Notes

Polymerizable Polyelectrolyte−Surfactant Complexes from Monomeric Ammonium Cations and Polystyrenesulfonate

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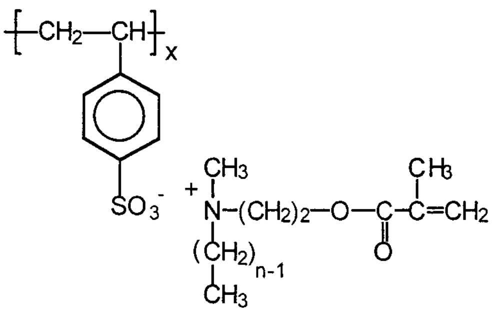
Introduction

The nature of polyelectrolyte−surfactant (p−s) interactions has been of long-standing interest, since both species are common in the washing process and as rheology modifiers, for example in the food industry, cosmetics, and fotografic film emulsions. Considerable efforts have been made in understanding the mechanistic principles of association between charged polymers and charged surfactants in solution and at interfaces.[1] Also, interactions between uncharged soluble polymers and surfactants have been studied and theoretically described.[2] Solid-state properties of p−s complexes have recently attained much interest, as it was shown that a 1:1 stoichiometric combination leads to spontaneous formation of highly organized assemblies.[3] The self-assembled bulk materials exhibit interesting properties such as thermotropic liquid-crystalline behavior, which results from long-range organization on a mesoscopic length scale.[4] If fluorinated surfactants are used, bulk materials or self-standing films with ultralow surface energies can easily be obtained.[5]

Not much is yet known on chemical reactions performed within p−s complexes. Only recently, Antonietti et al. reported on the UV radiation-induced degradation of complexes containing photolabile azo moieties incorporated into the self-organized assemblies.[6] Controlled photoablation of such materials could lead to nanometer-scale structures within a bulk film. Until now, the micro- and macroscopic properties of the irradiated material are mostly unknown, and the p−s complexes showed solubility in specific solvents. We now introduce a different pathway in order to obtain a mesoscopically structured material with improved mechanical, thermal, and solvent resistance. A combination of an anionic polyelectrolyte (sodium polystyrenesulfonate, Na−PSS) and polymerizable cationic surfactants of the 2-(methacryloyloxy)ethyl(dimethyl)(*n*-alkyl)ammonium bromide type (C*n*Br) was used for the complex formation. The introduction of monomeric surfactants into the self-assembly process leads to the possibility to create a stoichiometric polyelectrolyte−polyelectrolyte complex from a p−s complex by internal polymerization. It also reveals a novel example to conduct polymerization reactions in organized (liquid-crystalline) media.[7] It will be shown in the following that a 1:1 complex formation from aqueous solution leads to highly organized, monomeric p−s complexes. The mesoscopic dimensions can be tuned by variation of the length of the hydrophobic surfactant tails. The liquid-crystalline complex properties and their stability toward ^{60}Co γ-ray-induced polymerization will be described.

Materials and Methods

The preparation and workup of the p−s complexes was done according to ref 4a, using 2-(methacryloyloxy)ethyl(dimethyl)-(*n*-alkyl)ammonium bromide surfactants (C*n*Br) with *n* being 8, 10, 12, 14, and 16 instead of *n*-alkyltrimethylammonium bromide surfactants. Details on the preparation of the surfactant monomers can be found in ref 8. The PSS−C*n* complexes were obtained as white powders.



The structure and the thermal properties of the PSS−C*n* complexes were investigated using small- and wide-angle X-ray diffraction (SAXS, WAXS, Philips) and differential thermal calorimetry (DSC, Perkin-Elmer) as well as optical polarizing microscopy (OPM, Zeiss). ^{60}Co γ-radiation with a dose rate of 52 krad/h (0.52 kGy/h) was used for polymerization. Fourier transform infrared (FTIR) spectra of the samples were measured using a Perkin-Elmer Paragon 1000 spectrometer.

Results and Discussion

Figure 1 shows a representative WAXS diffractogram of the dried PSS−C14 complex before irradiation. Two characteristic, intensive peaks are visible: a small-angle peak and a broad peak at $2\theta = 20°$. Also, one can identify a less pronounced, broad peak at $2\theta = 40°$. The main peak corresponds to a Bragg spacing of about 0.44 nm, and very similar diffraction patterns were found for the other PSS−C*n* complexes. The results are in correspondence to earlier observations of p−s complexes with PSS and *n*-alkyltrimethylammonium counterions.[4a] The diffraction pattern can be interpreted as being typical for smectic layered structures, similarly to complexes with polyacrylates and anionic surfactant counterions.[4c] Since the peak at $2\theta = 20°$ is rather broad,

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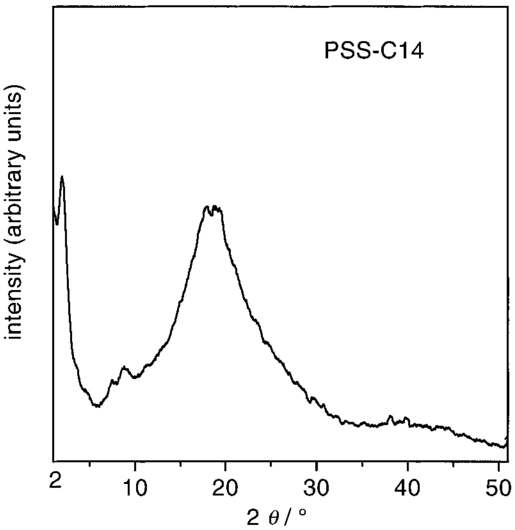

Figure 1. WAXS diffractogram of the PSS−C14 complex before irradiation.

the order within the alkyl chain domain is supposed to be quite low. Solid-state NMR investigations also revealed that at room temperature the surfactant tails in the lamellar layer are more likely in a liquidlike arrangement (smectic A) than in a frozen (smectic B) state.[9] In the OPM, the dried p−s complex samples were not easily processible. After swelling granular samples with *tert*-butyl alcohol, domain-free, colored textures became visible, indicating the long-ranging order of the bulk material. The textures result from small differences in the sample thickness. Under mechanical strain, the textures show alternate dark and bright lamellae. The mesoscopic order obviously is temperature-independent, since DSC measurements of the PSS−C*n* complexes showed no detectable phase transitions independent of the surfactant tail length *n* in a temperature range between 255 and 450 K. At even lower temperatures, a transition into the smectic B state is likely.[9] OPM investigations confirm that the materials are thermally degraded at about 480 K without prior transition into the isotropic state.

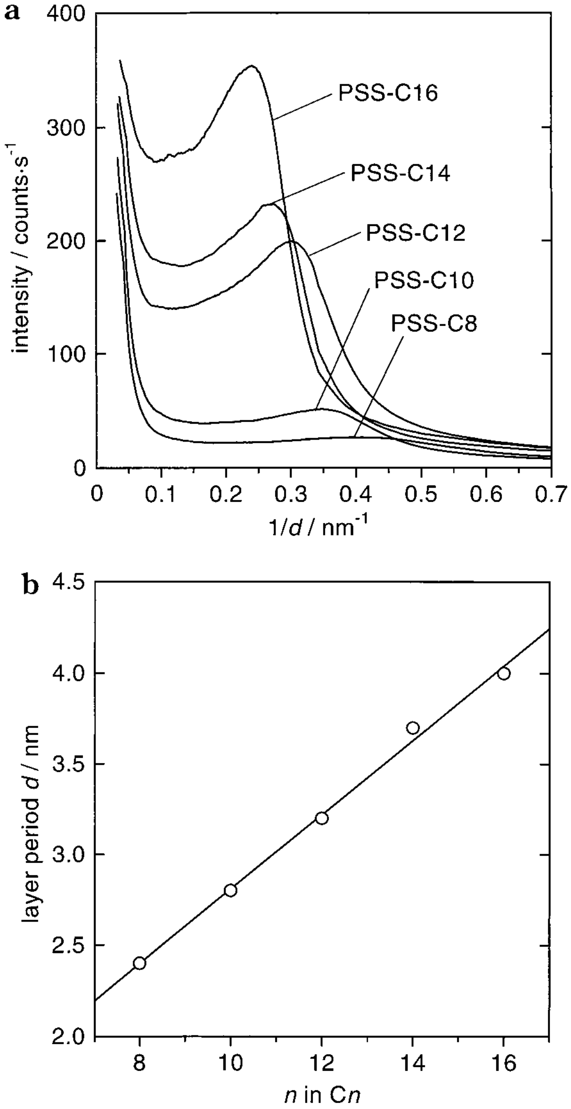

Figure 2. (a) SAXS diffractogram of the various PSS−C*n* complexes before irradiation. (b) Plot of the resulting layer periods *d* in nanometers versus the number of carbon atoms *n* in the monomeric surfactant tails.

Table 1. Comparison between the Theoretically Calculated Alkyl Chain Length *l* Resulting from Tanford's Formula and the Experimentally Determined Layer Spacing *d* Minus the Thickness of the Ionic Layer (1.4 nm, Refs 4a and 9)

p−s complex	theoretical *l* [nm]	experimental *d* − 1.4 [nm]
PSS−C8	1.17	1.00
PSS−C10	1.42	1.40
PSS−C12	1.67	1.92
PSS−C14	1.93	2.30
PSS−C16	2.18	2.76

SAXS measurements of the various complexes are shown in Figure 2a. It is obvious from the increase of the scattering intensity that the internal order of the different PSS−C*n* complexes is improved with increasing surfactant chain length. Also, the maxima in the SAXS curves are shifted to a smaller 1/*d* value, which means larger internal dimensions. In Figure 2b, the resulting layer periods *d* in nanometers are plotted versus the number of carbon atoms in the surfactant alkyl chain. A linear dependence is found, leading to the equation d [nm] $= 0.76 + 0.205n$ determined by a last-squares fit with a regression coefficient of 0.998 and standard errors of the *Y*-intercept and the slope being 0.095 and 0.008 nm, shown as a solid line in Figure 2b. If a constant thickness for the ionic layer (polyelectrolyte backbone, ionic headgroups) of 1.4 nm is assumed,[4a,9] the increase in the residual nonpolar layer determines the overall structure. It should be stressed that each hydrophobic layer consists of alkyl residues from two hydrophilic layers due to the internal compartmentation process. Compared to the maximum length of one fully extended surfactant alkyl chain which is given by the Tanford formula $l = 0.15 + 0.127n$,[10] it is obvious from Table 1 that the conformation of the surfactant chains in the nonpolar layer is predominantly interpenetrating or strongly disordered for *n* being 8 and 10. For larger chain lengths, the layer distance is larger than one theoretical all-trans chain, so that the degree of chain interpenetration is reduced and a more ordered chain conformation is present. Since there is no deviation observed from the linear slope in Figure 2b, the presence of undulated structures resulting from frustration effects within the smectic layers[3a] is questionable from our data.

The PSS−C*n* complexes were submitted to various ^{60}Co γ-radiation doses. After irradiation, no visible changes in the material conditions could be detected.

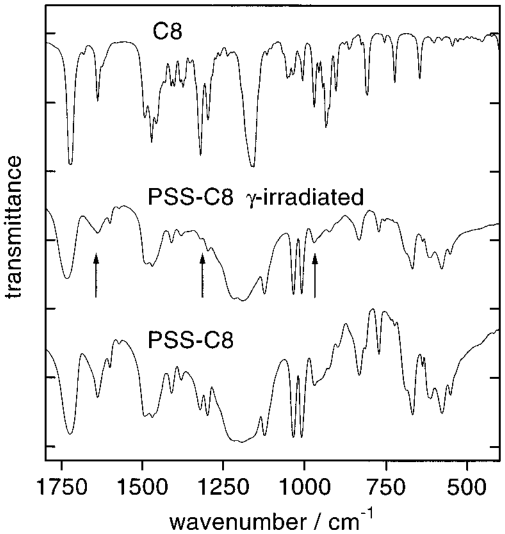

Figure 3. FTIR spectra of (a) C8 before irradiation, (b) the PSS−C8 complex after irradiation with a γ-ray dose of 40 Mrad, and (c) the PSS−C8 complex before irradiation. The arrows indicate changes in characteristic monomer IR bands.

Even after applying 40 Mrad (400 kGy), the samples showed no macroscopic changes, while a blind probe of the pure surfactant (10 wt % in aqueous solution) was completely converted into polymer after a 2 Mrad dose. While the nonirradiated p−s complexes can be swollen in solvents such as *tert*-butyl alcohol or dimethyl sulfoxide, a strongly reduced swelling tendency of the irradiated complexes was observed. This might indicate a successful polymerization of the surfactant monomers within the complex but may also be due to complete dehydration of the ionic layer.[9] WAXS and SAXS measurements did not show any changes in the layer distances as well as in the crystallinity of the complexes. DSC measurements also revealed no changes compared to the nonirradiated material. Since NMR measurements gave no meaningful results due to the low solubility of the samples, FTIR measurements were used in order to examine the molecular effects of the irradiation process. Figure 3 shows FTIR spectra of the monomeric surfactant C8, the PSS−C8 complex after applying a γ-ray dose of 40 Mrad, and the monomeric PSS−C8 complex. It can be seen from the decrease of the C═C valence band at 1630 cm^{-1} and the ═CH$_2$ deformation band at 980 cm^{-1} that the monomer amount in the complex is reduced after γ-irradiation. Also, a substantial decrease of the C−O valence band at 1290 cm^{-1} is observed (see arrows in Figure 3). The relative decrease of all three bands coincides very well and is detectable only at γ-ray doses above 10 Mrad. This gives rise to the assumption that the preferred reaction pathways during irradiation is not the direct polymerization of the surfactant monomers, which should, if possible, proceed much faster, but a decomposition of the monomer molecules. Obviously, the steric confinement is too large to directly build up a polyelectrolyte−polyelectrolyte complex from the monomer complex. One can suppose that a hindrance takes place of the monomer units to reach their neighbor molecules due to the electrostatic repulsion of the surfactant headgroups. The monomeric units might then act as additional short “tails”, so that the probability for a successful polymerization reaction is mostly restricted.

Conclusions and Outlook

It can be concluded that monomeric surfactants can be used to build up polymerizable p−s complexes with controlled mesoscopic properties and internal order. The treatment of the monomer complexes with ^{60}Co γ-radiation in order to initiate polymerization reactions within the smectic liquid-crystalline layers led to no changes in the macro- and mesoscopic properties of the complex materials. Therefore, it is assumed that monomer degradation is the preferred reaction due to the reduced mobility of the monomer units within the complex assembly.

In the future, improved pathways to control architecture and material properties of p−s complexes are of interest. First, surfactant monomers with enhanced flexibility of their monomer units or tail-functionalized monomers may be useful. Increase of the temperature might be another way to promote polymerization. If surfactant chains are long enough to build up steric restriction that leads to crystalline-like order, also solid-state polymerizations may be possible, for example if diacetylene surfactants are used, similar to the polymerization of diacetylene bolaamphiphiles in self-assembled multilayers.[11]

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