Polyelectrolyte–Surfactant Complexes: A New Type of Solid, Mesomorphous Material

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ABSTRACT: Polyelectrolyte–surfactant complexes made of poly(styrenesulfonate) and different alkyltrimethylammonium derivatives are "synthesized" by common precipitation in water. Redissolved in polar organic solvents, these complexes show polyelectrolyte behavior. Cast films of these complexes exhibit highly ordered mesomorphous phases which are characterized by X-ray diffraction. Depending on alkane chain length, different layered phase modifications with long periods between 2.9 and 4.1 nm are obtained.

(I) Introduction

Polyelectrolytes as well as surfactants are known to form interesting three-dimensional structures in aqueous solution. This structure formation is based upon the combination of a polymer backbone and electrostatic interaction or electrostatic and hydrophobic interactions, respectively.

For obvious reasons, the combination or mixing of polyelectrolytes with surfactants results not only in a zoo of different interactions but also in a bundle of different phenotypes of materials and applications. In the present work, we only consider the mixtures of polyelectrolytes (PE) and oppositely charged surfactants, which form stoichiometric, highly stable, but water insoluble complexes (PE–surfs).

Many publications can be found in the literature which describe the formation of these complexes in water as a function of experimental parameters such as ionic strength, stoichiometry, and concentration (see for instance, refs 1 & 2, or for a review, ref 3).

The essential results are just briefly summarized:

–The formation takes place already at extremely small concentrations (much smaller than the cmc of the surfactants) and is highly cooperative. A binding process neighboring a "docked surfactant" is much faster than the primary binding process, with a factor of up to 2000.

–Using less than stoichiometric amounts of surfactant results in many cases in a "string of pearls" like morphology of surfactant micelles lined up on the polymer backbone.

–Polyelectrolytes with a pronounced hydrophobic character of the backbone (e.g. poly(styrenesulfonate)) introduce only 50–70% of their ionic sites in the first cooperative binding step; the other sites require higher concentrations or more stringent binding conditions.

To our knowledge, only very little work related to the material properties of these PE–surf complexes has been published, although interesting solution properties (in organic solvents) and solid state effects might be expected.

Some of these expectations result from extrapolating the behavior of similar materials:

–Polyelectrolyte complexes made of two oppositely charged polyelectrolytes also spontaneously form complexes which underly strict stoichiometries and exhibit interesting material properties.[4–6] For instance, stable porous and selective membranes can be made by this complexation procedure. However, due to the double polymeric nature, a reprocessing via solution or the melt is impossible.

–Kunitake et al.[7] and Okahata et al.[8] have stabilized lipid bilayer membranes via complexation using natural polyelectrolytes or poly(styrenesulfonate). X-ray scattering on these systems revealed that the double layer structure is essentially maintained. The characteristic phase transitions of the membranes were just slightly shifted toward higher temperatures. Okahata et al. also showed[9,10] that the permeability of such polymer-supported membranes can be modulated by small electric fields.

–Zwitterionic polymers with long alkane side chains look very similar to PE–surf complexes, but show an additional covalent bond between the charges. With chosen architectures, they form well-defined micellar aggregates and solvate inorganic salts into the polymeric bulk phase.[11,12]

We expect very similar properties for the PE–surfs, having the advantage of a much simpler "synthesis" or accessibility and a wider range of structural variability.

For those reasons, this paper describes the isolation and purification of some model PE–surf complexes made of poly(styrenesulfonate) (PSS) and monofunctional cationic surfactants of the alkyltrimethylammonium type. In addition, we report some of the solution properties and experiments related to the solid state structure of these materials.

(II) Experimental Section

(II.1) Polymer Synthesis. The sodium salt of poly(styrenesulfonate) (PSS-Na) is made by sulfonation of anionically polymerized polystyrene ($M_w \approx 449\,000$ g/mol, $M_w/M_n < 1.05$) using H_2SO_4/P_2O_5 and the Vink procedure.[13] The degree of sulfonation is determined with elemental analysis and exceeds 0.90. The PSS-Na is dialyzed against pure water and freeze-dried.

For complexation, 5.0 g of PSS-Na is dissolved in 400 mL of 0.01 *m* Na_2SO_4 solution, and a 1.5-fold excess of surfactant (e.g. cetyltrimethylammonium chloride, CTMA, from Aldrich, or the other homologues (all from Aldrich)) in 100 mL H_2O is added dropwise.

The resulting white precipitate usually coagulates, and the water is removed. The crude complex contains large amounts of excess surfactant, salt, and water. For purification, this mixture

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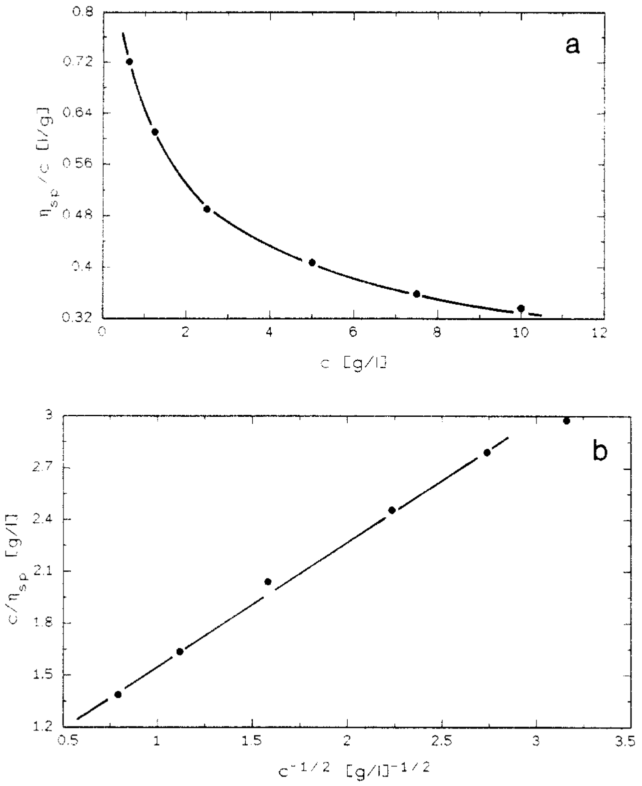

Figure 1. Viscometric data for PSS–C_{16} in ethanol at 20.0 °C in a linear (b) and a Fuoss–Strauss presentation (a).

is redissolved in 2-butanol, and water is added until a phase separation of a complex rich gel phase and a salt and surfactant rich water phase takes place.

After removal of the water phase, this phase separation is repeated until the water phase is practically free of halogenide ions (tested with $AgNO_3$). The pure gel phase can directly be processed. For a fine precipitation, it is slowly dropped in a 10-fold excess of bidistilled water. The resulting flocculous white powder is dried for 4 days in a vacuum oven at 40 °C.

Elemental analysis of all complexes results in sodium contents of 0.01% and bromide contents on the order of 0.005%. Therefore, we can exclude the presence of salt as well as a surplus of surfactant (by Br^-) or unattached repeat units (by Na^+); the pure 1:1 complex is obtained.

(II.2) Film Casting. The gel phase (or a redissolution of the isolated complex) is cast on a planar glass sheet coated with octadecyltrichlorosilane. The two-dimensional geometry of the film is controlled by a brass frame with variable dimensions which is mounted on top of the glass sheet. After slow evaporation of the solvent, the film is easily removed with the brass frame and cut.

(II.3) X-ray Scattering. All the SAXS curves were obtained with an Anton Paar compact Kratky scattering camera with a Phillips pw1830 generator as the source of Cu Kα incident radiation. Monochromatization was accomplished using a nickel filter and pulse height discrimination. The measurements where performed in an s range of 1.0×10^{-3} to 9.0×10^{-2} A^{-1} (the scattering vector s is defined as $s = 2/\lambda \sin \theta$ where 2θ is the angle between incident and scattered light). The data were corrected for parasitic scattering (maximum 2% of the signal). The beam profile was measured without a detector slit and convoluted with the detector slit profile. The resulting slit length profile and the corrected data were used for desmearing using a new method via generalized Laguerre orthogonal functions (GLOF) by Burger and Ruland.[14] No slit width correction was performed because of the small width of the primary beam (integral width of 1×10^{-3} A) compared to the width of the observed scattering peaks.

(III) Results and Discussion

(III.1) Solution Properties. Depending on alkane chain length and the hydrophilic/lipophilic balance, the complexes dissolve in different alcohols and halogenated and amidic solvents. To our surprise, we were unable to determine the molecular properties of the complexes with static and dynamic light scattering. In most solvents, the scattering power is very low, and the correlation function as well as its angular dependence is distorted in a manner known from polyelectrolytes in aqueous solution.[15,16] This "polyelectrolyte behavior" in polar *organic* solvents is vividly demonstrated in case of the viscometric experiments.

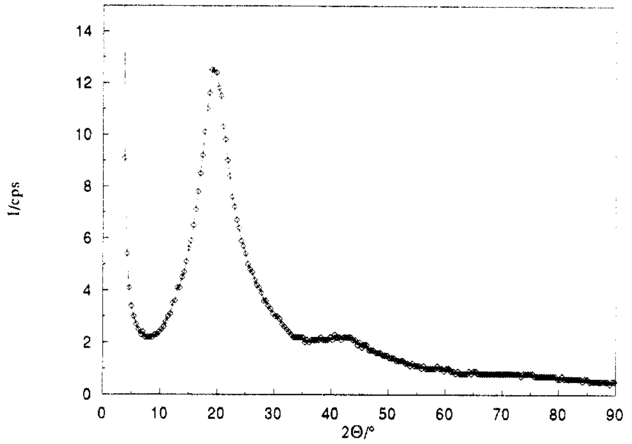

Figure 2. WAXS diffractogram of PSS–C_{14}. A Cu Kα source with λ = 0.1542 Å was used.

Figure 1 exemplarily presents the data for PSS–CTMA in ethanol in a standard presentation as well as in a Fuoss–Strauss plot.[17] The apparent divergence of the intrinsic viscosity following a $c^{-1/2}$ law is detected, which might result from concentration dependence of the Debye screening length. In addition, the absolute value of the intrinsic viscosity at a given concentration is very high and just slightly smaller than the corresponding one of the linear precursor polyelectrolyte in aqueous, salt-free solution.

From these similarities we have to conclude that a part of the charges of the PE–surf complexes dissociates in organic solvents; the chemical nature of the charge carrying species remains unclear. The comparatively low dielectric constant of the solvent surely prohibits a high number of charges, but at the same time, a larger electric field is obtained. The dissociation process and the Coulomb interaction also prohibit the characterization of molecular properties such as molecular weight and radius of gyration.

Very recently, MacKnight et al. published viscometric data from nonstoichiometric polyelectrolyte surfactant complexes of poly(N-ethylpyridinium bromide) and sodium dodecyl sulfate in chloroform.[18] In contrast to our data, they found comparably low reduced viscosities and a not polyelectrolyte-like behavior. This is possibly due to the lower polarity of their polymer/solvent system. A more extensive study of the effects of chain length and polarity in stoichiometric PE–surfs is in progress.[19]

(III.2) Solid State Properties. Solvent casting of the C_{12}–C_{18} derivatives results in flexible and highly transparent films. With differential scanning calorimetry, we observe neither a glass transition nor any phase transition. All films stay mechanically stable until they decompose. Such a behavior is not seen in statistically sulfonated polystyrene chains (1%–20% sulfonation) with surfactant counterions where a quasi-one-phase behavior and a depression of the glass transition temperature is described.[20] Cooperative neighborhood effects in fully converted PE–surf complexes obviously result in mi-

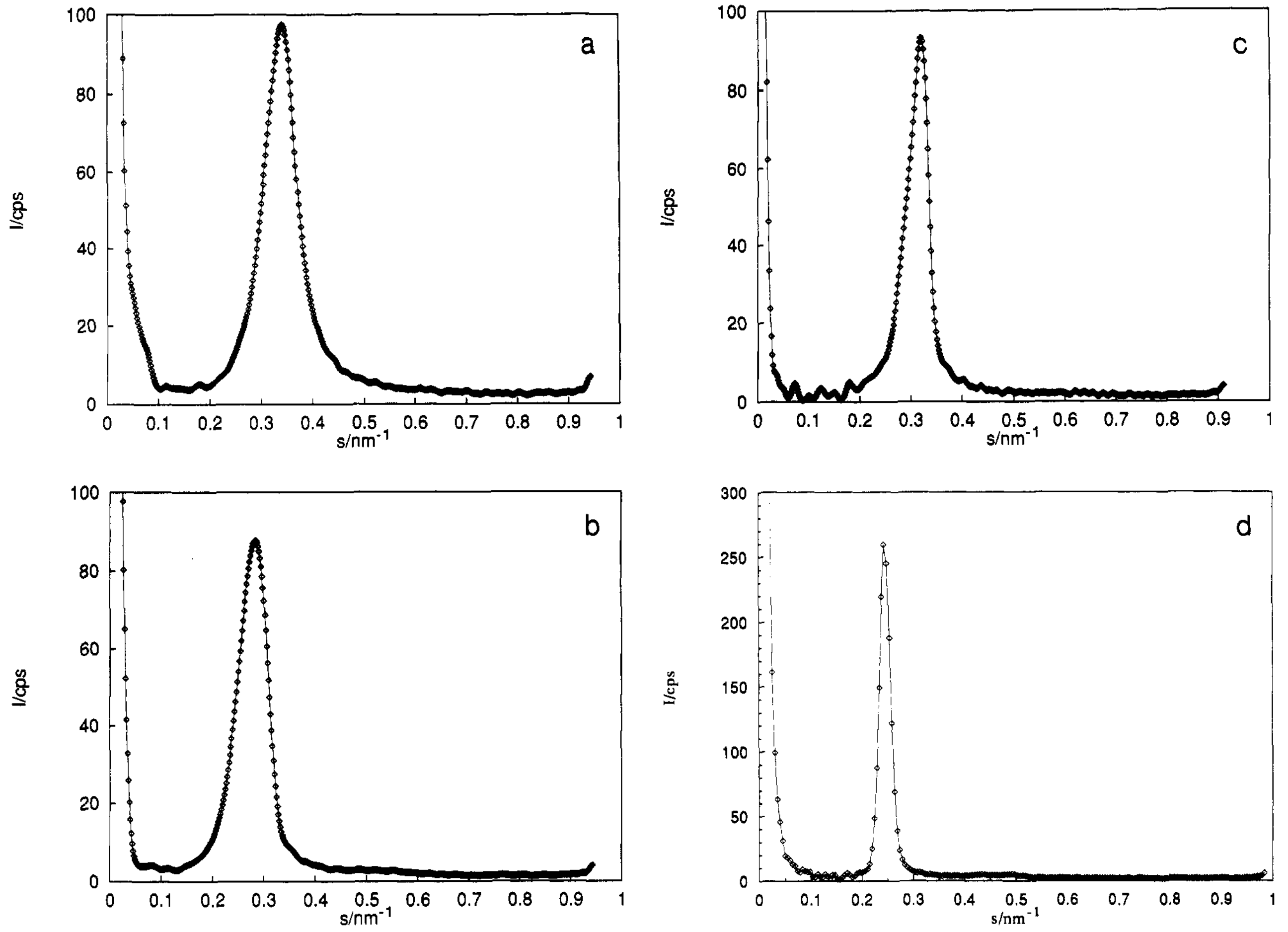

Figure 3. SAXS data for the homologous series of PE-surf complexes: (a) PSS–C_{12}; (b) PSS–C_{14}; (c) PSS–C_{16}; (d) PSS–C_{18}.

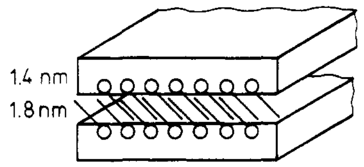

Figure 4. Structure model for the solid state structure of PSS–C_{14}. A sequence of ionic layers (polyelectrolyte, ionic head groups) and alkane layers (tails) is obtained where the hydrophobic tails of two layers must interdigitate. The thicknesses are taken from the long period and density calculations.

crophase separation being very different from the ionomer-type structures.

Figure 2 shows the WAXS diffractogram of PSS–C_{14} which can be regarded to be typical for all complexes. The material possesses no crystallinity, neither an overall nor a partial side chain crystallinity. The scattering peak, however, is narrower than expected for an amorphous polymer. The pronounced shoulder at higher angles and a second peak at $2\theta = 43°$ might even be interpreted as indications of higher order peaks.

Peaks with a similar structure are known for highly ordered liquids, e.g. smectic phases. The peak position corresponds to a Bragg spacing of about 0.43 nm, which is close to the known value for a densely packed alkane layer. (E.g. the area need of surfactants in compresed LB layers is very similar to $(0.43\ \text{nm})^2 = 0.188\ \text{nm}^2$.)

Parts a–d of Figure 3 present the results of small angle X-ray scattering for the four different complexes. PSS–C_{14}, for instance, produces an extremely narrow scattering peak with corresponds to a long period of about 3.2 nm. Both SAXS and WAXS data for this complex can be explained by a lamellar structure of alternating alkane and ionic layers where the alkane side chains of two layers are intercalated, as sketched in Figure 4.

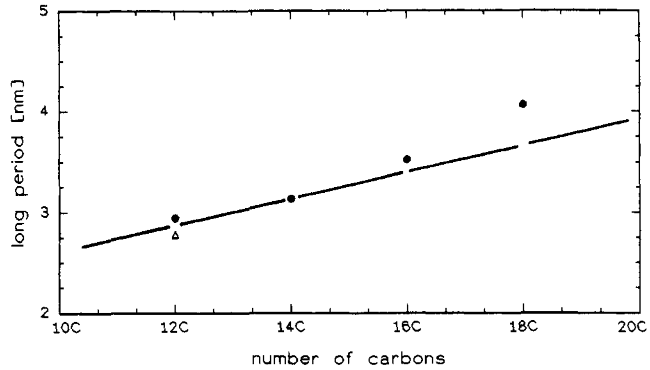

Figure 5. Long period of the different complexes: (●) pure systems; (△) cross-linked with 10% bola surfactant. The straight line is the expected behavior for a pure lamellar structure with extended alkane chains.

Assuming standard densities for the alkane ($\rho \approx 0.95$ g/cm^3, highly orderred) and polyelectrolyte layer ($\rho \approx 1.5$ g/cm^3, measured at tetramethylammonium–poly(styrenesulfonate) and knowing the 1:1 stoichiometry and the overall density of the complex ($\rho = 1.2$ g/cm^3), we can calculate the relative thicknesses of both layers to be 1.4 nm (ionic layer) and 1.8 nm (alkane layer), respectively. This symmetry also supresses a second-order peak which might be expected for such well-defined, layered structures.

Figure 5 and Table 1 present the long period dependent on the length of the surfactant chain. For many lamellae-forming systems (e.g. LB-multilayer, stiff main chain polymers with alkyl side chains), this standard exercise results in a straight line where the tilt angle of the side

Table 1. Long Period *d* Dependent on the Length of the Hydrophobic Tails

complex	PSS–C_{12}	PSS–C_{14}	PSS–C_{16}	PSS–C_{18}	PSS–bola
d/nm	2.94	3.13	3.52	4.07	2.78

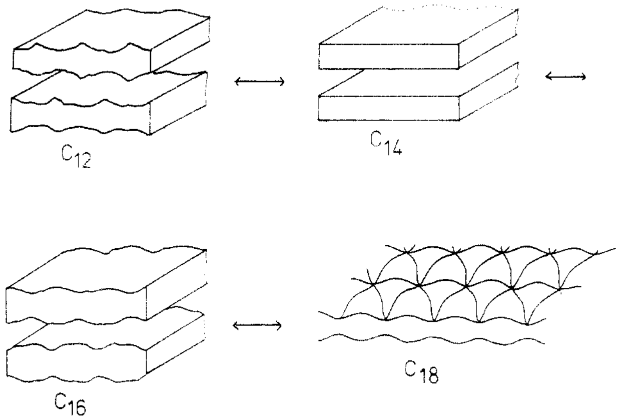

Figure 6. Structure transitions in lamellar amphotropic phases. Changing the volume ratio of the phases results in a spontaneous curvature of the interface with positive and negative values (a, c). Beyond a critical value, the ripples become localized which results in additional scattering peaks.

chains can be calculated from the slope m (m = 0.127 nm/carbon·cos ϑ with ϑ being the angle between the normal of the lamellae and the side chain). The intercept with the Y-axis determines the thickness of the non-alkane layers (see, for instance, ref 21).

The experimental data for the PSS–surf complexes clearly do not follow such a simple dependence. Moreover, the difference between the C_{14} and C_{16} derivatives as well as the difference between the C_{16} and C_{18} derivatives exceeds the maximal value of 0.254 nm. The straight line in Figure 5 compares the experimental values with this simple expectation as calculated from the C_{14} derivative and density calculations.

These data prove that the structures are not isomorphous; with changing surfactant length or alkane volume fraction the morphology has to change too.

A strict analogy to this behavior of PE–surf complexes has been observed for block copolymers (e.g. refs 22 and 23) or surfactants (for a review, see ref 24): increasing the alkyl length or the volume fraction of one phase induces a spontaneous interfacial curvature toward the other phase that destabilizes the lamellar morphology and finally leads to the appearance of new phase structures.

Transferring the behavior of these amphotropic liquid crystalline phases to the PE–surfs results in the scenario scetched in Figure 6.

Changing the spontaneous curvature toward small positive or negative values gives rise to a "rippling" of the phases which—on the average—only results in a broadening of the long period peak. This effect is known as frustration[25] or Landau–Peierls instability and is also well-known in thermotropic liquid crystals.[26,27]

A further increase of the spontaneous curvature to small positive or negative values deepens and localizes the ripples and causes (casually) the transition to different phase structures such as the "perforated layer" phase. In these cases, additional scattering peaks have to appear.

For PSS–C_{18}, we indeed observe small, but sharp, higher order peaks with a ratio of 1:1.71:2 which, for instance, can be related to a BCC arrangement of the ripples (see also refs 23 and 28). This change of the scattering profile or symmetry breaking is paralleled by a change of the optical behavior, as detected with polarization microscopy: PSS–C_{18}, in contrast to all other derivatives, is birefringent.

A hexagonal arrangement of dispersed cylinders as the structure for PSS–C_{18} can be excluded since smaller Bragg spacings and a lower film stability are expected for the hexagonal phase.

A clear structure proof by scattering on the unoriented sample solely is impossible, and additional experimental evidence such as electron microscopy or structure sensitive solid state NMR is surely needed. These experiments are currently in progress.

In one additional experiment, we have used a chemical modification to influence the phase behavior: 10% of the surfactant was replaced by its bola derivative, 1,12-bis(trimethylammonio)dodecane. Besides the gelation of the solutions above a critical concentration, this replacement was easy to perform, and transparent and stable films were obtained.

In the SAXS characterization, this cross-linking of the ionic layers results in a peak narrowing where the width of the peak becomes comparable to the one of PSS–C_{14}. The long period of the cross-linked sample is remarkably lower compared to its pure counterpart (PSS–C_{12}) and even below the "ideal" value expected for the pure lamellar structure. This is also shown in Figure 5 where the value for the cross-linked sample is included, too. Within our interpretation, the fluctuations of the interface are damped by incorporating remarkable amounts of cross-linker.

(IV) Conclusion and Outlook

We have demonstrated that polyelectrolyte–surfactant complexes are easily "synthesized" and possess interesting and unconventional material properties. Besides the fact that these complexes exhibit polyelectrolyte behavior in polar organic solvents, they show an extremely well-defined solid state structure which can be discussed as polyelectrolyte-stabilized surfactant phases.

In the present set of experiments where poly(styrenesulfonate) has been complexed with different alkyltrimethylammonium derivatives, all the phases were essentially layered, as seen by the film stability and the scattering behavior. As we know from other systems, this is just a small excerpt of the broad variety of phases which can be obtained. The variation of the polyelectrolyte (type of charge, charge density) or the surfactant (type of charge, number of tails, optical activity, sheet or disklike shape, etc.) results in interesting new amphotropic phases where the appearance of a distinct phase structure is mainly controlled by the mutual geometric fit of surfactant and polyelectrolyte, respectively.[29]

In addition, we plan for our future research a more stringent assignment of the structures by using EM and solid state NMR.

Considering the simplicity of the "synthesis" and the accessibility of the starting materials, this new class of highly ordered, self-organizing products may find its way in science and applications.

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