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Electron Transfer to Anionic Reactants Incorporated within Polycationic Coatings on Glassy Carbon Electrodes. Comparison of Random and Block Copolymers[†]

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Block and random copolymers containing varying ratios of styrene and *p*-(diethylaminomethyl)styrene were synthesized and used to coat glassy carbon electrodes. In acidic electrolytes the coatings become polycationic and incorporated electroactive ions such as $Fe(CN)_6^{4-}$ by anion exchange. With ratios of styrene to (aminomethyl)styrene groups up to ca. 2:1, the electrochemical responses exhibited by incorporated anions are very different in coatings prepared from random and block copolymer coatings of the same composition. As the quantity of protonated amino groups in the copolymer coatings increases, the electrochemical behavior of incorporated anions becomes more similar. The contrasting electrochemical behavior appears to originate in differences in the size of, and connections between, hydrophilic domains that are formed spontaneously within the coatings. Diffusion coefficients of the incorporated anions decrease sharply with the total quantity incorporated.

A variety of polyionic materials has been employed to coat electrode surfaces where they can be used to confine high concentrations of electroactive counterions on the surface.[1-13] Electrochemical measurements with such ion-containing coatings can provide useful information on their internal morphologies and behavior as ion exchangers. However, rather little attention has been paid thus far to the effects of systematic structural variations in the polymers on their capacities to retain counterions and to provide the facile ionic propagation rates within the coatings that are required to sustain high currents. Electrode coatings prepared from a blend of a ternary random copolymer and various homopolymers were described recently and shown to have several properties desirable in electrocatalytic and electrosynthetic applications.[12,14,15] An important feature of this blend was the spontaneous segregation into hydrophilic and hydrophobic domains exhibited by coatings prepared from it.[14] We have subsequently observed domain formation in coatings prepared from single-component polyelectrolytes containing both hydrophilic and hydrophobic groups. Such behavior is observed, for example, in coatings prepared from copolymers of styrene and *p*-(diethylaminomethyl)styrene under conditions where the amino groups are protonated. In this study a series of both random and block copolymers containing these two groups was synthesized and used to cast polycationic coatings on glassy carbon electrodes. The electrochemical responses obtained from electroactive anions incorporated into the coatings proved sensitive to both the structure and composition of the polyelectrolytes. Our new observations and suggested interpretations are presented in this report.

Experimental Section

Synthesis. The structures of the new polymers prepared as part of this study are shown in Figure 1.

(4-Vinylbenzyl)diethylamine (I). Seventy grams of (4-chloromethyl)styrene (Seimi Chemical Co., Tokyo) (0.46 mol) was added to 67 g of diethylamine (0.92 mol) in 100 mL of methanol, and the resulting mixture was refluxed for 2 h. The solvent was removed by evaporation, and 100 mL of 6 M HCl was added to the residue, which was subsequently extracted three times with diethyl ether to remove any unreacted (4-chloromethyl)styrene. Fifty grams of NaOH dissolved in 50 mL of H_2O was then carefully added to the aqueous layer, which was further extracted with ether. The ether extracts were dried with $MgSO_4$, and the solvent was evaporated. I (7.3 g) was obtained by distillation under reduced pressure: yield 84%; bp 85 °C at 1.2 mmHg. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.47; H, 10.18; N, 7.28. The NMR spectrum was in accord with the structure shown in Figure 1.

Block Copolymer II. The block copolymers corresponding to structure II in Figure 1 were obtained by anionic polymerization of styrene and I. Appropriate quantities of dry styrene (~25 mmol), dry I, and sodium naphthalide (~0.1 mmol) were prepared in separate aliquots of dry THF on a vacuum line. The sodium naphthalide solution was transferred to 100 mL of dry THF followed by the styrene solution, whereupon the color changed from green to cherry red indicating the presence of a "living" anion. After 1 h of stirring, the solution was cooled to −77 °C, and the solution of I in THF was transferred into the solution of living anion. The mixture was stirred for 23 h at −77 °C, the living anion was deactivated by addition of methanol, and the block copolymer was isolated by addition of aqueous methanol (the ratio of H_2O to MeOH was increased as the amine content of the copolymer decreased). The product was dissolved in benzene and freeze-dried. Typical yields were 80–85%. The compositions of the resulting ABA-type block copolymers were determined by elemental analysis and checked by NMR. Molecular weights were estimated by gel permeation chromatography (GPC). The results were summarized in Table I.

Random Copolymer III. The random copolymers were obtained by radical polymerization of styrene and I. Appropriate quantities of the two monomers were dissolved in benzene to obtain about 25 mL of a solution 1.5 M in total monomer. AIBN (azobis(isobutyronitrile)) (0.4 mol %) was added, and the mixture was allowed to react for 24 h at 60 °C in a previously degassed reaction ampule. Isolation, workup, and characterization procedures followed those employed with the block copolymer. Typical yields of random copolymer were 20–30%. The compositions of the set of random copolymers that were prepared are

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[†] Contribution No. 7356.

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TABLE I: Polymers Prepared as Part of This Study

		elemental analysis							
		C		H		N			
abbrev	polymer type[a]	found	calcd	found	calcd	found	calcd	amino group content,[b] %	$\bar{M}_w$[c]
B-30	II	88.00	87.98	8.80	8.78	3.12	3.24	30	88
B-46	II	86.47	86.30	9.21	9.19	4.58	4.51	46	67
B-80	II	83.52	83.67	9.77	9.83	6.55	6.50	80	84
R-19	III	89.34	89.34	8.63	8.45	2.18	2.21	19	89
R-30	III	87.83	87.98	8.73	8.78	3.27	3.24	30	37
R-36	III	87.33	87.32	8.92	8.94	3.77	3.74	36	132
R-50	III	85.98	85.95	9.27	9.27	4.75	4.77	50	51
R-63	III	84.76	84.87	9.36	9.54	5.46	5.59	63	149
R-81	III	83.47	83.60	9.63	9.84	6.45	6.55	81	52

[a] See Figure 1. [b] From elemental analysis. [c] Weight-average molecular weight in kilodaltons as estimated by gel permeation chromatography using polystyrene of known $\bar{M}_w$ as a standard.

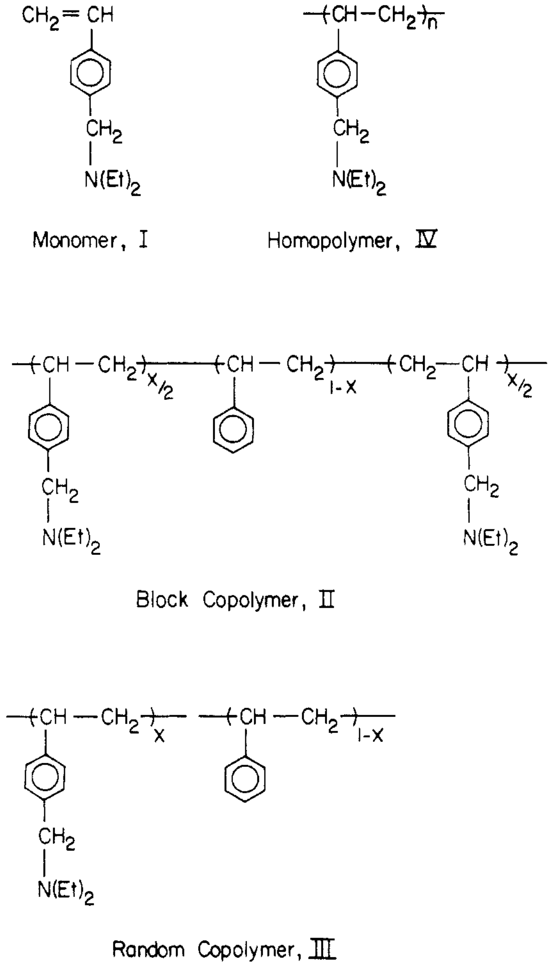

Figure 1. Formulas of the block and random copolymers examined in this study.

given in Table I.

Homopolymer IV. A homopolymer of I was obtained by radical polymerization following the procedure employed for the random copolymers. The product was precipitated by addition of acetone and freeze-dried from a benzene solution. MW = 86 000 Da (GPC).

Materials. Chemicals and reagents were used as received with the following exceptions: Sytrene (Matheson) was distilled just prior to use and dried for 2 days over CaH_2. AIBN (Polysciences, Inc.) was recrystallized from methanol. Tetrahydrofuran (THF) (Matheson) was prepared by refluxing 12–24 h over sodium and distillation into a storage flask that contained sodium and a trace of benzophenone, whose purple anion radical confirmed the absence of water. Just before polymerization the volume of solvent needed was transferred on a vacuum line, first into an ampule in which a sodium mirror had been deposited on the wall and subsequently into the reaction ampule. The polystyrene (Alfa) that was used to make blends with homopolymer IV had a molecular weight of 93 000 Da.

Procedures. Polymer coatings were cast on the surface of freshly polished (0.3 μm alumina) and subsequently sonicated glassy carbon electrodes (0.34 cm^2) by transferring 1 μL of 0.5 wt. % solutions of the polymers in THF to the surface and allowing the solvent to evaporate at room temperature for at least 15 min.

$Fe(CN)_6^{4-}$ anions were incorporated into the coatings by immersion in 0.1 mM solutions of the anion in 0.1 M acetate buffer adjusted to pH 4.5. The quantities incorporated were determined by coulometric assay immediately after the coated electrode was transferred to a pure supporting electrolyte solution. The charge passed was measured as the electrode potential was scanned at 50 mV s^{-1} from −0.2 to +0.4 V, where it was held until the flow of charge had decayed to background levels.

Diffusion coefficients for $Fe(CN)_6^{4-}$ within the coating were evaluated from the slopes of chronocoulometric charge–(time)$^{1/2}$ plots as previously described.[14] The chronocoulometric data were obtained with a commercial instrument (Bioanalytical Systems Model 100) and analyzed manually. The coating thicknesses required in order to calculate diffusion coefficients were estimated from micrometer measurements conducted with electrodes containing ca. 100-fold greater quantities of the polymers. The procedure has been previously described.[13]

Cyclic voltammograms were obtained with conventional procedures and instrumentation. Potentials were measured and are reported with respect to a sodium chloride saturated calomel electrode (SSCE). Solutions were prepared with distilled water that had been further purified by passage through a purification train (Barnsted Nanopure Organo-pure).

Transmission electron micrographs were obtained with a Phillips EM 201 instrument. Copper minigrids for the electron microscope were coated with polymers and stained with $IrCl_6^{2-}$ as described previously[14] except that a more concentrated solution (~0.1 mM) was employed. Aliquots (1 μL) of 0.5 wt % solutions of the polymer were employed to coat minigrids in each case. This 100-fold increase in the amount of polymer compared with our previous study[14] was required to obtain satisfactory images.

Results and Discussion

A list of the three block and six random copolymers examined in this study is given in Table I. The fraction of the monomeric groups that contained the protonatable amine function was varied between 30 and 80% for the set of block copolymers and between 19 and 81% for the set of random copolymers.

To compare the behavior of electrode coatings prepared from the various copolymers a standard procedure was adopted: Coated electrodes were cycled between −0.2 and +0.5 V in 0.1 mM solutions of $Fe(CN)_6^{4+}$ until the peak currents had stabilized at their maximum value. The electrode was then transferred to a solution containing only supporting electrolyte, where the quantity of electroactive counterion retained by the coating was measured immediately and again 45 min later to assess the ability of the coatings to retain the incorporated anions for extended periods. A qualitative indication of a coating's retention capability could also be judged from the magnitude of peak currents for voltam-

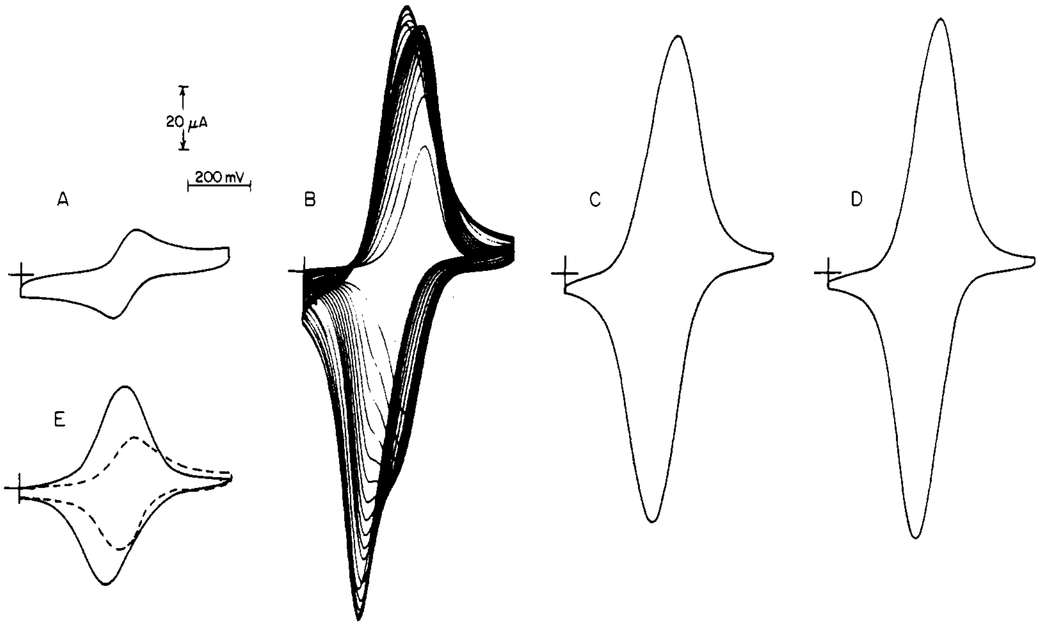

Figure 2. Cyclic voltammograms for 0.1 mM $Fe(CN)_6^{4-}$ at a glassy carbon electrode coated with block copolymer B-30 (Table I). (A) Bare electrode. (B) After electrode was coated with 3.0×10^{-8} mol cm^{-2} of B-30. Voltammograms recorded repetitively until a steady response was obtained. (C) Immediately after transfer of electrode used to record B to pure supporting electrolyte solution. (D) As in C, 45 min after transfer. (E) As in C (solid line) and D (dashed line) with coating cast from 1:1 THF–MeOH. Supporting electrolyte: 0.1 M acetate (pH 4.5). Potential scanned at 100 mV s^{-1} between −0.2 and 0.5 V.

mograms recorded immediately and 45 min after coated electrodes were transferred to pure supporting electrolyte.

Application of this protocol for testing the coating materials revealed striking differences between random and block copolymers. For example, the cyclic voltammograms in Figure 2 show the behavior of B-30, a block copolymer in which 30% of the monomeric units contain protonated amine groups. Figure 2A is a voltammogram for 0.1 mM $Fe(CN)_6^{4-}$ recorded at the bare glassy carbon electrode. Figure 2B was obtained with the same solution after the electrode had been coated with B-30. Incorporation of $Fe(CN)_6^{4-}$ into the coating by ion exchange leads to much larger concentrations at the electrode surface than in the bulk of the solution with a corresponding increase in peak currents. In addition, the peak potentials shift because the formal potential of the incorporated $Fe(CN)_6^{4-}$ couple, which dominates the response, is different from its formal potential in solution. Parts C and D of Figure 2 were recorded immediately and 45 min after the electrode was transferred to pure supporting electrolyte. The coating retains almost all of the incorporated $Fe(CN)_6^{4-}$ anions during the 45-min waiting period. Quantitative data on the incorporation and retention of $Fe(CN)_6^{4-}$ by B-30 coatings are summarized in the first row of Table II. The coating incorporated $Fe(CN)_6^{4-}$ anions to 63% of its theoretical capacity and retained all of them 45 min after transfer to pure supporting electrolyte. This behavior compares favorably with that of an unusually attractive two-component polymer blend described recently.[12,14]

Coatings prepared from R-30 (Table I), a random copolymer with the same fraction of protonated amine groups as B-30, exhibited very different behavior (Figure 3). There was essentially no incorporation of $Fe(CN)_6^{4-}$ by the coatings even after 1 h of exposure to a 0.1 mM solution (Figure 3A). Increasing the amine content of the random copolymer to 36% gave polycationic coatings that did incorporate $Fe(CN)_6^{4-}$ (Figure 3B). However, the incorporation rate was very low (14 h was required to obtain the peak currents in Figure 3B), and the coatings appeared to be less conductive because the separation between anodic and cathodic peak potentials was much larger than for coatings prepared from B-30. Speculation on the origin of the differences in behavior of these random and block copolymer coatings is reserved for a later section.

Higher Fractions of Amino Groups. When the amine content of the copolymers was increased to ca. 50%, the ion-exchange behavior of random and block copolymers became more similar (Figure 4 and Table II). The coatings derived from the random copolymer (R-50) incorporated and retained somewhat more than did the corresponding block copolymer (B-46) (Table II). The B-46 coating was also inferior to that prepared from B-30 with respect to both the quantity of $Fe(CN)_6^{4-}$ incorporated per protonated amine group and the retention of $Fe(CN)_6^{4-}$ in pure

TABLE II: Electrochemical Data for $Fe(CN)_6^{4-}$ Incorporated in Polymer Coatings on Glassy Carbon Electrodes

polymer[a]	$10^8\Gamma_p$,[b] mol cm^{-2}	$10^9\Gamma_o$,[c] mol cm^{-2}	$4\Gamma_o/\Gamma_p$[d]	Γ_{45}/Γ_o[e]	$10^4\phi$,[f] cm
B-30	3.0	4.9	0.63	1.0	0.30
B-46	4.2	3.7	0.39	0.91	0.43
B-80	5.7	4.4	0.36	0.86	0.58
R-50	4.4	5.3	0.48	0.97	0.24
R-63	5.2	2.8	0.21	0.86	g
R-81	6.1	2.8	0.18	0.90	g

[a] Abbreviations correspond to those in Figure 1 and Table I. [b] Quantity of amino groups in the polymer deposited on the electrode. [c] Quantity of $Fe(CN)_6^{4-}$ incorporated by the coating. [d] Fraction of the amino groups in the coating involved in electrostatic binding of $Fe(CN)_6^{4-}$. [e] Fraction of the originally incorporated $Fe(CN)_6^{4-}$ remaining in the coating 45 min after transfer to pure supporting electrolyte solution. [f] Coating thickness; estimated as described in the Experimental Section. [g] Coatings too unstable in aqueous electrolyte for ϕ to be measured.

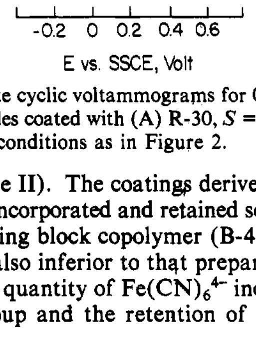

Figure 3. Steady-state cyclic voltammograms for 0.1 mM $Fe(CN)_6^{4-}$ at glassy carbon electrodes coated with (A) R-30, S = 30 μA and (B) R-36, S = 7.5 μA. Other conditions as in Figure 2.

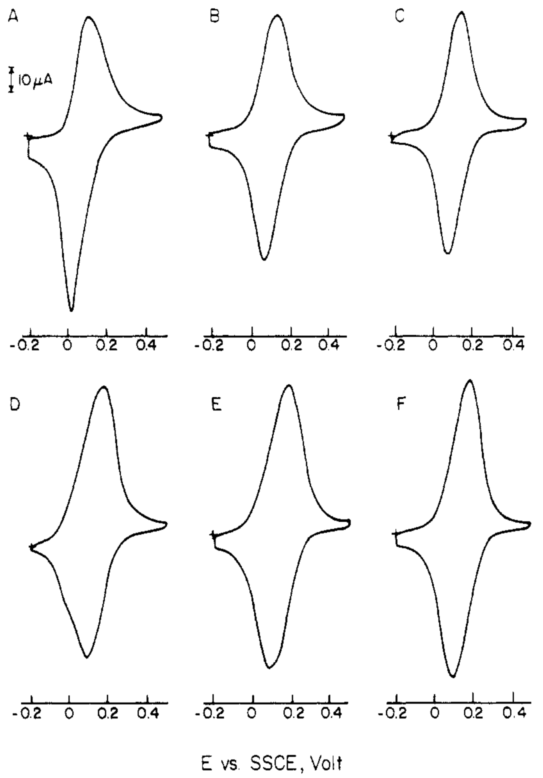

Figure 4. Steady-state cyclic voltammograms for 0.1 mM $Fe(CN)_6^{4-}$ at electrodes coated with B-46 or R-50: (A, B, C) B-46 coating before, immediately after, and 45 min after transfer, respectively, from 0.1 mM solution to pure supporting electrolyte; (D, E, F) repeat with electrode coated with R-50.

supporting electrolyte. The behavior of coatings of B-46 was subject to significant variation depending on the details of the casting procedure (slow vs. rapid solvent evaporation, temperature, etc.). However, there was no doubt that the reproducibly distinct differences between coatings of B-30 and R-30 were no longer present when B-46 was compared with R-50. Apparently, as the quantity of hydrophilic groups in the random copolymer increases, its coatings adopt structures in which increasing fractions of the protonated amino groups are accessible to the supporting electrolyte to participate in ion-exchange reactions.

When the hydrophilic content of the block or random copolymers is increased much above 50% the resulting coatings swell excessively and appear to dissolve partially in the supporting electrolytes. One result is a decrease in the quantity of $Fe(CN)_6^{4-}$ incorporated by electrodes coated with B-80, R-63, and R-81 (Tables I and II). However, the anions that are incorporated in the adherent portion of the coatings continue to be substantially retained after the electrodes are transferred to solutions containing only supporting electrolyte. Thus, there are optimum composition ranges for both random and block copolymers to obtain stable coatings with good ion-exchange capacities.

Comparison with Blends of Homopolymer. The desirable properties exhibited by the copolymers (B-30, B-46, and R-50) could not be matched by merely blending polystyrene and the appropriate homopolymer (polymer IV in Figure 1) in the same proportions as those present in the polymers. Coatings prepared from such blends exhibited significantly smaller ion-exchange capacities, and incorporated counterions were lost rather quickly following transfer of the coatings to solutions of pure supporting electrolyte.

Transmission Electron Micrographs. The structures assumed by coatings prepared from the block and random copolymers B-30 and R-30 were compared by means of transmission electron microscopy. The two micrographs shown in Figure 5 reveal the remarkably spherical shapes of domains into which both polymers apparently segregate. These spherical domains are dark because they are stained by the $IrCl_6^{2-}$ staining agent, which indicates that they probably represent hydrophilic portions of the coatings located within a featureless hydrophobic matrix. Formation of such spherical, segregated domains is to be expected in films cast from polymers containing both hydrophilic and hydrophobic groups.[17] For both of the films in Figure 5 the spherical domains appear fairly large with diameters of 1000–3000 Å. The difference between the two micrographs that we regard as most significant in the electrochemical experiments is the greater extent of apparent connections between the hydrophilic domains within the coatings prepared from the block (Figure 5A) compared with the random (Figure 5B) copolymer. The connecting hydrophilic channels within coatings of B-30 could provide the pathways over which the incorporated $Fe(CN)_6^{4-}$ anions diffuse to the underlying electrode surface to yield the larger cyclic voltammetric responses obtained (compare Figures 2B and 3A). The structural differences between block and random copolymers were not present in coatings prepared from B-46 or R-50, both of which had structures resembling that exhibited by B-30. The higher content of hydrophilic groups in R-50 is apparently sufficient to provide adequate channels for the facile diffusion of the incorporated $Fe(CN)_6^{4-}$ anions indicated by the voltammetric responses shown in Figure 4C.

The properties and morphology of ABA triblock copolymers are expected to depend markedly on the identity of the central block.[18] Thus, the behavior we observed with coatings prepared from the poly[(aminomethyl)styrene]–poly(styrene)–poly[(aminomethyl)styrene] block copolymer would not be expected to mimic that of coatings prepared from the BAB block copolymer poly(styrene)–poly[(aminomethyl)styrene]–poly(styrene).[19]

Effect of Casting Solvent. The domain structure of coatings of B-30 revealed in Figure 5A can be largely eliminated if the solvent from which the coatings are cast is changed. Mixing 1 μL of a 0.5 wt % THF solution of B-30 with 1 μL of methanol on the electrode surface produced a coating that exhibited the electron micrograph shown in Figure 6. A few large spherical domains are evident, but the majority of the stained (presumably) hydrophilic portions of the coatings have diameters of only ca. 100 Å and lie scattered throughout the coating with no evident connecting channels. THF is a good solvent for B-30. In THF solutions of the polymer the hydrophilic poly[(aminomethyl)-styrene] blocks that are separated by the poly(styrene) block are presumably able to expand and move relatively freely, which would promote their clustering together in hydrophilic domains as the solvent evaporated. Methanol is a rather poor solvent for B-30, so that the poly[(aminomethyl)styrene] blocks may have more difficulty in segregating into connected, hydrophilic domains in coatings cast from the mixed THF–MeOH solvent.

The differences in the structure of coatings cast from the mixed THF–MeOH solvent are also reflected in their electrochemical behavior: Fewer $Fe(CN)_6^{4-}$ counterions are incorporated, and they are not retained as well in pure supporting electrolyte. For example, the cyclic voltammograms shown in Figure 2E were obtained with coatings of B-30 that had been cast from the mixed THF–MeOH solvent. The smaller peak current and its 2-fold decrease within 45 min are in sharp contrast with the behavior of coatings of the same copolymer when cast from pure THF (parts C and D of Figure 2). Coating structures with large interconnected domains as in Figure 5A evidently favor the superior electrochemical responses apparent in Figure 2.

Diffusion Coefficients for Incorporated Anions. The maximum rate with which electronic charge can be carried across polymer coatings by means of incorporated redox couples is determined by the diffusion coefficient, D_E, of the ions comprising the incorporated couple.[16] It was therefore of interest to compare D_E values for $Fe(CN)_6^{4-}$ incorporated in random and block copolymer coatings. Table III summarizes diffusion coefficients evaluated

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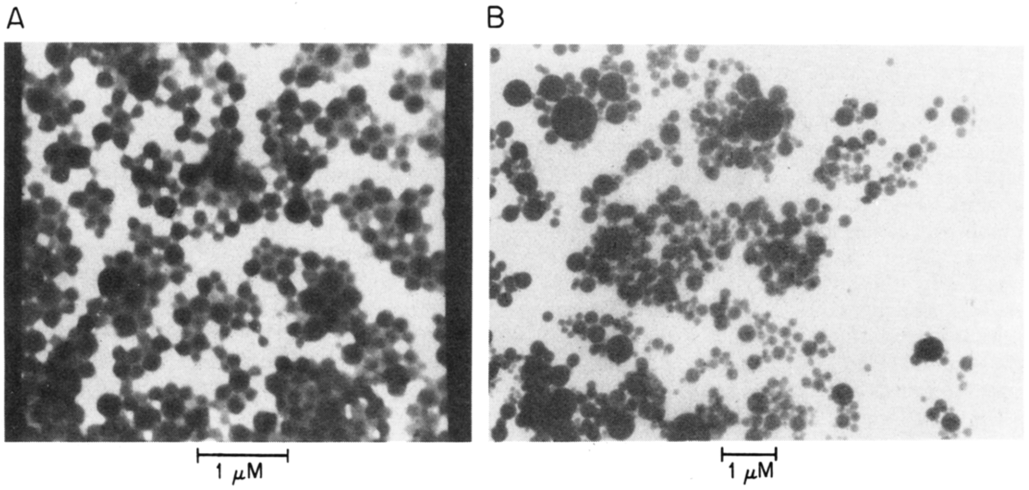

Figure 5. Transmission electron micrographs of random and block copolymer coatings: (A) block copolymer B-30; (B) random copolymer R-30. Coatings were cast from THF solutions of the polymers.

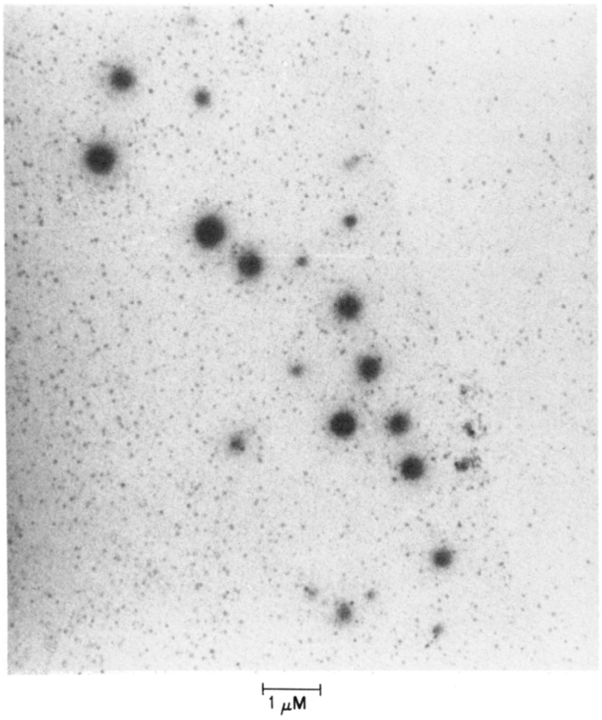

Figure 6. Transmission electron micrograph of a coating of block copolymer B-30 cast from 1:1 THF–MeOH.

for three block and one random copolymers by the procedure given in the Experimental Section. The 4-fold larger value of D_E for the B-46 than for the R-50 coating is significant. It means that even though these two copolymers have comparable ion-exchange and retention properties, the block copolymers could sustain much higher charge propagation rates. An additional point worth noting is the monotonic increase in D_E for the block copolymers as the fraction of hydrophilic groups increases. This could be a reason to prefer coatings prepared from B-80 over those prepared from B-46. However, B-80 yields less stable coatings with poorer counterion retention properties because of its greater solubility in aqueous electrolytes so that it is not an attractive coating material.

The magnitudes of the D_E values in Table III are somewhat larger than previous values reported for $Fe(CN)_6^{3-}$ incorporated into coatings of protonated poly(4-vinylpyridine).[20] In both cases, however, the diffusion coefficient decreases as the quantity of the ion incorporated in the coatings increases. For example, the steep, essentially linear decrease of D_E for $Fe(CN)_6^{4-}$ as its concentration is increased in a coating prepared from the block copolymer B-30 is shown in Figure 7. Such behavior has been ascribed to increasing electrostatic cross-linking by the multiply charged, incorporated counterions that results in increasing resistance to their diffusive motion within the coatings.[20,21]

TABLE III: Diffusion Coefficients for $Fe(CN)_6^{4-}$ Incorporated in Random and Block Copolymer Electrode Coatings

polymer[a]	$10^9\Gamma_o$,[b] mol cm^{-2}	$10^9 D_E$,[c] cm^2 s^{-1}
B-30	4.9	1.9
B-46	3.7	6.6
B-80	4.4	9.2
R-50	5.3	1.5

[a] Abbreviations correspond to those in Table I and Figure 1. [b] Quantity of $Fe(CN)_6^{4-}$ incorporated by the coating. [c] Diffusion coefficient evaluated from the slope of chronocoulometric charge–(time)$^{1/2}$ plots.

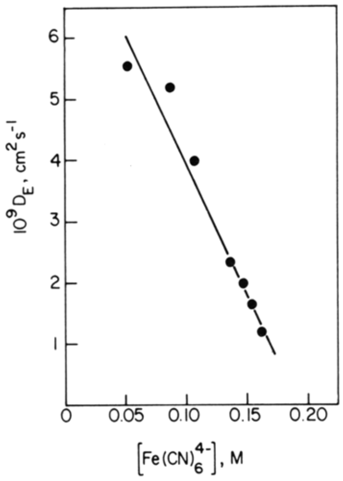

Figure 7. Diffusion coefficients for $Fe(CN)_6^{4-}$ incorporated in a coating of block copolymer B-30 on glassy carbon electrodes. After incorporation of each quantity of $Fe(CN)_6^{4-}$, the coated electrodes were transferred to pure supporting electrolyte (0.1 M acetate buffer at pH 4.5) for measurements of D_E.

Much larger values of D_E for $Fe(CN)_6^{4-}$ have been reported for coatings prepared from a blend of a ternary copolymer with a variety of homopolymers.[12,14] These coatings appeared to swell more than those employed in the present study, but the origin of the very high rates of diffusion of $Fe(CN)_6^{4-}$ anions within them has yet to be established.

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Conclusions

The combination of results presented here supports the idea that the internal structure of polyelectrolyte coatings on electrodes strongly influences the electrochemical behavior of electroactive counterions incorporated in them. For the particular combination of styrene and (dialkylaminomethyl)styrene monomer units examined in this study, the block copolymers yielded coatings with more desirable properties than did corresponding random copolymers if more than half of the styrene groups present were unsubstituted. However, with copolymers containing a larger proportion of amino groups the difference between block and random copolymers was not significant. Both types of polymer yield highly swollen, partially soluble, and therefore unstable, coatings when more than 70–80% of the styrene groups contain amine substituent groups. The electrochemical behavior exhibited by coatings, as well as their internal structures, was influenced strongly by the nature of the casting solvent employed. Diffusion coefficients for incorporated $Fe(CN)_6^{3-}$ anions are notably larger in block than in random copolymer coatings, although neither type of coating exhibits diffusion coefficients nearly as large as those reported recently for a ternary copolymer–homopolymer composite.[14] Understanding the reasons for this difference is one objective of continuing studies.

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Registry No. I, 3749-75-5; $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_6^{3-}$, 13408-62-3; C, 7440-44-0; 4-(chloromethyl)styrene, 1592-20-7; diethylamine, 109-89-7; styrene, 100-42-5.

Charge-Transfer Reactions in Pendant Viologen Polymers Coated on Graphite Electrodes and at Electrode/Pendant Viologen Polymer Film Interfaces

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Charge-transfer reactions in poly(styrene-*co*-chloromethylstyrene) pendant viologens (PMV) with various loadings (x = 3–34%) of viologen sites coated on graphite electrodes and at electrode/PMV film interfaces were examined by cyclic voltammetry and normal pulse voltammetry. The relevant parameters characterizing these charge-transfer reactions (i.e., apparent effective diffusion coefficient D_{app} for the homogeneous charge-transport process and standard rate constant k° and cathodic transfer coefficient α_c for the heterogeneous electron-transfer reaction) were obtained for the PMV films with various x's. As x was increased from 9% to 34%, which corresponds to the concentrations ($C_{MV^{2+}}^{obsd}$) of electroactive viologen sites from 6.7×10^{-5} to 3.3×10^{-4} mol cm^{-3}, D_{app} increased from 2.5×10^{-11} to 3.9×10^{-10} cm^2 s^{-1}, k° increased from 3.0×10^{-5} to 8.9×10^{-5} cm s^{-1}, and α_c was independent of $C_{MV^{2+}}^{obsd}$ (0.42 ± 0.04). The finding of the almost linear dependence of D_{app} on $C_{MV^{2+}}^{obsd}$ suggests the significant contribution of electron self-exchange between viologen redox couples confined in the polymer chain to the overall charge transport in the PMV films. On the basis of these results, the mechanism of the charge-transport process within PMV films is discussed.

Introduction

The mechanism and kinetics of charge-transport processes in thin polymer films on electrodes have become of considerable interest in the present stage of research in "polymer-coated electrodes".[1-13] Physical models for the mechanisms of charge transport in the polymer film, factors affecting their electrochemical response, and mathematical modeling have been presented and studied. The details of charge transport are hard to ascertain on a molecular level and probably differ for different systems. However, in a number of cases the charge transport seems to be adequately described phenomenologically by simple diffusion across a concentration gradient.[1-5,7a,8a,9a,b,12] Thus, apparent effective diffusion coefficients (D_{app}) have been obtained. An understanding of the obtained D_{app}'s is complicated because, in addition to electron-transfer reactions, we must consider polymer motion, diffusions of electrolyte and solvent, and changes in polymer layer structure with oxidation and reduction. In any case, charge (ion or electron) transport in redox polymer films is considered to occur via electron hopping between redox sites (species)[1a,b,2c-e,3e,i,4a,e,g,12,14,15] and/or the physical diffusion of redox species themselves.[1b,2a-c,3b,e,4b,c,h,i,5,9a] Especially when redox sites are covalently bonded to polymer chains, an electron-hopping charge-transport mechanism seems to be operative.

According to Dahms–Ruff's idea[14,15] proposed for charge transport in solutions, whenever electron self-exchange makes a significant contribution to the diffusion process, D_{app} should exhibit a linear dependence on the concentration (C) of electroactive sites in polymer films.[2d,3i,13] However, in most cases, such a concen-

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