Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Dewi, Eniya Listiani , Nakano, Hiroko , Oyaizu, Kenichi , Nishide, Hiroyuki and Tsuchida, Eishun(2003) 'Ion-Exchange and Apparent Diffusion Coefficients Within Cationic Polysulfonium Coatings Containing Ferricyanide', Journal of Macromolecular Science, Part A, 40: 1, 37 — 47

To link to this Article: DOI: 10.1081/MA-120016672

URL: http://dx.doi.org/10.1081/MA-120016672

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JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. 40, No. 1, pp. 37–47, 2003

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ABSTRACT

A cationic polyelectrolyte of various poly(arylenesulfonium salt)s were coated on the surface of glassy carbon electrodes with an incorporated ferricyanide anion from the electrolyte solutions. The apparent diffusion coefficients of $Fe(CN)_6{}^{3-}$ that are electrostatically bound were determined by chronoamperometry, chronocoulometry and mediated electron transfer from the rotating disk voltammetry. The complex incorporated by the S-cationic polyelectrolyte shows a high diffusion coefficient for the polyelectrolyte of poly(methylsufonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate). The diffusion of poly(arylenesulfonio triflate) depended on the ionic exchange of the S-cation which has an alkyl bond and the crystalline structure that influenced the electrostatic motion of the anion within the polyelectrolyte modified electrode.

Key Words: Cationic polyelectrolyte; Polysulfonium; Chronoamperometry; Chronocoulometry; Mediated electron transfer; Diffusion coefficient.

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DOI: 10.1081/MA-120016672 1060-1325 (Print); 1520-5738 (Online)

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INTRODUCTION

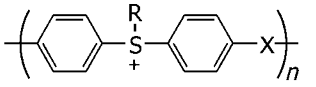
Mass transport within a cationic polyelectrolyte has been a subject of research during the past decade. Polyelectrolytes in many kinds of polymer were investigated because of their wide potential window, solubility in electrolyte solutions and permselectivity. The most popular polyelectrolytes are the SO_3-anionic and N-cationic polymers with their incorporated ions such as, Nafion (SO_3^-) with $Co(bpy)_3{}^{2+}$, $Ru(NH_3)_6{}^{2+}$,[1,2] and $Os(bipy)_3{}^{2+}$,[2,3] polystyrene sulfonate (SO_3^-) with $Os(bipy)_3{}^{2+}$,[4–6] poly(ester-sulfonate) with $Ru(bpy)_3{}^{2+}$, $Fe(bpy)_3{}^{2+}$, $Os(bpy)_3{}^{2+}$ and $Ru(bpz)_3{}^{2+}$,[7] protonated poly(4-vinylpyridine) (N^+) with $Fe(CN)_6{}^{4-}$, $Fe(CN)_6{}^{3-}$, $Mo(CN)_8{}^{4-}$, $W(CN)_8{}^{4-}$ and $IrCl_6{}^{2-}$,[8–10] polyviologen (N^+) with $Fe(CN)_6{}^{4-}$ and $Mo(CN)_8{}^{4-}$,[11] and copolymer (polystyrene sulfonate and vinylpyridine) with $Os(bipy)_3{}^{2+}$,[12] which can bind ions from solution, and also the diffusive motion within the films has been clarified. The S-cation modified polyelectrolyte was firstly described by Tsuchida et al.[13–15]

In an earlier report, Tsuchida et al. described the incorporation behavior of anions in a new type of cationic polyelectrolyte.[13] The anions have been concentrated in polysulfonium **1** as a matrix for immobilizing redox mediators on electrodes, and polysulfonium **1** offered several attractive features. As a polyelectrolyte, it affords the convenience of the electrostatic binding of redox centers ($Fe(CN)_6{}^{3-}$), and it appears to be electro-inactive over −0.6 to 1.2 V vs. Ag/AgCl and stable in a wide pH range (1.2–13). It have been clarified that the incorporation was due to the electrostatic interaction between the anionic complexes, and the cationic sulfonium sites of the polyelectrolyte show significant shifts in the formal potential to less positive values due to the stronger binding of ferricyanide by the polycation coating than that of ferrocyanide. This paper was intended to compare the diffusion coefficients of the polysulfonium films, and to observe the interaction responsible for the binding of the $Fe(CN)_6{}^{3-}$ ions to the sulfonio cation and the influence of the sulfide, oxide and imine groups. The apparent diffusion coefficient of the anionic reactant, $Fe(CN)_6{}^{4-}$, that was incorporated in the polysulfoniums with various arylene coatings on a glassy carbon electrode was evaluated by chronoamperometric, chronocoulometric and mediation in rotating ring disk electrode measurements.[16–18]

EXPERIMENTAL

Materials

Polysulfonium films (Fig. 1), such as poly(methylsufonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate) **1** ($Mn = 4.3 \times 10^4$, $Mw = 2.4 \times 10^5$),[14,19–21] poly(propylsufonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate) **2** ($Mn = 6.7 \times 10^4$, $Mw = 1.2 \times 10^5$),[22] poly(phenylsufonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate) **3** ($Mw = 1.5 \times 10^4$),[23] poly(methylsufonio-1,4-phenyleneoxy-1,4-phenylene trifluoromethanesulfonate) **4** ($Mw = 2.8 \times 10^5$),[21] poly(octadecylsufonio-1,4-phenyleneoxy-1,4-phenylene trifluoromethanesulfonate)



(a) X = S, R = CH_3 (**1**), C_3H_7 (**2**), C_6H_6 (**3**)
(b) X = O, R = CH_3 (**4**), $C_{18}H_{37}$ (**5**)
(c) X = N, R = CH_3 (**6**)

Figure 1. The copolymers used in this study.

5 ($Mn = 8.4 \times 10^3$, $Mw = 3.5 \times 10^4$),[24] and poly(methylsulfonio-1,4-phenyleneamine-1,4-phenylene trifluoromethanesulfonate) **6** ($Mn = 9.2 \times 10^3$, $Mw = 2.7 \times 10^4$),[25][†] were synthesized according to previous procedures as described and analyzed by IR, NMR and elemental analysis. The resulting polysulfonium was soluble in acetonitrile and sparingly soluble in acetone, DMSO and sulfonic acid. Distilled acetonitrile was used to dissolve the polymer to make a polyelectrolyte solution in order to modify the electrode in all of the experiments. $K_4Fe(CN)_6$ and $[Ru(NH_6)_3]_2$ were purified by crystallization in the usual manner. CH_3SO_3Na as the supporting electrolyte was commercially available in reagent grade and used without purification.

Apparatus and Procedure

The electrochemical analyses were done using a Nikko Keisoku DPGS-1 dual potentiogalvanostat and a Nikko Keisoku NFG-3 universal programmer with a Graphtec WX2400 X-Y recorder to obtain the voltammograms. A glassy carbon disk ($0.28\,cm^2$), a coil platinum wire and a saturated calomel electrode were used as a working, auxiliary and reference electrodes, respectively.

The modified electrode was mounted as previously described.[13] The polysulfonium coatings employed in electrochemical experiments were prepared using $5\,\mu L$ of a 1 mM solution of the polysulfonium in acetonitrile placed on a glassy carbon disk and allowing the solvent to evaporate slowly in air. The triflate counterions initially present in the coatings were removed by transferring the electrode to a 1 mM solution of $K_3Fe(CN)_6$ with 0.1 M CH_3SO_3Na as the supporting electrolyte in aqueous solution. The electrode potential was cycled over the oxidation and reduction waves of the anion ($-0.3 \sim 0.7\,V$) for 10 min at a rate of 25 mV until the desired amount was incorporated into the coating by ion exchange. The electrode was then removed and transferred to a pure supporting electrolyte solution for further measurements.

For the chronoamperometric and chronocoulometric experiments, the potential was stepped between -0.1 and $+0.3\,V$, and then back to $-0.1\,V$ for

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[†] The synthesis was done with the processes as described in the literature[20] to get methylsulfonio-1,4-phenyleneimino-1,4-phenylene sulfoxide monomer. Then the polymerization of 6 was done as Mullen Method.[26]

the $Fe(CN)_6{}^{4-/3-}$ couples. The experiments were conducted in air at 25°C. The potentials were measured and are reported with respect to the saturated calomel electrode (SCE). The quantities of the anions present in the coatings were measured by integrating the current that flowed as the electrode was scanned over the voltammogram and held at a value well beyond the peak potential until the current was stable at a maximum peak.

RESULTS AND DISCUSSION

When electrodes coated with polysulfonium **1** were immersed in solutions of $Fe(CN)_6{}^{3-}$, rapid exchange between the anion initially present in the coating and increasing of current was observed by cyclic voltammetry. After the anion exchange was complete, the electrode was transferred to a pure electrolyte where stable cyclic voltammograms for the incorporated anions were recorded. The electrochemical responses of polysulfonium **1** coatings were significantly influenced by the composition of the supporting electrolyte used to record the current-potential curves, thus CH_3SO_3Na has ideal anion permselectivities towards its polysulfonium-modified electrode, which were therefore employed for most of the measurements in this report.[13]

Chronoamperometry, chronocoulometry and the mediation effect analysis that measure the rate of such movement were used to measure the diffusion coefficients (D_{app}) of the anions that were incorporated in the polysulfonium membranes. The use of chronoamperometry to evaluate the diffusion coefficients within the polymer films of finite dimension has been described and practiced by Daum and Murray,[16,28] while chronocoulometry has been advocated by Anson.[29,30]

Chronoamperometry of Polysulfonium

The anionic reactant, $Fe(CN)_6{}^{3-}$, was incorporated in the polysulfonium **1–6** coatings on a glassy carbon electrode which was exposed to electrolyte and the apparent diffusion coefficient of the incorporated anions were evaluated by transient chronoamperometric measurements. A subsequent measurement of the quantity of $Fe(CN)_6{}^{3-}$ remaining in the coating showed that not more than 5% was lost during the slow potential scan by cyclic voltammetry due to the effective ionic exchange of the S-cation polymer. Figure 2(a) shows a current-time response in chronoamperometry for the oxidation and reduction of an anion within the polysulfonium **1**. The first half ($t = 0-1000\,\mathrm{ms}$) of the response corresponds to the oxidation of the incorporated $Fe(CN)_6{}^{4-}$. The second one ($t = 1000-2000\,\mathrm{ms}$) is for the reduction of the resulting $Fe(CN)_6{}^{3-}$. The apparent diffusion coefficient, D_{app}, for the electron process within the film was obtained from the cathodic limiting currents using the Cottrell equation, $i(t) = (nFAD_{\mathrm{app}}^{1/2}C_{\mathrm{o}}^{*})/(\pi^{1/2}t^{1/2})$,[27,32] where $F =$ Faraday constant, $A =$ electrode area and $D_{\mathrm{app}} =$ apparent diffusion coefficient. The Cottrell plots of current vs. $(\mathrm{time})^{-1/2}$ were linear at sufficiently short times and the values of $D_{\mathrm{app}}^{1/2}C_{\mathrm{o}}^{*}$, where $C_{\mathrm{o}}^{*} = \Gamma/d$ were calculated from the slopes of the plot (Fig. 2(a′)).

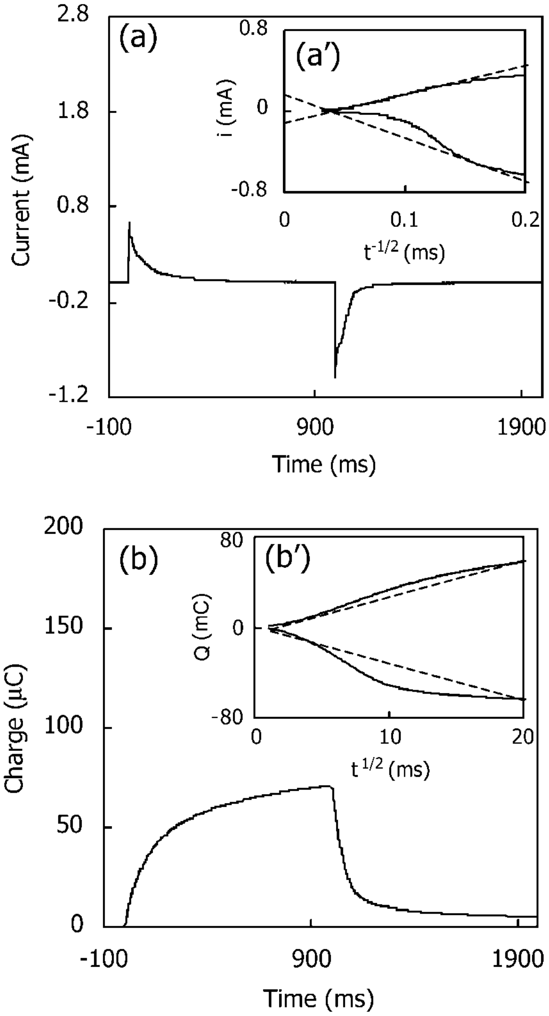

Figure 2. (a) Chronoamperometric plots for the oxidation and reduction of $\mathrm{Fe(CN)_6}^{4-/3-}$ in the modified electrode of **1**; (a′) Cottrell plots for redox of incorporated $\mathrm{Fe(CN)_6}^{4-/3-}$. (b) Charge-time response for oxidation and reduction of the $\mathrm{Fe(CN)_6}^{4-}$ and $\mathrm{Fe(CN)_6}^{3-}$ in a coating polymer **1**. (b′) Charge-time plots using Anson method. The electrode potential was stepped from -0.1 V to $+0.3$ V and back to -0.1 V. The coating electrode contained $3.4 \times 10^{-5}\,\mathrm{mol\,cm^2}$ of ferricyanide. Glassy carbon electrode area: $0.28\,\mathrm{cm^2}$. Electrolyte: H_2O containing 0.1 M CH_3SO_3Na as supporting electrolyte and 0.1 mM $K_3[Fe(CN)_6]$. Scan rate: $10\,\mathrm{mV\,s^{-1}}$.

The d is the film thickness and Γ is the quantity of the incorporated concentration of $\mathrm{Fe(CN)_6}^{3-}$ by each coating at saturation of anions that were coulometrically determined by integrating the current transients stepped across the reduction or oxidation wave from -0.1 V to 0.3 V of the anion. The apparent value for

Table 1. Comparison of incorporated anion and apparent diffusion coefficiens of various polycations.

Polymer[a]	Ferricyanide incorporated[b] ($\times 10^{-4}$ mol/cm^3)	D_0 calculated by PSCA[c] ($\times 10^{-11}$ cm^2/s)	D_0 calculated by PSCC[d] ($\times 10^{-11}$ cm^2/s)
1	4.3	21.3	5
2	4.8	3.9	2.8
3	3.8	2.9	2.7
4	0	—	—
5	0	—	—
6	6.9	0.12	0.15

[a] Under conditions where the coatings of 5μL of 1 mmol unit L^{-1} polymer are saturated with incorporated anion of 0.1 mM $K_3Fe(CN)_6$.

[b] Quantity incorporated as measured coulometrically after transfer to pure supporting electrolyte.

[c] Potential-step chronoamperometry.

[d] Potential-step chronocoulometry.

polysulfonium **1**, 2.1×10^{-10} cm^2/s, was much larger than that of the other polyelectrolytes as summarized in Table 1.

Chronocoulometry of Polysulfonium

Figure 2(b) shows a pair of charge-time responses typically obtained by chronocoulometry with the anion in the modified polysulfonium **1** electrode. The oxidation of the incorporated $Fe(CN)_6{}^{4-}$ and the reduction of the resulting $Fe(CN)_6{}^{3-}$ were observed by chronocoulometry. The incorporated anion appears to be readily accessible to the supporting electrolyte so that the anion rapidly responds to changes in the electrode potential. An Anson plot (Fig. 2(b′)) was used to calculate the apparent diffusion coefficient with the equation, $Q(t) = (nFAD_{app}^{1/2}C_o^* t^{1/2})/(2\pi^{1/2})$ for all of the mediated polysulfoniums. The D_{app} results are summarized in Table 1.

Mediation Effect of Polysulfonium

Polysulfonium **1**, that had the highest diffusion coefficient as described above, was used as the mediator in the rotating disk modified electrode containing electrostatically bound $Fe(CN)_6{}^{4-}$ to characterize the dynamics of the mediated oxidation of the ruthenium complex, $[Ru(NH_3)_6]^{2+}$. This system demonstrated that a flux of $[Ru(NH_3)_6]^{2+}$ arrives at the electrode surface by diffusion of electrons through the film.

Figure 3(A) shows the cyclic voltammogram of the initial redox of $[Ru(NH_3)_6]^{2+}$ at 0.15 V vs. SCE without modification of the glassy carbon electrode in the ruthenium complex electrolyte. An aqueous electrolyte solution containing 1 mM $[Ru(NH_3)_6]_2$ and 0.1 M CH_3SO_3Na as the supporting electrolyte were used. After the electrode was modified by the polysulfonium **1**, the cyclic voltammogram showed no

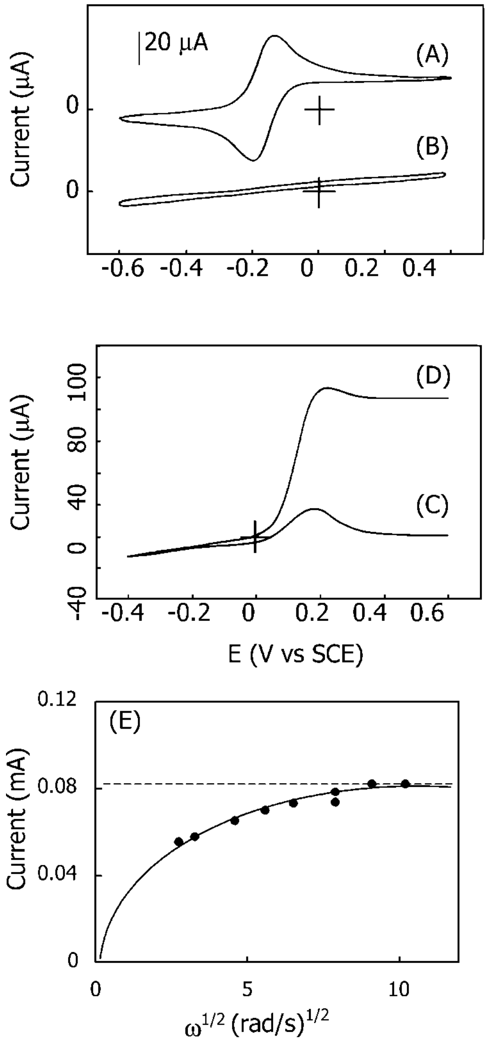

Figure 3. Cyclic voltammogram in aqueous solution of 1 mM $[Ru(NH_3)_6]_2$ with non-modified electrode (A) and modified electrode coated with 50 μL of 1 mM acetonitrile solution of **1** (B). The measurement was done under nitrogen. Rotating disk voltammogram of modified electrode of **1** containing incorporated $Fe(CN)_6{}^{3-}$ in pure aqueous electrolyte solution (C), and electrode of (C) observed in aqueous electrolyte containing $[Ru(NH_3)_6]^{2+}$ (D). Scan and rotating rates were 5 mV s^{-1} and 200 rpm, respectively. (E) Current potential response obtained from rotating ring voltammogram of (D) at −0.15 V vs. SCE. Electrolyte: H_2O containing 0.1 M CH_3SO_3Na as supporting electrolyte.

redox peak due to the electrostatic repulsion (Fig. 3(B)). When the anion exchange of ferricyanide was completely incorporated from the aqueous electrolyte solution containing $Fe(CN)_6{}^{4-}$, it was transferred to the aqueous electrolyte solution containing the ruthenium complex as described above. The oxidation of

$[Ru(NH_3)_6]^{2+}$ through the mediation performance of $Fe(CN)_6{}^{3-/4-}$ in polysulfonium **1** was observed by the increased current in the rotating disk voltammogram as shown in Fig. 3(D) comparing to the modified ferricyanide film 3(C). From the steady-state oxidation current of $[Ru(NH_3)_6]^{2+}$, the increasing current was found to be a maximum at 0.08 mA due to the rate-determining step of the mediation process (Fig. 3(E)). Based on Fick's second law, the diffusion coefficient of the mediator was calculated from the equation, $D_{app} = (i/FA) \times (\delta C/\delta x)$,[27,32] where $(\delta C/\delta x)$ was an incorporated concentration. The diffusion coefficient of $Fe(CN)_6{}^{3-/4-}$ within the polysulfonium **1** was thus calculated to be $3.1 \times 10^{-10}\,cm^2/s$.

The values calculated from the chronoamperometric and chronocoulometric measurements for $Fe(CN)_6{}^{3-}$ that are electrostatically bound within the coatings of the polysulfoniums on the glassy carbon electrodes are summarized in Table 1. The quantities of the incorporated anions and diffusion coefficients of the polysulfonium membranes were compared between the various polyarylenethiosulfides **1**–**3**, polyarylenethioethers **4**–**5** and polyarylenethioimines **6**. The S-cation with a long alkyl-chain has a highly electron donating nature which allowed the electrostatically anionic bonding and caused the ferricyanide ionic exchange observed in **1**–**3** and **6**. Although the polyarylenethioethers **4**–**5** that have methyl and octadecyl groups in the S-cation have a low electron density, they have no ionic exchange because of their highly crystalline structure, which is in agreement with the following observations. The DSC analysis of polysulfonium **5** was used to confirm the crystalline structure that produced the T_g at 43°C the first scan, and the T_c produced at 60°C in the second heat scan after cooling.[25] This suggests that **4** has the same structure with no incorporation anions within the polymers. However, polyarylenethioimine **6** has a highly incorporated concentration of ferricyanide which is about two times greater than that of the other polysulfoniums. The imine in **6** is easily protonated under acidified conditions hence much less nucleophilic,[26] thus, it was found that the ferricyanide causes the increasing ionic exchange within the polymer. The phenomenon of the incorporated concentration of polysulfonium **6** probably suggests that the motion of the diffusing

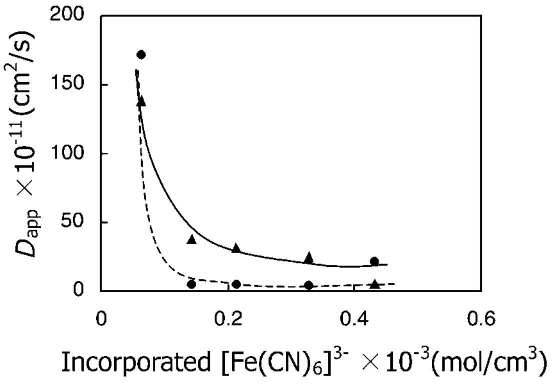

Figure 4. The apparent diffusion obtained with PSCA (▲) and PSCC (•) values vs. incorporated concentration of redox $Fe(CN)_6{}^{4-/3-}$ in different quantities of modified polysulfonium **1** (5, 10, 30, 50, 100 μL of 1×10^{-3} M polysulfonium solution). The other experimental conditions were as described in Fig. 2.

counter-ions accompanying the electron transfer within the coating film dominates the rate of the electron transfer.[28]

The obtained apparent diffusion coefficients were dependent of the quantities of the anion incorporated in the electrode. The D_{app} for the incorporated anions showed a strong decrease as the anion concentration within the coating increased up to a steady value of the anion concentration near 0.14 M as shown in Fig. 4 for polysulfonium **1**. Indeed, this phenomenon was also observed in the modified polysulfonium **2**–**3** electrodes. One factor contributing to the larger D_{app} value probably exists to a smaller extent for the electrostatic cross-linking of the anions with the surrounding polymer cation sites as the concentration of anions decrease.[28,30]

The diffusion coefficients applicable to such steady-state experiments can be very different from those evaluated in the typical chronoamperometric or chronocoulometric experiments.[10] The results in Table 1 shows apparent diffusion coefficients that increase as the concentration of the diffusant decreases which was described by Oyama for the diffusants of $Fe(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$ incorporated in coatings of poly(vinylpyridine).[31] However, the D_{app} values obtained for a low concentration of diffusant are intrinsically concentration dependent due to the effect of the self-exchange rate.[30] From Table 1, poly(arylenesulfonium triflate) shows the same values for the phenyl and propyl group sulfoniums.

CONCLUSION

The incorporated ions in polyelectrolyte coatings are due to the ion-exchange between the adjacent pairs of oxidized and reduced ions and was the only method rather than incorporation by the diffusive motion of the incorporated ion or counter ions. These same phenomenon were described by Oyama.[10] Furthermore, the effectiveness of the catalyst that is held on the surfaces of electrodes by incorporation into coatings of the polyelectrolyte deposited on the electrode was highly dependent on the mobility of the catalyst molecules within the polyelectrolyte,[4] thus there is no diffusion in a highly crystalline polymer. The diffusion of poly(arylenesulfonio triflate) was dependent on the ionic exchange of the S-cation which has an alkyl bond and the crystalline structure that influenced the electrostatic motion of the anion within the polyelectrolyte modified electrode.

ACKNOWLEDGMENT

Eniya L. D. acknowledges Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists (No. 05709).

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Received July 26, 2002