

# Polymer Films on Electrodes

## XXII. Electrochemical, Spectroscopic, and Transmission Electron Microscopic Studies of Morphological Changes in Films of Polymeric Surfactants

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### ABSTRACT

An electroactive polymeric surfactant with pendent long-chain viologen redox groups, PCMS-VC<sub>16</sub>, was synthesized by the reaction of poly(chloromethylstyrene) with N-hexadecyl-4(4'-pyridyl)pyridinium bromide. Films of this polymeric-surfactant on glassy carbon electrodes were studied by electrochemical, microscopic, spectroscopic (absorption-probe), and electron spin resonance techniques. The results suggest that upon reduction of the viologen groups in aqueous solution, the structure of the polymeric surfactant becomes more compact, probably because of reorganization induced by a decrease in the coulombic repulsive interaction. Spherical domains formed by the aggregation of the long-chain hydrocarbon groups were observed in the transmission electron micrographs of both the oxidized form and reduced form of the polymeric surfactants.

Studies of polymeric films on electrodes have been carried out to investigate the mechanism of mass and charge transport in polymeric layers, to characterize their redox properties, and for possible applications (e.g., displays, electrocatalysis) (1). Several investigations concerned the morphology of polymer films, the changes that occur upon oxidation and reduction, and how these changes affect film properties (2). The present study concerns the effect of oxidation and reduction of films of redox active polymeric surfactants. Polymeric surfactants, or polysoaps, have been studied extensively (e.g., in their application in the catalysis of chemical reactions) (3, 4). Related investigations of the electrochemistry of redox species incorporated in the micelles (5), and of vesicles with electroactive head groups (6a-c), have also been carried out. For example, Saji *et al.* (7), studied the formation and disruption of micelles by control of redox states of the (monomeric) surfactant ferrocene tail groups. However, no detailed study of the morphology of electroactive polymeric surfactants has been made. In this article, we describe studies of the polymeric surfactant, Scheme I, PCMS-VC<sub>16</sub>, containing

actions and large spectral changes upon reduction (8). In these polymers, the charge of the viologen groups can be switched reversibly between V<sup>2+</sup> (oxidized form) and V<sup>+</sup> (reduced form) electrochemically. The change in the structure of the polymer coatings was monitored by electrochemical, spectroscopic, and electron microscopic methods.

### Experimental Section

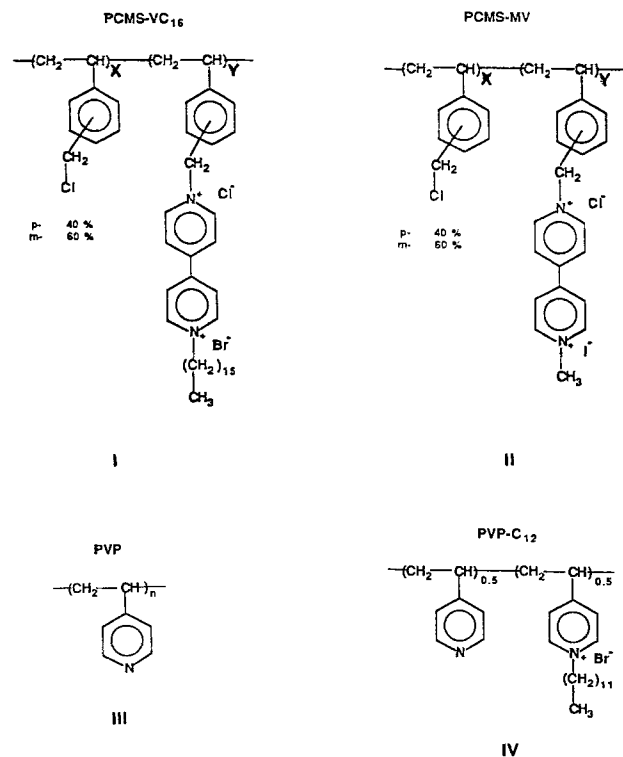
**Materials.**—4-Vinylpyridine (Polyscience, Inc., Warrington, PA) and chloromethylstyrene (60% meta, 40% ortho) (Aldrich, Milwaukee, WI) were distilled under reduced pressure. Poly(4-vinylpyridine), PVP, Scheme III, was synthesized by bulk polymerization of 4-vinylpyridine initiated by benzoyl peroxide (Polyscience, Inc.) at 50°C (9). It was purified by reprecipitation of the nitromethane solution with excess toluene. The molecular weight was  $4.9 \times 10^5$  (viscometry) (10). Quaternization of poly(4-vinylpyridine) with dodecyl bromide (Aldrich) was carried out in degassed 1:1 nitromethane-nitroethane at 50°C (3). The extent of quaternization was 50% (NMR). This product is designated here PVP-C<sub>12</sub>, Scheme IV. Poly(chloromethylstyrene) was synthesized (11) by radical chain polymerization in degassed benzene using AIBN (Polysciences, Inc.) as the initiator. It was purified by the precipitation of a benzene solution with MeOH. The average molecular weight was  $8 \times 10^4$  (GPC).

N-(n-hexadecyl)-4-(4'-pyridyl)pyridinium bromide was synthesized and characterized according to Ref. (12). <sup>1</sup>NMR(DMSO-d<sub>6</sub>), (ppm): 0.88 (t, 3H, —CH<sub>3</sub>), 1.1–2.3 (m, 28H, —CH<sub>2</sub>—), 4.7 (t, 2H, N—CH<sub>2</sub>); aromatic H-8.13 (d, 2H), 8.73 (d, 2H), 8.96 (d, 2H), 9.33 (d, 2H).

PCMS-VC<sub>16</sub>, I. N-hexadecyl-4-(4'-pyridyl)pyridinium bromide and poly(chloromethylstyrene) were heated at 80°C in dry degassed N,N-dimethylformamide (DMF) for 48h. The precipitate was collected, washed, and redissolved in warm MeOH. The MeOH solution was added dropwise to rapidly stirred dioxane and the resulting cloudy mixture was centrifuged. The precipitate was washed with dioxane, then acetone. A yellow powder was obtained by another reprecipitation of a MeOH solution with dioxane. The result of elemental analysis indicated that 40% of the chloromethylstyrene groups were functionalized with viologen groups. Elemental analysis for PCMS-V<sub>16</sub> (40%), 1 dioxane/monomer unit: Found: C, 66.8; H, 8.05; N, 3.32. Calcd: C, 66.4; H, 8.05; N, 3.25.

PCMS-MV, II, was synthesized according to the procedure for a similar polymer (12a). Elemental analysis indicated that the extent of substitution was 42%. PCMS-MV (42%), 1 dioxane/monomer unit: Found: C, 56.2; H, 5.74; N, 4.05. Calcd: C, 56.3; H, 5.66; N, 3.93.

**Apparatus.**—Electron spin resonance (ESR) measurements (X band) were made with a Varian E-9 spectrometer (100 kHz field modulation) equipped with a TE<sub>102</sub> dual-sample cavity. The ESR-electrochemical cell was a specially designed 1 mm thick flat ESR cell (13) suitable for



long-chain viologen side groups. Other polymers containing viologen (V<sup>2+</sup>) groups have been studied previously, because these groups show reversible electrochemical re-

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both electrochemical and ESR studies. Visible absorption measurements were obtained with transparent SnO<sub>2</sub> (PPG Glass) electrodes and an HP-8450A spectrometer. Electrochemical measurements were performed with a PAR Model 175 universal programmer, a Model 173 potentiostat, and a Model 179 digital coulometer (Princeton Applied Research Corp., Princeton, NJ). Current-time curves were recorded on a X-Y recorder or a Norland Model 3001 digital oscilloscope. Transmission electron micrographs were obtained on a JEOL 1200 EX STEM equipped with a Tracor 5500 energy dispersive spectroscope. The working electrode used in voltammetric experiments was a glassy carbon electrode with an area of 0.07 cm<sup>2</sup> (Bioanalytical Systems, West Lafayette, IN). The SnO<sub>2</sub> electrode was prepared by attaching a Cu wire to the conducting SnO<sub>2</sub> surface with silver paint and covering the contact with a non-conducting epoxy cement. The working electrode for the ESR experiment was a 0.3 × 0.6 cm Pt flag. The counter-electrode was a Pt wire and the reference electrode was a saturated calomel electrode (SCE), except in the simultaneous electrochemical-ESR (SEESR) experiment where an Ag/AgCl electrode was used as both the counter and reference electrode. Viscometry was performed with a Bausch and Lomb Viscomatic-1 viscometer.

**Procedures.**—The electrodes were prepared by covering the conducting substrates (C, Pt, SnO<sub>2</sub>) with an aliquot of the polymer solution (0.25% w/v); solvents were MeOH for PCMS-VC<sub>16</sub>, PVP, and PVP-C<sub>12</sub>, and DMF for PCMS-MV. Before every experiment the potential of the electrode was held at a positive value to oxidize any bromide in the polymer to bromate, and iodide to iodate. Both bromate and iodate are replaced by chloride from the supporting electrolyte solution very rapidly (12a). Samples for transmission electron microscopy were prepared by coating a thin polymer film on a carbon-coated copper grid. The films were then stained with a 2% aqueous uranyl acetate solution.

### Results and Discussion

**Electrochemical experiments.**—PCMS-VC<sub>16</sub> is a polymeric surfactant. The long-chain viologen groups are the charged pendent groups. Since the doubly charged viologen group can be reduced reversibly to the singly charged cation radical, this provides the opportunity to investigate the effects of charge on the morphology of the film of a polymeric surfactant. The cyclic voltammograms (CV) of a PCMS-VC<sub>16</sub> coating on a glassy carbon electrode are shown in Fig. 1. In Fig. 1a, the initial potential was set at -0.1V, where all the viologen groups were in the V<sup>2+</sup>, oxidized, form. On the other hand, in Fig. 1b, the initial potential was set at -0.6V, where they were in the V<sup>+</sup>, reduced, form. In both cases, the coated electrode was held at the initial potential for 30 min before the potential scan. Note that the shape of the CV waves depends upon the initial potential. In both cases the waves are those of a surface-confined species with the viologen groups being completely reduced (or oxidized) during each cathodic (or anodic) scan. Under these conditions, the shape and the width at half-height ( $\Delta E_{1/2}$ ) provides information about the extent of interaction between the reduced groups (14). In Fig. 1b, the width at half-height is 75 and 120 mV for the anodic and cathodic wave, respectively, while it is 95 and 120 mV, respectively, for Fig. 1a. The distinctly different  $\Delta E_{1/2}$  values for the anodic and cathodic wave in Fig. 1b indicate the morphology of the polymer in the reduced form is different from that in the oxidized form.

This voltammetric behavior can be understood by referring to the model for the analysis of the cyclic voltammetric behavior of polymer films on electrodes (14b). According to this model, the polymeric surfactant viologen film should be classified as a system containing electrochemically nonequivalent redox sites and the fractional distribution of the different classes of redox sites is a function of the redox state of the film. Since the charged viologen side groups are associated with long-chain hydrocarbon groups, the morphological structure depends on both hydrophobic and coulombic interactions. When the viologen groups are reduced ( $V^{2+} + e^- \rightarrow V^+$ ) the coulombic repulsion is decreased and the long-chain hydrocarbon groups

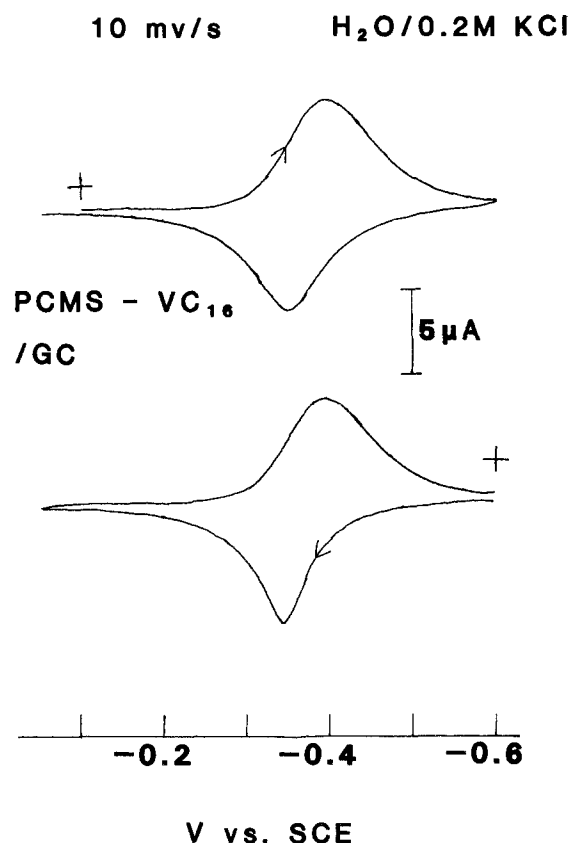
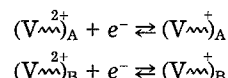


Fig. 1. Cyclic voltammograms of  $1.3 \times 10^{-8}$  mol cm<sup>-2</sup> (viologen groups) of PCMS-VC<sub>16</sub> film on a glassy carbon electrode. The electrode was (a) (upper) equilibrated at -0.1V before potential scan, (b) (lower) equilibrated at -0.6V before potential scan. Scan rate: 10 mV s<sup>-1</sup>. Supporting electrolyte: 0.2M KCl.

can approach one another more closely. Moreover, the extent of solvation depends upon the state of oxidation of the viologen centers; the V<sup>2+</sup> state would be more highly solvated than the V<sup>+</sup> state. Thus, reduction is probably accompanied by a loss of solvent from the polymer structure. Overall, reduction results in a significant enhancement of the hydrophobic interaction and the morphological structure changes to a more compact one.

We schematically represent the various processes as



where A and B represent a more extended (more swollen) and a more compact (less swollen) structure, respectively. The  $\Delta E_{1/2}$  of 75 mV for the anodic wave in Fig. 1b is smaller than  $\Delta E_{1/2}$  of 90 mV for noninteracting groups and points to the much stronger attractive interaction among the reduced viologen than that among the oxidized viologen groups in the more compact structure, B. This attractive interaction also causes a free energy change and, therefore, a formal potential shift in the positive direction relative to PCMS-MV, a polymeric methyl benzyl viologen (vide infra). On the other hand, in the more extended A form, the hydrophobic interaction is not as pronounced as in the B form, because of the penetration of water molecules into the hydrophobic domains to separate the long-chain viologen groups. To account for the  $\Delta E_{1/2}$  of 120 mV (larger than 90 mV) for the cathodic wave in Fig. 1a, it would be necessary to assume that in the A form, at least for the oxidized state, coulombic effects dominate the hydrophobic interaction and the overall interaction is repulsive. However, the situation may also be complicated by the existence of multiple classes of redox sites in the A form. The fact that the  $\Delta E_{1/2}$  value for the oxidation is larger (95 mV) when the scan occurs on reversal from an initial potential where all of the viologens are in the V<sup>2+</sup>-form (Fig. 1a) than it is (75 mV) when the viologen has been in the V<sup>+</sup> form for

a much longer time (Fig. 1b) indicates that the rate of change in polymer morphology from the A to the B form upon reduction is slow on the time scale of this CV experiment. The following experiment was performed to estimate the rate of change. The coated electrode was allowed to equilibrate at  $-0.1\text{V}$  and then the potential was scanned to  $-0.6\text{V}$  and held at this potential for different periods of time ( $\tau$ ) before it was scanned positively to obtain the anodic wave. For  $\tau$  longer than 4 min, the  $\Delta E_{1/2}$  was 75 mV and the shape of the wave did not depend on  $\tau$ . For smaller  $\tau$ -values,  $\Delta E_{1/2}$  was larger and the wave shape depended on  $\tau$ . Thus, the time required for the change in polymer morphology upon reduction is about 4 min.

Although the rate of change in polymer morphology is slow during reduction, the rate of change in polymer morphology upon reoxidation (i.e., from the B to the A form) is fast on the voltammetric time scale as indicated by the almost equal  $\Delta E_{1/2}$ -values for the cathodic waves in Fig. 1a and 1b. Different rates of change for expansion and contraction of charged polymers have been discussed previously (16). However, the present observation demonstrates that voltammetric methods can be used to study the kinetics of change in the morphology of a polymeric surfactant in aqueous solution.

The amount of electroactive species was determined from the areas of the voltammetric waves. This was typically 40-60% of the amount of polymer applied to the electrode, so that some of the viologen groups were not accessible for redox processes. However, those that were electroactive could be oxidized and reduced repeatedly without significant loss in electroactivity. The rate of charge transport through the films of PCMS-VC<sub>16</sub> was estimated by potential step chronoamperometry (15c). In this experiment, the potential was stepped either from  $-0.1$  to  $-0.6\text{V}$  (for measurement with the polymer initially in the oxidized form) or from  $-0.6$  to  $-0.1\text{V}$  (for the polymer initially in the reduced form), and the slope of the current ( $i$ ) vs.  $t^{-1/2}$  line for times ( $t$ ) of 0.8-1.4 ms was used to determine the effective diffusion coefficient,  $D_{\text{eff}}$ .  $D_{\text{eff}}$  was  $1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  for an initially oxidized form and  $1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  for an initially reduced form, respectively. The significant difference is consistent with a morphology change accompanying the redox process.

To demonstrate that the variation in  $\Delta E_{1/2}$  is due to the variation in the intensity of the hydrophobic interaction among the long-chain side groups, the same experiment was carried out with another viologen polymer, PCMS-MV. As shown in Fig. 2a and 2b,  $\Delta E_{1/2}$  for the two pairs of waves are all in the range of 138-145 mV. Since both reduced groups (cation radical groups) of PCMS-VC<sub>16</sub> and PCMS-MV undergo dimerization (vide infra), this finding supports the concept that the structural change associated with the variation in  $\Delta E_{1/2}$  upon reduction of PCMS-VC<sub>16</sub> is caused by the attractive interactions of the hydrocarbon chains, not by dimerization. The greater stabilization of the radical cation of PCMS-VC<sub>16</sub> by the attractive, hydrophobic interaction among the charged long-chain hydrocarbon groups is also reflected in the redox potential. The redox potential of PCMS-VC<sub>16</sub> is  $-0.38\text{V}$ , compared to that of PCMS-MV,  $-0.44\text{V}$  vs. SCE. The shape of the cyclic voltammetric wave for PCMS-VC<sub>16</sub> also depends on the solvent. In  $\text{CH}_3\text{CN}$ , nearly symmetrical waves were observed, and there is no indication of aggregation of the viologen groups. ESR experiments, described below, provide further evidence for this lack of interaction.

**Spectroscopic study with absorption probe.**—To gain more insight into the change in polymer morphology, spectroscopy in the visible region with and without methyl orange as an absorption probe was carried out. The absorption spectrum (Fig. 3) of the reduced form of PCMS-VC<sub>16</sub> film on an  $\text{SnO}_2$  electrode shows an absorption maximum at 540 nm, indicating predominantly dimeric species in the film matrix (17). The reduced form of PCMS-MV is also mainly comprised of dimeric species. The dimerization of the cation radical head groups could contribute to some extent to the more compact aggregation of the polymer in the reduced form, but we do not believe that it is the major factor (vide supra).

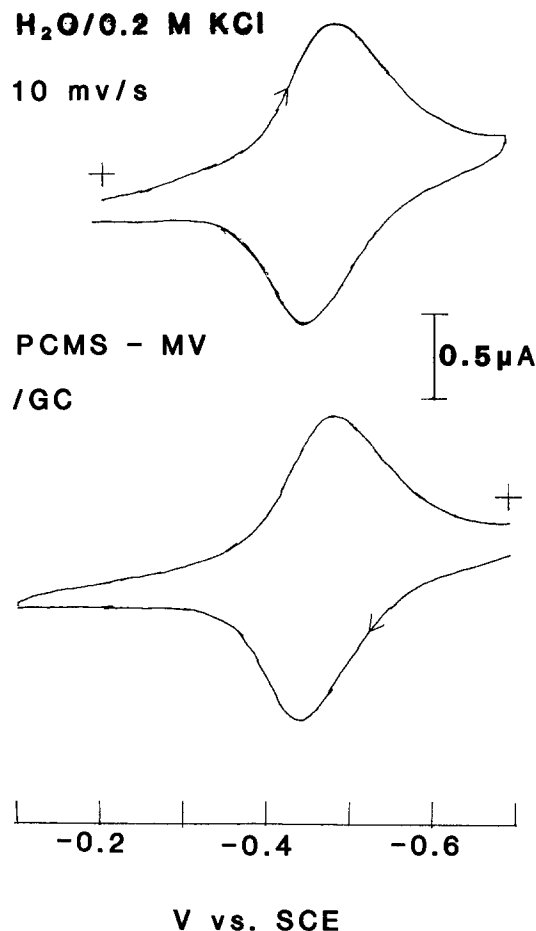


Fig. 2. Cyclic voltammograms of  $2.6 \times 10^{-9} \text{ mol cm}^{-2}$  (viologen groups) of PCMS-MV film on a glassy carbon electrode. The electrode was (a) equilibrated at  $-0.2\text{V}$  before potential scan, (b) equilibrated at  $-0.7\text{V}$  before potential scan. Scan rate:  $10 \text{ mV s}^{-1}$ . Supporting electrolyte:  $0.2\text{M KCl}$ .

Absorption probes, such as methyl orange, have been used to investigate the microenvironments in polymer matrices (18). For example, Martin and co-workers have applied this technique in several studies (18b-d). Methyl orange probes the hydrophobicity of binding sites (19); the absorbance maximum is 460 nm in water, but is 420-430 nm in organic solvents. For example, when it is bound to biopolymers or charged polymers, the absorbance maximum is at a shorter wavelength than 460 nm, thus indicating a higher hydrophobicity at the binding site. The difference spectra for methyl orange in PCMS-VC<sub>16</sub> coating on  $\text{SnO}_2$  electrodes is shown in Fig. 4. By taking the differ-

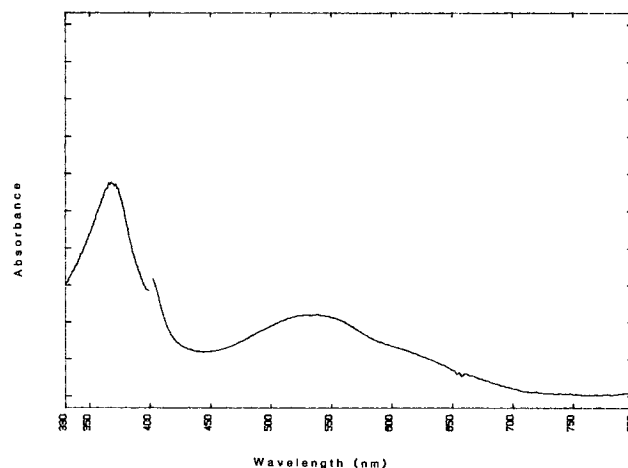


Fig. 3. Absorption spectrum of fully reduced  $2.5 \times 10^{-7} \text{ mol cm}^{-2}$  (viologen groups) of PCMS-VC<sub>16</sub> film on  $\text{SnO}_2$  electrode.

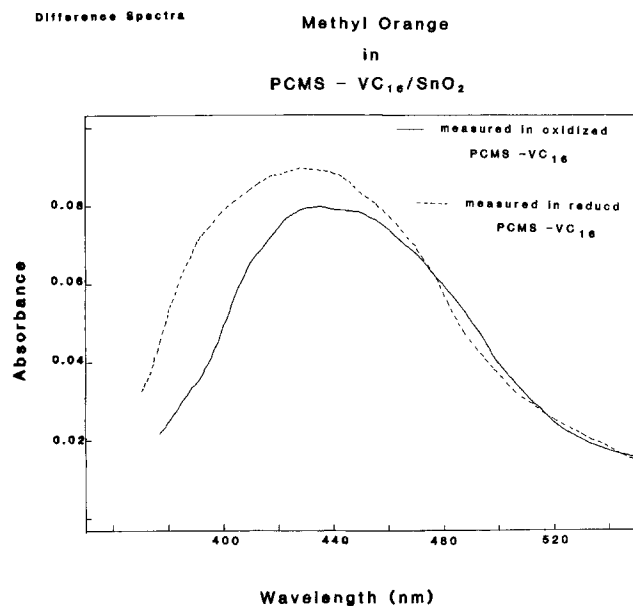


Fig. 4. Difference absorption spectra of methyl orange incorporated in the PCMS-VC<sub>16</sub> film of Fig. 3. Solid line, PCMS-VC<sub>16</sub> film fully oxidized; dotted line, PCMS-VC<sub>16</sub> film fully reduced. Supporting electrolyte: 0.2M KCl and 0.01M CH<sub>3</sub>COONa, pH = 5.6.

ence between the absorption spectrum of a PCMS-VC<sub>16</sub> coating alone and that of a PCMS-VC<sub>16</sub> coating in which methyl orange has been incorporated from a dilute solution, the contribution from the viologen groups is eliminated. Two difference spectra were taken by holding the potential of the electrode at -0.1V (oxidized form of PCMS-VC<sub>16</sub>), or at -0.6 (reduced form of PCMS-VC<sub>16</sub>). That the absorption spectrum of methyl orange incorporated in the reduced form of the polymer coating is blue shifted from that incorporated in the oxidized form indicates that the environment of the binding sites of methyl orange in the reduced form of the polymer is more hydrophobic. Thus, in the reduced form of the polymer, the long-chain hydrocarbon groups approach one another and form more compact hydrophobic domains. The result here is consistent with the conclusion drawn from the variations of  $\Delta E_{1/2}$  of the CV waves.

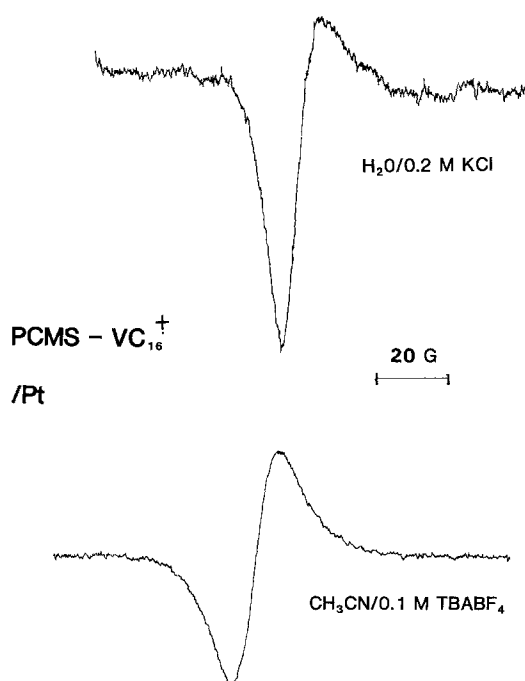


Fig. 5. ESR spectra of fully reduced  $1.4 \times 10^{-6}$  mol cm<sup>-2</sup> (viologen groups) of PCMS-VC<sub>16</sub> film on a Pt flag electrode: (a) in 0.2M KCl aqueous solution, (b) in 0.1M (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub> MeCN solution.

This is a clear demonstration of the effect of charge on the hydrophobicity of the binding sites (or the domains) associated with a polymer in aqueous solution. Previously, Ikemi *et al.* (20) used the shift of emission spectrum of the fluorescent probe, 8-anilino-naphthalene-1-sulfonate to study the effect of polymer concentration on the hydrophobicity of the hydrophobic domains formed by the triblock copolymer, poly(2-hydroxyethyl methacrylate)-poly(ethylene oxide)-poly(2-hydroxyethyl methacrylate).

**ESR experiment.**—The ESR spectra of the reduced form of PCMS-VC<sub>16</sub> are shown in Fig. 5 for (a) aqueous and (b) acetonitrile (MeCN) solutions. In MeCN (Fig. 5b) the usual spectrum of polymeric radicals, namely, an approximately symmetric single-line spectrum, is observed. The disappearance of the hyperfine structure exhibited by the monomer in dilute solution is caused by dipolar interactions and/or electron and spin exchange reactions in systems of high concentration of radicals (21). The ESR spectrum in aqueous solution (Fig. 5a) approaches the solid-state (or powder) spectrum (22) and indicates immobile radical cation side groups in the reduced PCMS-VC<sub>16</sub>. Thus, in aqueous solution the long-chain viologen radical cation side groups are embedded in very hydrophobic, only slightly swollen hydrocarbon domains. The rotational motion is severely retarded. The difference between the spectrum in aqueous and that in MeCN solution also points to the so-called hydrophobic effect—the aggregation of the amphiphilic molecules is only pronounced in those solvents with high strength of hydrogen bonding and high dielectric constant, such as water (23).

**Transmission electron microscopy.**—The size of micelles is generally in the range of 15-30Å (24). We were interested in investigating the size of the hydrophobic domains formed in polymeric surfactants and the effect of the charge on the size. Because of the film-forming property of polymeric surfactants, we were able to investigate the morphology of polymeric surfactants by transmission electron microscopy (TEM). Figure 6 shows the micrographs of several charged polymers. A polymer film cast on a carbon-coated copper grid, was stained with 2% uranyl acetate solution (Fig. 6a-e). The film of oxidized PCMS-VC<sub>16</sub> clearly shows continuous spherical domains, with typical domain diameters of about 200-500Å (Fig. 6a). The size of the domains is similar to those exhibited by synthetic vesicles (6). However, the domains in the films of vesicles are discrete, whereas in PCMS-VC<sub>16</sub>, the domains are close-packed. We believe the hydrophobic domains observed in the film of PCMS-VC<sub>16</sub> are formed both inter- and intramacromolecularly by the aggregation of the long chain viologen groups.

If the film of PCMS-VC<sub>16</sub> was first reduced chemically before staining with uranyl acetate, the size of the hydrophobic domains became smaller; the typical diameters were about 100Å (Fig. 6b). This is consistent with the results of electrochemical and absorption experiments, which indicates a more compact structure for the reduced form of the polymer.

Another polymeric surfactant PVP-C<sub>12</sub>, IV (see Experimental section), was also investigated for comparison. As shown in Fig. 6c, hydrophobic domains were also observed. However, in this case the domains showed an elliptical rather than a spherical shape. The origin of this difference is not clear. For charged polymers that do not have long-chain hydrocarbon groups, such as PCMS-MV (Fig. 6d) and sodium polystyrenesulfonate (Fig. 6e), domain structure was not observed. This supports the view that domains observed in the polymeric surfactant film are formed by the aggregation of long-chain hydrocarbon groups.

**Incorporation of hydrophobic compounds.**—We are particularly interested in the incorporation of organic molecules by polymeric surfactants for potential applications of such films in electrocatalysis. Conventional polyelectrolytes, such as protonated-polyvinylpyridine (19b), are capable of incorporating inorganic compounds (as catalysts or mediators) such as Fe(CN)<sub>6</sub><sup>3-/4-</sup> but do not incorporate organic substrates. We anticipated that the hydrophobic

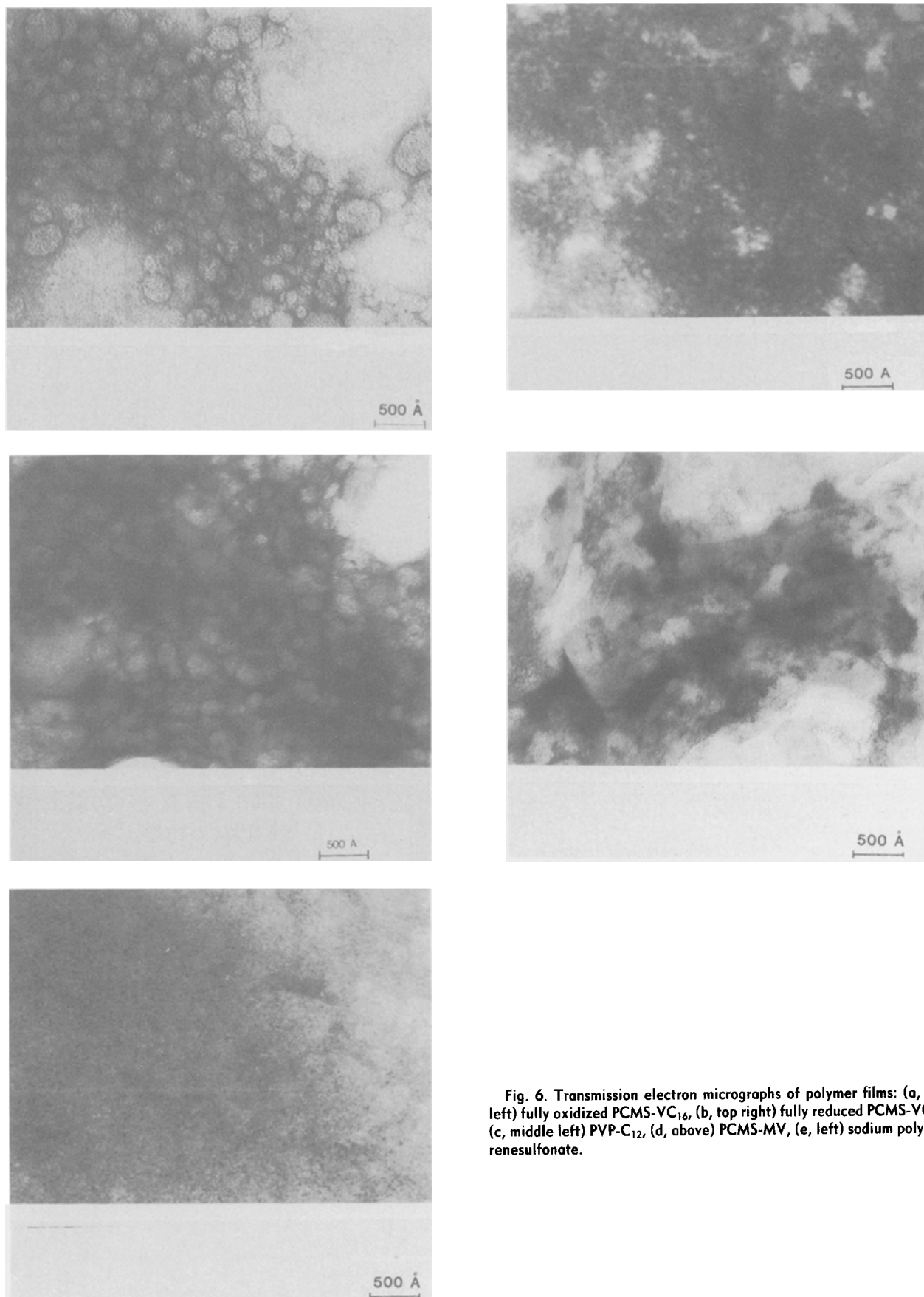


Fig. 6. Transmission electron micrographs of polymer films: (a, top left) fully oxidized PCMS-VC<sub>16</sub>, (b, top right) fully reduced PCMS-VC<sub>16</sub>, (c, middle left) PVP-C<sub>12</sub>, (d, above) PCMS-MV, (e, left) sodium polystyrenesulfonate.

domains formed by PVP-C<sub>12</sub> would incorporate organic compounds, and this was indeed observed. Previous studies of perfluorosulfonate (Nafion) and perfluoro-carboxylate (Flemion) (15, 18) indicated these perfluoro polyelectrolytes can incorporate both hydrophilic and hydrophobic compounds.

Figure 7a illustrates one such experiment. A PVP-C<sub>12</sub>-coated electrode was dipped in 1 mM anthraquinone- $\beta$ -sulfonate (AQS) aqueous solution and then transferred to a pure supporting electrolyte solution. The much larger response (reduction and reoxidation of AQS) (solid line) obtained compared with the response (dashed line) of a 1 mM

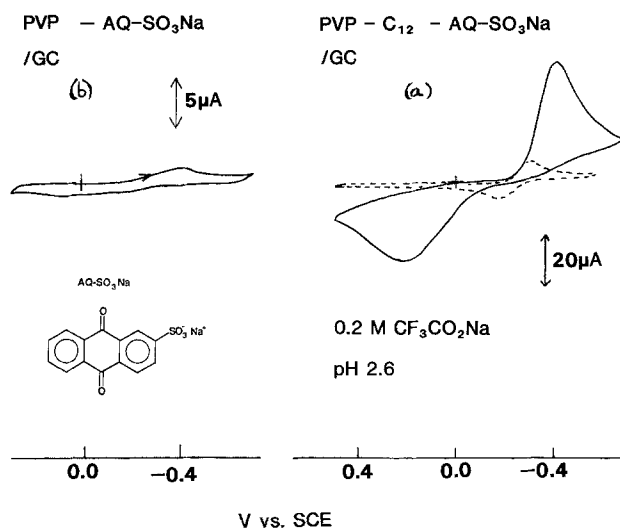


Fig. 7. Cyclic voltammograms for anthraquinone- $\beta$ -sulfonate (AQS): (a) dotted line, on uncoated electrode, 1 mM AQS; solid line, electrode coated with  $4.6 \times 10^{-7}$  mol  $\text{cm}^{-2}$  (dodecyl groups) of PVP- $\text{C}_{12}$ , dipped in 1 mM AQS solution, and replaced in pure supporting electrolyte solution; (b) repeat of (a) but with electrode coated with  $2.0 \times 10^{-6}$  mol  $\text{cm}^{-2}$  (pyridine groups) of PVP. Scan rate: 50  $\text{mV s}^{-1}$ . Supporting electrolyte: 0.2M  $\text{CF}_3\text{COONa}$ , pH = 2.6

AQS solution at an uncoated electrode indicates that a large amount of AQS has been incorporated into the PVP- $\text{C}_{12}$  coating. When the same experiment was carried out for a protonated PVP-coated electrode, the amount of incorporation was very small (Fig. 7b).

### Summary and Projections

The investigation of electroactive polymeric surfactants revealed a number of interesting properties. The film-forming property might make them more useful than micelles or even vesicles in some applications. Although vesicles do retain their structure after solvent evaporation, they do not form good films and the domains are discrete. These polymeric surfactants can behave as bound or immobilized micelles with both hydrophobic and hydrophilic domains. Films of Nafion also exhibit segregated hydrophobic and hydrophilic domains. It would be interesting to compare their behavior with those of the polymeric surfactants. These polymeric surfactants may also be useful as model systems for electron or energy transfer reactions in organized assemblies. With stable films, investigation by the combination of electrochemical, spectroscopic, and other techniques can be easily carried out.

The effects of charge on the side groups on the morphology of polymeric surfactants have been demonstrated, and it was shown that reduction of the viologen groups leads to a more compact structure in the polymer. Studies of the morphology and properties of blends of polymeric surfactants with other polymers should also be of interest.

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## Rotating Disk Characterization of Factors Limiting the Performance of Li/FeS<sub>2</sub> Cells

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### ABSTRACT

High resistance, which limited the power output, was measured for both the upper and the lower (voltage) discharge plateaus of a Li-Si/LiCl-KCl eutectic/FeS<sub>2</sub> cell. Seventy-five percent of the total resistance has been determined to reside in the porous FeS<sub>2</sub> electrode. A planar Fe electrode, which has a more uniform potential distribution than a porous electrode, was designed to investigate the controlling mechanisms which are responsible for this high resistance. Cyclic voltammetric experiments with a planar Fe rotating disk electrode were conducted. It was found that the electrochemical reaction associated with the lower discharge plateau of Li/FeS<sub>2</sub> cells is controlled by mass transport in the solid phase (X-phase), while the electrochemical reaction associated with the upper discharge plateau is controlled by mass transport in the molten salt. This implies that: (i) the particle size in FeS<sub>2</sub> electrodes has to be minimized in order to reduce the internal resistance observed for the lower plateau, and (ii) agitation of the molten salt is needed to reduce the internal resistance for the upper plateau.

During testing of 60 Ah Li-Si/LiCl-KCl eutectic/FeS<sub>2</sub> cells, high internal resistance, or high overpotential, has been observed (1). A small test cell (2) (0.6 Ah capacity) with a porous FeS<sub>2</sub> working electrode, a Li-Si counterelectrode, and two Li-Al reference electrodes was subsequently designed to study the contributions of various cell components to this internal resistance. The results (2) indicated that 75% of the overall resistance was associated with the FeS<sub>2</sub> electrode. However, it was not known whether this high resistance is caused by activation or mass-transfer control. Rotating disk experiments were thus required to differentiate between these two possible processes.

In the past, porous FeS<sub>2</sub> electrodes were employed (2-4) for studies on Li/FeS<sub>2</sub> cells. However, the current and potential distributions in a porous electrode are nonuniform. Moreover, it is very difficult to interpret rotating disk data obtained from a porous FeS<sub>2</sub> electrode. Therefore, a planar FeS<sub>2</sub> electrode, with more uniform current and potential distributions than those for a porous electrode, is needed to isolate causes for the high internal resistance of Li/FeS<sub>2</sub> cells.

The approach taken in this work was first to fabricate a planar Fe electrode and then to convert it electrochemically to FeS and FeS<sub>2</sub>. The Fe electrode was fusion-bonded to a molybdenum sleeve, nonreactive in the Li/FeS<sub>2</sub> cell environment, to prevent the electrolyte leakage. Cyclic voltammetry was then conducted with this rotating electrode, and the causes of overpotential were analyzed by comparing its behavior with that of a porous electrode under identical conditions.

### Experimental

**Cell configuration.**—The test cell is shown in Fig. 1. The distance between the capillary opening of the reference electrode and the working electrode was 1 mm. Therefore, the electrolytic resistance between the working and the reference electrodes was 0.022Ω at 430°C based on the reported (5) electrical conductance of pure LiCl-KCl eutectic electrolyte. Since the total current passed through the cell was in the milliamperage range, the ohmic loss between the working and the reference electrodes was negligible.

**Planar iron working electrode.**—For the planar Fe electrode, a 4.83 mm diam iron disk (99.999% pure) was fusion

bonded to a 7.94 mm od molybdenum sleeve. The fusion bonding process consisted of melting the iron disk under the inert atmosphere inside a helium-filled glove box using a welding torch. The temperature was measured by an optical pyrometer and was maintained at about 1600°C to minimize molybdenum diffusion into the iron. The electrode was then prepared by wet grinding on 600 grit paper and then polished using 1 μm alumina.

A scanning electron micrograph of the planar Fe electrode is shown in Fig. 2. Complete bonding between iron and molybdenum is observed. Figure 2 also shows a dendritic phase at the edge of the planar Fe electrode, indicating the possibility of molybdenum diffusion into the iron electrode during fusion bonding. A microprobe study of the electrode (Fig. 3) indicated that the molybdenum diffusion front was only 50 μm from the iron-molybdenum

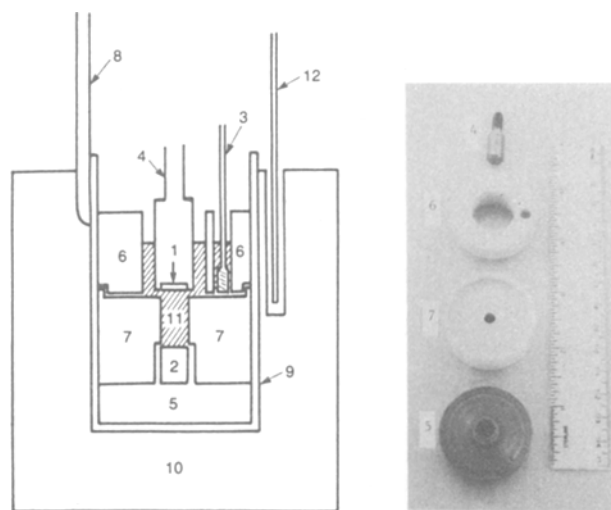


Fig. 1. Schematic diagram of a test cell. 1, Fe disk electrode; 2, Li-Si counterelectrode; 3, Li-Al reference electrode; 4, Mo sleeve; 5, stainless steel holder of counterelectrode; 6, boron nitride fixture 1; 7, boron nitride fixture 2; 8, counterelectrode lead; 9, stainless steel beaker; 10, alumina thermal mass; 11, LiCl-KCl eutectic saturated with Li<sub>2</sub>S; 12, thermocouple.