Communications to the Editor

Polymerization of Acrylamide in Lamellar, Hexagonal, and Cubic Lyotropic Phases

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Polymerization of lyotropic phases of different symmetries formed by surfactants in solution is focusing major interest among the scientific community. Several attempts[1-5] have been made to obtain new materials using lyotropic phases. Difficulties have often been encountered in conserving the long-range order of the phase upon polymerization.[1,2,5] We report on polymerization of acrylamide inside the water layer of lamellar, hexagonal, and cubic phases, conserving the liquid-crystal nature of the lyotropic arrangement. These results provide a unique method of obtaining polymers in a constraint environment, which can be applied to physical studies[6,7] as well as technical applications.[4]

The study of fluctuating interfaces and membranes is of considerable interest in physics. However although knowledge of linear polymers is well documented, the understanding of two-dimensional systems is only at its beginning.[6] Experimental studies have focused mainly on fluid membranes so far, while experimental rigid systems are still missing. In particular the possibility of obtaining *tethered* or solid membranes has been theoretically pointed out but only little experimentally demonstrated. For instance the crumpling[7] transition is still waiting for experimental evidences. One way to obtain such solid membranes is the polymerization of lamellar phases, using a monomer dissolved in (or bound to) one of the components of the lyotropic system.

Beyond such theoretical aspects, potential applications of polymerized lyotropic phases are numerous. Lyotropic phases are highly symmetrical, periodic systems, whose spacing can be continuously and very easily tuned. Upon polymerization one expects to retain the spatial organization of the lyotropic phase. Of special interest are the cubic phases which are bicontinuous systems, with a sharply monodisperse pore diameter, adjustable in a wide range. Polymerization of the cubic phase could provide microporous materials[4] with potential applications in ultrafiltration, catalysis, or enzyme immoblization for instance.

We have prepared phases of various symmetries, dissolving acrylamide (10% by weight) and methylenebis(acrylamide) (as a cross-linking agent, 0.3% by weight) in the water phase of amphiphilic systems. Lamellar phases have been obtained from the binary systems water/AOT (dioctyl sodium sulfosuccinate) and from the ternary water/AOT/isooctane, hexagonal phases from SDS (sodium dodecyl sulfate) and water, and cubic phases from the ternary system water/AOT/decanol. The polymerization has been initiated photochemically, using a dye/reducer couple as a photosensitizer.[8] The best results were found with a mixture of eosine and methylene blue, the reducing agent being ethanolamine.[9] Polymerization was completed in a few minutes upon irradiation by visible light (experimental details will be published in a forthcoming paper).

Comparison of phase diagrams for the AOT system with and without acrylamide (Figure 1) shows that acrylamide acts as a cosurfactant,[10] the lamellar domain being shifted when acrylamide is present. Nevertheless it is noteworthy that an overlapping region exists where the lamellar phase is stable with both pure water and water with acrylamide. Similar phase diagrams have been determined for the other surfactants, each showing the cosurfactant effect of acrylamide. We have observed that, in order to prevent phase separation during polymerization, samples to be polymerized must be chosen inside the overlapping region. Indeed, this fact could be explained considering that, due to the presence of the long alkyl chain, the polymer is not expected to act as a cosurfactant, or at least not at the same degree as the monomer. Consequently, as the polymerization process occurs, the consumption of the monomers drives the phase toward a new system without (or with less efficient) cosurfactant. In a first approximation this new system can be assimilated to the one without acrylamide. It is therefore fundamental to start the polymerization from a point in the phase diagram where the lyotropic phase is stable with and without acrylamide. The samples used for polymerization have always been prepared with composition lying inside the overlapping region.

The samples become slightly turbid upon polymerization. This could be explained as an increase of the scattering due to the grain boundaries. The degree of conversion, evaluated by weighing the polymer after precipitation and washing out of the surfactant and monomer in acetone, has been found to be usually ranging around 95%. The degree of conversion is lower for the cubic phase, on the order of 75%. For this latter phase, the overlapping of the stability domain is of very small size and care must be taken to avoid a two-phase polymerized system. The results presented in the following correspond to the samples for which polymerization gave one single phase. Polymerization of the lamellar phase, performed without methylene bis(acrylamide), has shown that, in this case, the estimated molecular weight of the polymer (determined by gel permeation chromatography) is higher than 10^5, which is a commonly obtained value for polyacrylamide. When possible, optical observation using a polarizing microscope indicates that the characteristic pattern of the lyotropic phase is conserved upon polymerization and no phase separation is apparent.

The similarity between the X-ray scattering spectra of the lamellar phase of AOT before and after polymerization (Figure 2) demonstrates that long-range order is preserved. The small (10%) decrease of the interlayer spacing in the polymerized system has to be related with the decrease of the specific volume of acrylamide upon polymerization.[11] Similar results have been obtained for the polymerization of swollen lamellar phases containing

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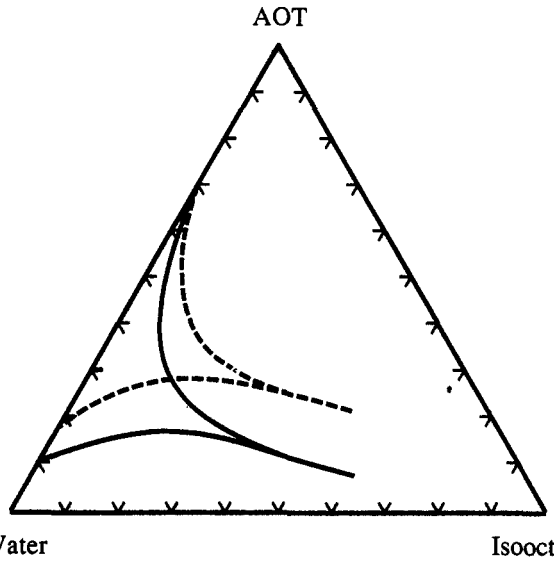

Figure 1. Schematic phase diagram of the ternary system water/AOT/dodecane (dark line) showing the existence domain of the lamellar phase. Superposed to this diagram, the existence domain of the lamellar phase of the quaternary system water/acrylamide/AOT/isooctane (with a ratio acrylamide/water of 0.1) is indicated with a dotted line.

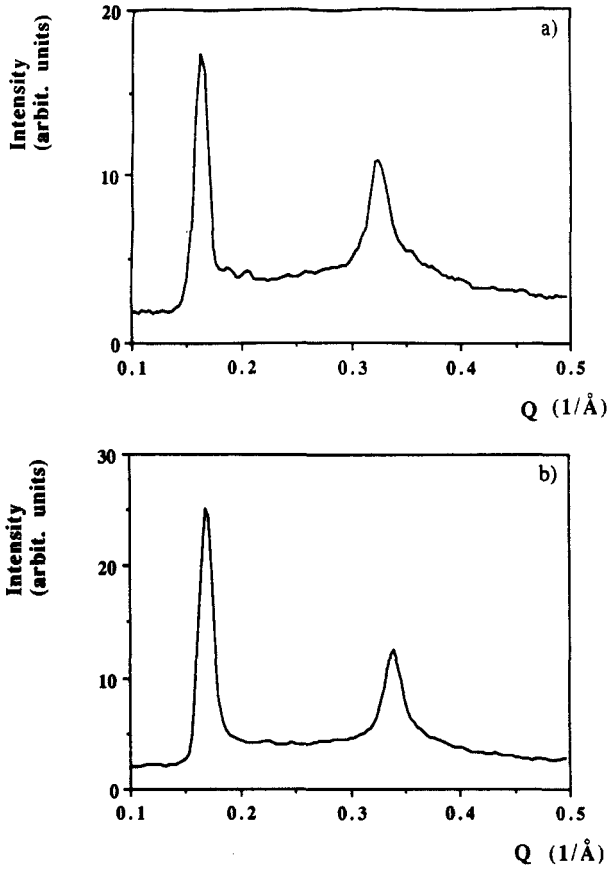

Figure 2. X-ray scattering spectra, obtained using the Cu Kα line of an 18-kW rotating anode, a graphite monochromator, and a scintillation counter, of the lamellar water (acrylamide)/AOT phases: (a) before polymerization; (b) polymerized. In each case the AOT mass fraction is 0.5. The positions of the Bragg peaks are characteristic of a lamellar symmetry. An increase in the wave vector of these peaks (decrease of the interlayer spacing) can be notice upon polymerization.

up to 8% isooctane. These results clearly show that acrylamide embedded in the water layers of a lamellar phase has been polymerized without disturbing the smectic order.

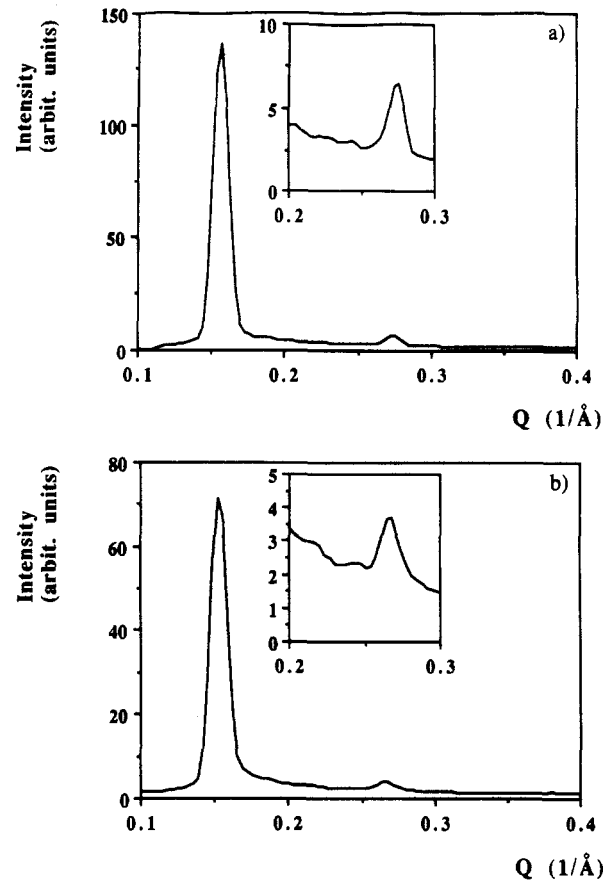

Figure 3. X-ray scattering spectra of the hexagonal phase of the water (10% acrylamide)/SDS system: (a) before polymerization; (b) polymerized. The SDS mass fraction is 0.477. The positions of the Bragg peaks (wave vector ratio $\sqrt{3}$) are in agreement with a hexagonal symmetry.

Other lamellar phases have been polymerized, using the same technique, with larger values for the interlayer spacing. In particular, swollen smectic phases made of C_{18}DMAO (octadecyldimethylamine oxide) and water, containing around 1% surfactant and thus brightly iridescent[12] due to an interlayer spacing ranging around 2000 Å, have been successfully polymerized, leading to a stiff iridescent polyacrylamide gel.

The X-ray spectra of the hexagonal phase of the SDS/water system are reported in Figure 3 before and after polymerization. The similarities between the monomer and the polymer spectra are remarkable, both showing the expected $\sqrt{3}$ ratio between the position of the first two peaks. The corresponding X-ray spectra for the cubic phase of the AOT/pentanol/water system are given in Figure 4. The ratio of the position of the two observed peaks ($\sqrt{3}/2$) is in agreement with an *Ia*3*d* symmetry and remains undisturbed after polymerization. In both cases, the optical microscopy did not reveal any trace of decomposition of the optical texture upon polymerization. This indicates that the polymerization of these two systems has been performed without disturbing the lyotropic order.

The phase diagram of the polymerized lamellar phase of AOT is schematically described in Figure 5. Dilution of the polymerized phase by isooctane retains the lamellar structure only for oil fractions lower than 12%. Such an observation is in agreement with the expected behavior of a more rigid membrane for which the undulation forces are less efficient.[13] Beyond this dilution, two phases, both containing polymers, are in equilibrium. An isotropic

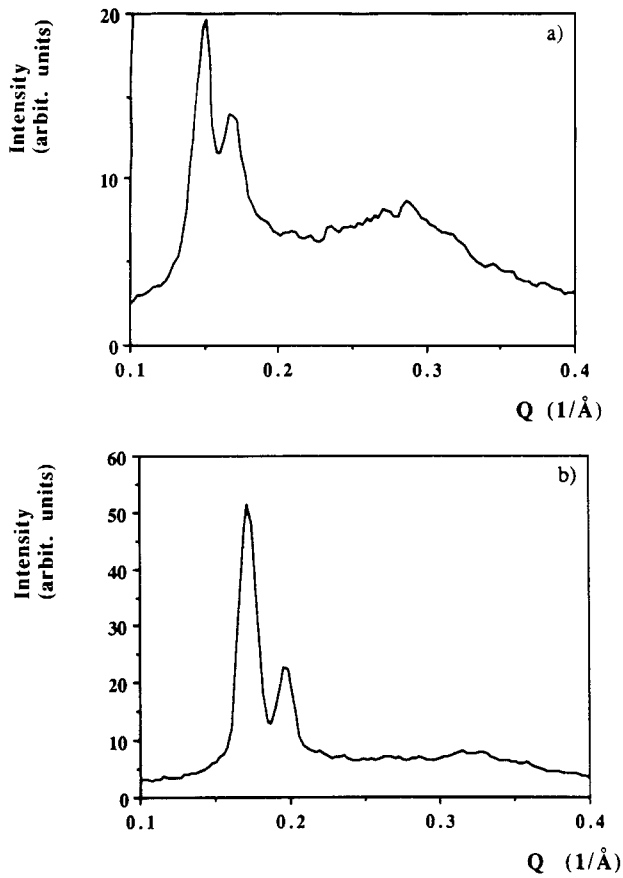

Figure 4. X-ray scattering spectra of the cubic phase of the water (10% acrylamide)/AOT/decanol (mass fraction 0.411/0.429/0.16) system: (a) before polymerization; (b) polymerized. The positions of the Bragg peaks (wave vector ratio $2/\sqrt{3}$) are in agreement with a cubic symmetry.

homogeneous phase is observed upon further dilution in isooctane beyond 92%. Moreover, the isolated (acetone-washed) polymer dissolves in water, giving a slightly bluish solution. This seems to indicate that the degree of cross-linking between layers is rather low and suggests that the obtained polymer is formed of polymerized layers embedded in the lamellar phase, rather than a 3D cross-linked polyacrylamide gel.

In conclusion this report indicates that it has been possible to use a general method to polymerize lyotropic phases of various symmetries obtained with different surfactants. One of the keys of its success has been to recognize that the phase to be polymerized must be stable with and without the monomer. Physical studies of the polymerized material, in particular using light scattering, are currently in progress.

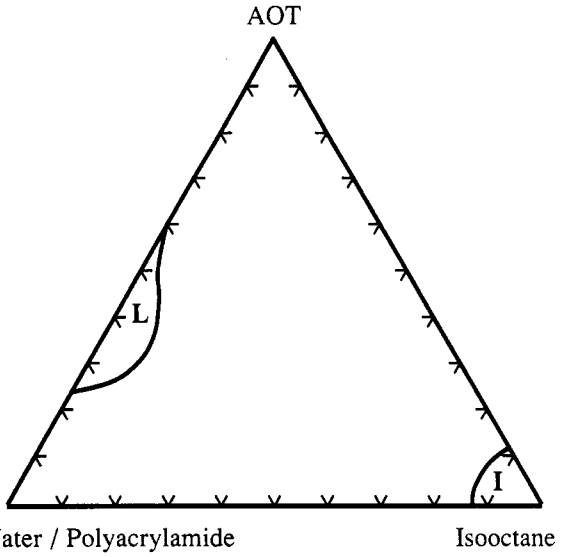

Figure 5. Schematic phase diagram of the AOT/isooctane/polyacrylamide in water system showing the lamellar (L) and isotropic (I) regions.

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References and Notes

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