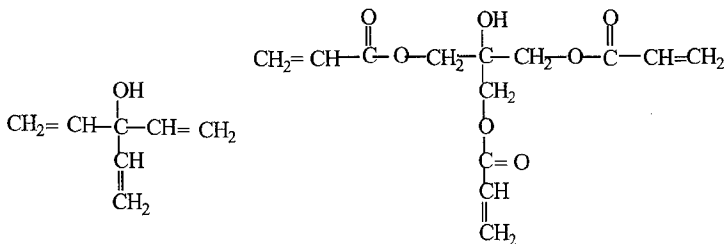
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**ABSTRACT**

The lamellar liquid crystalline (LLC) regions of sodium oleate (NaOL)/ water/ hexadecane/4-allyl-1,6-heptadiene-4-ol (AHD-ol) system and sodium oleate (NaOL) /water/ hexadecane/pentaerythritol triacrylate (PETA) system were determined when the weight ratio of NaOL to hexadecane was kept at 90:10. Copolymerization was accomplished in the LLC phases of the above systems. AHD-ol and PETA acted as the cross-linking agents between the double bonds on NaOL backbones in their systems respectively. Interlayer spacing determinations showed that the cross-linking agents, AHD-ol and PETA, were solubilized in the middle of the NaOL hydrocarbon chains in each LLC system. As a result, the copolymerization reactions were confined within each monolayer of the amphiphilic bilayer. The systems after the copolymerization were a mixture of water and LLC phase for the former system and a mixture of LLC phase and solid particles for the latter one. The aqueous solutions of copolymers exhibited surface activity, but with both higher CMC and surface tension values than NaOL aqueous solutions.

**INTRODUCTION**

In the two lamellar liquid crystalline (LLC) polymeric systems studied previously<sup>1,2</sup>, all the cross-linkers used had two reactive double bonds in each molecule. The cross-linker DVG, which was dissolved in the middle of NaOL hydrocarbon chains, was used to confine the copolymerization within each monolayer of amphiphilic bilayer although the copolymerization itself would somewhat disrupt the original ordered LLC structure. It showed that the copolymers formed still kept the surface activity in each system studied.



**AHD-ol**

**PETA**

4 - Allyl -1, 6 - heptadiene - 4 - ol (AHD-ol) and pentaerythritol triacrylate (PETA), which have three double bonds in one molecule respectively (as shown above), were selected as crosslinkers in this study. Both of the cross-linkers could be dissolved only in the middle of the hydrocarbon

chains in the LLC phase of NaOL/ water/ hexadecane system. Moreover, these crosslinkers have polar groups substituted next to the double bonds to promote their reactivity, which would facilitate the complete copolymerization. As a result, the copolymerization was confined only within each monolayer of the bilayer in the LLC phases of both NaOL/ water/ hexadecane/ AHD-ol and NaOL/ water/ hexadecane/ PETA systems.

## EXPERIMENT

Lamellar liquid crystalline phases of NaOL/ water/ hexadecane/ AHD-ol and NaOL/ water/ hexadecane/ PETA systems were polymerized with the initiation of BPO by heating at 72 °C for 48hrs under the protection of pure nitrogen. The molar ratios of double bonds between AHD-ol (or PETA) and (NaOL + OLA) were kept at 1:1.

The IR spectra were recorded on a Mattson Galaxy 202 Fourier Transform Infrared Spectrometer, casting the chloroform solutions of the systems after polymerization onto CaF<sub>2</sub> disks and letting the solvent evaporate. The solid sample of NaOL was determined in the form of a KBr pellet. Liquid samples of AHD-ol and PETA were measured by placing several drops between the two CaF<sub>2</sub> crystal windows. The partial phase diagrams of both the four-component systems containing NaOL/ water/ hexadecane/ AHD-ol and NaOL/ water/ hexadecane/ PETA were determined by optical observation of the samples both visually and with the aid of polarized optical microscopy. In these four-component systems, the weight ratio of hexadecane to NaOL was always kept at 10:90. The boundary of the liquid crystalline phase was confirmed by the results from small-angle X-ray diffraction. The surface tension of the aqueous solutions of NaOL and copolymers was measured by means of Fisher Surface Tensionmat Model 21. Liquid crystalline samples were observed with Olympus Polarized Optical Microscope (Model BHA-P) and microphotos were obtained with a Polaroid microcamera

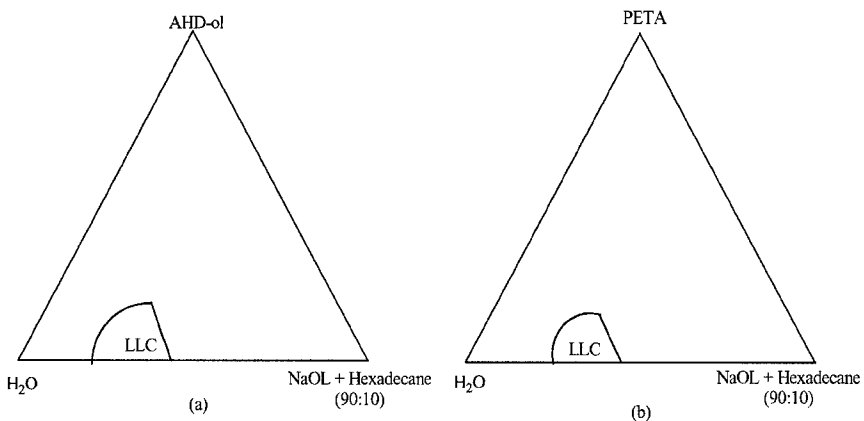
## RESULTS AND DISCUSSION

### LLC structure of NaOL/ water/ hexadecane/ AHD-ol system and NaOL/ water/hexadecane/ PETA system

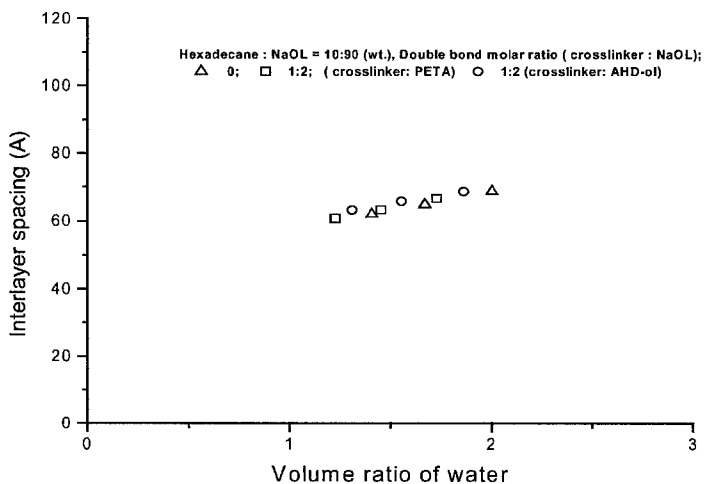
Figure 1(a) is the partial phase diagram for NaOL/ water/ hexadecane/ AHD-ol system. AHD-ol was solubilized into the LLC phase of NaOL/ water/ hexadecane system with its maximum solubility at 16(wt.)% when the weight ratio of water to (NaOL + OLA) was 56:28. Figure 1(b) is the partial phase diagram for the NaOL/ water/ hexadecane/ PETA system. PETA was also solubilized into the LLC phase of the NaOL/ water/ hexadecane system, but with its maximum solubility at 12(wt.)% when the weight ratio of water to (NaOL + OLA) was equal to 61:27.

Figure 2 shows the relationship of interlayer spacing with the volume ratio of water in the systems NaOL/ water/ hexadecane, NaOL/ water/ hexadecane/ AHD-ol, and NaOL/ water/ hexadecane/ PETA. In all three systems, the weight ratio of NaOL to hexadecane was kept constantly at 90:10. It was shown in Figure 4 that the addition of cross-linkers to the LLC phase of NaOL/water/hexadecane system did not affect the interlayer spacing, with or without water, of the LLC phase. Thus both of the cross-linkers used here, similar to DVG reported previously<sup>2</sup>, were solubilized in the middle of the hydrocarbon chains of the NaOL molecules.

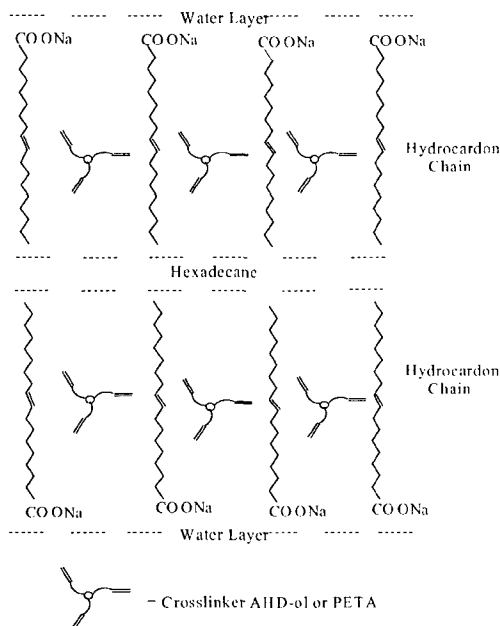
The bilayer structure of lamellar liquid crystalline system NaOL/ hexadecane/ water/ crosslinkers is shown in Figure 3.



**Figure 1.** Partial phase of (a) NaOL/ water/ hexadecane/ AHD-ol system and (b) NaOL/ water/ hexadecane/ PETA system



**Figure 2.** The change of the interlayer spacings with volume ratio of water in NaOL / water/ hexadecane, NaOL/ water/ hexadecane/ AHD-ol, and NaOL /water/ hexadecane/ PETA systems.



**Figure 3.** The bilayer structure of lamellar liquid crystalline system NaOL/ hexadecane/ water/ crosslinker

### LLC phase polymerization of NaOL/ water/ hexadecane/ AHD-ol and NaOL/ water/ hexadecane/ PETA system

Both of the systems changed from transparent to milky-white opaque during copolymerization between NaOL and cross-linkers, because of phase separation, as reported in the similar system<sup>3-4</sup>. There was water, about ten percent of the total polymerization system, precipitated from NaOL/ water/ hexadecane/ AHD-ol system when the copolymerization finished. After the water was removed from the system through centrifugation, the phase remained was lamellar liquid crystalline state. The copolymer synthesized from this system could be dissolved into water again. However, there was no water precipitated from NaOL/ water/ hexadecane/ PETA system when copolymerization completed. The phase after the polymerization was the mixture of LLC phase and solid particles in this system. The solid particles precipitated from polymerization system became not dissolvable in water.

IR spectra of NaOL, AHD-ol, and the copolymer formed from the LLC phase of NaOL/water/hexadecane/AHD-ol system showed that the C-H stretch of the double bonds in AHD-ol presented IR absorptions mainly at  $3077\text{cm}^{-1}$  and  $3007\text{cm}^{-1}$ . The C-H stretch of the double bonds in NaOL also presented absorption at  $3007\text{cm}^{-1}$ . These absorption bands decreased greatly after the copolymerization. IR spectra of NaOL, PETA, and the copolymer formed from

the LLC phase of NaOL/water/ hexadecane/PETA system also showed that the C-H stretch of the double bonds in PETA exhibited its IR absorptions mainly at  $3107\text{cm}^{-1}$  and  $3040\text{cm}^{-1}$ , which were higher in wavenumber than that of AHD-ol. This is because in PETA the double bonds connected directly to the carboxyl groups and could form a conjugation structure with them. These absorption bands, as well as the C-H stretch absorption in the double bonds of NaOL, decreased greatly after copolymerization. The carboxyl absorption for the cross-linker PETA appears at  $1726\text{cm}^{-1}$  while that for its copolymer at  $1736\text{cm}^{-1}$ , which was caused by the loss of the conjugation with the double bonds after copolymerization. The carboxyl absorption of NaOL appears at  $1560\text{cm}^{-1}$  because the carboxyl group in NaOL exists in the form of a  $-\text{COO}^{-1}$  ion. In the IR spectra of the copolymers, the absorption strength and area for these two kinds of carboxyl groups were almost the same. It means that there was same amount of the comonomer units existed in the copolymer. Thus all the solid particles precipitated from NaOL/water/ hexadecane/PETA system were the copolymer of NaOL and PETA since it is almost impossible for NaOL to execute homogeneous polymerization because of the steric hindrance in this kind of 1,2-disubstituted ethylene monomer structures. The alternative copolymer structure between PETA and NaOL was favored because there is big polarity difference between the two comonomers, which also helped to overcome the steric hindrance in NaOL molecule and to promote the copolymerization happened. There exist electron-drawing groups connected directly to the double bonds in the PETA molecules, which made its double bonds much more polar than those of NaOL. When the copolymer backbone propagated too long, it began to precipitate from the original LLC phase, which caused the whole system to be opaque. The IR spectra for these two systems showed that almost all of the three double bonds in these two cross-linker molecules polymerized with the double bonds in NaOL molecules, which proved the proposed copolymer structure. The IR spectra of copolymers also exhibited the carbonyl group absorptions in both monomers, which also proved the copolymerization between crosslinkers and NaOL molecule.

The small-angle x-ray diffraction determination of the LLC phase obtained from the polymerization of NaOL (33.0%)/water (62.5%)/ hexadecane (1.7%)/AHD-ol (2.8%) system gave the interlayer spacing as equal to  $39.0\text{\AA}$ . Compared with the interlayer spacing,  $62.6\text{\AA}$ , of the above system before polymerization, the value after polymerization decreased greatly. Increasing the amount of cross-linker, AHD-ol, used in the polymerization system would decrease the interlayer spacing of the polymer's LLC phase, as seen in Table I, but not significantly. The same things occurred in the NaOL/water/ hexadecane/ PETA system, as shown in Table II. Wide-angle x-ray diffraction determination of the two systems after polymerization also showed that there were only LLC structures formed from polymerization.

**Table I.** The interlayer spacing of the LLC phase of NaOL/water/ hexadecane/AHD-ol system before and after polymerization (NaOL: hexadecane = 90: 10 wt.; NaOL 0.35g; water 0.65g)

Molar ratio of AHD-ol to NaOL AHD-ol : NaOL	Interlayer spacing ( $\text{\AA}$ ) before	Interlayer spacing ( $\text{\AA}$ ) after
4 : 12	63.7	39.1
5 : 12	63.2	38.7
6 : 12	62.5	37.8
7 : 12	62.3	37.2
8 : 12	61.7	36.2

**Table II.** The interlayer spacing of the LLC phase of NaOL/water/ hexadecane/PETA system before and after polymerization (NaOL: hexadecane = 90: 10 wt.; NaOL 0.35g; water 0.65g)

Molar ratio of PETA to NaOL PETA : NaOL	Interlayer spacing (Å) before	Interlayer spacing (Å) after
1 : 12	64.3	40.8
2 : 12	63.3	40.4
3 : 12	62.3	39.7
4 : 12	61.9	39.2
5 : 12	61.4	39.0

The ordered and stiff arrangements of the hydrocarbon chains in the amphiphilic bilayer of NaOL/water/hexadecane system were distorted greatly by the polymerization with such branched cross-linkers as AHD-ol and PETA. Thus it can be expected that the interlayer spacing of LLC system after polymerization decreased greatly compared with that before polymerization.

#### Surface activity of the polymeric surfactants

The polymeric surfactant synthesized from NaOL/water/hexadecane/AHD-ol was dissolved into water. Thus the relationship between the surface tension and concentration was determined. The CMC of the polymeric surfactant aqueous solution was higher than that of NaOL aqueous solutions, and also the surface tension. Since the polymeric surfactant, synthesized from NaOL/water/hexadecane/PETA, was not able to completely dissolvable in water, the data were determined after dispersing the polymer by ultrasonic method. The surface tension of the aqueous solutions of this polymer changed quickly with time at first and then leveled off during the determination.

#### SUMMARY

Polymeric surfactants were synthesized from the LLC phase polymerization of NaOL/water/ hexadecane/ AHD-ol and NaOL/ water/ hexadecane/ PETA systems. AHD-ol and PETA acted as cross-linkers of the double bonds in NaOL molecules during polymerization.

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