VOLUME 31 NUMBER 12

ACCOUNTS of CHEMICAL RESEARCH®

DECEMBER 1998

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Self-Assembled Polyelectrolyte−Surfactant Complexes in Nonaqueous Solvents and in the Solid State

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Received November 17, 1997

Introduction

The central goal of macromolecular synthesis is preparation of materials with tailored macroscopic properties. With increasing frequency, synthetic strategies not only address the formation of requisite covalent bonds, but also utilize the capability of molecules to self-organize. Self-assembly is defined as spontaneous intermolecular association via noncovalent bonds (e.g., electrostatic interactions, hydrogen bonds, or hydrophobic interactions), resulting in thermodynamically stable, well-defined supramolecular structures with dimensions ranging from 10 nm to 10 μm.[1,2] Self-organizing systems are widely represented in nature, e.g., double-helical structures of nucleic acids and bilayers of lipids within cell membranes, with organization and intimately linked function.[3,4] Assembly through noncovalent interactions offers a number of advantages over chemical synthesis involving formation of covalent bonds: it does not require complicated preparative procedures, the reactions are typically fast,[5] and the resulting structures may be capable of reversible adaptive rearrangement in response to changes in environment (e.g., solvent or temperature). Control over organization of synthetic supramolecular structures by tuning the assembly processes opens fascinating possibilities in the manipulation of materials properties on the molecular scale. This may be particularly important for fabrication of multifunctional materials for technological applications where precise control of properties is essential, e.g., electronic devices, microsensors, separation membranes, catalysts, and biomaterials.

Among the best-known synthetic self-assembling polymeric systems are complexes of charged polymer chains (polyelectrolytes) and oppositely charged small amphiphilic molecules (surfactants) consisting of a polar "headgroup" and a nonpolar "tail".[6] The complexation process is an ion-exchange reaction driven by electrostatic attraction between the polymer chain units and the surfactant ions. Several major types of polyelectrolyte−surfactant complexes are described in the literature. Complexes of the first type are formed at the air−water interface if an amphiphile is spread on an aqueous solution of an oppositely charged polyelectrolyte.[7−12] Complexation occurs at the water surface and results in monolayer films considerably more stable than those of the amphiphile alone.[7,11,13] Complexes of another class are prepared by successive adsorption of a surfactant

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10.1021/ar960309g CCC: $15.00 © 1998 American Chemical Society
Published on Web 09/04/1998

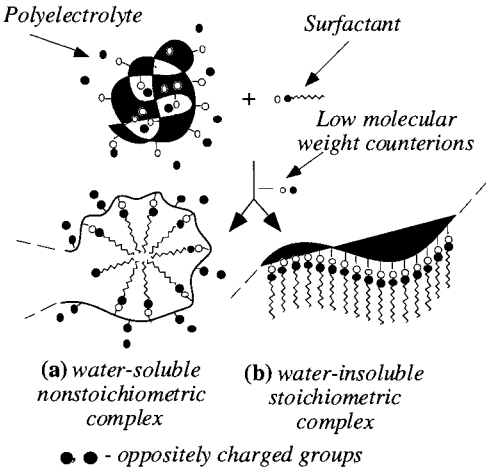


FIGURE 1. Scheme of formation of polyelectrolyte−surfactant complexes in aqueous solutions.

(typically with two headgroups separated by a nonpolar linker) and a polyelectrolyte on a solid substrate, resulting in multilayer films.[14−16] Complexes of the third type consist of polyelectrolytes with flexible chains and oppositely charged small amphiphiles with mesogenic groups, prepared by mixing solutions of the two components in polar organic solvents.[17−19] Such complexes exhibit liquid crystalline mesophases characteristic of the bound amphiphile, while the polymer chains enhance the thermal stability of the ordered structures.

Complexes of polyelectrolytes and oppositely charged surfactants with aliphatic chains are formed spontaneously if dilute aqueous solutions of the two components are mixed.[6,20,21] The complexation reaction occurs at concentrations considerably lower than the critical micelle concentration (CMC) of the surfactant, and is highly cooperative. The electrostatic driving force for complexation is reinforced by hydrophobic self-association of the surfactant chains in water.

Depending on the polymer to surfactant ratio in aqueous solution, the complexes formed are either stoichiometric or nonstoichiometric[6,20] (Figure 1). Nonstoichiometric complexes containing an excess of either charged polymer chain units or surfactant molecules are generally soluble in water. The formation and structure of water-soluble polyelectrolyte−surfactant complexes containing an excess of polyelectrolyte chain units have been studied in detail.[6,20] Such complexes form "mixed micelles" consisting of clusters of hydrophobic surfactant chains surrounded by the polar polyelectrolyte backbone (Figure 1a). An interesting property of such clusters is their ability to solubilize nonpolar organic molecules in water solutions, which has a number of technological applications.[6]

If equimolar amounts of charged polymer chain units and surfactant molecules are mixed in water, stoichiometric complexes are formed (Figure 1b). Such complexes are insoluble in water. Until recently, the interest in water-insoluble polyelectrolyte−surfactant complexes has been limited; however, the discovery that such complexes can be soluble in organic solvents has dramatically increased interest in this area.[22−24] The simplicity of synthesis of stoichiometric polyelectrolyte−surfactant complexes, their solubility in nonaqueous solvents, and the wide variety of available polyelectrolytes and surfactants provide attractive opportunities for preparation of materials with adjustable macroscopic properties.

Stoichiometric polyelectrolyte−surfactant complexes can be viewed as a new type of comb-shaped polymer, in which every polymer chain unit has an electrostatically bound "side chain". Such complexes combine in unique ways the properties of polymers with those of low molecular weight amphiphiles. The polymeric components can provide, for example, mechanical strength and thermal stability, while the surfactants retain their tendency to assemble in layered structures and their ability to crystallize. Research efforts in the area of water-insoluble polyelectrolyte−surfactant complexes have been focused both on understanding the influence of the electrostatically attached side chains on properties of the polymer chains (e.g., solubility and conformation) and on the effect of the polymer chain on the organization of the complexed surfactants.

To date, water-insoluble complexes containing two types of polymers have been investigated: conventional synthetic polyelectrolytes with flexible chains[23−33] and charged synthetic polypeptides.[34−37] In this Account, we will discuss the properties of water-insoluble complexes formed by charged polymers and oppositely charged amphiphilic molecules with aliphatic chains. We will present an overview of the large variety of structures and properties exhibited by such complexes and their possible applications.

Polyelectrolyte−Surfactant Complexes in Nonaqueous Solutions

Complexes of Conventional Polyelectrolytes. In order to understand the solution properties of polyelectrolyte−surfactant complexes, it is important to realize that they are amphiphiles, consisting of a nonpolar, hydrophobic part (the surfactant alkyl chains) and a polar part (the ionic groups of the polymer and the surfactant). The presence of structural elements of opposite polarity and, therefore, of different solubility allows one to manipulate the solution properties of the complexes, including the solubility and the conformation of the polymer chains.

Stoichiometric complexes are insoluble in water because the ionic groups of polyelectrolyte and surfactant are shielded from solvent by the nonpolar parts of the complex. However, stoichiometric complexes formed by polyelectrolytes with hydrophobic side chains[22] or even simple synthetic polyelectrolytes[23,24,26,27] (e.g., poly(styrenesulfonate) or poly(methacrylic acid)) and oppositely charged single- or double-chain surfactants can be soluble in organic solvents. In solvents of low polarity (e.g., benzene, chloroform, or dichloroethane), the complexes are soluble without dissociation, as shown by the linear dependence of the reduced viscosity on concentration in dilute solutions.[26] In solvents of higher polarity (e.g.,

dimethylformamide, ethanol, or isopropyl alcohol), the complexes dissociate in part into polyelectrolyte and surfactant ions, as indicated by a nonlinear increase in solution viscosity with dilution.[27]

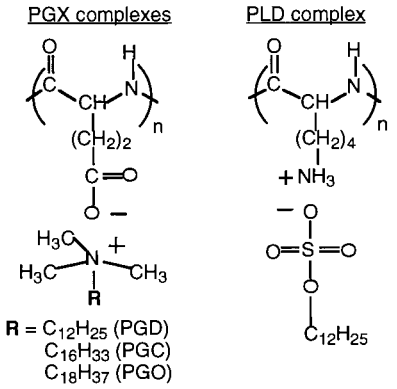
The conformational properties of polymer chains in polyelectrolyte−surfactant complexes in nonaqueous solutions have been investigated both theoretically[38] and experimentally.[26] Polymer conformation in complexes of conventional polyelectrolytes and surfactants in organic solvents is governed by two main factors: dipole−dipole interactions between ion pairs and steric interactions of the surfactant chains. Theory predicts a considerable stiffening of a flexible polymer backbone upon complexation with surfactants (at complex compositions close to stoichiometric), owing to crowding of bound surfactant chains. In a good solvent for the surfactant chains, the complex is described as a semiflexible rod, with the persistence length considerably exceeding the diameter of the rod. On the basis of calculations of the stiffness of polymer chains in such complexes, theory predicts formation of liquid crystalline phases in solution.[38a]

However, experimental studies of complexes of poly(*N*-ethyl-4-vinylpyridinium) cations and dodecyl sulfate anions in dilute solutions in low-polarity solvents suggest that the conformation of the polyelectrolyte chains in the complex is that of a flexible coil, on the basis of the value of the Huggins constant of 0.25 and the persistence length of about 5 nm, estimated from viscometry and flow birefringence data, respectively.[26]

Complexes of Synthetic Polypeptides. Most work in the area of water-insoluble polyelectrolyte−surfactant complexes has been concerned with complexes of conventional synthetic polyelectrolytes and low molecular weight amphiphiles. However, biopolymers may offer special advantages in the development of new polymer−surfactant complexes with useful properties. An attractive feature of polypeptides is their ability to form ordered secondary structures, the most common being the α-helix and the β-sheet.[39] The α-helix is stabilized by hydrogen bonds connecting amino acid residues along the helical axis, and the helical conformation confers rodlike character on the molecule.[40] β-Sheets are formed by nearly extended segments of polypeptide chains connected by lateral hydrogen bonds. Control over formation and disruption of hydrogen bonds (e.g., by solvent or temperature) may allow manipulation of polypeptide chain conformation and the related material properties.

We have been interested for some time in water-insoluble polyelectrolyte−surfactant complexes, consisting of synthetic homopolypeptides, specifically poly(α-L-glutamic acid)[35,36] and poly(L-lysine),[37] and single-chain surfactants (Chart 1). In order to gain an understanding of the role of noncovalent interactions in defining the polypeptide chain conformation and the supramolecular structure of the complexes, we have compared the behavior of these complexes to that of their covalent analogs—synthetic polypeptides with covalently attached

Chart 1. Polypeptide−Surfactant Complexes



side chains, e.g., the alkyl esters of poly(α-L-glutamic acid) (PALGs) and poly(L-lysine)s bearing acyl side chains (PALLs).

(1) Solubility in Organic Solvents. The solubility of polypeptide−surfactant complexes in organic solvents is governed by their amphiphilic properties and by the conformation of the polypeptide chains. Owing to the presence of polar groups in every chain unit, the range of low-polarity solvents for the complexes is greatly reduced compared to their covalent analogs. Poly(α,L-glutamate)-based complexes, which are predominantly α-helical in the solid state, are soluble in chloroform and a variety of more polar solvents, including benzyl alcohol, methanol, and dimethylformamide.[36] The solubility behavior of the corresponding esters of poly(α-L-glutamic acid) is quite different: PALGs are soluble in most common organic solvents, including *n*-alkanes and aromatic hydrocarbons,[40] which are nonsolvents for the complexes. Poly(L-lysine)-based complexes, which are in the β-sheet conformation in the solid state (when isolated after synthesis), are insoluble in most common organic solvents.[37] However, such complexes are soluble in mixtures of organic solvents of low polarity ($\epsilon = 2-6$) with small amounts (at least 1−2 vol %) of a solvent capable of breaking the interchain hydrogen bonds, e.g., trifluoroacetic acid (TFA). Dilute solutions of the complex formed between poly(L-lysine) and dodecyl sulfate (PLD) in chloroform−TFA mixtures have been extensively investigated.[37]

(2) Conformational Transitions in Solutions. Investigation of the solution properties of polypeptide−surfactant complexes has shown many similarities to the behavior of the covalent analogs of the complexes.

First, in dilute chloroform−TFA solutions, the PLD complex neither dissociates into polyelectrolyte chains and surfactant ions nor forms interchain aggregates, as indicated by viscometry.[37] The reduced viscosity depends linearly on the concentration of the complex (Figure 2). Depending on the TFA content of the chloroform solutions, the conformation of the PLD chains can be either a rigid rod or a flexible coil, as shown by the values of the Huggins constants (K) estimated from the slopes of the viscosity vs concentration lines. At low content of TFA (1 vol %) (Figure 2, curve a), the chains are rigid ($K = 0.12$);

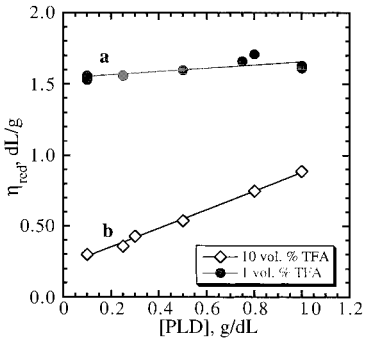


FIGURE 2. Concentration dependence of reduced viscosity of the PLD complex in chloroform solutions containing 1 vol % (a) and 10 vol % (b) trifluoroacetic acid.

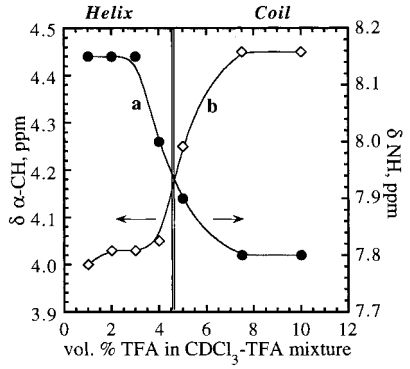


FIGURE 3. Dependence of the positions of the NH (a) and α-CH (b) resonances of the PLD complex on the trifluoroacetic acid content in deuterated chloroform solutions. Concentration of PLD solutions 10 mg/mL.

at high TFA contents (10 vol %), the chains are flexible (K = 0.66) (Figure 2, curve b).

Second, the polypeptide chains in the PLD complex can adopt ordered conformations in solution,[37] similar to the alkyl esters of poly(α-L-glutamic acid)[40] and to the poly(L-lysine) with acyl side chains.[41−43] Evidence for the ordered conformation is provided by ^{1}H NMR spectroscopy. At low TFA contents in chloroform solutions of the PLD complex, the α-CH and NH resonances of the complex are observed at 4.00 and 8.15 ppm, respectively, consistent with hydrogen-bonded (α-helix or β-sheet) conformations of the polypeptide chains (Figure 3). We believe that the poly(L-lysine) chains are in the α-helical conformation, considering the absence of aggregation in dilute solutions and the known propensity of β-sheets to aggregate in solution. PALLs and PALGs also adopt α-helical conformations in organic solvents, if no TFA is added.[40−43]

Third, the helix−coil transition of the polypeptide chains in the complex can be induced by adding a solvent capable of breaking hydrogen bonds, similar to other polypeptides.[40] An increase in the TFA content of chloroform solutions of the complex results in an upfield shift of the NH resonances, and a downfield shift of the α-CH resonances (Figure 3), consistent with disruption of hydrogen bonds and formation of a disordered conformation of the polypeptide.[37] The shifts in the proton resonances of the poly(L-lysine) backbone upon addition

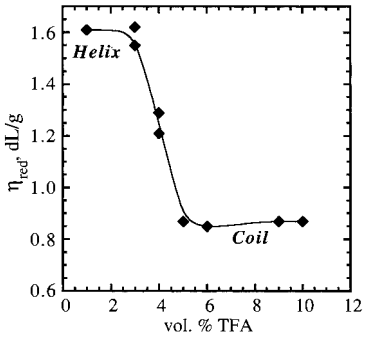


FIGURE 4. Dependence of reduced viscosity on the trifluoroacetic acid content in chloroform solutions of the PLD complex. Concentration of PLD solutions 10 mg/mL.

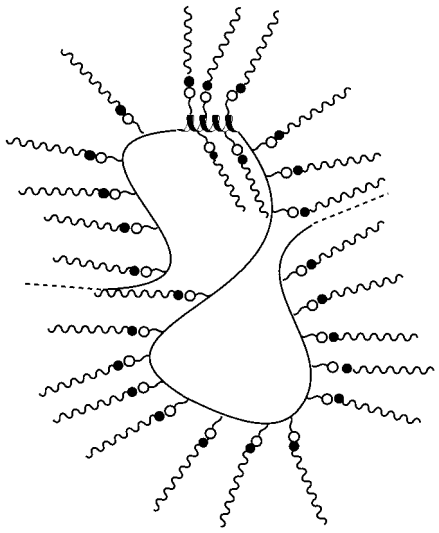


FIGURE 5. Schematic representation of the structure of the PLD complex in dilute chloroform solutions containing about 10 vol % trifluoroacetic acid.

of TFA coincide with an abrupt decrease in viscosity of the PLD solution between 4 and 6 vol % TFA (Figure 4). In PALLS with similar side chains, the helix−coil transition requires addition of 20−30 vol % TFA.[43] The lower stability of the of α-helix of the PLD complex toward addition of TFA can be explained by the repulsive dipole−dipole interactions between polar groups of the complex, which destabilize the intrachain hydrogen bonds of the helical conformation.

Correlation between the conformation of the PLD chains in chloroform−TFA solutions and segmental mobility was studied by measuring the proton spin−lattice relaxation times of the poly(L-lysine) backbone and the dodecyl sulfate chains.[37] The helix−coil transition of the PLD chains is accompanied by an increase in the mobility of the poly(L-lysine) segments, consistent with disruption of intramolecular hydrogen bonds. However, the mobility of the side chains remains unchanged. These results suggest that in the α-helical conformation, as well as in the disordered conformation of the polypeptide, the side chains are exposed to solvent, shielding the polypeptide backbone and the ionic groups (Figure 5). The structure of the stoichiometric complex in the disordered conformation in chloroform−TFA mixtures appears to be quite

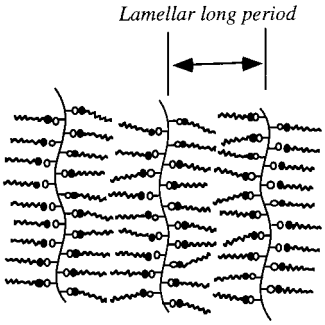


FIGURE 6. Scheme of a typical lamellar structure of a stoichiometric polyelectrolyte−surfactant complex in the solid state.

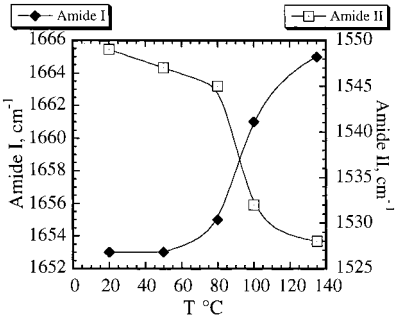


FIGURE 7. Temperature dependence of the frequencies of the amide I and amide II vibrations in the infrared spectra of PGD films.

different from that of nonstoichiometric polyelectrolyte−surfactant complexes in water, in which the polymer is exposed to solvent, shielding the surfactant chains[6] (Figure 1a).

Polyelectrolyte−Surfactant Complexes in the Solid State

Complexes of Conventional Polyelectrolytes. The solid state organization of complexes of flexible chain polyelectrolytes and oppositely charged surfactants is dominated by the tendency of the amphiphilic molecules to assemble in layered structures. Complexes formed by linear[24,28,30,31] or cross-linked[44] polyelectrolytes and oppositely charged single- or double-chain surfactants spontaneously adopt lamellar structures, consisting of alternating layers of polymer chains separated by layers of surfactant (Figure 6). The long period of the lamellae depends on the organization of the surfactant molecules within the layers, which is governed by alkyl chain length and chemical structure of the amphiphile. Surfactants with shorter chains (fewer than 16 carbon atoms) are typically disordered in the complexes,[24,32,44] while surfactants with longer chains (at least 16 carbon atoms) can crystallize in the complex.[44] In complexes of cross-linked polymethacrylate anions and hexadecyltrimethylammonium cations, the surfactant chains crystallize on a hexagonal lattice.[44] Surfactant crystallites in the complex are considerably smaller than those of the uncomplexed surfactants, as indicated by their lower melting temperatures. For complexes of poly(styrenesulfonate) with alkyltrimethylammonium surfactants, no crystalline order was observed for chains with up to 18 carbon atoms.[24,32] These data suggest that the polyelectrolyte chains impose restrictions on surfactant chain packing that decrease the tendency of the surfactant to form ordered structures.

Mechanical properties of polyelectrolyte−surfactant complexes have been shown to depend on the chemical structure of the amphiphile.[31] Complexes with double-chain surfactants in the amorphous state can exhibit mechanical properties similar to those of high-performance rubbery polymers, with elastic moduli in the range of 20−200 MPa.[29]

Stoichiometric polyelectrolyte complexes can be processed easily by casting from organic solvents. Melt processability is limited. The high density of ionic groups results in a high glass transition temperature (T_g), which exceeds the temperature of decomposition. An interesting approach to decreasing T_g by complexing surfactants with copolymers of ionic and nonionic monomers has been reported.[30] However, a significant reduction in T_g of complexes of alkyltrimethylammonium surfactants with polyacrylic acid was only observed at high contents of *N*-alkylacrylamide (80 wt %) in the copolymer.

Complexation of polyelectrolytes with surfactants capable of reversible structural rearrangement has been used to prepare membranes with controlled permeability. Membranes with permeability switched by small electric fields have been prepared from complexes of poly(styrenesulfonate) with viologen-containing dialkyl sulfates, in which the temperatures of the liquid−solid transitions of the alkyl chains can be controlled by redox reactions of the headgroups.[45,46]

Complexes of Synthetic Polypeptides. (1) Conformation of Polypeptide Chains. The capacity of polypeptides to adopt ordered secondary structures provides additional control over the properties of polyelectrolyte−surfactant complexes. In complexes based on poly(α-L-glutamate), the polypeptide chains are predominantly in the α-helical conformation at room temperature. Circular dichroism spectra of chloroform-cast films of the complexes exhibit a positive band at about 190 nm and two negative bands at 210 and 220 nm, as observed in the spectra of the alkyl esters of poly(α-L-glutamic acid) in the α-helical conformation.[36] FTIR spectra of the complexes are also consistent with the α-helical conformation (amide I and amide II vibrational modes are observed at 1653 and 1549 cm^{-1}, respectively, Figure 7). As the temperature is increased, the amide I band shifts to higher frequency and the amide II band shifts to lower frequency (Figure 7), indicating disruption of hydrogen bonds and a transition to a disordered conformation.[36] The conformational changes are completely reversible on cooling. Similar effects for the amide I and amide II bands have been observed for the benzyl ester of poly(α-L-glutamic acid) (PBLG).[36] However, the shifts in the amide I and amide II band positions with temperature are much less pronounced for PBLG than for the complex of poly(α-L-glutamate) anions with dodecyltrimethylammonium cations (PGD), in the temperature range studied. The lower stability of the α-helical conformation in the complex compared to the covalent analog is attributed to the repulsive dipole−dipole interactions in the complexes,

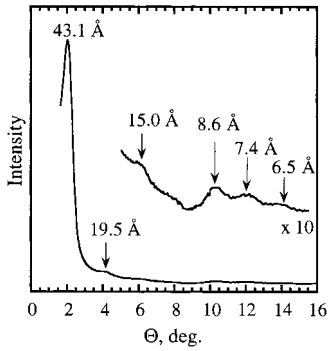


FIGURE 8. Small-angle X-ray diffractometer trace of the PLD powder.

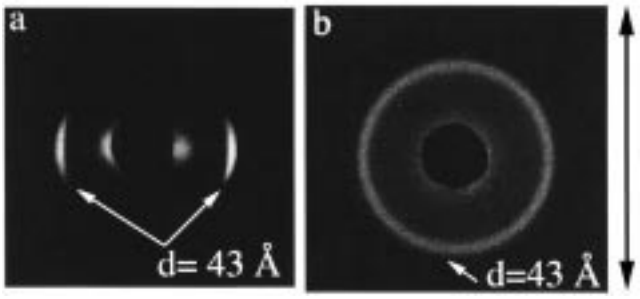


FIGURE 9. SAXD patterns of the PLD films cast from chloroform solutions containing 1 vol % (a) and 10 vol % (b) trifluoroacetic acid. The X-ray beam was parallel to the plane of the films. The arrow indicates the orientation of the film.

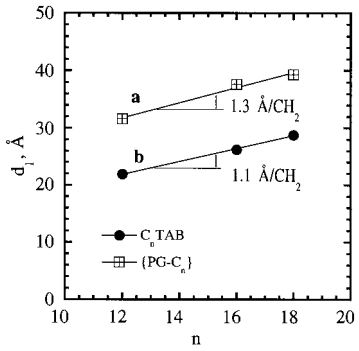


FIGURE 10. Dependence of the long period of the lamellae of the complexes (a) and of the corresponding surfactants (b) on the number of carbon atoms (*n*) in the surfactant chains.

which destabilize the helix and render the intramolecular hydrogen bonds more susceptible to thermal disruption.

In contrast to the poly(α-L-glutamate) complexes, which are α-helical at room temperature, poly(L-lysine) complexes can adopt either β-sheet or α-helical conformations in the solid state. In the powder form of the PLD complex as isolated after synthesis, the poly(L-lysine) chains adopt a β-sheet conformation, as shown by the positions of the amide I and amide II vibrations in the FTIR spectrum[47] (observed at 1629 and 1534 cm^{-1}, respectively). Poly(L-lysine) also adopts a β-sheet conformation in complexes with negatively charged lipids[34] and in the protonated form in the solid state.[47−49] However, covalent analogs of the PLD complex (PALLs) are α-helical in solid samples.[50] Casting of films from chloroform−TFA mixtures in which the poly(L-lysine) chains are disordered yields complexes in which the polypeptide chains are predominantly α-helical, as shown by the characteristic circular dichroism spectra.[51]

(2) Supramolecular Structure. Stoichiometric polypeptide−surfactant complexes adopt lamellar structure, similar to those of conventional polyelectrolyte−surfactant complexes.[34−37] A typical small-angle X-ray diffraction (SAXD) pattern consists of a relatively sharp peak of high intensity and several peaks of low intensity (Figure 8).[37] For the PLD complex, the ratios of the Bragg spacings are 1:1/2:1/3:1/5:1/6:1/7, indicating a lamellar structure. The long period of the lamellae does not depend on the conformation of the polypeptide chains, but the lamellar orientation is different for different conformations. Figure 9 presents SAXD patterns of the PLD films obtained with the X-ray beam directed perpendicular to the planes of the films. For films cast from chloroform containing 1 vol % TFA (where the polypeptide chains are predominantly in the β-sheet conformation), the reflections corresponding to the lamellar spacings are equatorial, indicating anisotropic orientation of stacks of the lamellae within the film (Figure 9a). At high TFA content (when the polypeptide chains are in the α-helical conformation in the solid state), the films are characterized by isotropic orientation of stacks of lamellae (Figure 9b).

All poly(α-L-glutamate) complexes studied to date possess similar lamellar structures. This is shown by the dependence of the lamellar spacing on the surfactant chain length[35,36] (Figure 10, curve a). The slope of the dependence is equal to projection of the C−C bond along the molecular axis in the fully extended alkane chain (1.3 Å per CH_2 group), suggesting that the surfactant chains in the complexes are nearly fully extended, interdigitated, and perpendicular to the lamellar surface. For the pure alkyltrimethylammonium bromides, in which the surfactant chains are tilted with respect to the lamellar surfaces, the increment of the lamellar thickness is about 1.1 Å per CH_2 group (Figure 10, curve b).

(3) Organizafion of Surfactant Chains. The organization of the surfactant chains in the polypeptide−surfactant complexes is similar to that in the complexes of conventional polyelectrolytes. In the poly(α-L-glutamate)-based complexes, two types of surfactant organization were observed: shorter chains consisting of 12 and 16 carbon atoms are positionally disordered, as shown by the wide-angle X-ray diffraction (WAXD) pattern characterized by a broad halo centered at a spacing of 4.6 Å (Figure 11, curve a).[36] The longer chains of 18 carbon atoms partially crystallize on a hexagonal lattice, as indicated by a relatively sharp WAXD peak with a Bragg spacing of 4.2 Å, superimposed on a halo centered at 4.6 Å (Figure 11, curve b).[35] The degree of crystallinity of the PGO side chains estimated on the basis of the WAXD data was about 30%.

The crystallization behavior of the surfactant chains in the polyglutamate-based complexes is different from that of their covalent analogs—alkyl esters of poly(α-L-glutamic acid). The minimum number of carbon atoms in the side chain required for crystallization is 10 in the case of the

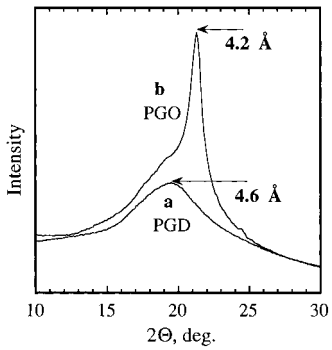


FIGURE 11. Wide-angle X-ray diffractograms of PGD (a) and PGO (b) powders.

PALGs[52] and 16 for the known complexes of conventional synthetic polyelectrolytes and oppositely charged surfactants. It is likely that, in the polypeptide−surfactant complexes discussed herein, the α-helical polymer backbone combined with the bulky headgroups of the surfactants imposes additional restrictions on alkyl chain packing and increases the minimum crystallization chain length.

The PGO complex with crystalline side chains undergoes a first-order transition on heating at 48 °C.[35] This transition correlates with considerable broadening of the WAXD peak of the complex and is attributed to the melting of the side chain crystallites. No thermal transitions were observed for the PGD and PGC complexes in the temperature range 0−170 °C, consistent with the observation of only broad halos in the WAXD patterns of the complexes. Thermal behavior of the poly(α-L-glutamate)-based complexes is dramatically different from that of their covalent analogs. PALGs with crystalline side chains undergo two first-order transitions on heating. The first transition corresponds to the melting of the side chain crystallites and transformation of the lamellar organization of the α-helical poly(α-L-glutamate) chains to a hexagonal packing, and the second transition corresponds to the formation of liquid crystalline melts with a cholesteric order. The absence of liquid crystalline melts for the PGO complex can be related to the strong preference of the bound surfactant chains to organize in layers, prohibiting reorganization of the polypeptide chains upon heating.

Concluding Remarks

We discussed stoichiometric water-insoluble complexes of polyelectrolytes and oppositely charged small amphiphilic molecules. Such complexes are readily synthesized by mixing equimolar amounts of the aqueous solutions of the two components. The simplicity of synthesis of such complexes, combined with the availability of a large variety of polyelectrolytes and surfactants, provides opportunities for the preparation of structures tailored to specific applications. Polyelectrolyte−surfactant complexes combine the properties of their components, such as polymeric nature and properties of low molecular weight amphiphiles, which makes them particularly promising as materials for molecular composites, separation membranes, solubilization, and compatibilization. At the same time, the complexes assembled through electrostatic interactions are individual compounds, which can exhibit properties characteristic of their covalent analogs.

We thank Professor A. B. Zezin (Department of Polymer Science, Moscow State University, Moscow, Russia) and Dr. K. N. Bakeev (International Specialty Products) for helpful discussions in the course of the research. The assistance of Dr. A. J. Waddon with the X-ray experiments and Dr. L. Charles Dickinson (both Polymer Science and Engineering Department, University of Massachusetts) with the interpretation of the NMR relaxation data is gratefully acknowledged. This work was supported by the NSF Materials Research Science and Engineering Center at the University of Massachusetts and the National Science Foundation (Grant DMR 9311658).

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AR960309G