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ORIGINAL CONTRIBUTION

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Polyelectrolyte-induced vesicle formation in lamellar liquid-crystalline model systems

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Abstract The object of the research was to investigate the influence of a semiflexible polyanion (carboxymethylcellulose) in the absence and presence of a more flexible cationic polyelectrolyte [poly(diallyldimethyl-ammonium chloride)] on structure formation in liquid-crystalline model systems consisting of sodium dodecyl sulfate (SDS)/decanol/water. Small-angle X-ray measurements in combination with electron microscopic investigations show the adsorption of the polycation on the SDS head groups. These polymer-modified lamellae form multilamellar vesicles. The semiflexible polyanion was embedded into the liquid crystal without macroscopic phase separation and multivesicular vesicles were formed on the supramolecular level. In combination the oppositely charged polyelectrolytes induce the formation of multivesicular structures where two lamellar structures coexist.

Key words Polyelectrolytes · Lamellar liquid crystals · Vesicle formation

Introduction

Polymers can be incorporated into self-assembled liquid-crystalline systems without macroscopic phase separation. Examples are given in nature by the formation of biomembranes, where protein–phospholipid interactions play a dominant role. Generally, polymers can influence the structure of cell membranes and model membrane systems [1–3]. Lamellar mesophases can be used as an anisotropic "solvent" for polymers, including polyelectrolytes [4–8]. The polymer can be solubilized in the water region [4] of the liquid crystal or localized entirely in the membrane [5]. Additionally, penetration through the bilayer has to be taken into account [6]; however, this process is controlled by the hydrophilic–hydrophobic balance of the polymer, on the one hand, and by the space required for the macromolecule, on the other hand [7]. The interaction forces between the surfactant head groups and the functional groups of the polymer also play a major role.

Turning to ionic surfactants, on the one hand, and charged polymers, i.e. polyelectrolytes, on the other hand, surfactant–polymer interactions are drastically enhanced [8]. Phase-separation phenomena can now be induced by attractive as well as by repulsive forces [9]. By adding two polymers the situation becomes more complicated. The structure formation process is now controlled by the preferential polymer–polymer and/or polymer–surfactant interactions. If the polymer–polymer interactions become dominant (e.g. by adding two oppositely charged polyelectrolytes) macroscopic phase separation is observed. Only by reducing the water contents incorporation of both components becomes possible [10]; however, a polyelectrolyte together with a noncharged polymer is much easier to incorporate into liquid crystals [11].

The aim of the present research is to investigate the influence of a less flexible polyanion (i.e. carboxymethylcellulose, CMC) in the absence and in the presence of the flexible polycation poly(diallyldimethylammonium chloride) (PDADMAC) on the resulting supramolecular structure of the lamellar liquid-crystalline model system sodium dodecyl sulfate (SDS)/decanol/water.

Experimental

Materials

The commercially available surfactant SDS (99% Fluka) and decanol (99% Merck) were used without further purification. PDADMAC-1 and PDADMAC-2 were synthesized according to Ref. [12] with molecular weights of M_n = 5,000 and 440,000, respectively. CMC-1, obtained by a "phase-separation induced" carboxymethylation in *N*,*N*-dimethylacetamide/LiCl according to Ref. [13], shows a block-like distribution of the functional groups along the backbone chain (degree of substitution: 1.76; M_q = 126,000) in contrast to a conventionally synthesized statistically distributed CMC-2 (degree of substitution: 1.78; M_q = 570,000).

Preparation

The components (i.e. SDS, decanol, water, polymer) were mixed in a glass vial and repeatedly stirred and centrifuged several times until the samples appeared to be homogeneous or did not phase-separate anymore.

Each sample contained SDS and decanol in a weight ratio of 1:1, 5–20 wt% polymer and different amounts of water (30–70 wt%). The percentage values refer to the total weight of SDS and decanol.

Microscopy

The lamellar phase was identified by its optical pattern using a Leica microscope with crossed polarizers.

For the freeze-fracture electron microscopy investigations a BAF 400 freeze-fracture apparatus (Balzers, Liechtenstein) equipped with an electron beam evaporator was used. After an etching time of 60 s at −100 °C the Pt/C evaporation was carried out. The replicas were cleaned in sulfuric acid and distilled water and examined using an EM 902 (Zeiss, Germany).

Alternatively, scanning electron microscopy (SEM) investigations of the freeze-etched samples were made with a LEO 1530 (LEO Oberkochern) cold field emission scanning electron microscope. The elemental microanalysis results were obtained with a Link-ISIS 300 energy dispersive X-ray microanalysis system from Oxford Instruments and a cold FE-SEM S-4700 from Hitachi.

Rheology

The rheological properties were investigated by using a low-stress rheometer (LS 100, Physica) with a cone–plate geometry (2° cone angle, 25-mm cone radius). The distance between the cone and the plate was adjusted to 50 μm for all measurements. The temperature of the samples was kept constant at 25 °C.

Small-angle X-ray scattering (SAXS)

The interlayer spacing was determined by SAXS measurements with a Kratky-Compakt small-angle camera system (A. Paar). The samples were placed in a sample holder and measured with Cu Kα X-ray radiation (λ = 0.1542 nm) filtered by Ni foil. The signals were detected with imaging plates from Fuji and read by an IPR-420 dip-scanner from MAC Science.

Results and discussion

Polyanion-modified liquid crystals

On mixing SDS, decanol and water in the presence of CMC-1 or CMC-2 up to a polymer concentration of 5% by weight no phase-separation phenomena were observed. All samples with water contents of 40–70% by weight were birefringent showing Maltese crosses and oily streaks under the polarizing microscope. The interlayer spacings calculated from the first-order Bragg peaks in a classical way were plotted versus the weight ratio of water:SDS/decanol. The slopes of these curves are of the same order as those without polymer, but the absolute values are somewhat smaller (Fig. 1). Electron microscopic investigations revealed the formation of a supramolecular structure in the sense that the individual lamellae rearrange to form multivesicular vesicles of size 1–10 μm (Fig. 2). In rheological experiments the CMC-modified samples show hysteresis, revealing their ability to reconstruct the original structure by decreasing the shear stress (Fig. 3). Generally, the good "solubility" of the semiflexible CMC can be explained by the embedding of the polyelectrolyte into the supramolecular structure under the preferential formation of multivesicular structures.

Polycation-modified liquid crystals

The influence of the cationic polyelectrolyte PDADMAC on the structure formation at the molecular level in the SDS/decanol/water system was already outlined in Ref. [14]. Based on the SAXS measurements a flat adsorption of the PDADMAC on the SDS head groups of the individual lamellae can be assumed, resulting in a "nonswelling" liquid crystal with a constant interlayer spacing of about 4 nm.

Starting from this information, the PDADMAC concentration was gradually increased to 20% by weight. SEM micrographs show the formation of spheres of the 2–5 μm (Fig. 4). A decrease in the polymer concentration leads to an increase in the diameter of spheres with an

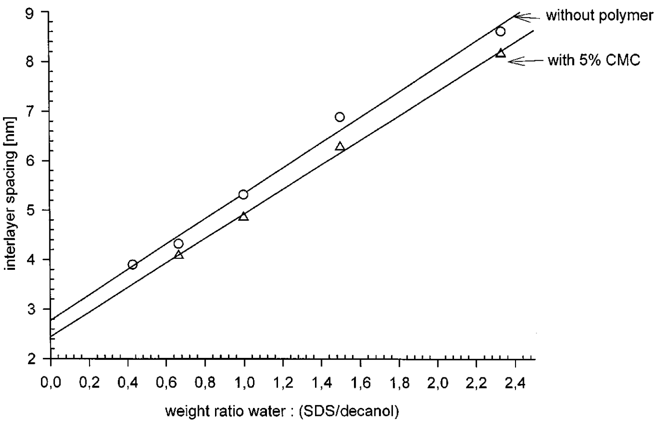

Fig. 1 Interlayer spacing versus weight ratio of water:decanol + sodium dodecyl sulfate (*SDS*) in the absence and in the presence of 5 wt% carboxymethylcellulose sample 1 (*CMC-1*)

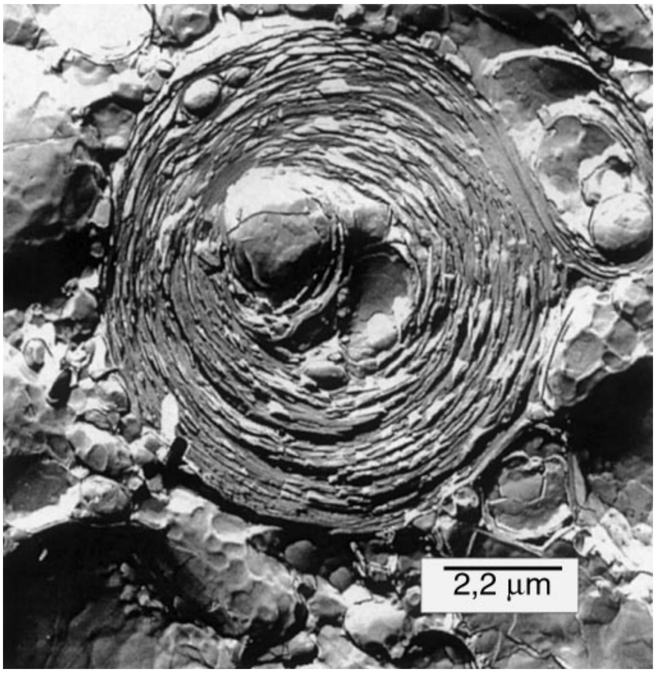

Fig. 2 Freeze-fracture electron micrograph of the SDS/decanol/water CMC-1 system (weight ratio water:decanol + SDS = 1; CMC-1 concentration: 5 wt%)

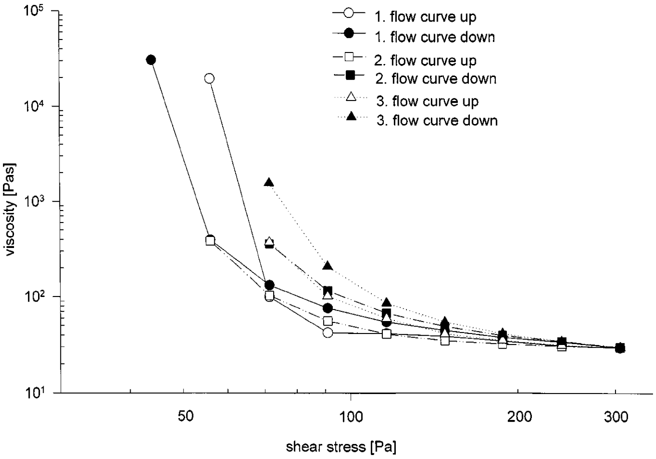

Fig. 3 Repeated flow-up and flow-down curves of the SDS/decanol/water/CMC-1 system (weight ratio water:decanol + SDS) = 1; CMC-1 concentration: 5 wt%)

onion-like inner structure (Fig. 5). It can be expected that the individual shells of the onion (about 4 nm) are PDADMAC-adsorbed individual lamellae, but experimental evidence is needed. The presence of a N peak in the energy dispersive X-ray (EDX) diagram (Fig. 6) of spot 3, marked in Fig. 7, demonstrates the presence of PDADMAC in the spheres.

The polymer-induced formation of spheres can now be explained as follows. The cationic flexible polyelectrolyte adsorbs (independently of the molecular weight) at the head groups of the SDS bilayer and a constant interlayer spacing of about 4 nm results. The adsorption of the polycation is responsible for the nonswelling of the bilayer and the change in the spontaneous curvature. Consequently, spheres with an onion-like structure, i.e. compact multilamellar vesicles, are predominantly formed.

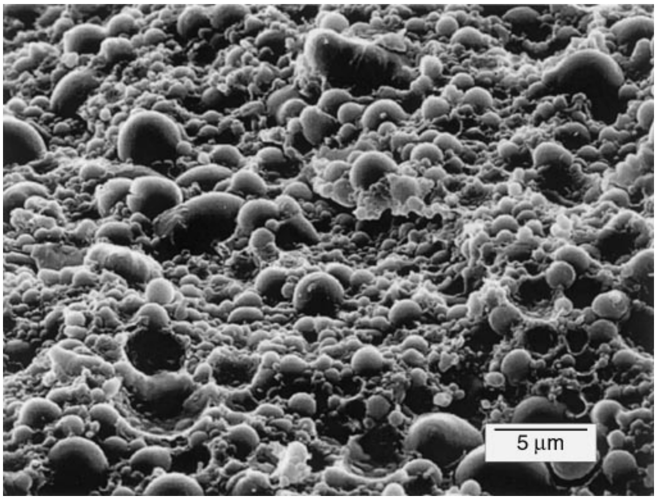

Fig. 4 Cryo-scanning electron micrograph of the SDS/decanol/water/poly(diallyldimethylammonium chloride) (*PDAD MAC-1*) system (weight ratio water:decanol + SDS) = 1; PDADMAC-1 concentration: 20 wt%)

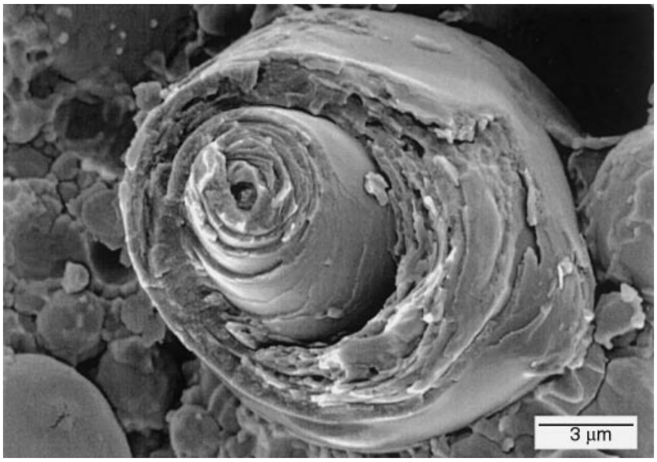

Fig. 5 Cryo-scanning electron micrograph of the SDS/decanol/water/PDADMAC-1 system (weight ratio water:decanol + SDS = 2.3; PDADMAC-1 concentration: 5 wt%)

Polyanion–polycation-modified liquid crystals

By adding CMC and PDADMAC to the SDS/decanol/water system two coexisting lamellar liquid-crystalline

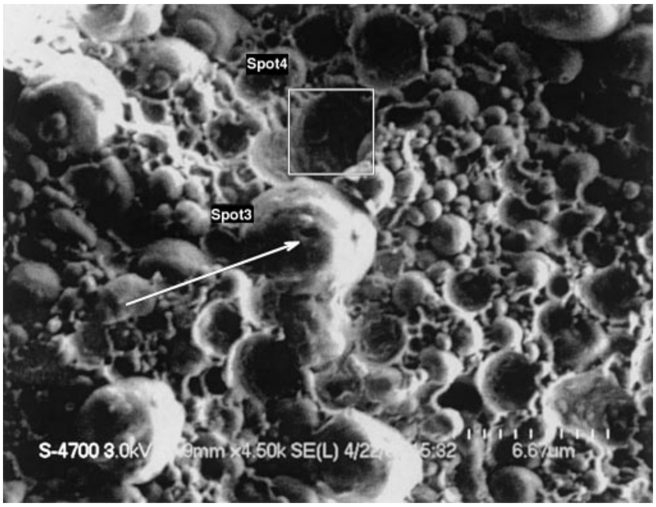

Fig. 6 Cryo-scanning electron micrograph of the SDS/decanol/water/PDADMAC-1 system (weight ratio water:decanol + SDS) = 1; PDADMAC-1 concentration: 20 wt%)

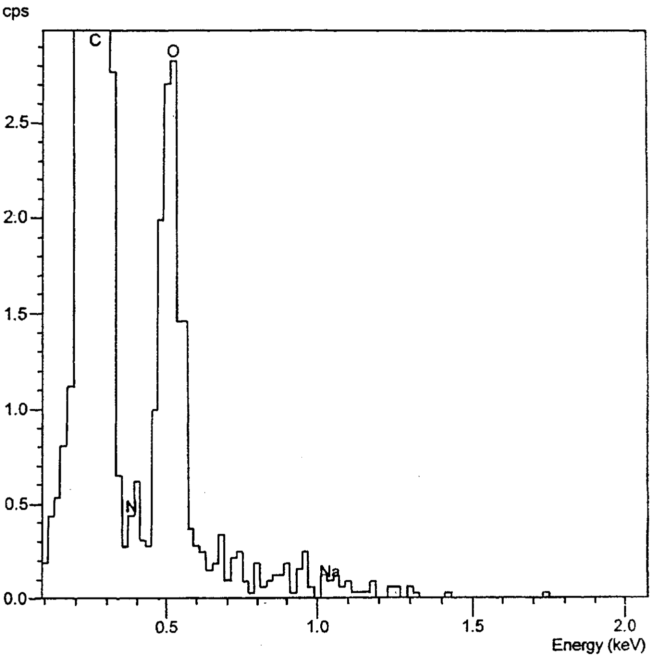

Fig. 7 Energy-dispersive X-ray elemental analysis of "spot 3" according to Fig. 6

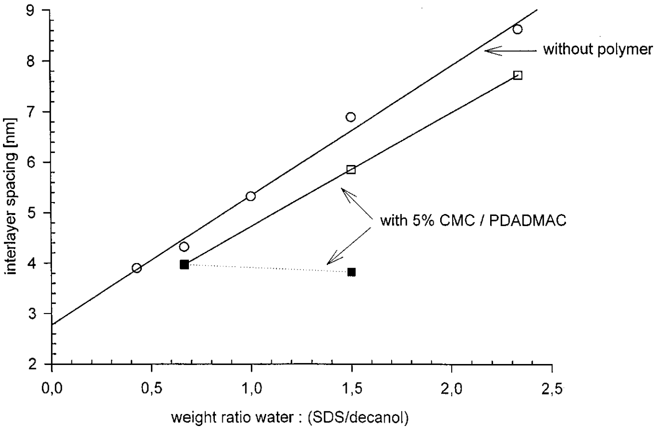

Fig. 8 Interlayer spacing versus weight ratio of water:decanol + SDS in the absence and in the presence of 5 wt% CMC-1/PDADMAC-1

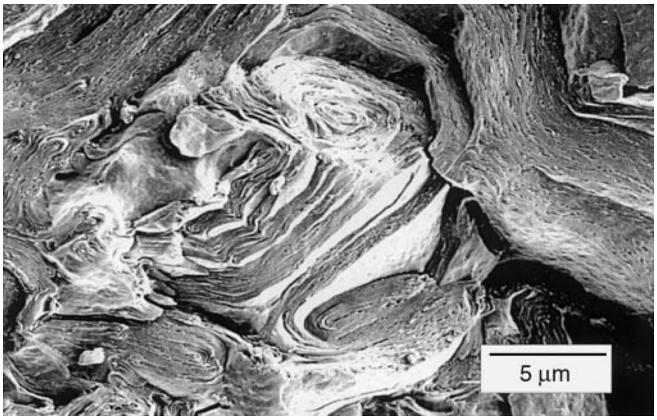

Fig. 9 Cryo-scanning electron micrograph of the SDS/decanol/water/CMC-1/PDADMAC-1 system (weight ratio water:decanol + SDS = 0.54; CMC-1/PDADMAC-1: 5 wt%)

phases were detected by SAXS measurements (Fig. 8), i.e. a nonswelling (in agreement with the PDADMAC reference system) and a swelling one. Compared to the CMC-based reference system the swelling is reduced. Both phases coexist without a macroscopic phase separation, which is usually assumed; however, similar coexisting lamellar structures have already been found [11, 15, 16]. SEM micrographs reveal the formation of multivesicular "stringlike" supramolecular structures (Fig. 9). Rheological measurements show that the shear-stress-induced deformation is reversible and that the original structure can be reconstructed by decreasing the shear stress. That means, the rheological behaviour is quite similar to the CMC-based lamellar system.

One can explain the experimental data as follows. On the one hand, the PDADMAC is partly adsorbed at the SDS head groups resulting in the nonswelling behaviour, as already discussed. On the other hand, a second swelling lamellar liquid-crystalline structure coexists and as for the CMC-modified system the formation of multivesicular structures becomes dominant on the supramolecular level. However, these results clearly show that the polymer–polymer interactions do not play a major role in the five-component system investigated here. Consequently, the observed phenomena can be understood on the basis of strong competition between both polymer components for the water. The water is partly consumed, the swelling is less than in that of the system without polymer and the system becomes more disordered.

Conclusions

Generally, we have to differentiate between two levels of structure formation in the liquid-crystalline system, i.e. a "molecular" and a supramolecular level. From the modified swelling behaviour of the bilayer, obtained by SAXS measurements, one can conclude the location of the polymer components on the "molecular" level. SEM is a useful method for identifying the individual bilayers on the "molecular" level as well as supramolecular structures. EDX measurements give evidence for polymer-modified bilayer structures.

The investigations have shown that due to the adsorption of the more flexible oppositely charged cationic polyelectrolyte on the SDS head groups the swelling of the bilayer is suppressed. The polymer-modified individual lamellae now tend to form spherical supramolecular structures, i.e. multilamellar vesicles. The more rigid anionic CMC alone is embedded into the liquid crystal without a significant change in the swelling behaviour of the individual bilayer. On the supramolecular level a multivesicular structure becomes dominant. If both polyelectrolytes are added a part of the PDADMAC adsorbs again on the SDS head groups, resulting in a nonswelling structure, together with a swelling structure. On the supramolecular level the formation of spheres is weakened and string-like multivesicular structures occur. A strong influence of the molecular weight of the polyelectrolytes could not be observed. Only the size of the multivesicular structures should be influenced by the molecular weight of the CMC.

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