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# Foams from Aqueous Systems of Polymerizable Surfactants

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Polymerization was made in aqueous foams stabilized by a combination of a polymerizable surfactant, sodium ( $\omega$ )-acrylamidoundecanoate (NaAAU), and oleyl alcohol. The common two-phase foams stabilized by a monomolecular layer of surfactant were not sufficiently stable to allow polymerization in foamed form, nor were such foams obtained in the two-phase region of aqueous solution and the liquid crystalline phase of hexagonally packed cylinders. Sufficient foam stability was found first when the lamellar liquid crystal formed by the combination of oleyl alcohol, the NaAAU, and the water. These foams were polymerized and shown to retain the liquid crystalline structure after polymerization. © 1987 Academic Press, Inc.

## INTRODUCTION

Polymerized foams enjoy a huge market with diverse applications in carpet backing, upholstery, etc., and the literature in the area is rich and varied describing foams produced from latex dispersions (1, 2) and the urethane foams (3–6) formed directly from the monomer solution.

The manufacturing of these foams rests on well-established technologies having been developed from the original rubber processes and the rules for stability and for obtaining foams with different properties of the final foam have been well established.

It appears that the fact that liquid crystals act as excellent stabilizers also for aqueous foams (7) should open a new avenue for polymerization of foams, because liquid crystals may be readily polymerized retaining their structure (8–10).

We found a preliminary investigation into the potential of polymerized foams using this technique well justified in order to evaluate the relative stability during polymerization of aqueous foams stabilized with a monomeric surfactant layer (11–15) versus those stabilized with a multilayered structure (16). With this paper we present our first investigation into that field. We investigated the combination of

water, a polymerizable surfactant, sodium ( $\omega$ )-acrylamidoundecanoate (NaAAU), and a long-chain alcohol, oleyl alcohol, to establish the phase regions for the micellar and liquid crystalline association structures. The stability of foams for different combinations of these phases was determined and the foams from the combination with optimal stability were polymerized. Optical microscopy in polarized light was used to detect liquid crystalline regions in the foams before and after polymerization.

## EXPERIMENTAL

### *Materials*

Materials used were acrylonitrile (+99% purity, Aldrich), 10-undecenoic acid (99% purity, Aldrich), cyclohexane (+99% purity, Aldrich), carbon tetrachloride (A.C.S. certified, Fisher), sulfuric acid (95% purity, Fisher), ethanol (punctilious grade, U.S. Industrial Chemical Co.), acetone (A.C.S. certified, Fisher), and oleyl alcohol (B.P. 205°/13 mm, Kodak).

### *Synthesis of the Polymerizable Surfactant*

The polymerizable surfactant (NaAAU) was prepared by the modified Ritter reaction (14),

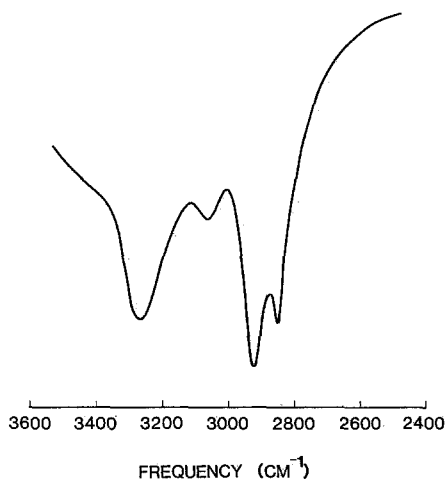
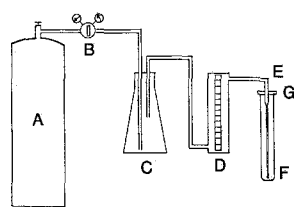


FIG. 1. Infrared spectra with the weak absorbance at  $3050\text{ cm}^{-1}$  showed the double bond to remain after the reaction of undecenoic acid and acrylonitrile.

in which sulfuric acid, acrylonitrile, and undecenoic acid were mixed together and the temperature was retained below  $20^\circ\text{C}$  during the reaction. The reaction vessel was kept at  $30^\circ\text{C}$  overnight to complete the reaction. The  $(\omega)$ -acrylamidoundecanoic acid (AAUA) was obtained after removal of the extra sulfuric acid by water rinses and extraction of the unreacted organic material by carbon tetrachloride. A final extraction was made with cyclohexane to remove trace amounts of carbon tetrachloride. IR spectroscopy showed that the vinyl double bond of AAUA at  $3050\text{ cm}^{-1}$  still



A - nitrogen gas cylinder  
B - pressure regulator  
C - humidifier bottle  
D - flow meter  
E - capillary tube  
F - test tube  
G - cap of tube

FIG. 2. The foaming equipment.

TABLE I

Sample Compositions for Foam Stability Measurement

Symbol	Composition		
	NaAAU (wt%)	Oleyl alcohol (wt%)	H <sub>2</sub> O (wt%)
▲	40.0	4.0	56.0
●	55.0	5.5	39.5
★	60.0	6.0	34.0
□	62.0	2.0	36.0
☆	58.0	10.0	32.0
△	55.0	16.0	29.0

existed after synthesis (Fig. 1). The AAUA was then neutralized with sodium ethoxide solution to a pH of 10. The soap was precipitated from the ethanol by addition of a few drops of acetone and dried under vacuum with a nitrogen gas flow.

#### Determination of Phase Regions

The phase diagram of the system (NaAAU/water/oleyl alcohol) was determined by mixing various ratios of NaAAU with a 20-ppm aqueous solution of hydroquinone and titration with oleyl alcohol. The boundary lines in the phase regions were checked by using a polarized microscope and high speed centrifuge.

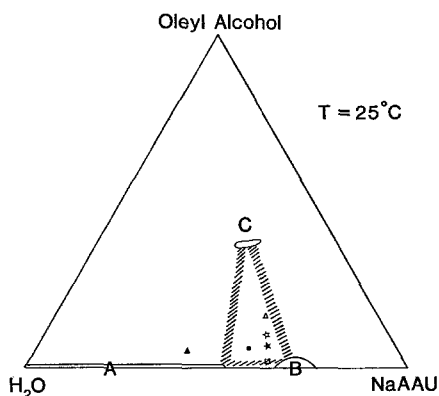


FIG. 3. The system water (H<sub>2</sub>O), sodium  $(\omega)$ -acrylamidoundecanoate (NaAAU), and oleyl alcohol gave three phase regions. (A) An aqueous solution. (B) A liquid crystal of hexagonally close-packed cylinders. (C) A lamellar liquid crystal.

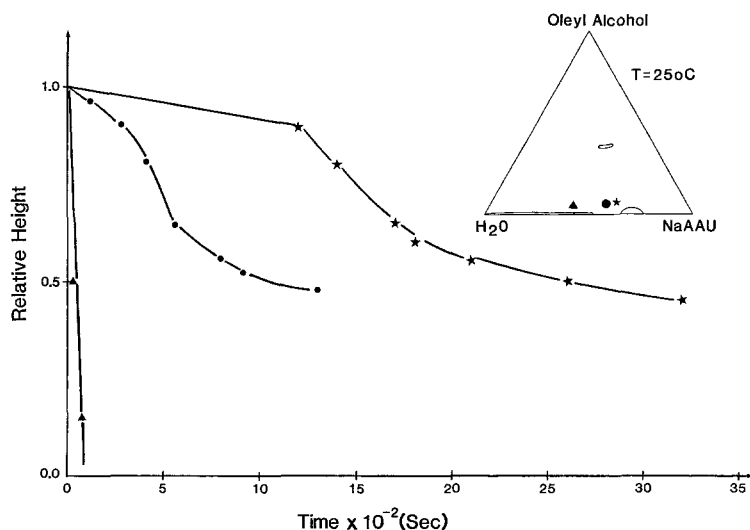


FIG. 4. The stability of foams with only the aqueous micellar solution and oleyl alcohol involved ( $\blacktriangle$ ) was extremely low. Compositions within the three-phase region with the liquid crystals ( $\bullet$ ,  $\star$ ) gave improved stability.

#### Foam Stability Study

The foam stability study used a foaming apparatus (Fig. 2) with nitrogen gas, whose flow rate was controlled at 6.5 ml/min by a pressure regulator and a flow meter. The gas bubbles were formed from a capillary. The

identical size of the bubbles was monitored by adjusting the dimensions of the capillary. The foam stability was estimated from the relative foam height with time.

The main concern of the investigation was to find the influence of liquid crystals on the stability of foams during polymerization. With

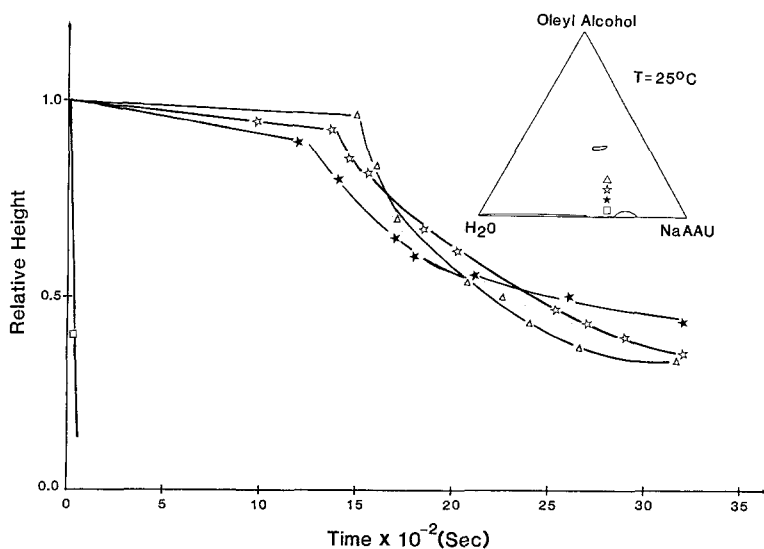


FIG. 5. Once within the three-phase region the ratio between the lamellar phase (C) and the hexagonal (B) did not influence foam stability.

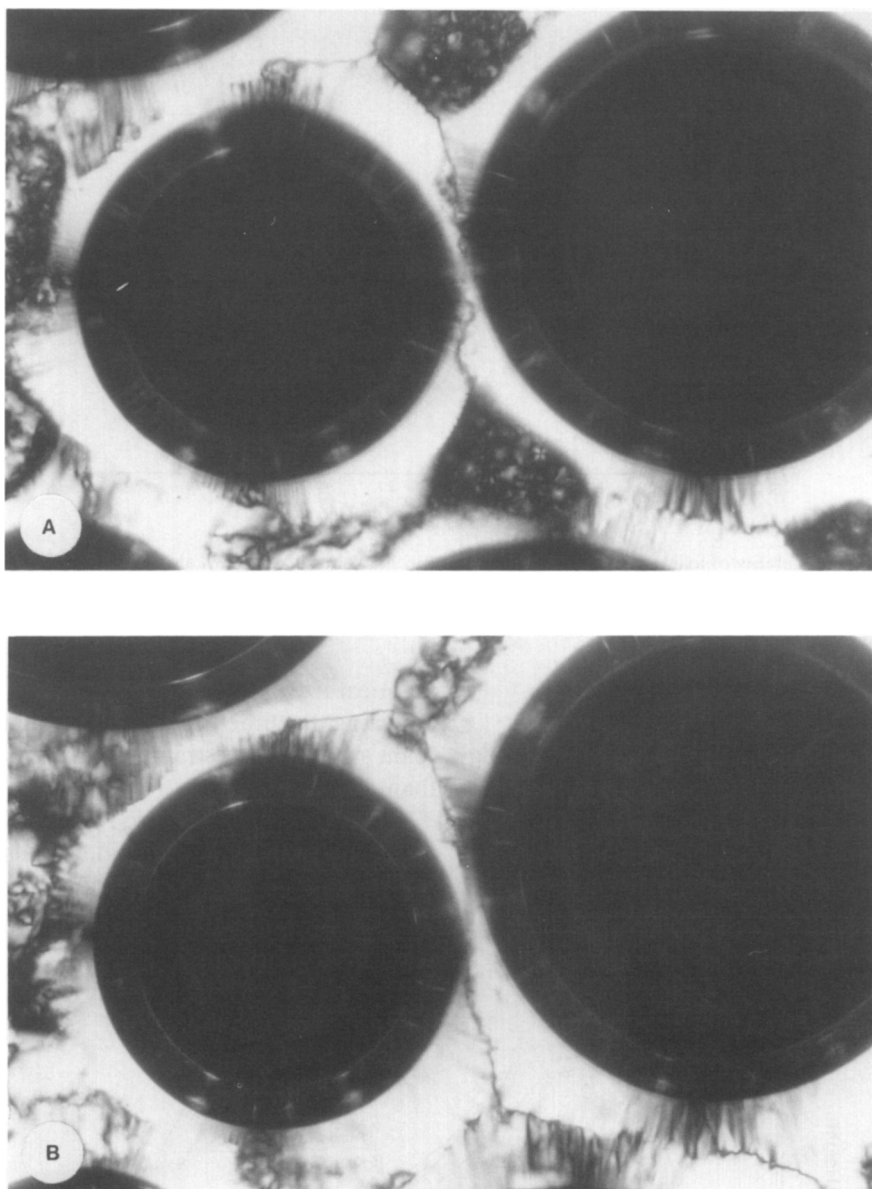


FIG. 6. Microscopy photos of two-dimensional foams during polymerization. Time after initiation of polymerization. (A) 0, (B) 30 h, (C) 44 h, (D) 50 h.

this in mind the compositions of the samples to be foamed were chosen with a constant oleyl alcohol/sodium ( $\omega$ )-acrylamidoundecanoate ratio. A reduction in the water content gave samples with and without liquid crystals. (Samples are marked in Fig. 4.) The other

condition of interest was the influence of the structure of the liquid crystal. Series No. 2 was chosen with a varied ratio of "hexagonal" and lamellar liquid crystal. The composition of each sample for foam stability measurement is listed in Table I.

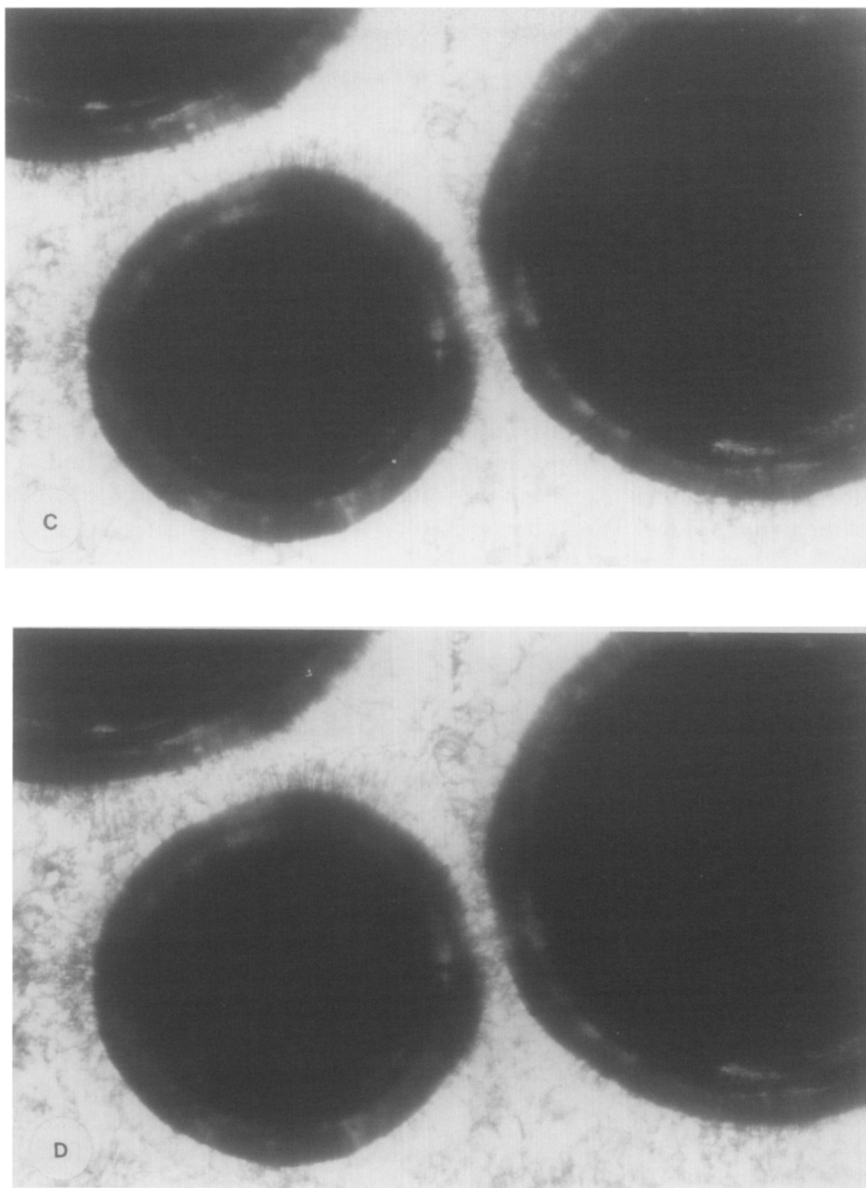


FIG. 6—Continued.

#### *Polymerization in Two-Dimensional Foams*

These foams were formed on a microscope glass slide (75/25 mm) with a framework of four glass chips (20/4 mm). The samples with 0.023 *m* potassium persulfate were foamed using a fine capillary tube through which ni-

trogen gas was passed. A cover glass was added to give a two-dimensional view and the sample was observed in a microscope with polarized light during polymerization. Rigid polymerized foam was obtained at room temperature in 50 h.

### *Polymerization in Three-Dimensional Foams*

Three-dimensional polymerized foams were made in a 1-cm diameter vial, with the same composition as that used in the two-dimensional polymerized foams. After polymerization, the foams were rigid, they were sliced, and the optical pattern was observed with a microscope using polarized light.

#### *Polarizing Microscope Study and X-Ray Diffraction Measurement*

An Olympus microscope (Model BH) was used to observe the structure during polymerization of the two-dimensional foams and the structure of three-dimensional foams after polymerization.

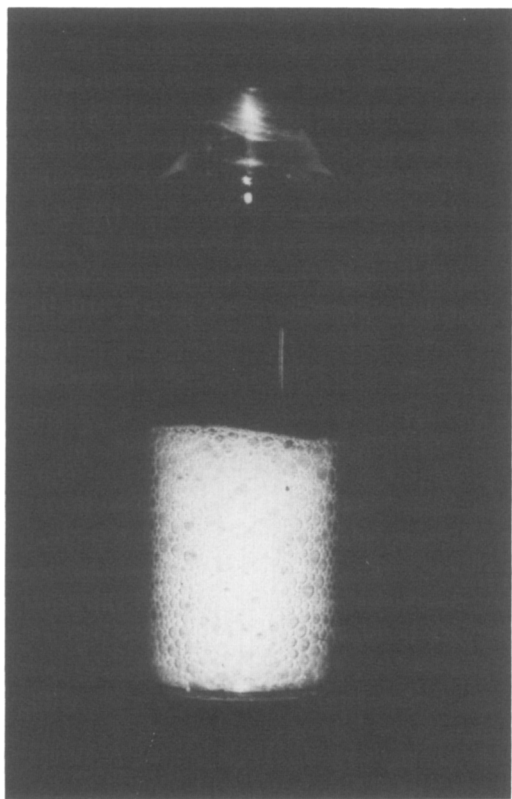


FIG. 7. The three-dimensional foam was optically anisotropic.

X-RD7 (GE Brand) powder X-ray diffractometer was used to obtain the X-ray pattern of the samples before and after polymerization.

## RESULTS

### *Phase Diagrams*

The phase diagram of the system sodium ( $\omega$ )-acrylamidoundecanoate (NaAAU)/water/oleyl alcohol is shown in Fig. 3. The NaAAU dissolved in water to 52% by weight in an isotropic normal micellar solution. Between 65 and 76% by weight of NaAAU, a hexagonal liquid crystalline phase was found. A small lamellar liquid crystal region was formed at 35% oleyl alcohol.

### *Foam Stability*

The foam stability was determined in order to evaluate the influence of the two liquid crystals in the system. The exact phase conditions were not determined because of the uncertainty of the "purity" of NaAAU due to partial polymerization. Hence, two- and three-phase areas indicated on Fig. 4 are approximate, but even in their approximate form, they allow the determination of the influence of the liquid crystal on the foam stability.

The combination of water and the surfactant alone gave an aqueous micellar solution and a liquid crystalline phase of hexagonally packed cylinders (B, Fig. 3). These phases alone or in combination gave foams with insufficient stability to retain the foam structure during polymerization.

The series with an oleyl alcohol/NaAAU ratio of 1/10 gave a combination of the aqueous micellar solution (A, Fig. 3) and oleyl alcohol solution for water contents in excess of 47 wt%. Between 29 and 47 wt% water, the series gave three phases: the aqueous micellar phase (A), the hexagonal liquid crystal (B), and a lamellar liquid crystal (C). The first sample in this series, Fig. 3 ( $\blacktriangle$ ), contained no liquid crystals and the foam stability, Fig. 4, was ex-

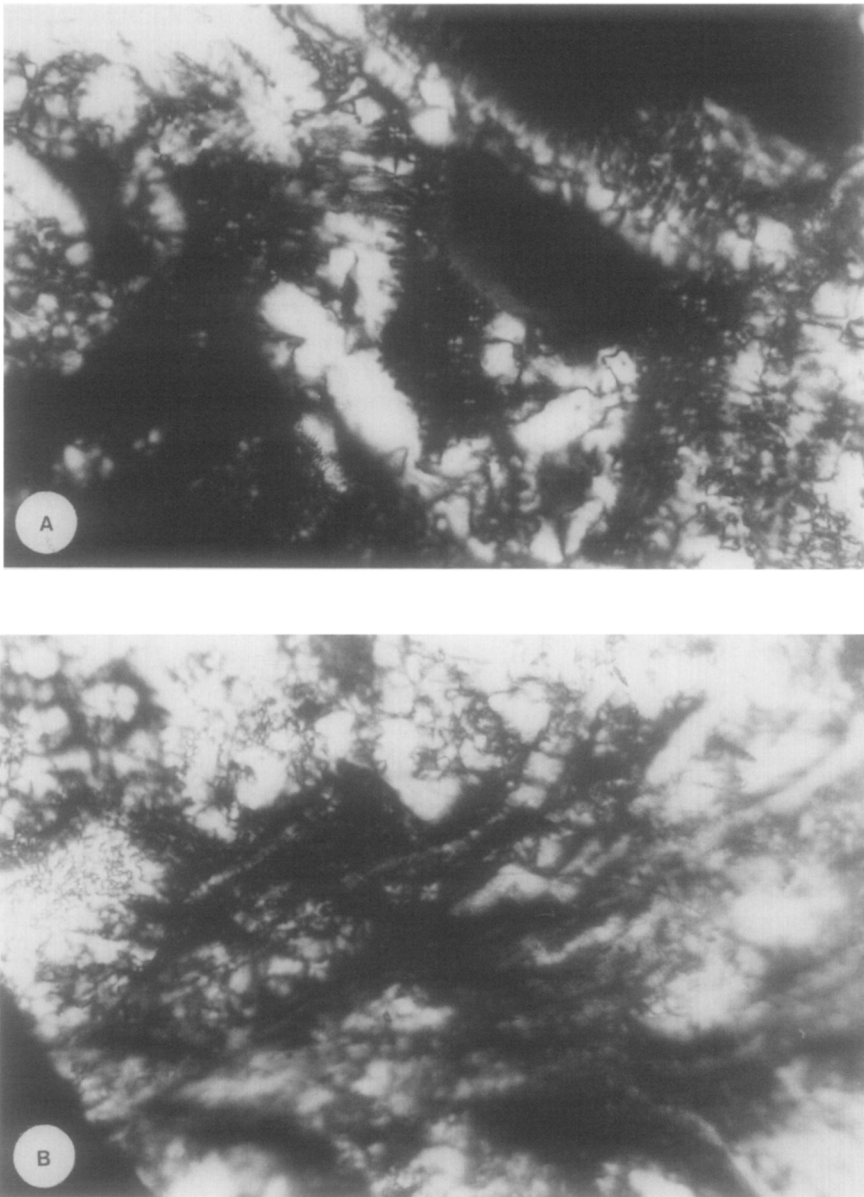


FIG. 8. In the three-dimensional foam the optical pattern in polarized light also remained after polymerization.

tremely low with a half-life of less than 1 min. The foams with increased liquid crystalline content, Fig. 3 (●) and (\*), were considerably more stable with half-lives of approximately 15 and 40 min., Fig. 4.

The next series now with a changed oleyl

alcohol/NaAAU ratio showed the specific influence of the structure of the liquid crystal. The results, Fig. 5, gave identical foam stabilities for the three samples investigated.

Based on these results a composition of 60% NaAAU, 34% water, and 6% oleyl alcohol was



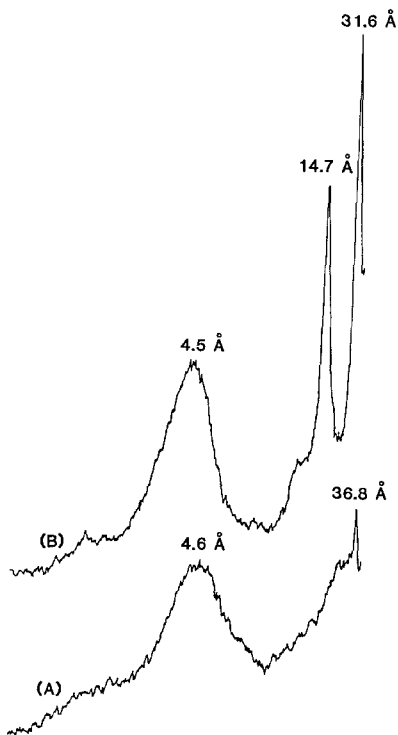


FIG. 9. The x-ray diffraction pattern before (A) and after (B) polymerization.

selected for the investigations on structural changes in the foam during polymerization.

In the microscope study of the two-dimensional foams, the lamellar liquid crystal was observed directly in the foams (Fig. 6A–D). The air bubbles appear black on the pictures as do areas with isotropic solution while the liquid crystalline parts appear radiant. The photos, Fig. 6A, clearly show the liquid crystal to be adsorbed predominantly at the surface of the gas bubbles.

The orientational influence of the surface on the liquid crystal is demonstrated by the fact that each liquid crystalline layer between the coalesced bubble surfaces (low right, Fig. 6A) is identified as belonging to one of the bubbles. The line where they meet is observed as an irregular line in the middle of the film separating the two bubbles.

The junctions joining the thin films contain the isotropic liquid with dispersed liquid crys-

tal. Radiant “oily streaks” and a single Maltese cross are easily observable in Fig. 6A.

This site was followed during polymerization and the changes are illustrated in Figs. 6B–6D. In Fig. 6B, the lower junction to the right of isotropic liquid with dispersed liquid crystal in Fig. 6A has now disappeared and has been replaced by a liquid crystal. It is interesting to note that the liquid crystalline layers are continuously growing from the surface of the liquid crystalline layers present in Fig. 6A. The separation line from the coalesced part in Fig. 6A (low right part) now continues uninterrupted to the center of the lower junction in Fig. 6B.

In Fig. 6C, the upper junction has also been filled with birefringent material as well as the huge space to the left in the figures. The line separating the liquid crystalline layers from each bubble may still be observed but with difficulty. The continued polymerization has fractionated the smooth optical pattern in Fig. 6B. The final state, Fig. 6D, showed very little change from that in Fig. 6C; the dimensions are slightly more shrunk, but the pattern from Fig. 6C is intact.

The foam from the three-dimensional polymerization was optically anisotropic; its radiance, when photographed between crossed polarizers, is evident from Fig. 7. The contour of the glass vial in which the foam was polymerized is not visible in the photograph, but the foam is very conspicuous with its strong radiance.

The optical pattern from thin films from the three-dimensional foam, Fig. 8B, demonstrates the anisotropy also in this foam. The borders to the air bubbles are very distinct and the characteristic Maltese crosses are present in multitude.

The X-ray diffraction patterns showed the characteristic diffuse reflection around 4.6 Å before and 4.5 Å after polymerization, Figs. 9A and 9B. This reflection is characteristic of the disordered state of the hydrocarbon chains in a liquid. The small-angle part of the pattern gave one reflection at approximately 40 Å be-

fore polymerization; after polymerization reflections at 14.7 and 31.6 Å were found. The ratio between the latter is approximately 1:2.

#### DISCUSSION

These initial results clarified several conditions concerning polymerized foam from aqueous solutions of polymerizable surfactants.

The first condition is concerned with the relation between foam stability and the aggregation state of the surfactant. The results show the foams from the aqueous solution not to be sufficiently stable to polymerize with retained stability of the foam. The monomolecular film on the aqueous micellar solution does obviously not have sufficient resilience to retain its stabilizing action during the polymerization, nor were the structures formed during polymerization of the micellar aggregates sufficient support to retain the foam stability.

The macroscopically thick layers of liquid crystal, Fig. 6A, provided sufficient stabilization to give polymerized foams, Fig. 7. It is obvious that stabilization is not a problem after polymerization, Fig. 7; now the foam films are solid and are able to support the foam indefinitely. The critical time is during the initial polymerization when the formation of the intermolecular bridges of the structure shown in Scheme 1 remove the translational and rotational freedom of the layered structure and in addition impose their own conformational demands. The multilayered structure of the liquid crystalline phase retained both its location and its identity during this process as is made obvious by a comparison of Figs. 6A and 6B. The results even indicate that the liquid crystalline phase formed during polymerization took place with the prepolymerized

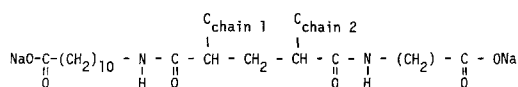
liquid crystalline layer as a template; the pattern of the radiant areas in Fig. 6B continued from the birefringent parts in Fig. 6A in an uninterrupted manner.

The disruption of the "ordered" pattern in Fig. 6B to the one in Fig. 6D indicates a perturbation of the structure. At present, there is no solid experimental evidence to clarify why this happens, but removal of water would mean a pronounced shrinkage of the structure as well as an introduction of directional forces in the polar part of the structure.

The optical pattern strongly supported the interpretation of a retained layered structure after polymerization but give no information on a crystalline or amorphous packing of the hydrocarbon chains. The X-ray diffraction results, Fig. 9, present evidence that no crystallization takes place; the diffuse reflection at 4.5–4.6 Å is a conspicuous feature in both Fig. 9A and 9B. The small-angle pattern in Fig. 9B with its ratio of 1:2 may at first be taken as the usual interlayer distance between the polar parts in a lamellar phase (14) or approximately equal to double the amphiphilic molecular chain length. The value 14.7 Å excludes such an interpretation; in fact, the distance corresponds well with the length of one chain only.

An interlayer distance of one chain length may be interpreted as a structure in which the hydrocarbon chains of opposite layer are completely intermingled with each other, Fig. 10A, and such structures for lamellar liquid crystals have been suggested (16). However, in the present case, the fact that the terminal groups are the polymerized entities makes such an interpretation less probable; it is difficult to envision polymerization leading to enhanced mixing of the alkyl chains.

A more probable structure is the one in Fig. 10B. The polymerized layer consists of a large proportion of nitrogen and oxygen atoms with polar bonds. It appears reasonable to assume that this layer reflects the X-rays to a degree comparable to that of the carboxylic group layers. In this way, the reduction in interlayer spacing receives a reasonable explanation.



SCHEME 1.

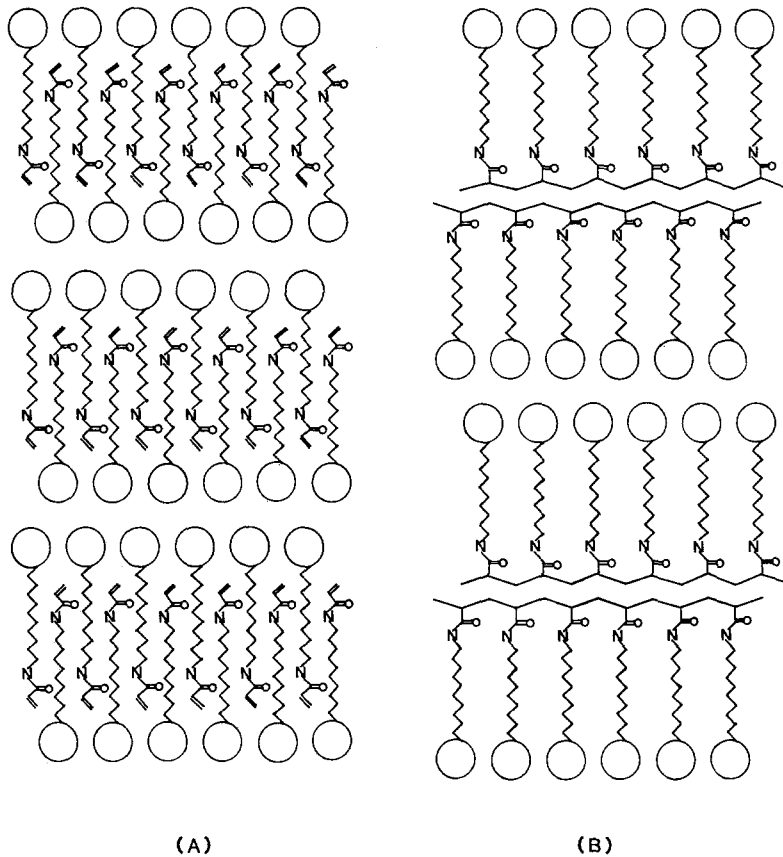


FIG. 10. Two kinds of lamellar structures: (A) Complete mixing of chains from opposite amphiphiles. (B) The polymerized chain forms a layer.

#### ACKNOWLEDGMENT

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