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Solid-state Polyelectrolyte Complexes of Branched Poly(ethylenimine) and Sodium Lauryl Sulfate

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Three lamellar phases (two crystalline and one liquid crystalline) were identified by X-ray diffraction, DSC, and polarizing optical microscopy in an ionic complex obtained by precipitation on mixing sodium lauryl sulfate (SLS) and branched poly (ethylenimine) (PEI). One of the crystalline structures, which has an orthogonal, bilayer, orthorhombic (crystal E-like) morphology, is attributed to a small amount of non-complexed, phase-separated SLS. The PEI-SLS complex is characterized by a smectic C bilayer mesophase that is stable up to degradation temperatures, in contrast to the much lower stability of complexes with carboxylate surfactants. It also shows a low degree of crystallinity at lower temperatures, attributed to tail-end crystallization of the complexed side-chains, the crystalline phase having a tilted bilayer lamellar structure with hexagonal packing (F or I-type mesophase). In general, ionic interactions in PEI-surfactant complexes result in nanophase segregation into ionic and alkyl sublayers giving rise to lamellar liquid crystalline structures whose stability depends on the strength of the ionic interactions.

Keywords complexes, polyelectrolytes, amphiphilic surfactants, poly(ethylene imine), sodium lauryl sulfate

Introduction

Complexes of flexible polar or ionizable polymers and polyelectrolytes with amphiphilic surfactants form a novel class of supramolecular materials that exhibit an interesting combination of phase structure and properties (1–5). Such complexes have been extensively studied over the past two decades, especially in solution (1, 5–8) and, increasingly, in the solid-state (see, for example, References 2–5, 9–14). This interest in both solution and

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Address correspondence to Gregory B. Kharas, DePaul University, Chemistry Department, 1036 West Belden Avenue, Chicago, IL 60614, USA. E-mail: gkharas@depaul.edu solid-state systems is driven by their wide range of applications in various technological formulations, such as coatings, inks, adhesives, hair preparations, drug delivery systems, and foodstuffs.

Polyethylenimine (PEI) has been used a number of times in studies of blends of polyelectrolytes and surfactants (6–15), and has most often been obtained from commercial sources (6–13). Whereas the majority of investigations of polyelectrolyte-surfactant complexes have involved linear polymers (2–5, 14, 15), the commercial grades of PEI are highly branched polymers formed by the acid-catalyzed opening of ethyleneimine and containing three different types of amino groups: secondary and tertiary amino groups in the main chain, and secondary and primary amino groups in the side chain. They exhibit high cationic activity when protonated due to a carbon:nitrogen ratio of 2 : 1 and generally have a nitrogen functionality ratio of 1 : 2 : 1 (primary:secondary:tertiary) (6). Of the PEI-surfactant systems studied in the solid-state to date, the surfactant is in the acid-form, carboxylic (9, 11–15) or sulfonic (10). Therefore, the complexation proceeds via proton transfer from the surfactant to PEI to give ion pairs (that may also implicate hydrogen-bonding). It gives rise to ordered supramolecular lamellar structures, often with liquid crystalline characteristics, the details depending on the surfactant used.

In the present study, a complex of branched PEI with an anionic surfactant, sodium lauryl sulfate (sodium dodecyl sulfate) (SLS), is prepared. To promote complexation, the PEI is protonated by the addition of HCl such that ion exchange with elimination of the Na and Cl microions can take place. This should result in ammonium-sulfate ion pairs holding the two components together. The thermal and structural characteristics of the complex are investigated.

Experimental

Materials

Poly(ethylenimine) (PEI), in the form of a 50 wt% solution in water, was obtained from Aldrich. The polymer was reported by the supplier to have an average M_w of ca. 750,000 (light scattering). The surfactant, sodium lauryl sulfate (SLS) (98%, Aldrich), was used without further purification.

Complex Preparation

The PEI-SLS complex was prepared by mixing the desired amount of water solutions of PEI (adjusted to pH 5.2 by the addition of HCl in order to protonate the nitrogens) and SLS at equimolar ratio and a total concentration of $6.3 \cdot 10^{-5}$ mol/L at room temperature. The resulting precipitate was isolated by filtration, washed with water, and dried in vacuum at 60°C until constant weight was achieved.

General Procedures

Thermogravimetric analysis (TGA) was conducted with TA Instruments 2090 TGA from ambient temperature to 1000°C at 20°C/min. Thermal transitions in the complex were measured with a TA Instruments 2010 differential scanning calorimeter (DSC). The thermal scans were performed in the −50 to 200°C range at a heating and cooling rate of 10°C/min. Birefringence in the PEI-SLS complex was observed by a Leitz polarizing microscope equipped with a Mettler FP90 hot stage. The sample was prepared as a thin film between two glass slides. The sample was photographed on the second heating at 140°C. The X-ray diffraction studies were carried out with a Bruker diffractometer (Siemens Kristalloflex 760 generator), using sealed tube Cu Kα (1.542 Å) radiation collimated by a graphite monochromator and a 0.8 mm pinhole; the diffraction pattern was recorded with a Bruker AXS two-dimensional wire-grid detector. The temperature was controlled fairly crudely by a Watlow 988 controller and oven supplied by Bruker. Powdered samples were packed into 1.0-mm diameter Lindemann capillary tubes (Charles Supper Co.).

Results and Discussion

The complex was obtained by ion exchange between ionized PEI (protonated by HCl) and the Na-neutralized surfactant. The Na and Cl microions, along with uncomplexed SLS, is expected to have been washed out during the purification process. Since PEI is strongly associated with SLS through electrostatic interactions, the thermal stability of PEI may be affected by complexation. Figure 1 shows the TGA thermograms of the PEI-SLS complex, PEI, and SLS under nitrogen atmosphere. PEI shows an initial weight loss of a little over 30%, which can be attributed to the loss of bound water (one water molecule per nitrogen corresponding to 30 wt% water) (15). In comparison, the complex shows very little initial weight loss, indicating that it is essentially water-free, as is SLS. The onset of degradation occurs above 200°C for all of the materials, with that for the complex being between those for the two components and just a little higher than for SLS.

The thermal behavior was probed by DSC analysis. The DSC thermogram obtained on second heating of a PEI-SLS complex is shown in Figure 2. It displays several

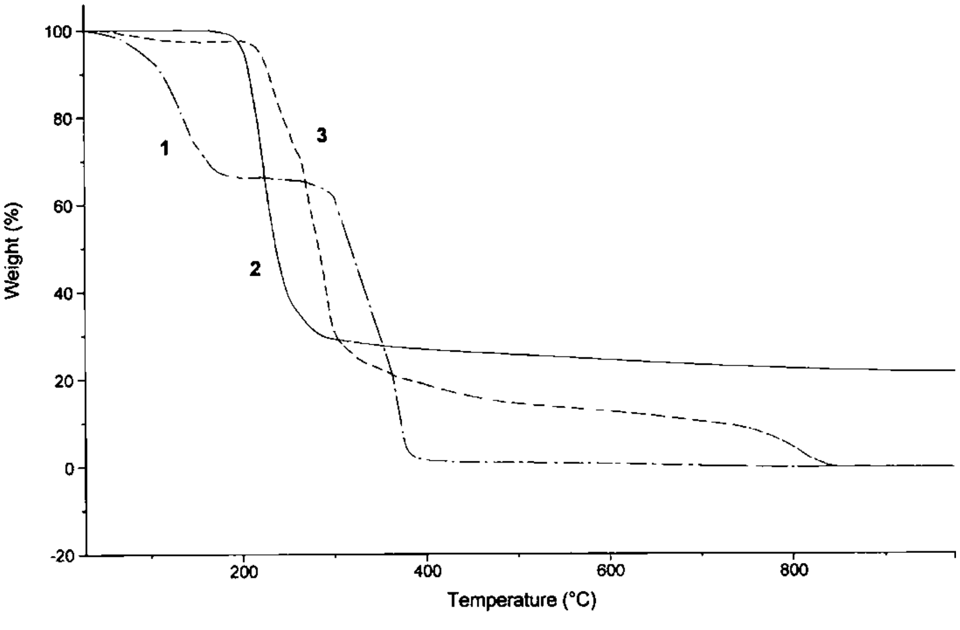

Figure 1. TGA thermograms of PEI (1), SLS (2), and the PEI-SLS complex (3).

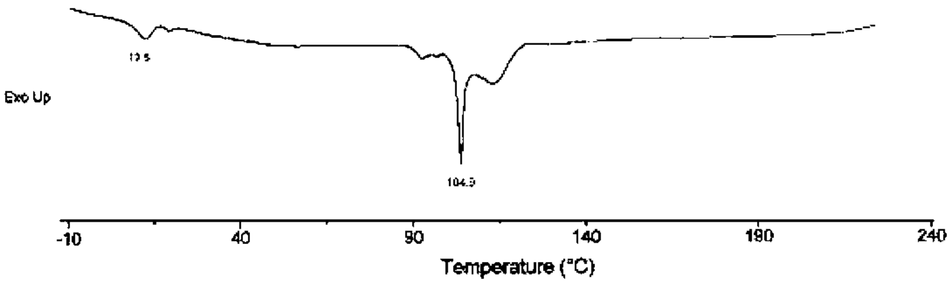

Figure 2. DSC thermograms of a PEI-SLS complex (second heating curves).

endothermic transitions. Low intensity peaks, at 13 and 18°C, are similar to those found for complexes of branched PEI and alkanoic acids (6). Higher intensity transitions lie in the 100–115°C range, with a maximum at 105°C and are related to melting of crystalline phases, as will be shown later. In comparison, the melting point in SLS occurs at much higher temperatures (204–207°C) and PEI is amorphous. Significant supercooling occurs in the cooling curves. Moreover, the number and precise locations of the transitions observed are sensitive to the thermal history of the sample, which was not investigated in detail.

Polarizing optical microscopy shows that the complex softens in the 100–115°C range, confirming that it is a melt region. However, it remains birefringent up to degradation temperatures, indicating anisotropy until degradation. Figure 3 shows a typical micrograph taken at 140°C after shearing the complex between two glass slides. The shearability of the sample after 115°C combined with the birefringence indicates that the complex is liquid crystalline up to degradation.

To probe the structural characteristics of the complex, X-ray diffraction studies were undertaken. Two sets of X-ray diffraction data were obtained, one for a sample aged for several months at ambient temperature in a sealed vial (designated "as received") and one for the same sample redried in a 60°C vacuum oven for 3 days (designated "redried"). These are shown in Figure 4. The evolution with temperature is complex, paralleling the complexity of the DSC data. Three distinct lamellar phases (labeled as L1, L2 and L3), each with three diffraction orders, can be distinguished. After cooling to ambient temperature, the diffractograms are not identical to those obtained initially, as is often observed when comparing melt-crystallized samples with solution crystallized samples.

L1 and L2 are present at ambient temperature in both the "as received" and "redried" samples, but L1 appears dominant in the "as received" sample and L2 appears dominant in the "redried" sample. The corresponding wide-angle region indicates that L1 and L2 are crystalline phases. L1 shows two main diffraction peaks corresponding to about 4.3 and 4.1 Å, respectively (the exact values vary somewhat with temperature), indicative of orthorhombic packing (such as given by a crystal E-type mesophase) and L2 shows a single diffraction peak at about 4.2 Å, indicative of hexagonal packing (such as given by B, F or I-type mesophases) (13, 16). The diffraction peaks are relatively weak and an amorphous halo is also present, indicating a low amount of crystallinity.

Both the L1 and L2 phases fade out as the temperature is increased to the region of the higher temperature DSC transitions (the melt region), and the third lamellar phase, L3, becomes prominent. In fact, L3 is present also at the lower temperatures, particularly

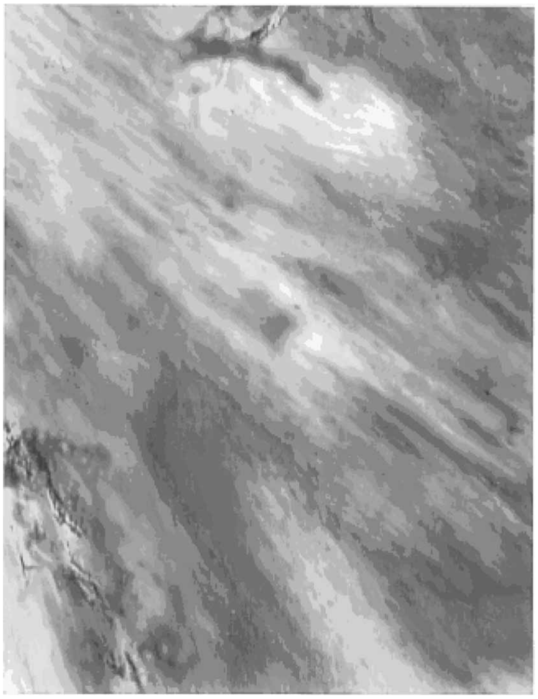

Figure 3. Polarized optical micrograph of a complexed PEI-SLS sample after shearing at 140°C.

apparent through its second-order diffraction peak. It is stable up to the highest temperature recorded, nominally 130°C. This phase gives an amorphous halo at wide angles. Thus, it must be a disordered liquid crystalline phase of the smectic A or C type. (In the "as received" series, the halo is superposed by a very weak peak, indicating a very low amount of crystallinity remaining - possibly the L1 phase, judging from the residual L1 small angle peaks also still present).

The lamellar spacings (Bragg distances) determined by the small-angle peaks are 38 and 32 Å for L1 and L2, respectively, and range from 29 to 32 Å in order of increasing temperature for L3. In comparison, the extended molecular length of lauryl sulfate is about 18 Å. This indicates that all of the lamellar phases above are bilayer structures. L1, at twice the molecular length of the complex repeat unit (PEI-SLS), is a full bilayer structure, and is therefore an orthogonal phase with no interdigitation. This is consistent with the crystal E-like structure suggested by the wide-angle data. L2 and L3 are somewhat less than twice the molecular lengths, which can be rationalized by either tilting of the molecules in the lamellar plane or by partial overlap (interdigitation) of the side chains. In contrast to L1, whose lamellar spacing is almost constant with temperature (it actually decreases slightly with increasing temperature, as is characteristic of orthogonal phases), the lamellar spacing of L2 increases a little and that of L3 increases very noticeably with increasing temperature, a phenomenon which is often associated with tilted phases. Thus, the L2 mesophase can be thought of as a bilayer F or I mesophase (although a partly interdigitated orthogonal bilayer B mesophase cannot be definitively excluded), whereas that of L3 may be concluded to be a smectic C mesophase.

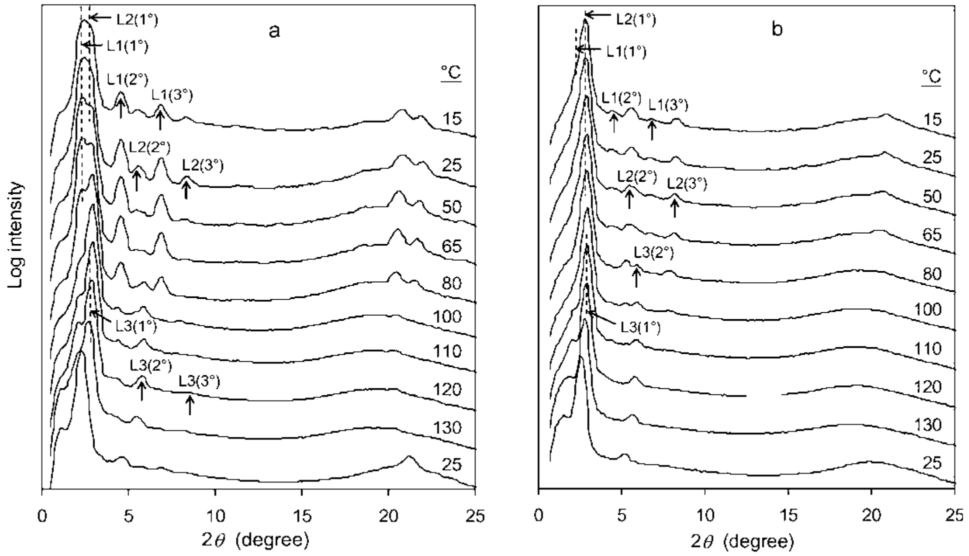

Figure 4. X-ray diffractograms for (a) the "as received" sample and (b) the "redried" sample at the nominal temperatures indicated, taken in order from top to bottom. The labels L1, L2 and L3 indicate three different lamellar phases (see text for details), with the number in brackets identifying the diffraction order. The arrows identifying second and third-order peaks are indicated for representative curves only.

It is not uncommon for comb-like polymers to be polymorphic, and display more than one crystal structure (see, for example, Reference 16 and references therein). This was also reported for PEI-octadecanoic acid complexes, where the crystal structure was shown to depend on the molar ratio of the components (13, 14). In other PEI-surfactant complexes studied (involving n-alkyl carboxylic acids of 12 carbons or greater, those of shorter chains showing no crystallization), only the tilted hexagonal structure was observed (11, 12).

On the other hand, it is unusual that two crystalline structures exist simultaneously outside of the transition range. Furthermore, it is noted that pure SLS gives an X-ray diffraction pattern almost identical to that of the L1 structure (17). This suggests that the sample may contain uncomplexed SLS, supported by elemental analysis indicating the presence of a small amount of Na (1.4%). In this case, it can be concluded that the complex itself is characterized by the L2 structure at lower temperatures and the smectic C structure at higher temperatures, whereas the L1 structure results from phase-separated, uncomplexed SLS (with the relative weakness of the wide-angle peaks associated with the L1 structure indicating low amounts).

The partial crystallinity in the complex (L2 structure) is consistent with what is frequently observed in side-chain polymers and complexes with sufficiently long side-chains. This has been attributed to crystallization of the side-chain tail-ends (15, 16). The weakness of the wide-angle peak associated with the L2 structure in the complex of the present study is consistent with the SLS having a side-chain length that is just beyond the minimum required to permit tail-end crystallization (12).

As final remarks, it should be mentioned that a smectic A or C mesophase was identified in various PEI-surfactant complexes studied previously (9–12). Reference 9 showed that PEI complexes with short-chain alkyl carboxylates ($\leq$12 carbons) possess a bilayer smectic A mesophase, whereas the longer chain complexes possess a bilayer smectic C mesophase. It is noteworthy that the surfactant of the present complex, which, as we just concluded, also shows a bilayer smectic C, has a total length that falls in the range of the longer chain complexes of reference 9. Reference 9 also showed that the isotropization temperatures of the alkyl carboxylate-PEI complexes are relatively low (ranging from 40 to 120°C for 6- to 18-carbon carboxylates). This contrasts with the much greater mesophase stability of the sulfate complex of the present study (up to degradation), observed also for a PEI-dodecylbenzenesulfonate complex (10). This may be ascribed to the much stronger ionic interactions of the latter.

Conclusions

Three phases with lamellar morphology were identified by DSC, polarizing optical microscopy and X-ray diffraction in the ionic complex obtained by precipitation on mixing sodium lauryl sulfate (SLS) and branched poly(ethylenimine) (PEI) ionized by HCl. The thermal behavior is correspondingly complex. One of the crystalline structures, which has an orthogonal, bilayer, orthorhombic (crystal E-like) morphology, is attributed to a small amount of non-complexed, phase-separated SLS. In this case, it can be concluded that the PEI-SLS complex is characterized by a very low degree of crystallinity at lower temperatures, giving what appears to be a tilted bilayer lamellar structure with hexagonal packing (F or I-type mesophase), attributed to tail-end crystallization of the side-chains, and a smectic C bilayer mesophase that is stable until degradation temperatures. Other long-chain PEI-surfactant complexes studied in the literature likewise display a crystalline phase at lower temperatures in addition to a liquid crystalline (smectic A or C) phase. Compared to surfactants with carboxylate groups, the sulfate (like the sulfonate) surfactant gives rise to a much more stable liquid crystalline mesophase, existing up to degradation temperatures. This can be attributed to the stronger ionic interactions of the latter. In all cases, the ionic interactions in the PEI-surfactant complexes result in nanophase segregation into ionic and alkyl sublayers, giving rise to a lamellar liquid crystalline structure whose stability depends on the strength of the ionic interactions.

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