Templating Polymerization of Dodecylammonium Surfactants with Polymerizable (Meth)acrylate Counter Ions

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Summary: Both dodecylammonium acrylate (I) and dodecylammonium methacrylate (II) are reactive surfactants in which the polymerizable group is the organic counterion. Templating polymerization of I and II from the lyotropic liquid crystalline (LLC) lamellar phase was successfully performed with conservation of the supramolecular structure. A 20 wt% aqueous solution of II formed cubic bicontinuous phases, even upon addition of divinyl benzene (DVB). Polymerization from the cubic phases was attempted without and with DVB (3 wt%). Bicontinuous cubic phases always evolved toward lamellar structures upon polymerization.

Keywords: surfactants; templates

Introduction

Surfactants are amphiphilic molecules characterized by their tendency to adsorb at interfaces. One of the most well known properties of surfactants is their ability to form micelles in water above the critical micelle concentration (CMC). In more concentrated aqueous solutions, surfactants can self-assemble into lamellae, hexagonally packed coil-like micelles, or cubic phases[1].

Due to a proton transfer from the acid to the amine, mixture of alkylamines and carboxylic acids can form amphiphilic species[2-4]. Depending on the lengths of the alkyl chains, the resulting salts are considered as catanionic surfactants[5-16] or surfactants with an organic counterion[17-20]. In a previous paper[21], we have shown that both species dodecylammonium acrylate and dodecylammonium methacrylate can be considered as surfactant species with reactive organic counterions. Depending on the nature of the counterion (i.e. acrylate or methacrylate) and on the relative ratios dodecylamine/(meth)acrylic acid/water, these systems can form bicontinuous cubic structures or lamellar lyotropic liquid crystalline (LLC) phases. This paper deals with the

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ability of both surfactants to polymerize from such organized LLC phases to give a patterned copy of the original structure.

Polymerizable surfactants ("surfmers") have been extensively studied for their wide range of applications[22-24]. All the different types of organized phases have been successfully templated by polymerization of various surfmers[25-33]. Generally, the polymerizable groups of surfmers are either in the hydrophobic tail or around the polar head. To our knowledge there is only one example of a surfmer with a polymerizable organic counterion (i.e. 4-vinylbenzoate) used in templating polymerization[34]. In this unique example, the authors polymerized the counterion of cetyltrimethylammonium 4-vinylbenzoate from hexagonal LLC structures, giving rise to the formation of discrete cylindrical micelles. Dodecylammonium acrylate or methacrylate surfactant presents the advantage of being a cheap reactive surfactant that is very easy to prepare.

Materials and Methods

Materials

Benzoin methyl ether (BME) (99%, Aldrich) was used as received. Acrylic acid (99%, Aldrich), methacrylic acid (99%, Aldrich) and divinyl benzene (DVB) were freshly distilled and deoxygenated prior to use. Water (w) was distilled, deionized and deoxygenated immediately before use. Dodecylamine (≥ 98%, Fluka) was deoxygenated by flushing with nitrogen above its melting point.

Analytical Methods

Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements were performed at 298 K. SAXS experiments were carried out in a transmission configuration. A copper, rotating anode X-ray source (functioning at 4 kW) with a multilayer focusing "Osmic" monochromator giving high flux (10^8 photons/sec) and punctual collimation was employed. An "Image plate" 2D detector was used. Diffraction curves were obtained, giving diffracted intensity as a function of the wave vector q. D-spacings were calculated using the relation $d = 2\pi/q$.

Fourier transform infrared spectroscopy (FTIR) was performed using a Perkin-Elmer Paragon 1000 FTIR, using a photo acoustic cell.

Phase Diagrams

Compositions in phase diagrams are given in weight percent (wt%). The straight lines drawn in the phase diagrams (marked by 1:1) correspond to an equimolar ratio between acid and amine. Phase boundaries and the nature of the liquid crystalline phases were determined by POM[35]. The nature of the different phases was confirmed by ^{2}H NMR and SAXS measurements. The construction of the phase diagrams has been detailed elsewhere[21].

Polymerization

Equilibrated aqueous solutions of surfmers containing 0.5 mol% of BME were placed in quartz vials and flushed with nitrogen. The quartz vials were sealed and exposed to UV light (254 nm) for 48 hours. Polymerized samples were stored in sealed vials.

Results and Discussion

The ternary phase diagrams for the systems dodecylamine/acrylic acid/water and dodecylamine/methacrylic acid/water are shown in Figure 1[21]. The phase diagram that includes acrylic acid comprises a lamellar LLC phase (annotated D) and a large isotropic solution region (annotated L). The phase diagram of the system that includes methacrylic acid exhibits a lamellar LLC phase, a solution phase, a cubic phase (annotated cub.) and a large area in which a phase separation occurs (annotated 2Φ), with two isotropic layers. In both systems, hydrated crystals of dodecylamine formed along the dodecylamine axis and the water-rich part of the (meth)acrylic acid axis (areas annotated crist.). SAXS patterns of lamellar phases and of the cubic phase are shown in Figure 2-a. D-spacings of the observed lamellar phases formed by dama 1:1/w 0.80/0.20 and daaa 1:1/w 0.80/0.20 were equal to 2.58 and 3.08 nm, respectively (dama 1:1 and daaa 1:1 meaning respectively an equimolecular ratio of dodecylammonium/methacrylic acid and an equimolecular ratio of dodecylammonium/acrylic acid). The observed peak of dama 1:1/w 0.20/0.80 shown in Figure 2-a (i.e. q 1.18 nm^{-1}) is most likely a second order peak originating from the cubic phase. This proposal is based on the diffractograms observed at very small angle scattering with similar cubic systems; they show a sharp peak at about 10.5-11.5 nm (cf. Figure 2-b, c, d). According to this, first order q^{-1} of the cubic system of dama 1:1/w 0.20/0.80 was calculated to be 0.59 nm^{-1}, with a corresponding d-spacing of 10.65 nm.

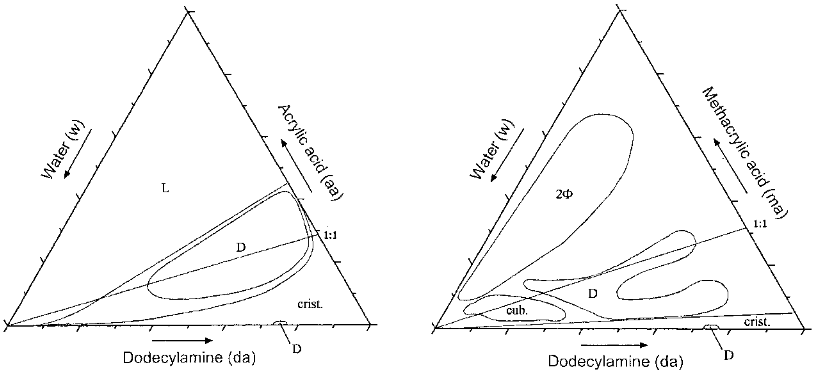

Figure 1. Ternary phase diagram for the systems dodecylamine/acrylic acid/water (left) and dodecylamine/methacrylic acid/water (right) at 298 K (2Φ: two isotropic phases region; L: solution; D: lamellar; cub.: cubic; crist.: crystals).

On adding small amounts of DVB, the two systems dama 1:1/w 0.20/0.80 (3) and dama 1:2/w 0.20/0.80 (6) maintained a cubic feature. Samples displayed high viscosities (gels) and optical isotropy for DVB contents up to 3%. The apparent viscosity decreased from 4%, and the hydrogel collapsed with 5% DVB. The bicontinuous cubic feature of systems 3 and 6 with 3% DVB was confirmed by SAXS, as shown in Table 1 (4 and 5) and Figure 2 (b and c, solid curves).

Templated polymerization was performed from samples containing 0.5 mol% photo initiator (BME). Compositions of the prepared samples are tabulated in Table 2. Samples were exposed to UV light (254 nm) for 48 hours at 25 °C. Average molar weights could not be determined by size exclusion chromatography (SEC) as the resulting polymers were soluble neither in tetrahydrofuran (THF) nor chloroform. Polymerization was confirmed by FTIR; the vibration band of the (meth)acrylic double bonds disappeared.

Table 1. Wave vectors (q) and d-spacing of the diffraction peaks of SAXS patterns before and after UV curing. (s: sharp; l: large; c: calculated; *Second order peak).

Entry	Name	Before polymerization			After polymerization		
		Struct.	q (nm^{-1})	D (nm)	Struct.	q_{pol} (nm^{-1})	d_{pol} (nm)
1	dama 1:1/w 0.80/0.20	D	q_1 2.44 (s) q_2 14.03 (l)	d_1 2.58 d_2 0.45	D	q 2.14 (s)	d 2.93
2	daaa 1:1/w 0.80/0.20	D	q_1 2.04 (s) q_2 14.14 (l)	d_1 3.08 d_2 0.44	D	q 2.00 (s)	d 3.14
3	dama 1:1/w 0.20/0.80	cub.	q_1 0.59 (c) q_2 1.18 (s)* q_3 19.6 (l)	d_1 10.65 (c) d_2 5.27 d_3 0.32	n/a	n/a	n/a
4	dama 1:1/w 0.20/0.80 + DVB	cub.	q_1 0.60 (s) q_2 1.21 (s)*	d_1 10.47 d_2 5.19	D	q_1 1.89 (s) q_2 14.28 (s)	d_1 3.33 d_2 0.44
5	dama 1:2/w 0.20/0.80 + DVB	cub.	q_1 0.54 (s) q_2 1.09 (s)*	d_1 11.14 d_2 5.56	D	q_1 1.89 (s) q_2 14.38 (s)	d_1 3.33 d_2 0.44
6	dama 1:2/w 0.20/0.80	cub.	q_1 0.54 (s) q_2 1.09 (s)*	d_1 11.59 d_2 5.75	D	q_1 1.82 (s) q_2 13.72 (l)	d_1 3.45 d_2 0.45

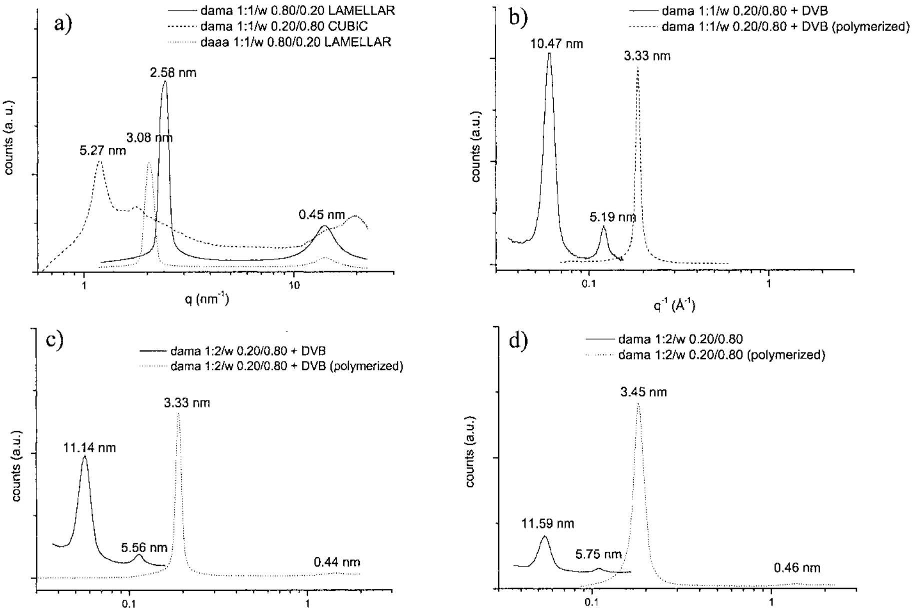

Figure 2. SAXS patterns. a) Non-polymerized cubic and lamellar phases. b) dama 1:1/w 0.20/0.80 + DVB before after polymerization. c) dama 1:2/w 0.20/0.80 + DVB before and after polymerization. d) dama 1:2/w 0.20/0.80 before and after polymerization.

Polymerization from lamellar phases (entries 1 & 2) yielded polymers looking the same as the original LLC solutions (waxy). The polymers were however no longer soluble in DMSO, water, THF and $CHCl_3$, as the original surfactants were. A nearly total disappearance of the acrylic and the methacrylic double bonds confirmed that polymerization had taken place. Typical mosaic textures were observed by polarized light microscopy (POM) for the original (non-polymerized) solutions 1 and 2, and for sample 2 after polymerization (cf. Figure 3). On the other hand, the observed texture of 1 after UV curing was not clear enough to conclude undoubtedly to the subsistence of a lamellar phase. However, SAXS experiments confirmed that both systems 1 and 2 maintained a lamellar feature upon polymerization. A slight increase in d-spacing accompanying the polymerization of both LLC lamellar phases 1 and 2 was however observed (cf. Figure 4).

Table 2. Preparation of the samples. (da: dodecylamine; ma: methacrylic acid; aa: acrylic acid; w: water; dama 1:1 = dodecylammonium methacrylate; daaa 1:1 = dodecylammonium acrylate; D: lamellar; cub.: cubic; DVB: divinyl benzene; BME: benzoin methyl ether).

Entry	Name	Molar ratio da : (m)a	Struct. before polymn.	Mass ratios				DVB (wt.%)	BME (mol.%)
				da	aa	ma	w		
1	dama 1:1/w 0.80/0.20	1:1	D	0.54	-	0.26	0.20	-	0.5
3	daaa 1:1/w 0.80/0.20	1:1	D	0.58	0.22	-	0.20	-	0.5
2	dama 1:1/w 0.20/0.80	1:1	cub.	0.14	-	0.06	0.80	-	0.5
4	dama 1:1/w 0.20/0.80 + DVB	1:1	cub.	0.14	-	0.06	0.80	3%	0.5
5	dama 1:2/w 0.20/0.80 + DVB	1:2	cub.	0.14	-	0.06	0.80	3%	0.5

Polymerizations from cubic phases were performed from a sample without DVB (6) and from samples containing 3 wt% DVB as crosslinking agent (4 and 5). DVB appeared to be a suitable crosslinking agent. Indeed, it is well know that aromatic compounds localize in the outer part of surfactant aggregates. The macroscopic feature of the samples changed in the course of polymerization, as the initially isotropic hydrogel became turbid after only 4 h of UV curing. The polymerization process yielded a white solid suspension in water. A FTIR spectrum of the solid in suspension indicated a nearly total disappearance of (meth)acrylic double bonds, and a large decrease in the vibration band of DVB's ethylenic double bonds (> 85%).

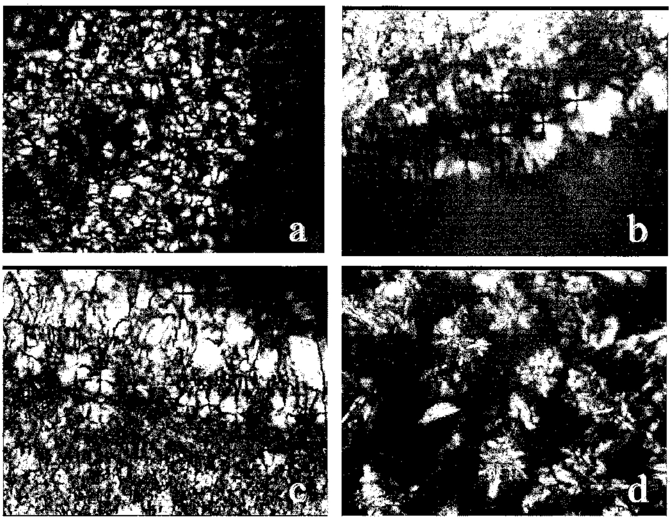

Figure 3. Textures observed by POM. (a) daaa 1:1/w 0.80/0.20 before and (b) after polymerization. (c) dama 1:1/w 0.80/0.20 before and (d) after polymerization.

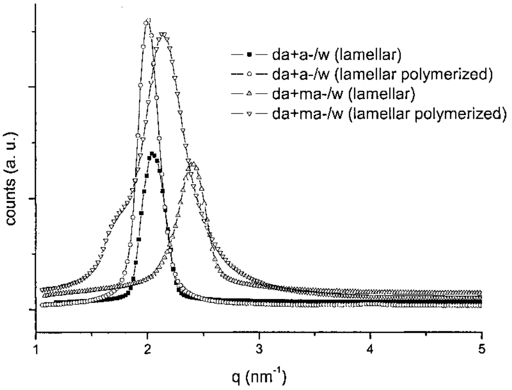

Figure 4. Overlay of SAXS patterns of LLC lamellar phases before and after polymerization.

SAXS patterns of the polymerized samples were very different to those of the corresponding non-polymerized samples. As shown in Figure 2-b-c-d, a sharp peak appeared around $q = 1.8\ nm^{-1}$ ($d \sim 3.4$ nm), while the typical peaks of the original cubic phases disappeared. The d-spacing of the new sharp peak is of the same order of those observed with lamellar phases. Despite the absence of any second order peak, one can assume that the three systems evolved toward a lamellar structure in the course of polymerization. Despite polymerized samples displayed an optical anisotropy, as determined by POM. Nevertheless, the determination of any typical texture of LLC lamellar phase was not possible because of the difficulty encountered in preparing samples that were thin enough. The change in organization during polymerization probably arises from a change in both packing parameter and entropy of the system occurring during the earliest stage of polymerization (initiation step and commencement of propagation step). Bicontinuous phases collapsing is likely favoured by a decrease in the entropy of the system, the more organized lamellar phase being favoured. The lamellar phase is then probably locked as the molecular weight increases during the latter stages of polymerization (propagation, cross linking, and termination). Insolubility of all of the obtained polymerized lamellar structures in water and organic solvents, even when polymerized without DVB, probably arises from a stabilisation of the lamellae, arising from in-situ formation of an equivalent of a polyelectrolyte-surfactant complex[36-39]. Furthermore, a possible inter-lamellar distribution of the "polyacrylate" chain arising from the in-situ polymerization of the counterions would explain the insolubility of the polymerized samples by an increase in the stability of the lamellae[25, 26].

Summary

Polymerizations of reactive organic counterions of dodecylammonium acrylate and dodecylammonium methacrylate were studied in concentrated aqueous solutions. Templated polymerization from LLC lamellar phases was successfully performed for both types of counterions. Conservation of the lamellar feature was confirmed by POM and SAXS. A slight increase in the d-spacing occurred upon polymerization. Attempts at templating polymerization from bicontinuous cubic phases formed with dodecylammonium methacrylate were made with and without DVB as a crosslinking agent. Bicontinuous phases always evolved toward lamellar phases. This is probably due to a change in the packing parameter of the surfactant, becoming oligomers in the earliest stage of the polymerization.

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