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ORIGINAL CONTRIBUTION

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Polymerisation in lyotropic liquid-crystalline phases of dioctadecyldimethylammonium bromide

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Abstract The polymerisation of styrene in lyotropic liquid-crystalline (LC) phases of dioctadecyldimethylammonium bromide (DODAB) in water is explored. Amphiphile concentrations between 20 and 50 wt % are employed. The study is set out as a model study for polymerisation reactions in nonstabilised, nonfunctional bilayer systems. X-ray characterisation was used to assess the phase behaviour of the lyotropic mesophases before, during and after polymerisation. The DODAB/water system forms the lamellar phase within the concentration range considered. Addition of styrene to the lamellar phase of DODAB at an equimolar ratio induces a phase shift to a bicontinuous cubic phase at elevated temperatures near the phase-transition temperature. Upon polymerisation within this cubic phase, the phase structure is maintained if the system is kept at constant temperature; however, if the polymer/amphiphile phase is cooled, the lamellar phase, being typical of the DODAB/water system, is restored. It is concluded that, as a result of phase separation between the polymer and the amphiphile phase, the polymerisation in lyotropic LC phases does not provide a stable copy of the templating amphiphile phase. This is in analogy to the observations for polymerisations in other lyotropic phases.

Key words Polymerisation in lyotropic surfactant phases · Interaction of polymers with lyotropic surfactant phases · Ternary cubic phases of dioctadecyldimethylammonium bromide

Introduction

Polymerisation in lyotropic liquid-crystalline (LC) phases comprises the polymerisation of monomers which are inserted in the hydrophobic part of a LC matrix. In principle, after polymerisation of the inserted monomer one should obtain a polymeric "copy" of the templating surfactant phase; however, in reality, such experiments appear to be more involved. Complex phase changes are mostly encountered in the course of the polymerisation reaction, often frustrating the concept of direct "templating".

A vast amount of research activity during the last few years was directed towards polymerisation in diverse surfactant phases [1]. Most of these studies deal with microemulsion phases and only a few examples of polymerisations in other phases have been reported. One successful example is the polymerisation of styrene and methyl methacrylate in cubic phases of didodecyldimethylammonium bromide (DDAB)/water/monomer systems which seemed to yield a cubic polymer structure [2, 3]. Early attempts of Herz et al. [4] to polymerise standard monomers within lamellar phases of fatty acids failed and resulted in polymer latices.

Another highly promising templating approach to the synthesis of an ordered polymer morphology was presented recently by Hillmyer et al. [5]. These authors accomplished the polymerisation of a thermosetting epoxy resin within a hexagonally ordered block-copolymer phase without experiencing any change of phases. Though this approach utilises a thermotropic instead of a lyotropic LC phase as the template, it illustrates that the templating approach can be successful if there is a thermodynamic match between matrix and monomer and between matrix and polymer and/or if the kinetics of phase separation is slowed down. Here, we want to focus on polymerisation reactions of styrene in lyotropic LC phases of dioctadecyldimethylammonium bromide (DODAB) in water.

Previously, we have proved that polymerisation in nonfunctional, nonstabilised vesicle bilayers inevitably leads to some form of phase separation between the polymer and the surfactant matrix, resulting in peculiar vesicle–polymer morphologies [6]. Now, we investigate the influence of the surfactant concentration and the surfactant phase on the polymerisation process. It is anticipated that the polymerisation in lyotropic LC phases will expose some analogies to the polymerisation reaction in vesicles as the bilayer membrane constitutes the common structural element of vesicles and lamellar phases. However, there are also important differences between vesicles and more concentrated lyotropic LC phases. The highly ordered stacking of membrane lamellae involves trans-bilayer interactions, electrostatic forces, hydration repulsion and fluctuational effects [7].

The phase behaviour of the lyotropic LC phases can be monitored advantageously by X-ray diffraction methods [8, 9, 10, 11]. Simultaneous small- and wide-angle in situ scattering measurements can be performed to shed light on the putative phase changes of the surfactant matrix occurring on the time scale of polymerisation. This X-ray study was developed in four steps. First, the phase behaviour of pure DODAB was established. Next, the DODAB/water binary system was examined prior to studying the solubilisation in the DODAB/water/styrene ternary system. Finally, thermally induced polymerisations of styrene were carried out.

Experimental

Materials

DODAB (Acros) was used as received. Super-Q water (Millipore) was used to prepare the samples. Styrene (Merck, >99%) was distilled under reduced pressure and stored at –18 °C. The initiator α,α'-azobis(isobutyronitrile) (AIBN, Fluka) was used as received.

Sample preparation.

The samples were prepared by weight in small vials which could be sealed by rubber, Teflon-lined septa. The total mass of the sample amounted to about 4 g. DODAB was first weighted into the vial. Next, water was added and the sample was capped. To homogenise them, the mixtures were kept at 70 °C for at least 2 days. In order to prepare the ternary systems, a desired amount of styrene was injected through the septum into the hot DODAB/water sample. The styrene contained either an inhibitor (hydroquinone) when the polymerisation had to be suppressed or an initiator (5–10 wt% AIBN) when polymerisation was intended. These samples were then vigorously stirred by a small stir bar within the sealed vials and kept at 70 °C for another 4 days before they were allowed to cool to room temperature.

X-ray scattering measurements

Synchrotron X-ray scattering experiments were performed at the A2 beamline at Hasylab, Hamburg, Germany, and at the ID1 station at ESRF, Grenoble, France. The scattering angle, θ_s, was determined experimentally and is referred to as "2 theta" in our study; it was calculated for all experiments for a reference wavelength of 0.15 nm.

A2, Hasylab

A detailed description of the beamline can be found elsewhere [12, 13]. The samples were contained in small brass cells having kapton windows (Goodfellow, 0.025-mm thickness) on both sides. These cells were mounted in a thermostatted holder which was inserted in the beam within an evacuated chamber. The beam had a standard wavelength of 0.15 nm (8 keV). A one-dimensional gas-filled detector was positioned at various distances from the sample (70, 120, 190 cm) to record the small-angle X-ray scattering (SAXS) pattern. Another detector was placed about 25 cm from the sample to detect the wide-angle scattering. The SAXS detector was calibrated using the reflections of rattail collagen, while the wide-angle X-ray scattering (WAXS) detector was calibrated using the peaks of poly(ethylene terephthalate). The exposure time of one sample was typically 2 min for measurements at constant temperature and about 0.5 min for temperature scans and time-resolved measurements.

ID1, ESRF

Details concerning the beamline are given elsewhere [14]. Measurements at ID1 were carried out using a wavelength of either 0.099 nm (12.5 keV) or 0.044 nm (28 keV). The samples were contained in small, round, brass cells having kapton windows (Goodfellow) on both sides. These cells could be fixed on a thermally controlled microscope hot stage (Linkam, Tadworth, UK) which was screwed on a goniometer head. The moveable two-dimensional gas-filled wire detector was located in an evacuated tube at a sample-to-detector distance of 70 or 430 cm. Silver behenate was used as a calibration standard [15]. Exposure times of the samples were typically 1 or 2 min. Data correction was carried out as described by Bösecke and Diat [16].

Results and discussion

Dioctadecyldimethylammonium bromide

Before studying the lyotropic LC phases of DODAB in water, it is worthwhile to examine first the phase behaviour of pure DODAB. SAXS and WAXS measurements of DODAB as a function of temperature are shown in Fig. 1. The corresponding spacings are summarised in Table 1. Unexpectedly, the SAXS pattern at 30 °C exhibits three peaks, which are equivalent to distances of 2.7, 3.3 and 3.7 nm, the first one being the

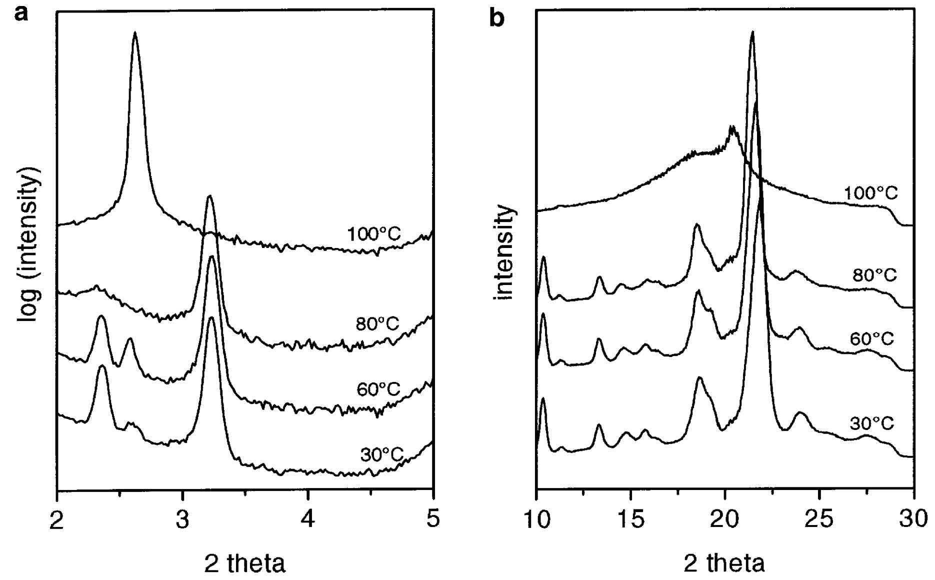

Fig. 1 **A** Small-angle X-ray scattering (*SAXS*) and **B** wide-angle X-ray scattering (*WAXS*) patterns of pure dioctadecyldimethylammonium bromide (*DODAB*) at different temperatures

Table 1 Overview of important small-angle X-ray scattering (*SAXS*) and wide-angle X-ray scattering (*WAXS*) peaks for systems of dioctadecyldimethylammonium bromide (*DODAB*), water, styrene and polystyrene (*PS*). The lattice parameter, *a*, is calculated from the strongest peak

DODAB (%wt)	Water (%wt)	Styrene (%wt)	*T* (°C)	Phase	*d* (SAXS) (nm)	a (nm)	*d* (WAXS) (nm)
Pure DODAB							
100	–	–	30	Lamellar	2.7, 3.3, 3.7		0.36, 0.40
100	–	–	100	Lamellar	3.3		0.42
DODAB/water							
20–50	80–50	–	30	Lamellar	3.7		0.42
20	80	–	60	Lamellar	17.5		0.45
30	70	–	60	Lamellar	15.4		0.45
40	60	–	60	Lamellar	8.4		0.45
50	50	–	60	Lamellar	7.0		0.45
DODAB/water/styrene							
19.4–46.2	77.4–46.2	3.2–7.6	30	Lamellar	3.7		0.42
19.4	77.4	3.2	60	*Ia*3*d*	18.8, 16.6, 11.8, 9.8, 9.1, 6.3	46.1	0.45
28.6	66.7	4.7	60	*Im*3*m*	13.0, 9.2, 7.5, 5.8, 5.3, 4.9	18.4	0.45
37.5	56.3	6.2	60	*Im*3*m*	9.4, 6.6, 5.4, 4.1, 3.8, 3.5, 3.0	13.3	0.45
46.2	46.2	7.6	60	*Im*3*m* (?)	7.2, 5.9, 4.1, 3.6	10.2	0.45
DODAB/water/PS							
19.4–46.2	77.4–46.2	3.2–7.6	30	Lamellar	3.7		0.42
19.4	77.4	3.2	60	Lamellar	14.6		0.45
28.6	66.7	4.7	60	Lamellar	11.6		0.45
37.5	56.3	6.2	60	Lamellar	8.4		0.45
46.2	46.2	7.6	60	Lamellar	6.4		0.45
DODAB/water/PS, on-line polymerisation							
19.4	77.4	3.2	70	*Ia*3*d*	16.2, 14.3, 8.4, 7.8, 5.6	39.7	0.45
28.6	66.7	4.7	70	*Im*3*m*	11.2, 9.2, 7.8, 6.4, 5.4	15.8	0.45

most prominent. With increasing temperature, the larger periods disappear and only the peak at 2.7 nm remains constant up to 80 °C. Within this temperature interval, the WAXS spectrum exhibits a differentiated pattern. Two strong peaks at 0.36 and 0.40 nm, similar to those obtained from alkane crystals, may be attributed to alkyl chain crystallisation, whereas the other reflections indicate a high degree of order in the head group plane. At 100 °C, the long-spacing extends to 3.3 nm and the alkyl chains seem to adopt a hexagonal packing of molten alkyl chains characterised by a broadened WAXS signal at 0.42 nm.

At first sight, the appearance of three different periods for crystalline DODAB below 80 °C is confusing; however, by referring to the detailed crystallographic study of Okuyama et al. [17], the peak at 3.7 nm can be identified as the DODAB · H_2O spacing. These authors found that the crystal structure of the DODAB · H_2O consists of regularly stacked bimolecular layers having a periodicity of 3.68 nm. By considering the length of an extended DODAB molecule to be 2.6 nm, it becomes obvious that the molecules have to be tilted in the bilayer surface at an angle of about 45° [18].

The shorter spacings of the SAXS pattern obviously belong to less hydrated (3.3 nm) or even anhydrous (2.7 nm) DODAB phases. In fact, prolonged evacuation of the sample at higher temperatures and cooling to 30 °C leaves only the periodicity at 2.7 nm, whereas longer spacings vanish. We therefore ascribe the period of 2.7 nm to the pure anhydrous DODAB crystal, where the alkyl chains are fully interdigitated and tilted to the bilayer surface [20].

Heating to 100 °C obviously induces a change in the chain packing of the anhydrous DODAB. The increased long-spacing to 3.3 nm reveals that the chains are not fully interdigitated but are still tilted. A loss of chain crystallinity is seen in the broad WAXS reflection centred at 0.42 nm. According to differential scanning calorimetry (DSC) measurements of Kajiyama et al. [19], the melting temperature of pure DODAB is 83 °C.

The DODAB/water system

Next, we investigated the phase behaviour of the DODAB/water system. Detailed information on the thermal phase behaviour of DODAB and its chloride analogue dioctadecyldimethylammonium chloride in water can be found in the literature [19, 20, 21, 22, 23, 24]. Several research groups have unanimously confirmed that the phase transition of DODAB/water systems occurs at about 51–55 °C for all concentrations between 3 and 83 wt% DODAB [19, 20].

In our study, we applied DODAB concentrations between 20 and 50 wt% for scattering experiments. It turned out that below the phase-transition temperature and independent of concentration all systems exhibit the characteristic period of 3.7 nm (Fig. 2). This spacing identifies DODAB · $2H_2O$ as the equilibrium crystal at the given temperature [20]. As the spacing is not dependent on concentration, it can be concluded that the lamellar dihydrate phase coexists with an excess water phase. This is corroborated by the DSC measurements of Schulz et al. [20], where the crystallisation of excess water is manifested. Furthermore, macroscopic phase separation between a white and grainy surfactant phase and an excess water phase is directly visible.

The wide-angle scattering of the dihydrate (Fig. 2) is characterised by a large number of peaks, which originate partially from the packing of the head groups and partially from the packing of the alkyl chains. Above the phase-transition temperature, the cationic head groups become fully hydrated and the alkyl chains melt as seen by a diffuse WAXS band at 0.45 nm. For all concentrations ranging from 20 to 50 wt% DODAB, a lamellar phase is established, while the spacing linearly decreases with increasing concentration of DODAB (Fig. 3). It is interesting to note that these lamellar phases swell infinitely and do not reach a maximal swellability as is known for zwitterionic lipids such as dipalmitoylphosphatidylcholine [25]. Therefore, a single-phase L_α region is discerned between 20 and

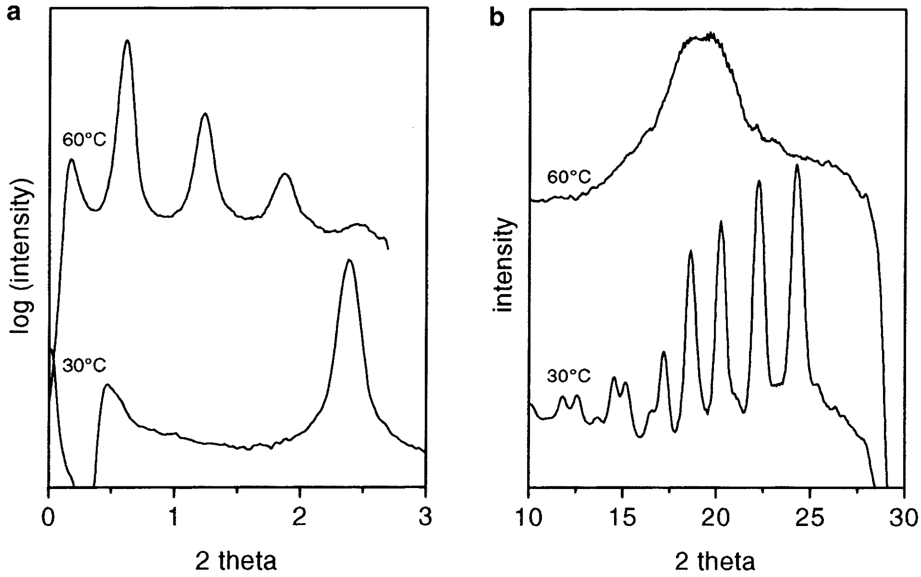

Fig. 2 **A** SAXS and **B** WAXS patterns of a 20 wt% DODAB/water system below and above the phase-transition temperature

50 wt% at temperatures above the phase-transition temperature.

More details concerning the phase changes with temperature are seen in complete temperature scans. SAXS and WAXS patterns that were recorded as a function of temperature for a sample of 30 wt% DODAB are displayed in Fig. 4. A heating and cooling rate of 1 K/min was applied for these scans. The transition from the dihydrate to the L_α phase occurs quickly between 53 and 55 °C; however, upon cooling, the dihydrate is only restored at about 41 °C. A similarly strong hysteresis was noticed by Kodama et al. [21] in their DSC study. Interestingly, these authors found two different transitions in the down-scan (at 44 and 40 °C) that were assigned to two different processes, namely the transition from the LC phase to the metastable gel phase (44 °C) and to the stable coagel phase. Here, we only discern one transition from LC back to the dihydrate, i.e. the coagel phase, without any obvious intermediates.

The DODAB/water/styrene system

Subsequently, we studied the phase behaviour of the DODAB/water/styrene ternary systems while keeping a constant molar ratio of DODAB concentration to styrene concentration of 1:1 and applying DODAB/water concentrations between 20 and 50 wt% as before.

Remarkably, hardly any influence of styrene can be detected at low temperatures, i.e. between 10 and 20 °C. Independent of DODAB concentration, lamellar phases ($d = 3.7$ nm) identical to those of the DODAB/water systems are found (Fig. 2, 30 °C). At temperatures above 50 °C, however, the ternary systems show rather diverse and complicated behaviour. While DODAB concentrations lower than 20 wt% lead to lamellar bilayer phases, cubic phases are formed at concentrations higher than 20 wt% in the presence of styrene. Some examples of diffraction patterns originating from cubic phases which were observed at 60 °C after at least 30 min of annealing are shown in Fig. 5. The extremely slow buildup of these phases and the weak appearance of higher-order peaks made the unambiguous determination of the actual phases difficult. Often, especially for high concentrations of DODAB, the small-angle scattering changed even after annealing the sample for more than 1 h. This is typical of highly viscous cubic phases [11]. In many instances we encountered the simultaneous appearance of different phases, often a cubic phase and a lamellar phase.

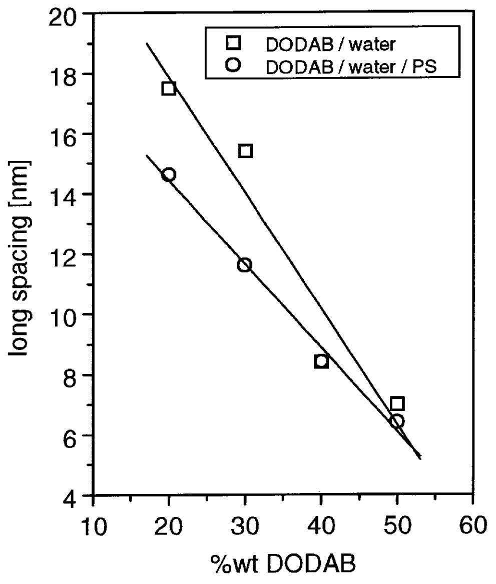

Fig. 3 Long spacings of the lamellar phases above the phase-transition temperature, before and after polymerisation

The occurrence of cubic phases in the ternary system of DODAB/water/styrene at high temperatures is not unexpected as it exhibits some analogies to the ternary systems of the shorter-chain surfactant DDAB with

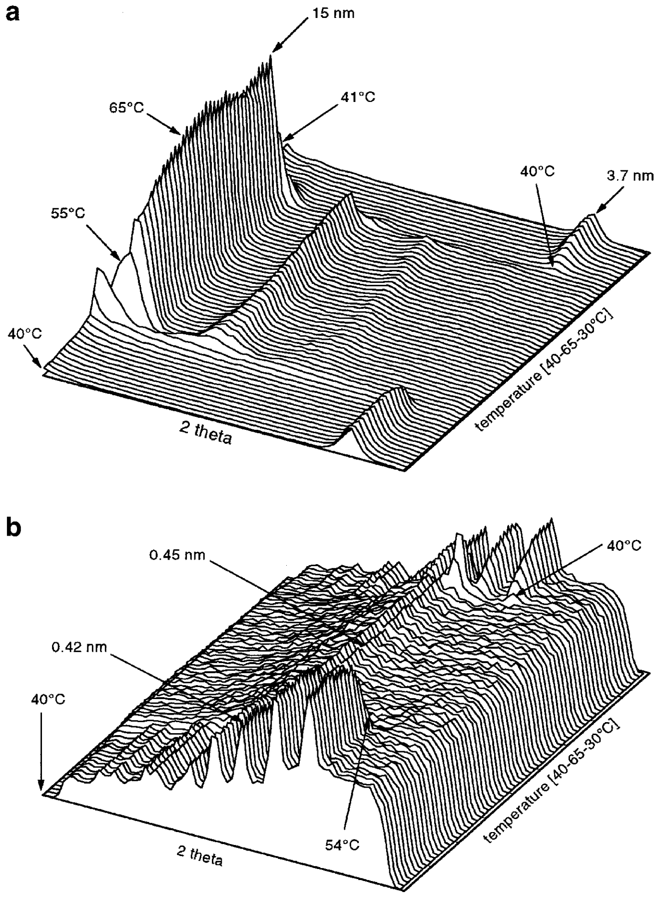

Fig. 4 **A** SAXS and **B** WAXS patterns of a 30 wt% DODAB/water system as a function of temperature. The scan speed was 1 K/min

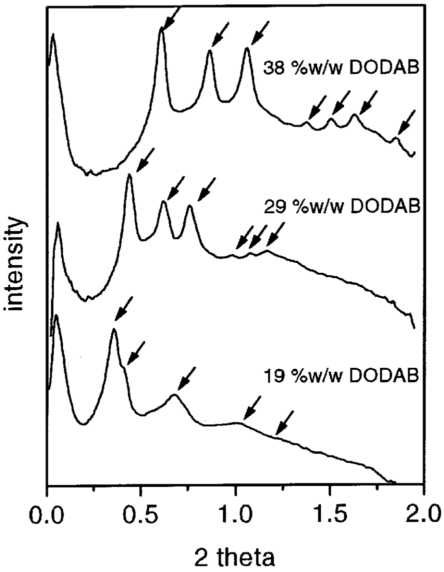

Fig. 5 SAXS patterns of different cubic phases in the ternary phase diagram of DODAB/water/styrene at 60 °C. The *Ia*3*d* space group is observed for lower concentrations of DODAB (19 wt%), while *Im*3*m* symmetry is seen for higher concentrations (29–46 wt%) of DODAB

water and various hydrocarbons at 20 °C [26, 27]. A thorough study of Anderson and Ström [3] revealed that the DDAB/water/styrene system has five separate bicontinuous cubic phases, which could be identified with respect to their space groups. In contrast to DDAB systems, the cubic phases in DODAB systems only exist at higher temperatures when the longer alkyl chains start to melt, the hydration of the head groups change and the chain volumes consequently increase.

We attempted an indexing of the of the observed reflections using the equation for a cubic element cell, $\sin^2\theta = \lambda^2/4a^2(h^2 + k^2 + l^2)$, where a is the lattice parameter.

Let us consider the pattern of the sample 19.4/77.4/3.2 (Fig 5, Table 1). The spacings match the ratio $\sqrt{6}:\sqrt{8}:\sqrt{16}:\sqrt{22}:\sqrt{26}:\sqrt{30}$. These values lead to the following indexing (221), (220), (400), (332), (431), (521) and a lattice parameter, a, of 46 nm. Such an indexing would coincide with the space groups *Ia*3*d* (no. 230), where the reflections with lower indices are extinguished [28, 29]. According to Rançon and Charvolin [30], the epitaxial relationship between the lamellar phase and the bicontinuous *Ia*3*d* phase is a transformation of the (100) plane (lamellar) to the (211) plane in *Ia*3*d*, i.e. the lattice parameter divided by $\sqrt{6}$ should provide the equivalent lamellar spacing. In our case this comes down to a distance of 18.8 nm, which is slightly longer than the original spacing of the DODAB/water (1/4) phase of 17.5 nm. The increase in the spacing can be explained by the insertion of styrene.

The bicontinuous *Ia*3*d* cubic phase is known to occur in many lyotropic [31] and thermotropic [32] liquid crystals, commonly those built by lipids [33, 38] or even block copolymers [28, 34]. The geometry is often visualised as a structure where short-rod aggregates are joined, three and three at each end, and form an interwoven but otherwise independent three-dimensional network.

A different cubic phase has been identified for systems with higher concentrations of DODAB at 28.6–46.2 wt%. Here, the proportions of the main peak positions are $\sqrt{2}:\sqrt{4}:\sqrt{6}:\sqrt{10}$: $\sqrt{12}:\sqrt{14}:\sqrt{18}$, as is nicely illustrated for the sample 37.5/56.3/6.2. Such a pattern is in good agreement with the symmetry of the space group *Im*3*m* (no. 229), sometimes called the "plumber's nightmare" [38] (Fig. 5). This is another frequently encountered cubic phase in lipid systems [35, 36].

In order to get an insight into the formation of the cubic phases, we studied the evolution of phases with temperature for this specific example (DODAB/water/styrene = 28.6/66.7/4.7, Fig. 6). Starting with the lamellar dihydrate phase at 25 °C (d = 3.7 nm), a second lamellar phase with longer spacings develops in a temperature interval from 37 to 50 °C, leading to a probably biphasic lamellar system. Further heating induces the buildup of a cubic phase of the *Im*3*m* space group. The formation of the cubic phase is accompanied by the melting of the alkyl chains and the head groups as seen in the WAXS spectrum (Fig. 6B). Upon cooling, the initial lamellar phase is quickly restored at 37 °C, now without showing the intermediate lamellar phases (X-ray patterns not shown). Note, that the second lamellar phase is built long before the crystal structure is lost! We suspect that this lamellar phase results mainly from insertion of styrene into the hydrophobic membrane part.

To resolve the intermediate structures in more detail, we slowly heated the sample to distinct temperatures, tempered for 10 min and collected the diffraction pattern (Fig. 7). Again, we observed the appearance of a second phase at about 20 °C, i.e. at temperatures far below the actual phase transition of the DODAB/water system. The broadened peak of this phase is located at 4.5 nm. This phase may be of lamellar morphology but a globular superstructure (small micelles) may also be possible. Further heating sharpens this reflex and at 40 °C two smaller peaks at larger angles (2.6 and 2.2 nm) rise while keeping residuals of the dihydrate (3.7 nm). Interestingly, the ratios of the spacings of these newly evolved peaks to the larger spacing correspond to $1:\sqrt{3}:\sqrt{4}$, hence suggesting a coexisting hexagonal phase. A similar picture is seen at 45 °C, although the long spacing of the hexagonal phase shifted to larger spacings of 5.4:3.1:2.7 nm. Finally, at 50 °C a cubic phase is established that smoothly changes upon further annealing to the equilibrium structure shown in Fig. 5. A direct lamellar–hexagonal–cubic transition is, however, improbable as the cubic structure is known to exist between

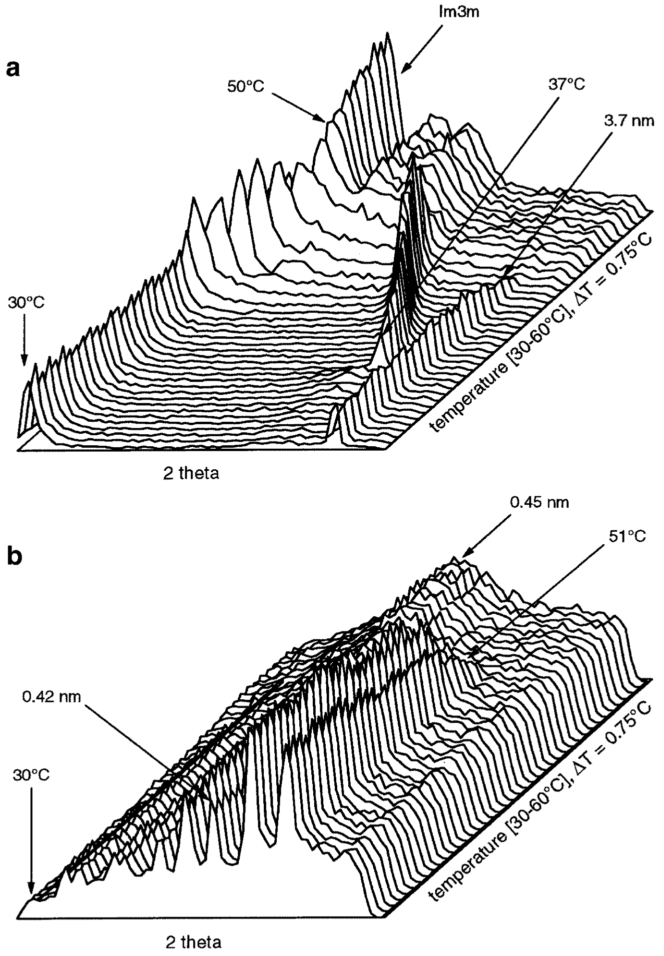

Fig. 6 Evolution of **A** SAXS and **B** WAXS patterns as a function of temperature for the DODAB/water/styrene ternary system (28.6/66.7/4.7). The dihydrate phase is transformed into the cubic phase via an intermediate biphasic lamellar phase. The scan rate was 2 K/min

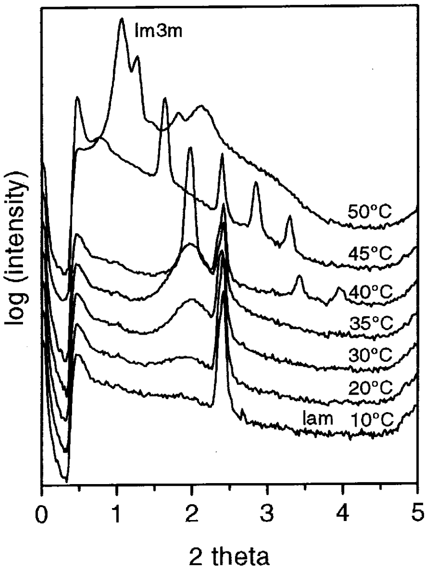

Fig. 7 Evolution of the SAXS pattern as a function of temperature for the DODAB/water/styrene ternary system (28.6/66.7/4.7). The transformation of a biphasic lamellar phase into the cubic phase is illustrated

the lamellar and the hexagonal phase and we thus have to assume that we deal here with impure nonequilibrium phases. We observed, nonetheless, that independent of the DODAB concentration, the transition of the lamellar hydrate phase to the cubic phase appeared to occur in a similar manner via the development of a second lamellar phase.

Anyhow, it is interesting to note that the low-temperature phase in the ternary system is identical to the low-temperature phase of the DODAB/water system. The structure of the DODAB hydrate is obviously not affected by the presence of styrene. We conclude that the system is macroscopically phase-separated and that styrene is not inserted in the strong DODAB · $2H_2O$ crystal lattice. At about 30 °C, i.e. 25 °C below the normal chain-melting temperature of DODAB, styrene starts to intrude in the DODAB · $2H_2O$ lamellae, most probably in the vicinity of the head group, although crystallinity is maintained up to about 50 °C. The concomitant increase in chain volume must then be compensated by an increase in head group area and hydration. Consequently, the lamellar distances grow until the lamellae spontaneously reorganise to a cubic order.

In the literature, the formation and the characterisation of these cubic phases has been a highly discussed topic of colloid and surfactant science during the last 10 years [37, 38]. In fact, undulating bilayer lamellae in the L_α phase are envisioned as precursors for the formation of cubic phases.

The DODAB/water/polystyrene system

Polymerisations of styrene within the lyotropic LC phases were studied using the DODAB/water/styrene systems described previously. The samples were polymerised at 70 °C in gas-tight vials for 4 days, then cooled to room temperature and stored at room temperature for 2 weeks before X-ray measurements. Size-exclusion chromatography of the obtained polymer revealed a rather broad molecular-weight distribution ($M_w/M_n \approx 4$) of high-molecular-weight material ($M_w \approx 400{,}000$).

Surprisingly, the SAXS and WAXS measurements of these samples as a function of temperature hardly differed from those of the pure DODAB/water systems, except for a slight decrease in the long-spacing (Table 1, Fig. 3). The cubic phases of the DODAB/water/styrene system were replaced by the lamellar phases of the

DODAB/water system. Since no influence of the polymer on the phase behaviour, the transition temperatures and chain crystallisation could be observed, we assumed that the polymer and the surfactant phase were macroscopically phase-separated. Indeed, visual inspection of the samples indicated macroscopic phase separation. This is in contrast to the findings of Anderson and Ström [2, 3], who reported the maintenance of cubic phases after polymerisation of styrene or divinylbenzene in ternary systems with DDAB and water. From a thermodynamic viewpoint, the polymerisation reactions in DDAB or DODAB systems should be indistinguishable; therefore, we can only speculate that the cooling to temperatures far below the reaction temperature, and implicitly far below the phase-transition temperature, could induce the collapse of the non-cross-linked original structure in our case.

In order to determine whether the phase separation occurred on the time scale of polymerisation or possibly after cooling to room temperature, we monitored thermally induced polymerisations on-line in the sample chamber. Repeated polymerisation experiments at 70 °C using ternary systems of 19 and 29 wt% DODAB demonstrated that the initial cubic phases change slightly with progressing polymerisation but maintain, in essence, their structure (Fig. 8). More detailed analysis of the *Ia*3*d* phase observed for 19 wt% DODAB reveals that the lattice parameter shifted to a smaller value of 40 nm compared to 46 nm for the unpolymerised system. We ascribe this shrinkage to the polymerisation and possibly to the loss of water from the sample as a consequence of the prolonged heating.

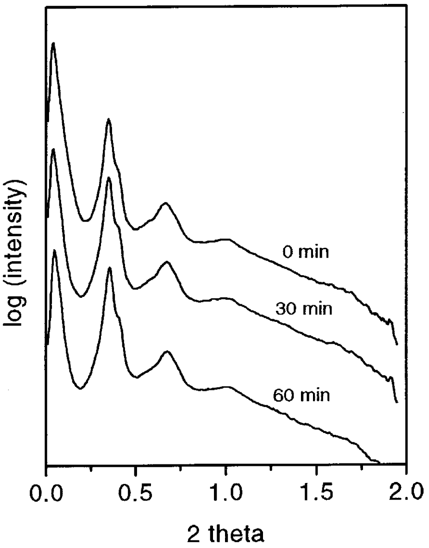

Fig. 8 SAXS pattern of on-line polymerisation of styrene in the ternary system at 70 °C at some stages of polymerisation for the system 19.4/77.4/3.2. The *Ia*3*d* cubic phase is maintained throughout the process of polymerisation

Anyhow, upon cooling and reheating of these samples, the cubic structure disappeared and was replaced by the lamellar phase. Again, we take this as a strong indication of the phase separation between the polymer and the surfactant phase. The surprising fact that the phase reorganisation only occurs upon temperature cycling is attributed to hindered diffusion in the highly viscous surfactant phase. In other words, the thermodynamic phase separation can be hindered kinetically in the cubic phase. It is hence reasonable to assume that a cross-linked polymer could maintain the structure of the surfactant matrix as described by Anderson and Ström [2, 3]. In the present case, however, dealing with non-cross-linked polymer chains, we surmise that the phase separation – even at higher temperatures – is only a matter of time. Note, that the initially hosted polymer will possess a glass-transition temperature below that of the bulk polymer owing to the constraints of a the cubic lattice [39] and to the presence of the alkyl chains of DODAB [40]. A rearrangement of the polymer chains to an eventually phase-separated polymer phase should therefore be facilitated.

Conclusions

The solubilisation and the polymerisation of styrene in lyotropic LC phases of DODAB in water was studied by X-ray diffraction. Within the concentration range investigated (20–50 wt% DODAB), the presence of styrene causes the formation of bicontinuous cubic phases for temperatures near and above the phase-transition temperature. Polymerisation of styrene within these phases does not disrupt the amphiphile structure as long as the temperature is kept constant at elevated temperatures. However, cooling and storing the polymerised sample at temperatures well below the phase-transition temperature seems to induce phase separation between the polymer and the surfactant phase. Obviously, the nature of the viscous cubic phases can prevent an expulsion of polymer in the first place, although polymer expulsion is expected to occur on longer time scales.

It is very instructive at this point to compare these results to our earlier results on polymerisation of styrene in DODAB vesicle bilayers [6]. There, the single vesicle bilayer could not restrict polymer growth in two dimensions. It seems now that the phase separation can be initially suppressed by polymerising in the cubic phase owing to the rigidity of the three-dimensionally ordered bilayer geometry; however, an eventual phase separation between the polymer and the surfactant matrix is observed under equilibrium conditions for both the colloidally dispersed lamellar phase, i.e. vesicles, and the more concentrated lyotropic LC phases.

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