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SHORT COMMUNICATION

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Polymerization of aqueous liquid-crystalline allyldimethyldodecylammonium bromide

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Abstract Allyldimethyldodecylammonium bromide was polymerized by γ-ray irradiation in both hexagonal and cubic mesophases, and the conversion–time curves were obtained. The maximum conversion was about 35%, and the polymer remained in the liquid-crystalline structure formed by the nonpolymerized monomers. The influence of polymerization on the distribution of water in the different types related to the hydrophilic surfaces of microstructures was studied using Fourier transform infrared spectroscopy. The incomplete polymerization was explained by steric constraints in the liquid-crystalline structures.

Key words Allyldimethyldodecylammonium bromide · Liquid crystals · Polymerization · Polymerizable surfactant

Introduction

There is increasing interest in polymerizable surfactants which can form microstructures such as micelles [1–5], vesicles [6, 7], mesophases [4, 5, 8–10], microemulsions [11] and adsorbed monolayers [12]. The polymerization and preservation of such microstructures offers the possibility of obtaining materials with unique ordering, shapes and properties for specific applications. As an example, the polymerization of cubic liquid crystals has allowed the preparation of membranes with extremely well defined pores [13]. Polymerizable amphiphilic compounds carry a vinyl double bond together with hydrophilic and hydrophobic moieties in a molecule. The active double bond may be situated either in the hydrophobic chain or in the hydrophilic headgroup, which may be cationic, anionic or nonionic. In some cases, spontaneous polymerization occurs above the critical micelle concentration in water [14–16].

In this paper the polymerization of aqueous allyldimethyldodecylammonium bromide (ADDAB) liquid crystals by γ-ray irradiation is reported. This surfactant has a reactive double bond near the headgroup. Its polymerization in molecular and micellar solutions has been reported elsewhere [1, 17–19]. Its temperature–composition phase diagram and rheological properties have been reported in previous papers [4, 20]. McGrath and Drummond [4] polymerized ADDAB mesophases both photochemically and thermally and found an upper limit of about 35% for the degree of polymerization; however, the polymerization was very fast and no kinetics data were obtained.

Experimental

ADDAB was synthesized according to a literature procedure [1], and dried under reduced pressure over phosphorous pentoxide. Water was doubly distilled and deonized.

Samples were prepared by weighing ADDAB and water in glass ampoules. These ampoules were closed with rubber stoppers and placed into a water bath at 60 °C for 2 days where they were frequently shaken to homogenize the mixture. Then the samples were frozen with liquid air and degassed by the freeze–pump–thaw technique to remove as much oxygen (a polymerization inhibitor) as possible. Then the ampoules were flame-sealed while still under vacuum. Two series of samples were studied, one with 65 wt% ADDAB, which corresponds to a hexagonal liquid crystal, and the other with 90 wt% ADDAB, which was a cubic liquid crystal [20].

The samples were irradiated with γ rays (6.84 kGy/h) for different times at room temperature. The progress of the polymerization was monitored as a function of time by stopping the irradiation of different ampoules with samples of the same composition at the desired times. Aliquots of the irradiated samples were desicated to constant weight to obtain the water content. Then these samples as well as the nondried ones, were studied using Fourier transform IR (FT-IR) spectroscopy. One sample was polymerized catalytically with 2,2′-azobis(isobutyronitrile).

FT-IR studies were performed using a Nicolet FT-IR 5ZDA spectrophotometer. Liquid crystal samples were sandwiched between IRTRAN-4 windows as capillar films. Dried samples were studied in KBr pills. The state of water in the samples were studied in the 2700–3800 cm^{-1} range. The water bands were superimposed with those of symmetric and asymmetric tension of methyl and methylene groups, and that of asymmetric tension of the $-CH{=}CH_2$ group at 3080 cm^{-1}. The polymerization was verified by comparing the decrease in the 1035 cm^{-1} peak area (=C-H bending) with that of the peak at 720 cm^{-1} [$(CH_2)_{n>4}$ deformation], which was invariant when samples were irradiated. All peaks were deconvoluted using the Peakfit program.

Electron micrographs were obtained with a Jeol 35CF scanning electron microscope on dried samples.

Results

State of water

The deconvoluted spectrum of water in a polymerized sample is shown in Fig. 1. Elsewhere it has been reported that the broad OH stretching water band in surfactant systems is a combination of three bands that correspond to three different "types of water" [21–25]. The band with a maximum absorption wavenumber at 3290 ± 20 cm^{-1} corresponds to "free" or "bulklike water"; that at 3490 ± 20 cm^{-1} belongs to "interfacial" water, and that at 3610 ± 10 cm^{-1} is due to "trapped water" [25]. Three types of water in surfactant liquid-crystalline systems have been reported in the literature [26–28].

Figures 2 and 3 show the number of molecules of each type of water per surfactant molecule ($R = n_w/n_s$) as a function of the percentage of polymerization in samples with 65 and 90 wt% ADDAB. It can be seen in Fig. 2 that the amount of water associated with the hydrophilic surface (R_{surf}) is almost independent of the degree of polymerization in samples with 65 wt% ADDAB ($R_{total} = 10$, hexagonal liquid crystal); however, the amount of water trapped in interstices of the structure (R_{trap}) increased while that of bulklike water (R_{bulk}) decreased with increasing degree of polymerization. Samples with 90 wt% ADDAB ($R_{total} = 2$, cubic liquid crystal) showed a similar trend for R_{trap} and R_{bulk}, but R_{surf} first increased and then decreased with increasing irradiation (Fig. 3).

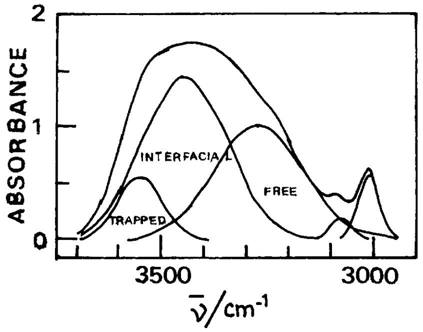

Fig. 1 Fourier transform (*FT*) IR spectrum of water -OH stretching bands in a 34.3% polymerized sample of hexagonal allyldimethyldodecylammonium bromide (*ADDAB*) liquid crystal (65 wt%), showing the bands of *free*, *interfacial* and *trapped* water

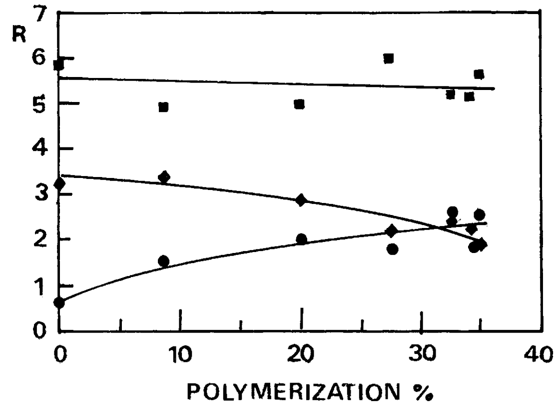

Fig. 2 The number of molecules of water per surfactant molecule *R*, as a function of the percentage of polymerization (% polym.) for different types of water. Samples with 65 wt% ADDAB. The tendency curves are drawn. Bulk water (♦) [$R_{bulk} = -0.001(\%\ \text{polym.})^2 - 0.0066(\%\ \text{polym.}) + 3.438$, $r = 0.9481$]; surface water (■) [$R_{surf} = -0.006(\%\ \text{polym.}) + 5.566$, $r = 0.1844$]; trapped water (●) [$R_{trap} = -0.0013(\%\ \text{polym.})^2 + 0.089(\%\ \text{polym.}) + 0.714$, $r = 0.8849$]

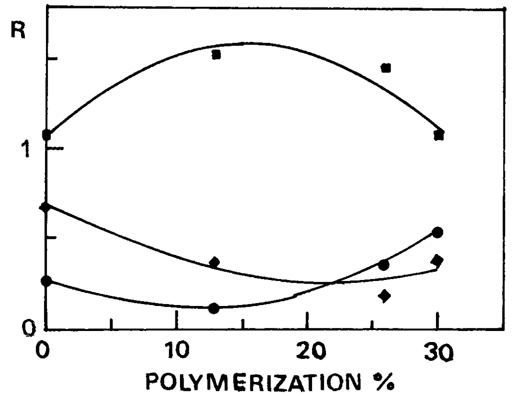

Fig. 3 *R* for different types of water as a function of the percentage of polymerization (% polym.). Samples with 90 wt% ADDAB. The tendency curves are drawn. Bulk water (♦) [$R_{bulk} = 0.0009(\%\ \text{polym.})^2 + 0.068(\%\ \text{polym.}) + 1.065$, $r = 0.9494$]; surface water (■) [$R_{surf} = -0.002(\%\ \text{polym.})^2 - 0.04(\%\ \text{polym.}) + 0.675$, $r = 0.9413$]; trapped water (●) [$R_{trap} = 0.0012(\%\ \text{polym.})^2 - 0.027(\%\ \text{polym.}) + 0.259$, $r = 0.9989$]

No bulk water was detected calorimetrically in ADDAB liquid-crystalline samples above 53 wt% [20]. Then, the "bulk" water detected by IR was strongly affected by the presence of surfactant aggregates and its properties were different from those of pure water, a situation which is common in concentrated liquid crystals [29].

Polymerization

The catalytically polymerized hexagonal sample produced a conversion of 34%. Electron micrographs of nonpolymerized and polymerized samples are shown in Figs. 4 and 5. The appearance of both samples is clearly different. Polymerized and unpolymerized samples did not show changes in texture when observed with a polarizing microscope.

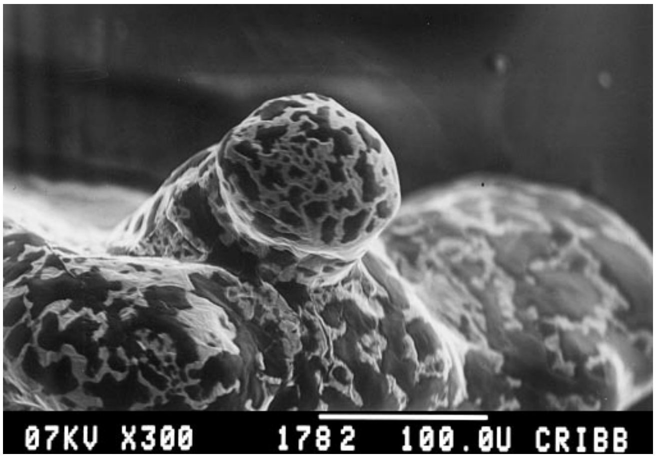

Fig. 4 Electron micrograph of nonpolymerized ADDAB

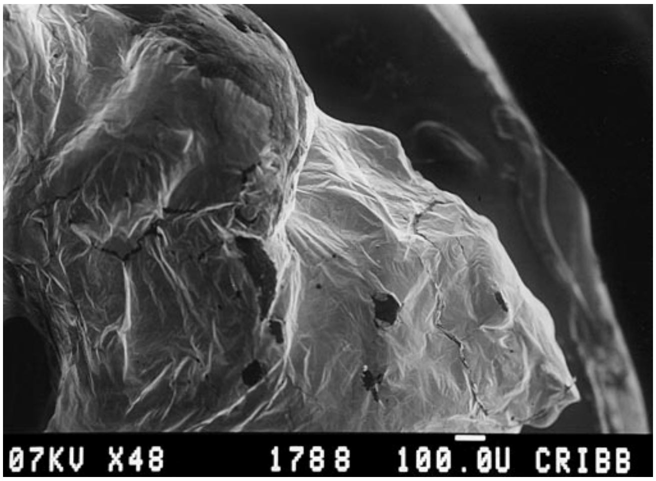

Fig. 5 Electron micrograph of 34% polymerized ADDAB

Figure 6 shows the reference peak and Fig. 7 shows the bands between 1075 and 925 cm^{-1} in a dried sample with 35% polymerization. The same zone in a liquid-crystalline sample is shown in Fig. 8. It can be seen that the interaction of the allyl group with water makes it difficult to study the degree of polymerization in wet samples. The percentage of polymerization as a function of time is shown in Fig. 9. The initial curves (up to 10 h) fit the following quadratic equations.

Hexagonal liquid crystal:

$$\text{Percentage polymerization} = 0.190t^2 + 2.399t + 0.0434, \quad r = 0.9999$$

Cubic mesophase:

$$\text{Percentage polymerization} = 0.322t^2 + 0.443t + 0.232, \quad r = 0.9983$$

r being the correlation factor and t the time in hours.

Above 9 hours of irradiation, the curve of the hexagonal mesophase tends to about 35% polymerization and that of the cubic mesophase to about 30% polymerization. When the reaction rate [r = d(percentage polymer)/dt, in percentage polymer/hour) was

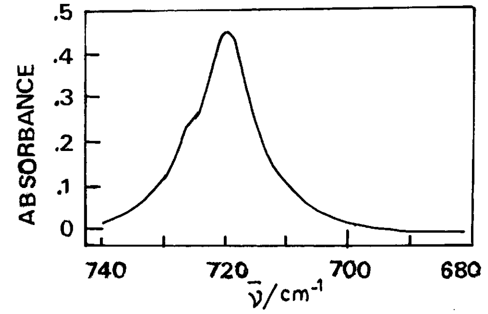

Fig. 6 FTIR reference peak at 720 cm^{-1} [$(\mathrm{CH_2})_{n>4}$ deformation], which was invariant when samples were irradiated

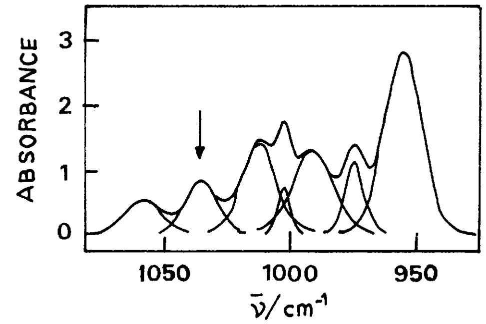

Fig. 7 FTIR peaks between 1075 and 925 cm^{-1}. The *arrow* indicates the 1035 cm^{-1} peak (=C-H bending), the intensity of which decreases with the degree of polymerization. Sample with 34% polymerization

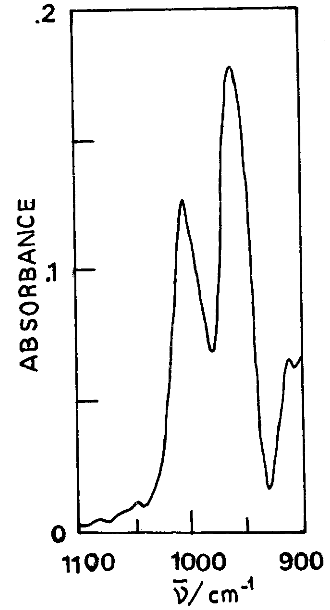

Fig. 8 The same FTIR wavelength number range as in Fig. 7, in a nondried sample of 65 wt% ADDAB with 34% polymerization

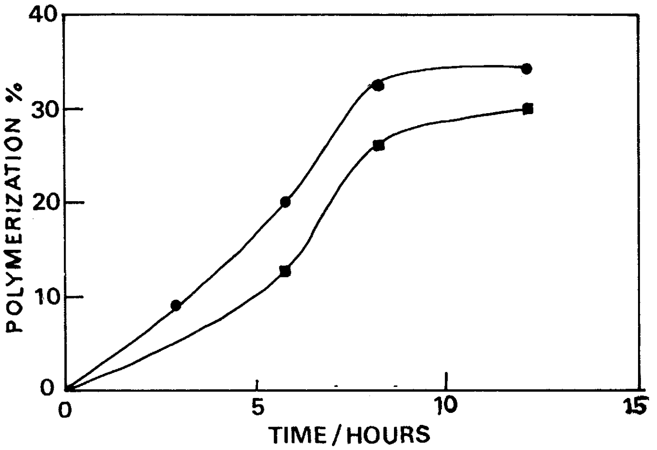

Fig. 9 ADDAB degree of polymerization versus irradiation time. Hexagonal mesophase (●) (65 wt% ADDAB); lamellar mesophases (■) (90 wt% ADDAB)

plotted versus the percentage of remanent monomer [% mon.], the following linear equations fitted the data.

Hexagonal liquid crystal:

$$r = -0.0473[\%\ \text{mon.}] + 7.207, \quad r = 0.9933$$

Cubic liquid crystal:

$$r = -0.0805[\%\ \text{mon.}] + 8.616, \quad r = 0.9933\ .$$

Some irradiated samples became bright yellow or orange, which was due to decomposition of a small amount of monomer [4].

Discussion

The results of this work indicate that polymerization which has been activated either by γ-ray initiation or catalytically gave almost identical results. This conclusion is in agreement with the findings of McGrath and Drummond [4], who polymerized hexagonal and cubic ADDAB mesophases photochemically and thermally and found the same limit of about 35% in the degree of polymerization. The γ-ray irradiation was slower than the other polymerization procedures. The conversion limit was attained in about 8 h, enabling us to determine the polymerization kinetics curve. Similar conclusion may be made by looking at the results of Paleos et al. [17] for the γ-ray irradiation of ADDAB micelles and monomeric (non-micellized) solution, although they obtained 100% conversion. The experiments of McGrath and Drummond [4] using thermal and photochemical polymerization of ADDAB mesophases with UV radiation resulted in very rapid rates which reached a plateau almost immediately.

Paleos and coworkers [1, 17, 19] polymerized ADDAB in molecular and in micellar aqueous solution, obtaining 100% polymerization, both radiolytically and catalytically; however, McGrath and Drummond [4] could not reproduce their results. In addition, it seems that ADDAB polymerization in the liquid-crystalline phase cannot achieve a conversion beyond about 35%, as confirmed by our results and those of McGrath and Drummond [4].

Why was ADDAB 100% polymerized in the micellar state but could not be polymerized beyond 35% in the liquid-crystalline state? It is probable that the alignement of the surfactant molecules imposed by the liquid-crystalline phase geometry was unfavourable to the polymerization. The crystalline structure of ADDAB is formed by interdigitated layers with a considerable separation among polar headgroups in the same layer [20]. This situation may be retained in the fluid structure of mesophases. In addition, polymerization of unsaturated nonamphiphilic quaternary ammonium compounds is extremely difficult and thermal polymerization in aqueous solution using water-soluble initiators is not possible for monomers containing only one allyl group [30–36]. This intrinsic resistance to polymerization of the allyl group is enhanced by its placement near the charged centre of the surfactant and the ordered structure of the polar headgroup layer; however, these factors exist both in micellar and liquid-crystalline states. It seems probable that the time elapsed to the reformation of the original carbon–carbon double bond is shorter than that needed to form another carbon–carbon double bond in the appropriate orientation with respect to an activated double bond in mesophases. The lateral mobility of the monomers in these microstructures is probably reduced due to a tighter packing of surfactant molecules in mesophases than in micelles, and this situation might obstruct the monomers capacity to orientate themselves with respect to a neighbour-activated centre. This situation may be more favourable to termination reactions than propagation.

Polymerization of ADDAB mesophases gave neither a phase separation nor a phase transformation during polymerization, as was found by McGrath and Drummond [4] using different polymerization techniques. However, changes in the distribution of the different types of water with the degree of polymerization, together with the polarizing microscope observations indicate that, while no major changes in the mesophase microstructure were induced by the inclusion of polymerized surfactant in the non-polymerized surfactant matrix, some slight change occurred at the polar headgroup layers, because there was an increase in the amount of water trapped in the interstices of the microstructure. These water molecules were recruited from the bulklike water, whereas the amount of interfacial water remained almost constant. Slight differences in the dependence of the *R* values on the percentage of polymerization may be due to the different structures of the aggregate/water interface in hexagonal and cubic mesophases.

Concluding remarks

- ADDAB polymerization by γ-ray irradiation was slow enough to obtain the conversion–time curve, which was not possible using other polymerization techniques.
- The upper limit of polymerization in ADDAB mesophases was about 35%, while it was 100% in micelles. The difference may be caused by differences in molecular mobility in the different microstructures favouring the termination reactions.
- Polymerized ADDAB remained included in the nonpolymerized liquid-crystalline structure; however, slight differences in the structure of the polar headgroup layers occurred, as revealed by changes in the state of water.

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