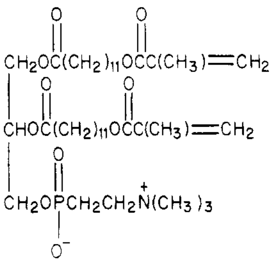
Chart I



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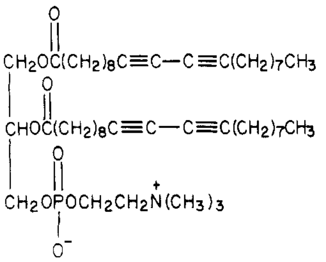

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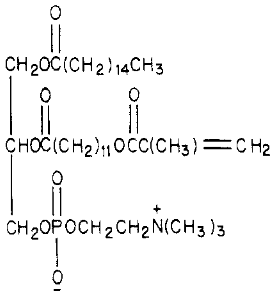

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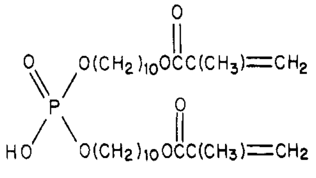

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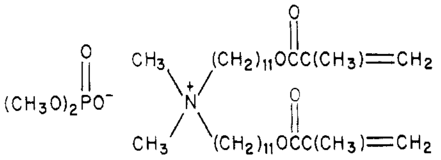

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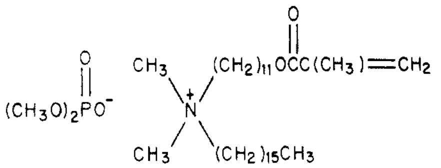

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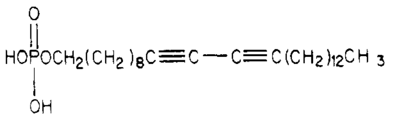

7

alyzing, quantitatively, the surface roughness and true surface area of solid organic polymers.[9] A related problem is that it is not possible to discern whether the coatings extend over the "hills and valleys" of a polymer surface, or whether they traverse the "hills". In our earlier work, we did not not claim a method for coating solid surfaces with ordered polymerized monolayers.[2,10] We also made no claims regarding the generality or synthetic scope of this technique. We in fact stated: "The question of whether or not a polymerized phosphatidylcholine monolayer of **1** or **2** has been attached to polyethylene cannot be answered unambiguously at the present time. However, the above results, taken together, *strongly suggest that a polymeric structure at least approaching monolayer coverage is present*". In this prior publication we also demonstrated that our method is very sensitive to the precise structure of the surfactant and concentrations used. Recently, it has been reported that compound **7** failed to produce a uniformly hydrophilic surface on Teflon and on polypropylene by using procedures and conditions which were similar to those described above.[10] These negative results cannot be used, in any way, to draw inferences regarding either the surface structure that exists in PE/**1**, PE/**2**, PE/**4**, and PE/**5** or the generality of this technique. This compound is substantially different in structure from those surfactants which we have successfully employed. Moreover, these films differ significantly in surface structure and composition.

A broad study aimed at examining the synthetic scope of this technique as well as elucidating surface structure is now in progress. Complete experimental details including synthetic procedures used for the preparation of **1–6** will be reported shortly.

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Registry No. 1 (homopolymer), 90064-68-9; **2** (homopolymer), 90046-25-6; **4** (homopolymer), 90046-27-8; **5** (homopolymer), 90046-29-0; PE, 9002-88-4.

References and Notes

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(3) Film provided by Luetzow Industries, Milwaukee, WI, was cleaned by using procedures previously described.[2]

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(5) Unless indicated otherwise, surface areas referred to in this work are geometrical and not true surface areas.

(6) The phosphorus content in this work for PE/**1** and PE/**2** is slightly greater than that reported in ref 2, due to an adjustment made in the phosphorus calibration curve.

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Quasi-Elastic Light Scattering of Polyelectrolyte–Micelle Complexes

The association between surfactants and synthetic polymers has been the subject of increasing attention, partly because these interactions may resemble phenomena in biological assemblies,[1] but also because of their bearing on certain applications of water-soluble polymers, e.g., in enhanced oil recovery.[2] The most intense association occurs between strong polyelectrolytes and oppositely charged amphiphiles; however, studies with these compounds have been carried out only well below the cmc,[3–5] primarily because precipitation commonly occurs at higher surfactant concentrations. Nonionic polymers, which do not exhibit such phase separation, have been extensively examined,[6–9] but the nature of their interaction with surfactants is somewhat obscure and relatively weak.

We have recently observed that the phase separation of

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polyions with oppositely charged surfactants above the cmc can be attributed to Coulombic interactions between micelle and polymer, inasmuch as this association can be modulated via ionic strength or mixed micelle surface charge density.[10] Thus, the phase boundary for solutions of poly(dimethyldiallylammonium chloride)—a strong polycation—in the presence of Triton X-100 and sodium dodecyl sulfate—a nonionic and anionic surfactant, respectively—is determined by the ionic strength and the mole fraction of anionic surfactant and is independent of total surfactant or polymer concentrations.[11] At conditions just short of phase separation the time independence of turbidity values and their reversibility with respect to surfactant composition indicate the presence of equilibrium polyion–micelle aggregates.[11] We describe here preliminary quasi-elastic light scattering (QELS) data that confirm the existence of such aggregates and provide further information about their structure. While QELS studies have yielded significant insight into both the solution behavior of polyelectrolytes[12–14] and the dimensional properties of surfactant micelles,[15–17] no reports have appeared on the application of this technique to polymer–surfactant complexes.

Solutions containing poly(dimethyldiallylammonium chloride) (PDMDAAC, Calgon Corp., MW = 2×10^5) and 20 mM Triton X-100 (Rohm & Haas Co.) in 0.40 M NaCl were titrated with 40 mM sodium dodecyl sulfate (SDodS, Fluka) in 0.40 M NaCl. The initial polymer concentrations C_p were 0.50, 1.0, 1.5, and 2.0 g dm^{-3}. Turbidities were read as 100 – % T with a Brinkmann PC600 probe colorimeter (2-cm path length, 420 nm). Aliquots were removed after each addition of titrant for QELS measurement and returned to the titration vessel prior to addition of further SDodS. After an initial mixing period of about 1 min, both turbidity and QELS values were stable for at least several hours, with the exception of those solutions containing microscopically visible particles (see below). All sample preparations and measurements were made at 22 °C.

Mean diffusion coefficients were obtained by QELS from 90° scattering data using a Coulter (Model N4) spectrometer equipped with a 5.0-mW He–Ne laser and a 32-channel autocorrelator. Sample times ranged from 3 to 100 μs. The normalized intensity autocorrelation function for homodyne detection arising from a single diffusive process is[18]

$$g^{(2)}(\tau) = 1 + A \exp(-2\Gamma\tau) \qquad (1)$$

where A is an instrument constant, and Γ, the decay constant, is given by $\Gamma = D_T\kappa^2$, with D_T the translational diffusion coefficient and κ the magnitude of the scattering wave vector, a function of refractive index, incident wavelength, and scattering angle. Analysis of the autocorrelation function $g^{(2)}(\tau)$ was done automatically to yield the mean diffusion coefficient D_T and thence, from the Stokes–Einstein expression, the apparent mean hydrodynamic radius R_h.[19] Both of these quantities were reproducible to better than 5%. The value for $2R_h$ for a polystyrene latex with an average diameter of 198 nm (electron microscopy, Dow Chemical Co.) was 194 nm. For Triton X-100 micellar solutions, R_h was 3.8 ± 0.2 nm, in good agreement with the mean radius of 40 Å determined[20] on the basis of intrinsic viscosity and light scattering data.

The deviation of ln $[g^{(2)}(\tau)]$ vs. τ from linearity was automatically analyzed in terms of sample polydispersity by fitting a second-order equation for ln $[g^{(2)}(\tau)]$ to a generalized Pearson Five distribution[21] using the method of cumulants.[22] Because of the uncertainty associated with this assumed distribution, the calculated polydispersities were used for qualitative comparisons only.

To obtain further information on particle size distributions, measurements were made at 30° and 90° with a correlation spectrometer assembly comprised of a Spectra-Physics (Stabilite Model 1248) 15-mW He–Ne laser, a Brookhaven (B1200SM/BIDS) goniometer/photomultiplier unit, and a Brookhaven (M2000) 128-channel autocorrelator.

Optical density and QELS data are summarized in Figures 1 and 2, in which the turbidity (as 100 – % T) and the apparent hydrodynamic radius R_h, respectively, are plotted vs. Y = [SDodS]/([SDodS] + [Triton X-100]), i.e., the mole fraction of anionic surfactant. Barring a nonlinear dependence of the degree of micelle counterion binding of Y, this quantity should be proportional to the mixed micelle surface charge density.[11]

Association of polyions and micelles is evidently negligible until a critical micelle surface charge density is attained, corresponding to $Y_c = 0.22$ for this particular ionic strength, 0.40 M. At lower values of Y the presence of polymer has no effect on either turbidity or R_h. The dimensions of the mixed micelles are significantly greater than those of the nonionic micelles, but both are small compared to the size of polymer–surfactant aggregates formed above Y_c.

The maxima with respect to Y in the turbidity plots are reflected with reasonable fidelity in the QELS curves for C_p = 0.5–1.5 g dm^{-3}. Since the presence of free micelles must contribute to some extent to the measured R_h values (see below), an unambiguous interpretation of these maxima cannot be offered. However, limited viscosity data suggest the possibility of contraction of soluble aggregates prior to precipitation,[11] so that the maxima in R_h may indeed correspond to maxima in soluble aggregate size. Since the overlap concentration $C^* \approx 1/[\eta]$[23] is about 10 g dm^{-3} for the polymer molecular weight and ionic strength of this study, most of the conditions here correspond to large interpolymer separation. This consideration supports the perception of intrapolymer micelle binding as the primary association phenomenon and—in view of the relatively small value of the Debye length κ^{-1} = 5 Å at this ionic strength—also encourages us to neglect any ordering effect from interpolymer repulsive forces.

Turbidity plots obtained in 0.6 and 0.8 M NaCl do not display maxima.[11] While we have not systematically studied this aspect of the influence of the ionic strength, I, it can be noted that while Y_c increases linearly with I,[11] Y_p is rather insensitive to I in the range 0.4–0.8 M. Thus the soluble aggregate range of Y shrinks with increasing ionic strength. It is furthermore plausible that the diminution of the range of Coulombic forces (e.g., κ^{-1}) at larger I reduces the sensitivity of the aggregation state to changes in Y and so limits the magnitude of changes in the turbidimetric titration curves between Y_c and Y_p.

Computed size distributions for many of the samples were narrow and remarkably close to the breadth of the distributions of the polymer-free micellar solutions ($M_w/M_n = 2.1$). In other cases, indicated by the flagged data points of Figure 2, the deviation from linearity of the logarithmic correlation function could not be fit by the assumed size distribution, a situation consistent with multimodal distributions.[21] These observations were also supported by limited angular dependence measurements at 1.0 g dm^{-3} polymer: for solutions at Y = 0.28, 0.30, and 0.35, the calculated Stokes radii at 30° and 90° were the same to within 5–10%. At Y = 0.23 and Y = 0.39 (where no monomodal distribution could be fit to the correlation

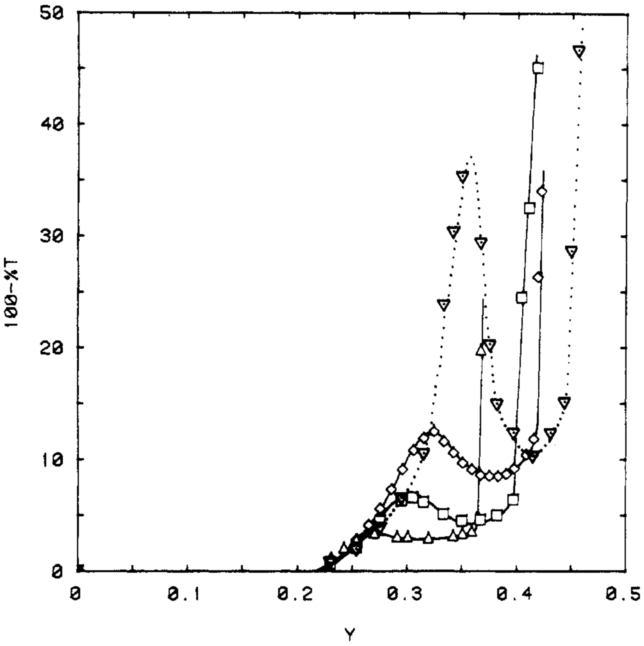

Figure 1. Turbidity, as 100 − % *T*, vs. mole fraction anionic surfactant (*Y*) in 0.4 M NaCl for initial polymer concentrations of (△) 0.5, (□) 1.0, (◇) 1.5, and (▽) 2.0 g dm^{-3}. Initial concentration of nonionic surfactant 20 mM. All values corrected for turbidity measured in absence of polymer.

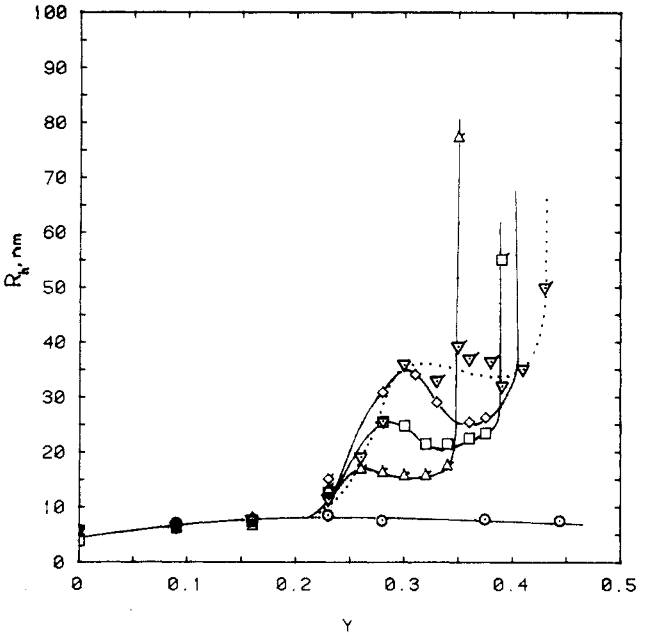

Figure 2. Apparent mean hydrodynamic radius R_h vs. *Y* for conditions described in the legend of Figure 1: (○) values obtained in the absence of polymer.

function with the Coulter N4 programs), $R_h(30°)/R_h(90°)$ was 1.4 ± 0.05 and 3.5 ± 0.5, respectively.

We interpret these findings on polydispersity as follows. Free, uncomplexed, micelles are always present at $Y \approx Y_c$ since complexes are first formed under these conditions. The second transitionary range, Y_p, corresponds to the irreversible formation of large particles, i.e., precipitation, and these mixtures are necessarily multimodal. For the lowest polymer concentration (0.50 g dm^{-3}), the apparently high polydispersity for $Y_c < Y < Y_p$ may also result from free micelles, if micelle concentration exceeds polymer binding capacity. Angular dependence results for these samples were unfortunately ambiguous.

At polymer concentrations above 1.5 g dm^{-3}, turbidity values become exceptionally large between Y_c and Y_p and display pronounced maxima with respect to *Y*. Microscopic observations of these solutions reveals liquid droplets, 1–75 μm diameter. Because of the angular disymmetry of Mie scattering,[24] these coacervate droplets affect the tubidity (i.e., global scattering) to a far greater extent than the right-angle scattering. In fact, removal of the coacervate by centrifugation was found to reduce the value of $\bar{R}_h$ by no more than 20%, despite the relative enormity of these droplets. The role of micelle composition and polymer:surfactant stoichiometry in the coacervation process is under further investigation.

In conclusion, QELS data confirm the presence of stable supramolecular aggregates with hydrodynamic diameters ranging from 30 to 70 nm, in solutions of polycations and oppositely charged mixed micelles at high ionic strength. Aggregate size increases with polymer concentration to a maximum value of $R_h \approx 35$ nm at $C_p = 1.5$ g dm^{-3}. At higher polymer concentrations these aggregates are in equilibrium with a polymer-rich liquid phase (coacervate).

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Registry No. PDMDAAC, 26062-79-3; Triton X100, 9002-93-1; SDS, 151-21-3.

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