Self-Assembled Complexes of Synthetic Polypeptides and Oppositely Charged Low Molecular Weight Surfactants. Solid-State Properties

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ABSTRACT: Solid-state properties of the stoichiometric complexes formed by sodium poly(α,L-glutamate) and oppositely charged low molecular weight surfactants (alkyltrimethylammonium bromides) were examined by circular dichroism, infrared, and X-ray diffraction techniques. The polypeptide chains in the complexes were shown to be predominantly in the α-helical conformation at room temperature. At higher temperatures, weakening or disruption of intramolecular hydrogen bonds stabilizing the α-helical conformation was observed. The polypeptide−surfactant complexes were shown to adopt lamellar structures in the temperature range 20−150 °C. The lamellae consist of alternating layers of polyglutamate chains and bimolecular layers of surfactant, with the surfactant alkyl chains aligned perpendicular to the lamellar surfaces and interdigitated.

The concept of self-assembly has attracted considerable interest in the last decade in polymer science,[1−11] and assembly processes based on electrostatic interactions,[2−4] formation of hydrogen bonds,[5−8] or charge transfer[9−11] have been shown to lead to spontaneous formation of ordered structures in solution or in the solid state. Assembly through noncovalent interactions offers advantages over chemical synthesis in that it does not involve complicated preparative procedures, equilibrium structures can often be realized, and adaptive rearrangement of the structure may be possible if the external conditions (e.g., solvent or temperature) are changed.

Among the best known self-assembling polymeric systems are complexes consisting of synthetic polyelectrolytes and oppositely charged low molecular weight amphiphilic molecules. These complexes are formed spontaneously if dilute aqueous solutions of the two components are mixed (see, for example, refs 12−14), and assembly involves electrostatic interactions between the polymer chain units and oppositely charged amphiphiles as well as hydrophobic self-association of the surfactant. If equimolar amounts of charged polymer chain units and surfactant are used, the stoichiometric complexes precipitate from water. Stoichiometric complexes consisting of hydrophobically modified polyelectrolytes and double chain surfactants,[15] as well as complexes formed by conventional polyelectrolytes and oppositely charged amphiphilic molecules,[16,17] can be redissolved in some common organic solvents of low polarity ($\epsilon = 4-10$) without dissociation. Solubility of stoichiometric polyelectrolyte−surfactant complexes in relatively polar solvents (*N*,*N*-dimethylformamide, dimethyl sulfoxide, aliphatic alcohols) has also been reported.[18,19] Complexes consisting of linear[14,18,20] or slightly cross-linked[21,22] polyelectrolytes and oppositely charged amphiphiles adopt lamellar structures in the solid state, with lamellae believed to consist of alternating layers of polymer chains and surfactant molecules. Formation of unusually stable monolayers of low molecular weight amphiphiles at the air−water interface via complexation with oppositely charged polymers has also been reported.[23,24] The wide variety of available polyelectrolytes and surfactants, coupled with the relatively simple procedures for synthesizing stoichiometric polyelectrolyte−surfactant complexes, has motivated recent interest in this area. Polymer−surfactant complexes are anticipated to exhibit interesting properties in organic solvents and in the solid state owing to the combination of their polymeric nature with the amphiphilic nature of the surfactants.

In this paper we report an investigation of the solid-state properties of stoichiometric complexes formed by a synthetic polypeptide−sodium poly(α,L-glutamate) and oppositely charged low molecular weight surfactants. We compare the behavior of these complexes with that of their covalent analogs, the alkyl esters of poly(α,L-glutamic acid). Poly(γ-alkyl α,L-glutamates) have been widely investigated as liquid crystals and ordered monolayers.[25−28] The stiff, helical polyglutamate backbone promotes formation of ordered structures in solution and in the solid state, while the flexible side chains promote solubility in a wide range of organic solvents. In the solid state, hexagonal or layered packing of α-helices is observed.[25] If the side chains are long enough, they may crystallize at low temperatures and melt at higher temperatures, to provide a liquid-like environment for the rods and thus enable the formation of thermotropic liquid crystals. Owing to their unique combinations of physical properties, such as high solubility and the ability to form liquid crystal phases, rod-like polypeptides with flexible side chains show promise as materials for optoelectronics, separation membranes and molecular composites.

We report herein an investigation of stoichiometric complexes formed from sodium poly(α,L-glutamate) and the oppositely charged surfactants dodecyl- and cetyltrimethylammonium bromides. We refer to such complexes as PGD and PGC, respectively.

Experimental Section

Materials. Poly(α,L-glutamic acid) sodium salt (PGNa) with weight-average degree of polymerization (DP_w) (provided

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by the supplier) of about 600 and cationic surfactants with formula $RN^+(CH_3)_3\ Br^-$ (where R = dodecyl (DDTAB) and cetyl (CTAB)) were purchased from Sigma Chemical Co. For comparison, we also used poly(γ-benzyl α,L-glutamate) (PBLG) with DP_w about 450 (Sigma). The solvent for film casting was HPLC grade chloroform (Aldrich Chemical Co.). All chemicals were used as received. Water used in the synthesis of the complexes was distilled and deionized in a "Milli-Q" water purification system (Millipore Corp.).

Sample Preparation. Complexes were prepared by mixing equal amounts of 0.05 M (for PGD complex) or 0.01 M (for PGC complex) aqueous solutions of PGNa and surfactant at room temperature at pH 8. The molarity of the polymer solutions was based on the repeating unit equivalent weight. The resulting white precipitates were isolated by filtration or centrifugation, washed several times with water to remove low molecular weight counterions, and dried in vacuum for at least 48 h at 45 °C. The complexes thus obtained were resuspended in water, filtered, and dried in vacuum under the same conditions as above. The compositions of the complexes were estimated by elemental analysis and by high-resolution ^{1}H NMR spectroscopy. Elemental analysis showed $(C/N)_{calcd}$ = 8.57, $(C/N)_{found}$ = 8.72, Na_{found} < 0.05% (PGD complex) and $(C/N)_{calcd}$ = 10.24, $(C/N)_{found}$ = 10.58, Na_{found} < 0.05% (PGC complex). From the ratios of the integrated peak intensities of the α-CH protons (δ = 4.0 ppm) of the polymer and the protons of the surfactant alkyl chains (δ 0.82 (CH_3, 3H), 1.19−1.26 (CH_2, 16H (PGD) or 24 H (PGC)), 3.27 (CH_3, 9H), 3.37 (CH_2, 2H)) it was found that 97 ± 4% of the polymer chain units were paired with surfactant ions. The complexes were analyzed immediately or stored in vacuum up to 2 weeks. Under these conditions the structural and spectroscopic properties of the samples remained stable. Upon prolonged storage, slow changes in properties were observed.

Films of the complexes for X-ray experiments were cast from chloroform solutions (concentration about 2−3 wt %) on Teflon plates. Powder samples for X-ray analysis were sealed in thin glass capillaries. For X-ray experiments at higher temperatures, the samples were heated for 1 h prior to recording the patterns. Oriented samples were prepared by stretching by hand the films of the complexes. The draw ratio did not exceed 2. For circular dichroism (CD) and Fourier transform infrared (FTIR) measurements, films were cast from chloroform solutions on quartz windows and on KBr plates, respectively.

Measurements. ^{1}H NMR spectra were recorded on a Bruker AMX 500 MHz instrument. Circular dichroism spectra were recorded using an Aviv 62DC spectrometer. FTIR spectra were obtained on a Nicolet IR 44 spectrometer. The samples for infrared experiments were purged with nitrogen for 1 h prior to measurements. X-ray diffraction patterns were recorded using either an evacuated Statton camera or a Siemens D500 diffractometer in transmission mode with a scintillation counter scanning through the appropriate 2θ range (where θ is the Bragg angle). In both cases Ni-filtered Cu Kα (λ = 1.5418 Å) radiation was used. The measurements were performed with the scattering vector s in the range 1.1 × 10^{-2} to 3.4 × 10^{-1} Å^{-1} ($s = 2/\lambda \sin\theta$). Optical microscopy studies were conducted using an Olympus BX 50 polarizing optical microscope. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC 7 system. The samples were examined at a scanning rate of 10 °C/min. Heating and cooling scans were performed twice for each sample, and in all cases both first and second scans were essentially identical. Thermogravimetric analyses were performed using a Perkin-Elmer TGA 7 system at a scanning rate of 20 °C/min.

Results and Discussion

PGD and PGC complexes are soluble in chloroform and in a variety of more polar solvents, including benzyl alcohol, methanol, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF). In polar solvents polyelectrolyte−surfactant complexes are likely to be partially dissociated,[18,19] while in solvents of low polarity such complexes are expected to remain tightly associated.[16,17]

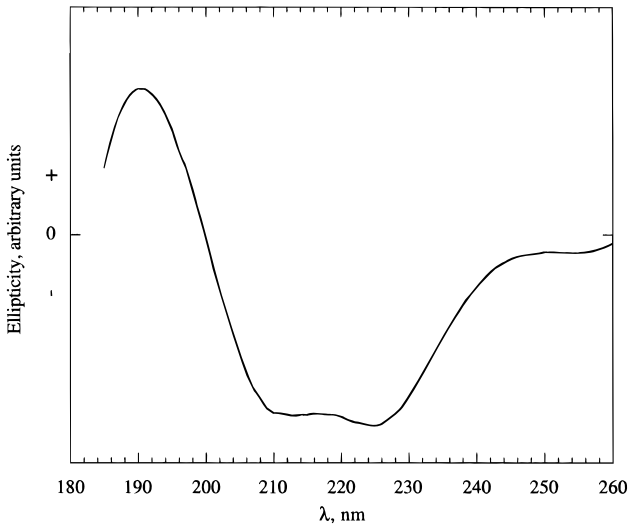

Figure 1. Circular dichroism spectrum of PGD film at 20 °C.

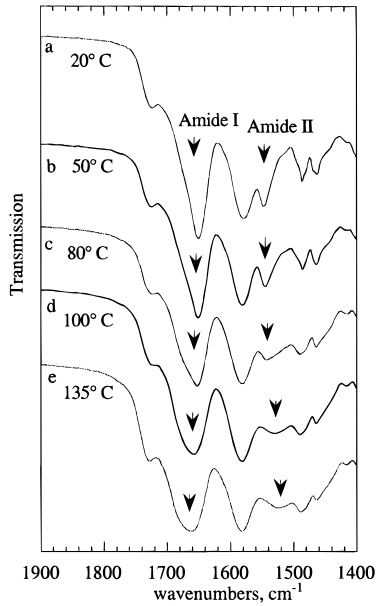

Figure 2. FTIR spectra of PGD films at 20 (a), 50 (b), 80 (c), 100 (d), and 135 °C (e) in the 1400−1900 cm^{-1}region.

The solubility behavior of the PGD and PGC complexes is in agreement with results published recently for complexes consisting of conventional synthetic polyelectrolytes and oppositely charged surfactants.[15,16,18] The solubility behavior of the corresponding esters of poly(α,L-glutamic acid) is quite different: poly(γ-alkyl α,L-glutamate)s (PALGs) are soluble in most common organic solvents, including *n*-alkanes and aromatic hydrocarbons,[26,28] which are nonsolvents for the complexes.

The conformation of the polypeptide chains in the complex was determined by CD and FTIR methods. Figure 1 presents a CD spectrum of a PGD film cast from chloroform solution. The signs and positions of the major bands in the spectrum of the PGD complex essentially coincide with those reported for polypeptides in the α-helical conformation[26,29] and we conclude that the polyglutamate chains in the surfactant complex are predominantly α-helical in the solid state. This conclusion is supported by the FTIR spectra of the PGD and PGC complexes. Figure 2 curve a presents the FTIR spectrum of the PGD complex at room temperature. The amide I and amide II bands are observed at 1653 and

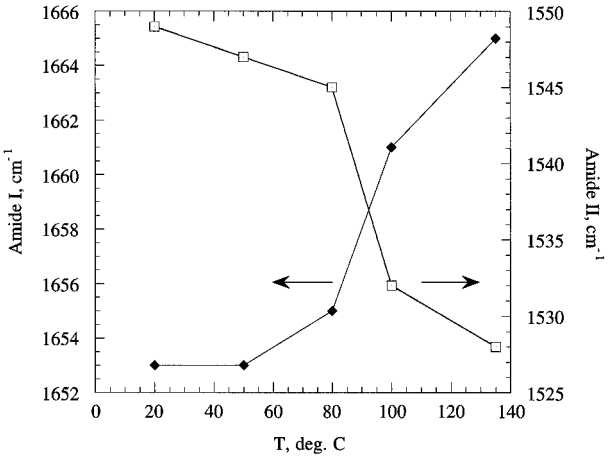

Figure 3. Temperature dependence of the frequencies of the amide I and amide II vibrations in the infrared spectra of PGD films.

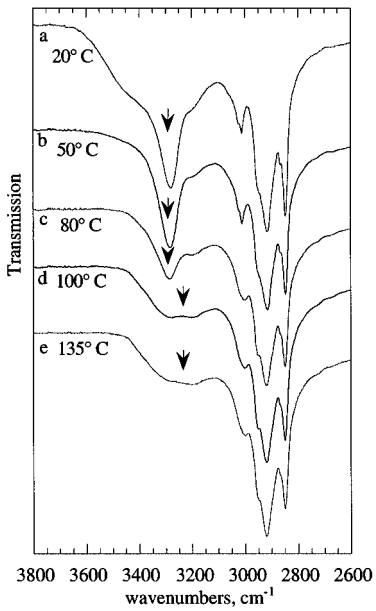

Figure 4. FTIR spectra of PGD films at 20 (a), 50 (b), 80 (c), 100 (d), and 135 °C (e) in the 2600−3800 cm^{-1} region; arrow indicates amide A band.

1549 cm^{-1}, respectively, consistent with the α-helical conformation.[26] Figure 2 curves b−e present FTIR spectra of the PGD complex at elevated temperatures. As the temperature is increased, the amide I band shifts to higher frequency , while the amide II band shifts to lower frequency (Figure 3). These effects are accompanied by a broadening and decrease in intensity of the amide I and amide II peaks and by a dramatic decrease in intensity of the amide A band (Figure 4). All of these spectral changes are completely reversible on cooling and all of these effects are identical for the PGD and PGC complexes.

The observed effects can be explained by weakening or even disruption of intramolecular hydrogen bonds as the temperature is increased. Disruption of hydrogen bonds is expected to shift the amide I band to higher energy and the amide II band to lower energy.[30] Broadening of all peaks upon heating may result from a broadening of the distribution of hydrogen bonds of different geometries and strengths.

Similar effects for the amide I and amide II bands have been reported for the benzyl and methyl esters of poly(glutamic acid).[30] The values of the shifts in

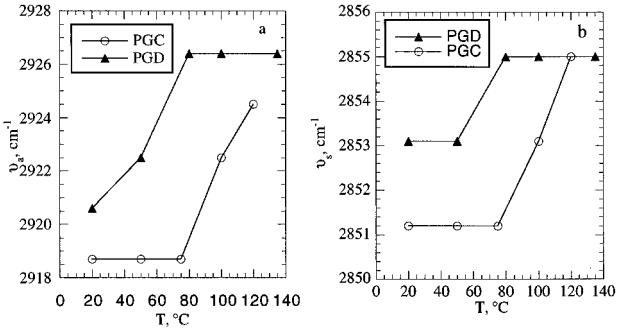

Figure 5. Temperature dependence of the frequencies of asymmetric (a) and symmetric (b) C−H stretching vibrations in the infrared spectra of PGD and PGC films.

Table 1. Frequencies of Amide Bond Vibrations (cm^{-1}) of PBLG and of the PGD Complex at Different Temperatures

	20 °C		115 °C	
	PBLG	PGD	PBLG	PGD
amide I	1654	1653	1657	1663
amide II	1549	1549	1547	1527

vibrational frequencies with temperature have not been reported, but changes in the IR spectra with temperature were correlated with increases in the X-ray diffraction spacings characteristic of the residue translation of the α-helix.[30] The overall effect is ascribed to weakening of the intramolecular hydrogen bonds leading to the expansion of α-helices along their long axes.

We carried out FTIR experiments with PBLG for comparison. The shift in amide I and amide II band positions with temperature is much less pronounced than in the case of the PGD complex in the temperature range studied (Table 1).

The difference in the behavior of the esters of poly(glutamic acid) and the complexes of polyglutamate with surfactants is likely to be related to the differences in stability of the α-helical conformation. The repulsive dipole−dipole interactions in the complexes are likely to destabilize the helix and render the intramolecular hydrogen bonds more susceptible to thermal disruption. This effect finds analogy in the difference in the conformations of poly(α,L-glutamic acid) and its salts in the solid state. While poly(α,L-glutamic acid) itself can adopt both α-helical[31,32] and β-sheet[33] conformations in the solid state at room temperature, the sodium salt is essentially disordered under the same conditions.[31,34] On the other hand, in the case of multivalent cations, such as calcium, strontium, or barium, poly(α,L-glutamic acid) salts can be crystallized in the β-form.[33]

FTIR spectra also provide information about the conformation of the surfactant alkyl chains in the complexes. The C−H asymmetric and symmetric stretching vibrations of the surfactant chains are observed at 2921 and 2853 cm^{-1} (PGD complex) and at 2919 and 2851 cm^{-1} (PGC complex), respectively, at room temperature. This indicates that in the case of the PGC complex, the surfactant chains are in a "solid-like", extended conformation, while in the case of the PGD complex the surfactant chains are likely to be slightly less extended.[35,36] As the temperature is increased, the C−H stretching vibrations are shifted to higher frequencies (Figure 5) indicating the transformation of the surfactant alkyl chains to a "liquid-like" state.[35,36] Similar shifts in C−H stretching vibrations are observed in the case of pure surfactants upon melting of their crystals; e.g., DDTAB exhibits asymmetric and sym-

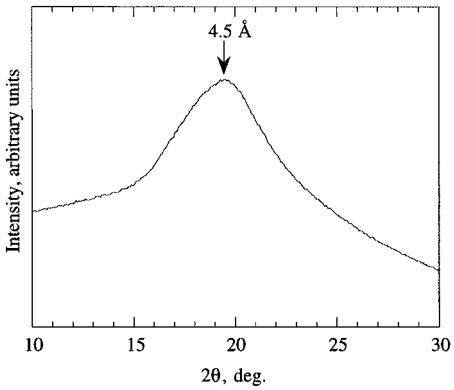

Figure 6. Wide-angle X-ray diffractogram of PGD powder at 20 °C.

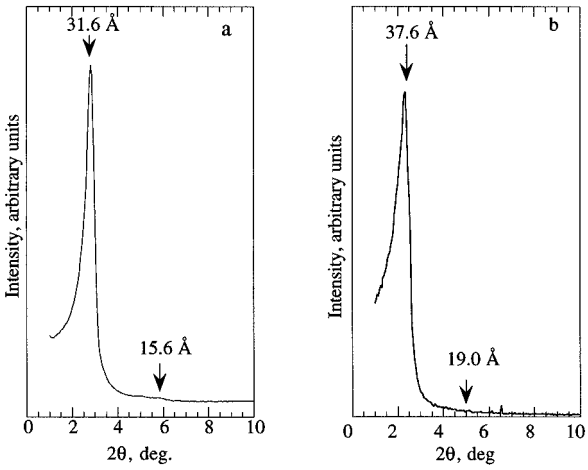

Figure 7. Small-angle diffractograms of PGD (a) and PGC (b) complexes at 20 °C.

metric C−H stretching vibrations at 2919 and 2851 cm^{-1}, respectively, in the temperature range 25−90 °C, while a shift of these bands to 2925 and 2855 cm^{-1} is observed at 100 °C. Disordering of the alkyl chains upon heating appears to precede the loss of helicity of the polyglutamate backbone in the case of the PGD complex; e.g., the transition monitored by the C−H stretching region is complete by 80 °C (Figure 5) at which point only minor changes are apparent in the amide stretching vibrations (Figure 3).

Evaporation of the PGD and PGC solutions in chloroform results in the formation of flexible, deformable, and transparent films. The films are optically isotropic when examined between crossed polarizers. The X-ray patterns of the solution-cast isotropic films are essentially the same as those of the powder samples. The wide-angle diffractogram (WAXD) of the PGD complex (Figure 6) consists of a broad halo, corresponding to a Bragg spacing of about 4.5 Å, which is close to the value known for the lateral packing of alkyl chains of various amphiphiles (see, for example, ref 37). This indicates that only short-range order is present in the lateral packing of the surfactant chains. A similar WAXD pattern is observed in the case of the PGC complex. The small-angle diffractograms (SAXD) of the PGD and PGC complexes (Figure 7) exhibit narrow peaks with Bragg spacings of 31.6 ± 0.6 and 37.6 ± 0.8 Å, respectively. The outer reflections, corresponding to Bragg spacings of about 15.6 and 19.0 Å, respectively, are quite weak, but they can be easily observed with the Statton camera (not shown). The ratio of the spacings of the inner and outer reflections suggests that the signals arise from

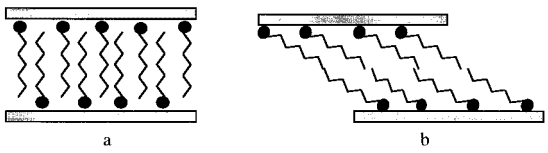

Figure 8. Possible arrangements of the surfactant molecules with respect to the lamellar plane of the complex.

lamellar structures of the PGD and PGC complexes with long periods of 31.6 and 37.6 Å, respectively.

It is reasonable to propose that both complexes possess lamellar structures consisting of alternating layers of α-helical polyglutamate chains and bimolecular layers of surfactant molecules. The fact that films of the complexes are transparent and appear optically isotropic between crossed polarizers suggests that the stacks of lamellae are randomly oriented within the sample and are much smaller than the wavelength of visible light.

The diameter of the rod-like poly(α,L-glutamic acid) chain, including both the polypeptide backbone and the side chain carboxyethyl groups, is about 13 Å.[27] The lengths of fully extended DDTAB and CTAB molecules are about 16 and 21 Å, respectively.[38] Thus, the experimental values of the long periods of the lamellae of the complexes suggest that the surfactant tails bound to the polypeptide chains lying in adjacent layers should be either interdigitated and perpendicular to the lamellar surface (Figure 8a) or tilted with respect to the layers without being interdigitated (Figure 8b).

Information about the orientation of the surfactant alkyl chains with respect to the lamellar surface can be obtained from the dependence of the long period spacing on the number of methylene groups in the side chain, provided the overall structure does not change dramatically with alkyl chain length. In the case of comb-like polymers,[39] the reported increment of lamellar thickness with side chain length is about 1.25 Å per methylene group if the alkyl chains are fully extended and perpendicular to the lamellar plane. The increment is less than 1.25 Å if the side chains are tilted. The observed difference in the long period spacings of lamellae of the PGD and PGC complexes is about 1.5 Å per methylene group; therefore we conclude that the surfactant alkyl chains are perpendicular to the lamellar plane. Similar increments of lamellar thickness with side chain length are observed in the case of PALGs with $n \geq 10$.[25] Extrapolation of the dependence of the long period of the lamellae on the number of methylene groups (n) in the side chain to $n = 0$ allows an estimate of the thickness of the polymer backbone layer.[39] In the case of the PGD and PGC complexes, this value is equal to 13.6 Å, which is in good agreement with the value expected for the diameter of the α-helical poly(α,L-glutamic acid) chain (*vide supra*).

Films of the polypeptide−surfactant complexes can be easily oriented by stretching. Oriented samples appear negatively birefringent when viewed between crossed polarizers in the optical microscope: the direction of highest refractive index, determined using a full wavelength plate inserted at a 45° angle to the direction of the polarizers, is perpendicular to the direction of stretching. The direction of highest refractive index in the case of comb-shaped polymers with long side chains is expected to be parallel to the direction of the side chains. Thus, stretching of the PGD films leads to the alignment of the lamellae and of the polymer chains parallel to the direction of orientation, while the side

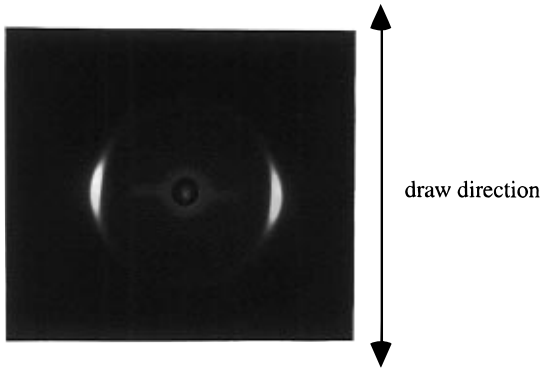

Figure 9. SAXD pattern of stretched PGD film at 20 °C. The equatorial arcs correspond to the lamellar repeat of the complex.

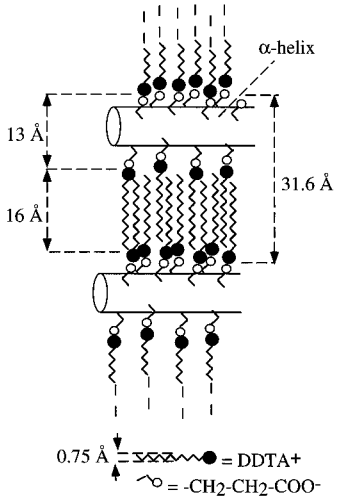

Figure 10. Proposed scheme of the lamellar structure of the PGD complex, viewed parallel to the layers and perpendicular to the long axes of the α-helices. The structure of the PGC complex is believed to be similar.

chains are perpendicular to the draw direction. This conclusion is supported by the SAXD pattern of the stretched PGD film (Figure 9): the sharp reflection corresponding to the long period of the lamellae is equatorial, indicating that the plane of lamellae is parallel to the stretching direction. Additionally, the broad halo on the WAXD pattern of the stretched complex (not shown) has increased meridional intensity, supporting the conclusion regarding the perpendicular orientation of the surfactant chains.

Thus, the stoichiometric polypeptide−surfactant complexes are characterized by lamellar structures consisting of layers of α-helical polymer chains separated by layers of surfactant. It is plausible that the side chains associate on opposite sides of the α-helices in order to form a layer, similar to the alkyl groups of poly(glutamic acid) esters,[25] as proposed by Watanabe and co-workers. The surfactant molecules are likely to be perpendicular to the lamellar surface and are significantly interdigitated (Figure 10). We have no information concerning the packing of the α-helical polymer chains within the layers.

The structures of the PGD and PGC complexes are similar to those of complexes formed by conventional linear synthetic polyelectrolytes and oppositely charged low molecular weight surfactants,[18,19] but differ from those of the corresponding esters of poly(glutamic acid). In the latter case, the α-helices are arranged in layers with the side chains located between the layers and interdigitated,[25] but those with alkyl side chains of ten or more carbons form alkane-like crystallites. The structures of the PGD and PGC complexes are also strikingly different from those of the corresponding surfactants in their bromide forms. Both DDTAB and CTAB adopt crystalline structures in the solid state[21,38] and DDTAB is reported to form a monoclinic lattice[38] with interdigitated chains.

The lamellar structure of the complexes remains intact in the temperature range 20−150 °C although disordering of alkyl tails and loss of helicity of the polyglutamate backbone are observed upon heating. Films prepared from the complexes remain mechanically stable until thermal degradation begins, with onset of weight loss at about 200 °C. No thermal transitions are observed by differential scanning calorimetry in the temperature range between 15 °C and the onset of degradation. The lamellar structure of the complexes is stable at temperatures higher than the melting temperatures of the corresponding surfactants (according to our experiments, 103 °C for DDTAB and 107 °C for CTAB); thus the complexes can be considered as lamellar phases of surfactants stabilized by the polymer.

The thermal behavior of the polypeptide−surfactant complexes is quite different from that of the alkyl esters ($n \geq 10$) of poly(glutamic acid), which undergo two first-order transitions.[24] The first transition corresponds to the melting of the side chain crystallites, while the layered packing of the α-helices is preserved. At the temperature of the second transition, flow is observed and melts with cholesteric order are formed. In the corresponding surfactant complexes examined herein (with chain lengths up to C_{16}), no "side chain" crystallization is observed, probably owing to dipolar and steric repulsion that prevents ordered packing of surfactant tails.

Concluding Remarks

Stoichiometric complexes of poly(α,L-glutamate) chains and alkyltrimethylammonium surfactants have been prepared and have been shown to be soluble in solvents of low polarity (e.g., chloroform). The polypeptide backbone in such complexes adopts an α-helical conformation in the solid state, similar to that of the esters of poly(α,L-glutamic acid). Intramolecular hydrogen bonds in the complexes are more sensitive to temperature changes than those characteristic of the esters, and the surfactant "side chains", attached to the polyglutamate backbone electrostatically, do not form alkane-like crystal lattices (for chain lengths up to C_{16}). The lamellar structures of the PGD and PGC complexes, stable in the temperature range 20−150 °C, are similar to those of complexes of conventional polyelectrolytes and oppositely charged surfactants. The lamellae consist of layers of polymer chains separated by layers of surfactant molecules. The surfactant chains are perpendicular to the lamellar surface and interdigitated.

Studies of the solution behavior of complexes formed by poly(α,L-glutamate) and oppositely charged surfactants are in progress.

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