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Hyperbranched Ferrocenyl Polymer Film with High Charge Transport Efficiency

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The electrochemical behaviors of hyperbranched poly(ferrocenyl-methylsilane) (HPFMS) and linear oligo-(ferrocenyldimethylsilane) (LOFS) films were studied systematically by cyclic voltammetry and chronocoulometry under different polymer coverage and solvents. Both poly(ferrocenylsilanes) show stable cyclic voltammographs in LiClO$_4$ solutions. Compared with LOFS films, HPFMS films exhibit higher charge transport efficiency because of their hyperbranched structure: peak current (i_p) and apparent diffusion coefficient (D_{app}) for HPFMS films are larger than those for LOFS films, especially at high polymer coverage (3.8×10^{-11} vs 3.9×10^{-12} cm^2/s for HPFMS and LOFS film at the coverage of 2.1×10^{-6} mol Fc/cm^2). The conceptual models of electrode processes for HPFMS and LOFS films were proposed to account for higher charge transport efficiency of HPFMS films. It is also found that a solvent with the appropriate solubility parameter and polarity, lower viscosity, and higher dielectric constant is in favor of charge transport through polymer films, which is consistent with the proposed model of electrode process for HPFMS films. These results imply that hyperbranched ferrocenyl polymers have the potential to be excellent chemical sensor materials with convenient synthesis and high sensitivity.

1. Introduction

Electrodes modified with special functional compounds, that is, chemically modified electrodes (CMEs), possessing particular catalytic, photoelectric, and electrochromic properties,[1,2] have been widely used in catalysis,[3–5] molecular recognition,[4,5] electrochromic devices,[6,7] synthesis of nanocrystal,[8–10] and so on. Therefore, the study of CMEs has become a creative and hopeful research area for chemistry and relative frontier subjects and has promoted the rapid development of electrochemistry and electroanalytic chemistry. As a typical sensor material for CME, ferrocenyl polymers have attracted much attention.[11–13,15–17,22–28] Calvo et al.[11] prepared an Au electrode modified with poly(allylamine)ferrocene and glucose oxidase by layer-by-layer self-assembly, which exhibited high catalytic oxidation activity to glucoses. Armada et al.[12] prepared amperometric biosensors by immobilizing glucose oxidase or lactate oxidase onto the ferrocenyl polymer modified electrode, and the resultant electrodes could be used to determine the concentration of glucose or lactate. They also found that a platinum electrode modified with siloxane-based ferrocenyl homopolymer had the ability to electrocatalytically detect hydrogen peroxide. Sun et al.[13] modified a gold electrode with poly(allylamine)- ferrocene to oxidize ascorbic acid. However, linear ferrocenyl polymer modified electrode has a shortcoming that its electrocatalytic efficiency is relatively low, leading to low sensitivity and efficiency for an electrochemical sensor system. The possible reason is that linear polymer chains are wrapped together and many ferrocenyl groups are buried in polymer chains,[14] which results in the counterion penetrating into polymer film with difficulty and just part of redox centers participating in electrochemical reactions. Dendrimers with the sphere structure have circumvented the above-mentioned prob-

lem. Losada et al.[15] prepared ferrocenyl dendrimer/glucose oxidase modified carbon paste electrodes, and the prepared electrodes showed higher sensitivity to glucose concentration as compared with linear ferrocenyl polymer modified electrodes.[16,17] However, dendrimers often require multistep syntheses, especially for higher generation,[18–20] which makes it necessary to find another candidate for sensor materials with both high sensitivity and convenient synthesis.

In contrast to dendrimers, hyperbranched polymers can be prepared by a one-step polymerization of AB$_x$ type multifunctional monomers or A$_2$ + B$_3$ type comonomers,[18,19,21] and they possess similar structures with dendrimers.[19,21] Our previous results[21] and others[14,22–24] have indicated that hyperbranched ferrocenyl polymers possessed electrochemical properties similar to those of their dendritic analogues. Cuadrado's group[24] has exploited the electrocatalytic behavior of hyperbranched ferrocenyl polymer modified electrodes. In order to systematically study the charge transport property of hyperbranched polymer and find a good candidate for sensing materials, herein we investigated the electrochemical behaviors of hyperbranched ferrocenyl polymer (HPFMS) films and their linear analogue (LOFS) films (the structures of HPFMS and LOFS are shown in Figure 1) as a comparison, where the hyperbranch structure and solvent effect on the charge transport through polymer films were observed. The possible models of electrode processes for ferrocenyl polymers with different structures were proposed to account for high charge transport efficiency of the HPFMS film.

2. Experimental Section

2.1. Instruments and Reagents. ^{1}H NMR spectra of polymers were recorded with a 500 MHz AVANCE NMR spectrometer (model DMX500) in CDCl$_3$ using TMS as the standard. The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) with a laser scattering detector and an Ultrastyragel column with pore

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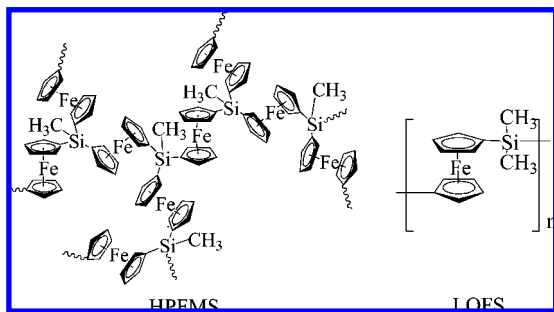
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Figure 1. Structures of HPFMS and LOFS.

sizes of 10^3–10^5 Å. The eluent was THF at a flow rate of 1.0 mL min^{-1}. A detection wavelength of 632.8 nm and the refraction index increment value of the polymer solutions dn/dc = 0.20 were used for laser scattering detection.

The electrochemical measurements were performed with a CHI-600B electrochemical analyzer (CH Instruments, Inc., Austin, Texas). A one-compartment, three-electrode cell with a Teflon-shrouded glass carbon working electrode (Φ = 3 mm; geometric area = 0.071 cm^2), a Pt wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode were used. All electrodes were purchased from CHI. The working electrode surface was hand-polished to a mirror finish with 0.05 μm Al$_2$O$_3$ paste on felt, and it was washed by an ultrasonic wave with 0.1 M NaOH, 1.0 M HNO$_3$, double-redistilled water, and anhydrous ethanol in succession. Before the measurements, the solutions were filtered with a 0.45 μm micropore filter and purged for at least 10 min with prepurified nitrogen. All of the electrochemical measurements were carried out at room temperature. All chemicals were purchased from commercial sources and were of analytical or pure grades.

2.2. Synthesis and Characterization of HPFMS and LOFS. HPFMS and LOFS were synthesized according to the literature,[21] and their structures are shown in Figure 1. The ^{1}H NMR spectrum of HPFMS shows one broad resonance peak between 3.46 and 4.65 ppm for the cylcopentadienyl protons and one broad peak around 0.60 ppm for the methyl protons attached to silicon; the ^{1}H NMR spectrum of LOFS shows two resonance peaks at 4.00 and 4.27 ppm for the cylcopentadienyl protons and one peak at 0.45 ppm for the methyl protons attached to silicon. The molecular weights and molecular weight distribution of HPFMS are M_w = 1.76 × 10^4 and M_w/M_n = 2.29; the corresponding data of LOFS were M_w = 2.49 × 10^3, M_w/M_n = 1.35.

2.3. Preparation of Polymer film. HPFMS or LOFS film was prepared by dripping an amount of a solution of HPFMS or LOFS in THF onto the glassy carbon disk electrode and then allowing the solvent to evaporate at room temperature. The polymer coverage of film was approximately estimated as the material quantity of ferrocenyl polymer per unit area of glass carbon electrode surface.

3. Results and Discussion

3.1. Electrochemical Behaviors of HPFMS and LOFS Films in Aqueous Solution. *3.1.1. CV Behaviors of HPFMS and LOFS Films.* Our previous study[22,25] has proved that, in LiClO$_4$ aqueous solution, stable and reproducible cyclic voltammograms (CVs) for ferrocenyl polymers could be recorded; therefore, LiClO$_4$ was used as the supporting electrolyte for all studied electrochemical systems here. Like other redox polymer systems,[27,28] the electrochemical behaviors of HPFMS or LOFS films should undergo a break-in period to reach a stable state,

the time of which depends on film thickness. Therefore, each cyclic voltammogram discussed here was a stable one, unless otherwise stated. The typical cyclic voltammograms of HPFMS and LOFS films in 1.0 M LiClO$_4$ aqueous solutions are shown in Figure 2. Figure 2 (C and D) shows two pairs of redox peaks for the LOFS film, indicating that weak interaction exists between redox centers, but one pair of redox peaks are observed in the CVs of the HPFMS film, similar to the electrochemical behavior of its solution.[21] The electrochemical data of polymer films are listed in Table 1. Compared with LOFS, redox peak potentials of HPFS films are smaller, and the redox peaks are more symmetric, possibly suggesting that charge transport through the hyperbranched polymer films is more convenient than in linear polymer films.[29]

The stability of ferrocenyl polymer films was examined by continuously scanning CV curves for five cycles in 1.0 M LiClO$_4$ aqueous solutions (Figure 2B and D). Cyclic voltammograms of HPFMS film show little change in the peak current and peak potential: anodic peak currents only decrease by 5.5% from the first cycle to the fifth cycle, cathodic peak currents show no appreciable change during five cycles, and those of the LOFS film for five cycles show no appreciable change both in the anodic and cathodic peak current/potentials.

3.1.2. Influence of Polymer Coverage on CV Behaviors of HPFMS and LOFS Films. Polymer coverage (or film thickness), is an important factor influencing the charge transport through film and characteristics of polymer film.[28] Figure 3 shows the cyclic voltammograms of HPFMS and LOFS films with different coverage.

We find that film thickness remarkably influences the peak shape, redox peak current, and peak potential of the cyclic voltammogram, and its tendency varies with polymer structure (Figure 4). For HPFMS, one pair of redox peaks are observed at the test range of coverage; but for LOFS, the double redox peaks are seen at low coverage, and one pair of peaks is observed at high coverage (such as Γ = 1.4 × 10^{-6}). More interestingly, large differences between peak currents of HPFMS and LOFS films at the same coverage are observed from the dependences of the peak current on film thicknesses (Figure 4). At low ferrocenyl polymer coverage, the difference between the values of i_{pa} of HPFMS and LOFS is inconspicuous. However, when the coverage is over 7.1 × 10^{-7}, the tendency varies with polymer structures: i_{pa} decreases with the increase of coverage for LOFS film, i_{pa} continues to increase until the coverage is over 1.4 × 10^{-6} for HPFMS, and $i_{pa, \text{HPFMS}}$ outclasses $i_{pa, \text{LOFS}}$. The results possibly show that there are more redox centers participating in electrochemical reactions for HPFMS than for LOFS.

The kinetics of electrode processes of HPFMS and LOFS films were studied from the dependence of i_{pa} on the square root of scan rate or the scan rate of HPFMS (Figure 5A) and LOFS (Figure 5B) at different polymer coverage. At low coverage ($\Gamma \leq 5.2 \times 10^{-7}$), a plot of i_{pa} of poly(ferrocenylsilane) film shows a linear relationship versus the scan rate, which is a criterion of the fast kinetics of the adsorbed species.[28,29] As the film thickness increases, the resistance of charge transport through the film increases, and i_{pa} is linear with the square root of the scan rate, indicating that the electrode process is controlled by diffusion.[25,26,28]

3.1.3. Influence of Polymer Coverage on Apparent Diffusion Coefficient of the Electrode Processes for HPFMS and LOFS Films. There are many factors affecting the charge transport within films,[28] such as the supporting electrolyte and its concentration,[29–31] solvent,[32] film thickness,[25,26] tempera-
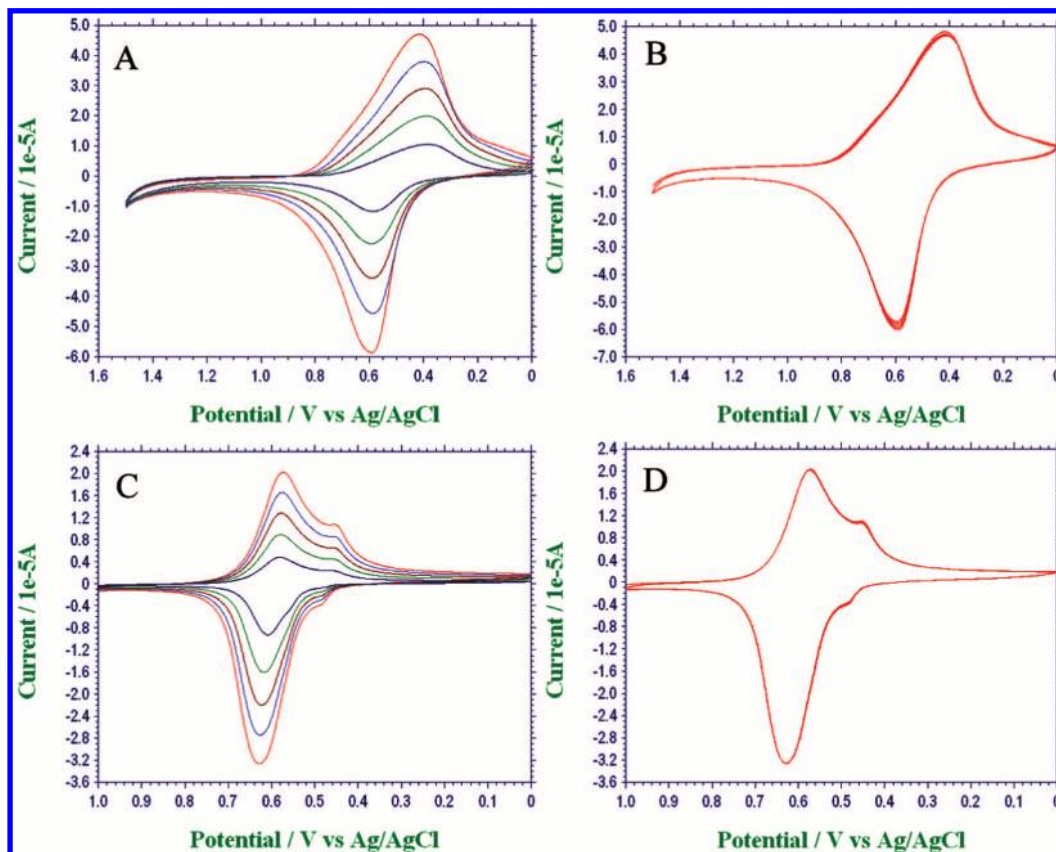
Figure 2. Cyclic voltammograms of HPFMS (A and B) and LOFS (C and D) films in 0.1 M LiClO₄ aqueous solution. (A and C) Scan rate = 20, 40, 60, 80, and 100 mV/s from inner to outer; (B and D) scan rate = 100 mV/s for five cycles. Coverage $\Gamma = 1.4 \times 10^{-7}$ mol/cm² of ferrocene site.

TABLE 1: Electrochemical Data of HPFMS and LOFS Films

electrochemical system	E_{pa} (mV)	E_{pc} (mV)	ΔE_p (mV)
HPFMS film[a]	592	413	179
LOFS film[a,b]	630	573	57

[a] Coverage $\Gamma = 1.4 \times 10^{-7}$ mol/cm² of ferrocene site; scan rate = 100 mV/s; concentration of electrolyte = 0.1 M LiClO₄ aqueous solution. [b] Another redox peak potential was omitted as it was difficult to numerate.

ture,[26] and so on. Among these factors, the supporting electrolyte and its concentration, solvent, and temperature[26,28−32] are common subjects, but few studies have been focused on the influence of film thickness on electrochemical behavior, especially on the charge transport process.[25,26] However, an important application of the chemically modified electrode is electrocatalysis or chemical sensor, and the concentration of redox centers is a key point for the sensor system. If the concentration is too high, the resistance of charge transport through the film would increase, and consequently, the catalytic efficiency would decrease.[28] As a result, an appropriate film thickness must be adopted. Therefore, we investigated the influence of film thickness on apparent diffusion coefficient (D_{app}) for two ferrocenyl polymers: HPFMS and LOFS.

There are many methods to derive D_{app}, such as cyclic voltammetry, chronoamperometry, chronocoulometry, impedance spectroscopy, steady-state voltammetry, and so on.[25,26,33] Among these means, chronocoulometry is one of effective methods to determine D_{app} since the resistance effect can be overcome by using larger potential steps.[33] As a result, chronocoulometry was used to calculate D_{app} here. As the film

thickness could not be measured accurately, we assumed that redox centers were distributed homogeneously within the polymer film, and the density of LOFS or HPFMS was similar to that of linear poly(vinylferrocene), that is, the film thickness was about 450 Å for a coverage of 3×10^{-8} mol Fc. cm⁻²,[34] and the film thicknesses at different coverages were estimated for our systems.

The typical chronocoulometric responses of HPFMS and LOFS are presented in Figure 6A, which shows a linear charge, Q, versus $t^{1/2}$ dependence. According to Cottrell eq 2, charge passed in reducing the diffusing reactant has a linear relationship with $t^{1/2}$ as shown below:

$$Q = \frac{2nFAD_{app}^{1/2}C^*}{\pi^{1/2}}t^{1/2} = \frac{2nFAD_{app}^{1/2}\Gamma}{\pi^{1/2}d}t^{1/2} \quad (1)$$

where n, F, A, D_{app}, Γ, and d represent electrochemical stoichiometric number of electrons, Faraday constant (C·mol⁻¹), surface area of the electrode (cm²), apparent diffusion coefficient (cm²·s⁻¹), surface coverage of redox centers (cm²·mol⁻¹), and film thickness (cm), respectively.

Accordingly, the apparent diffusion coefficients, D_{app}, under different coverage of redox centers can be determined from the plots of Q vs $t^{1/2}$ (shown in Figure 6). To validate the accuracy of D_{app} from chronocoulometry, D_{app} was also measured by cyclic voltammetry from the relationship between peak current/ peak potential and scan rate (Table S1, Supporting Information). It is found that D_{app} from chronocoulometry is about four times that from cyclic voltammetry, but the profiles of D_{app} vs coverage from both methods are similar. The larger difference between D_{app} from the two methods was also observed by
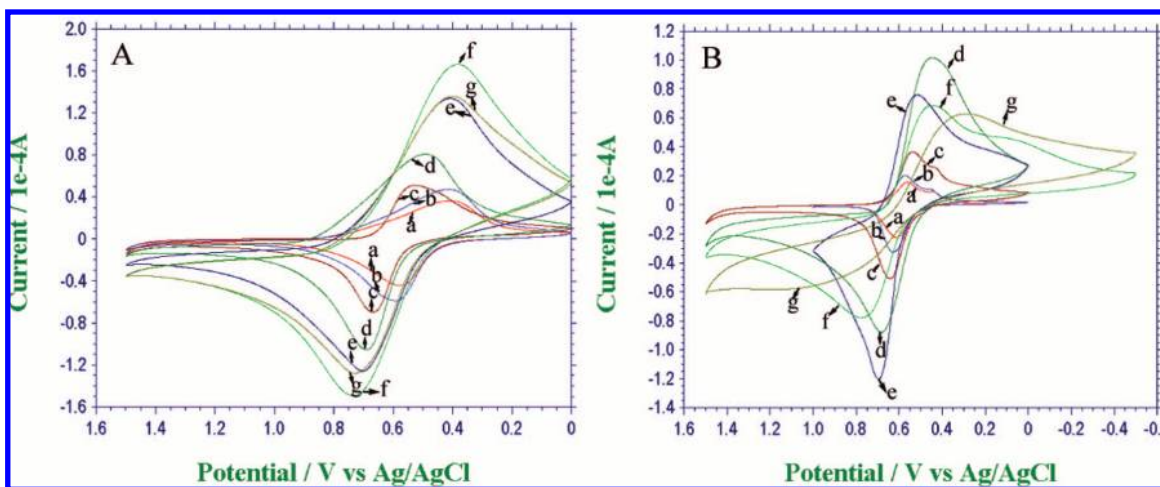
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Figure 3. Cyclic voltammograms of HPFMS (A) and LOFS (B) films with different film coverage. Coverage $\Gamma = 7.1 \times 10^{-8}$ (a), 1.4×10^{-7} (b), 2.8×10^{-7} (c), 4.2×10^{-7} (d), 7.1×10^{-7} (e), 1.4×10^{-6} (f), and 2.1×10^{-6} (g) mol/cm^2 of ferrocene site; 0.1 M LiClO$_4$ aqueous solution; scan rate $v = 100$ mV/s.
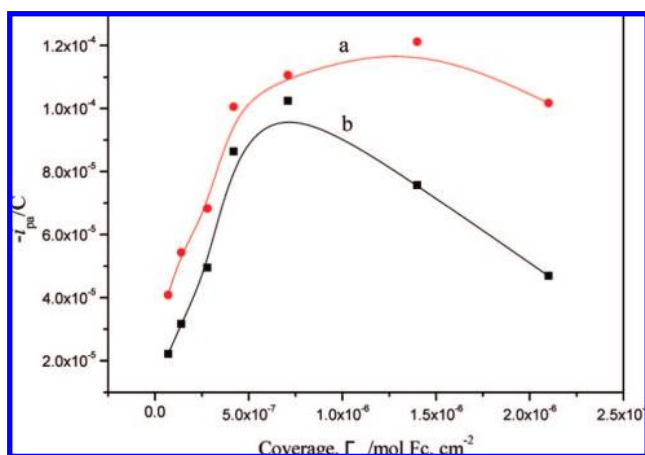

Figure 4. Influence of polymer film coverage on i_{pa} of HPFMS (a) and LOFS (b). 0.1 M LiClO$_4$ aqueous solution; scan rate $v = 100$ mV/s.

English[33] and Forster,[35] who explained that the difference resulted from the long range ion migration in cyclic voltammetry, but short range in chronocoulometry. Compared with D_{app} obtained from the same polymers in solutions ($\sim 10^{-5}$ cm$^2 \cdot$s^{-1}), the values are relative smaller but are of the same order of magnitude of D_{app} obtained from other similar systems (10^{-12}–10^{-11} cm$^2 \cdot$s^{-1}).[22,25,31] Figure 6B shows the dependences of D_{app} of HPFMS and LOFS films on the surface coverage of redox centers, which gives a similar trend with peak current vs coverage. The similarity implies that the decrease of peak current with increasing film thickness is possibly ascribed to the slow charge transport through the film. Interestingly, although $D_{app,HPFMS}$ is larger than $D_{app,LOFS}$ at the range of test coverage, there is no large difference between D_{app} of HPFMS and LOFS at low coverage. However, as the film thickness increases, a larger difference is observed, suggesting that the hyperbranched structure is more convenient for charge transport than the linear structure.[14,24] For example, at the coverage of 2.1×10^{-6} mol Fc/cm^2, D_{app} of HPFMS film (3.8×10^{-11} cm^2/s) is about 10 times greater than that of the LOFS film (3.9×10^{-12} cm^2/s). The distinct differences of D_{app} at different coverage probably resulted from the diverse controlling factor for each electrode process. At low coverage, the electrode process is a fast charge transfer process, which is not directly determined by the polymer structure. Whereas the high coverage electrode process is limited by the counterion flowing into polymer film, the polymer structure plays an important role in charge transport and makes a large difference between D_{app} of HPFMS and LOFS films (Figure 5). The possible mechanism of charge transport through ferrocenyl polymers film with different structures will be discussed below.

3.1.4. Hyperbranched Structure Effect on the Charge Transport of Electrode Process for Polymer Films. As discussed above, i_{pa} and D_{app} for HPFMS films outclassed those for LOFS films, especially at high coverage, which might be due to the different structures of polymer. In consideration of the results, the electrode process was mainly controlled by diffusion, including electron hopping, counterion flowing into polymer film plus solvent swelling, or motion of polymer chain.[30–38] Kaufman's group[37] has demonstrated that the kinetic process of oxidation in the tetrathiafulvalene polymer film was limited by ionic flow into the polymer phase by changing the concentration and the nature of the electrolyte. Murray et al.[36] also claimed that the counterion diffusion played an important role in the charge transport through the poly(vinylferrocene) film. Our group[30,38] previously investigated the electrochemical behaviors of high molecular weight poly(ferrocenylsilanes) in different aqueous electrolyte solutions. We found that the size of counterion drastically influenced the electrochemical behaviors of poly(ferrocenylsilanes), which proved that counterion permeation into polymer film was an important step during the charge transport process. As a result, the counterion permeation in film with different structure is possibly the direct reason for the large difference between the peak currents (or apparent diffusion coefficient) for HPFMS and LOFS films.

Bard et al.[39,40] and Saveant et al.[38,41] have proposed that the processes of substances flowing into the polymer films obeyed the membrane permeation model that the polymer film with infinitesimally small channels can be considered as a uniform phase through which the counterion could homogenously diffuse or penetrate. As infinitesimally small channels uniformly distribute at the polymer film first, it is difficult for electrolyte ions to flow into the polymer film, which causes the break-in phenomenon;[37] following solvent swelling, motion of polymer chain, and charge transport through the film, a succession of pores or channels with different sizes will form[42] so that the counterions can diffuse or penetrate through the polymer film. These results indicate that charge transport can be controlled by the state of the polymer film. There are many factors
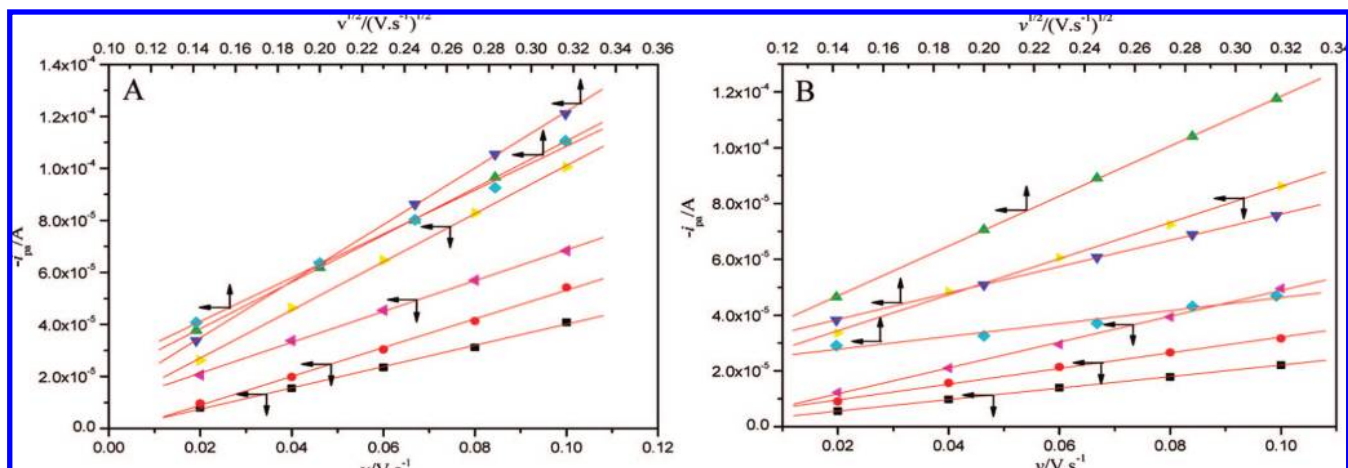
Figure 5. Dependence of i_{pa} on the square root of scan rate or the scan rate of HPFMS (A) and LOFS (B) at different polymer coverage. Coverage $\Gamma = 7.1 \times 10^{-8}$ (■), 1.4×10^{-7} (●), 2.8×10^{-7} (left facing triangle), 5.2×10^{-7} (right facing triangle), 7.1×10^{-7} (▲), 1.4×10^{-6} (▼), 2.1×10^{-6} (◆) mol/cm² of ferrocene site; 0.1 M LiClO₄ aqueous solution.
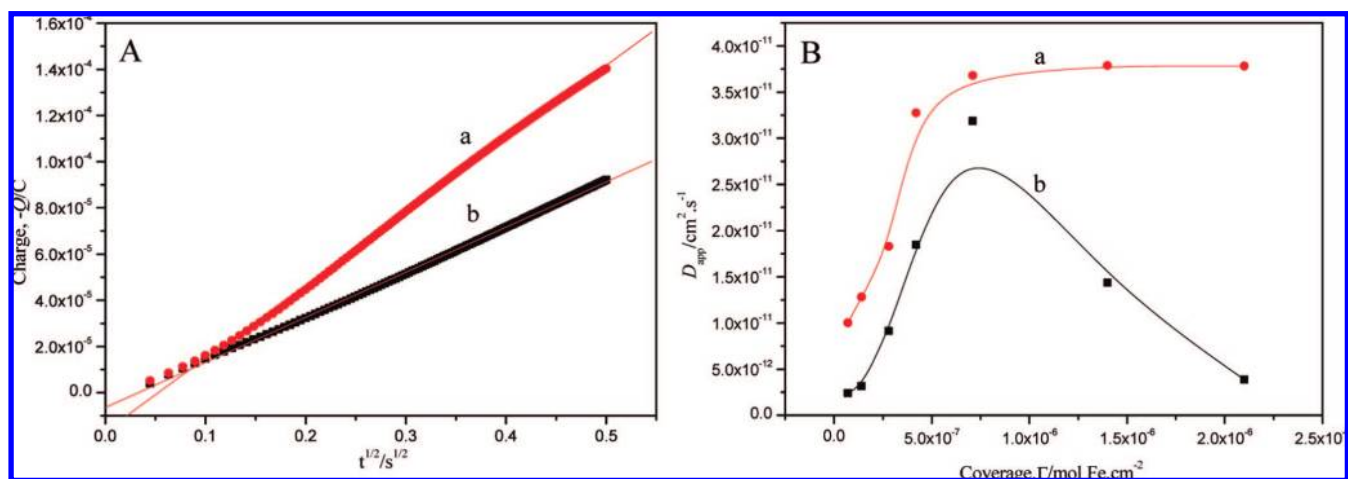

Figure 6. (A) Chronocoulometric responses Q vs $t^{1/2}$ of HPFMS (a) and LOFS (b) films for potential steps from 1.5 to 0.0 V; coverage $\Gamma = 1.4 \times 10^{-6}$ mol/cm² of ferrocene site; 0.1 M LiClO₄ aqueous solution. (B) Influences of polymer film coverage on D_{app} of HPFMS (a) and LOFS (b) films. 0.1 M LiClO₄ aqueous solution; D_{app} was calculated from chronocoulometric responses.

determining the state of a polymer film, such as the polymer structure, preparing method and condition, and so on. Among these factors, the polymer structure is of the most importance. Taking these facts into consideration, we speculated that high charge transport efficiency of HPFMS film might be attributed to its hyperbranched structure. Flory[43] has induced that the conformation of amorphous linear polymers in bulk, similar to that in solution, was in a random coil state and that polymer chains were entangled together so that it was difficult for polymer chains to move freely and that it was also difficult for the solvents and counterions to diffuse into the film. By contrast, hyperbranched polymers[44,45] were in the sphere-like conformation, and there was little entanglement among the polymer chains contrary to the linear polymer. Therefore, the HPFMS film can form larger pores or channels after the polymer film was swollen by solvents so that the counterions can diffuse easily into the polymer film, which results in high charge transport efficiency (conceptual models for the electrode processes of HPFMS and LOFS films are shown in Scheme 1).The hyperbranched effect could be further confirmed by the different CV curves of HPFMS and LOFS films through the repetitious scans of polymer modified electrodes (shown in Figure S1A and B, Supporting Information): the electrochemical behavior of HPFMS film arrives at stability after about 10 scan cycles, but that of LOFS film do not become stable until 25 cycles were scanned.

As a result, the charge transport through polymer film for HPFMS is more convenient than that for LOFS, and peak current and apparent diffusion coefficient of HPFMS are larger than that of LOFS, especially at high polymer coverage.

The similar branched effect on the gas permeability of polymer films has been reported by other groups.[45–48] Bruening et al.[46] deposited PAMAM dendrimer/PAA films on porous alumina substrates and found that the fluxes of all the tested gases (He, O₂, N₂, H₂, CO₂, and CH₄) were several orders of magnitude higher than those through PAH/PAA multilayer films. Bershtein et al.[48] demonstrated that ethylene glycol diglycidyl ether cross-linked amine-terminated hyperbranched polyimide membranes exhibited better air gas permeability and selectivity as compared with those for linear polyimide. In addition to the present result, the hyperbranched polymer exhibited better substrate permeability and thus more efficient charge transport through the polymer film compared to linear polymer, which may find widespread applications in various areas, such as chemical sensor or in electrocatalytic reduction and oxidation of substrate, and so on.

3.2. Solvent Effect on Electrochemical Behaviors of HPFMS Films. As solvent swelling is always accompanied by ion flowing through polymer films, and many reports[32,37] have claimed that the solvent significantly influenced electrochemical behaviors of redox polymers, it is indispensable to study the

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SCHEME 1: Conceptual Model of HPFMS and LOFS Film Electrode Processes: HPFMS (A) and LOFS (A′) Films, and the Magnifying Surface of HPFMS (A) and LOFS (A′) Films before and after Counterion Plus Solvent Diffusion
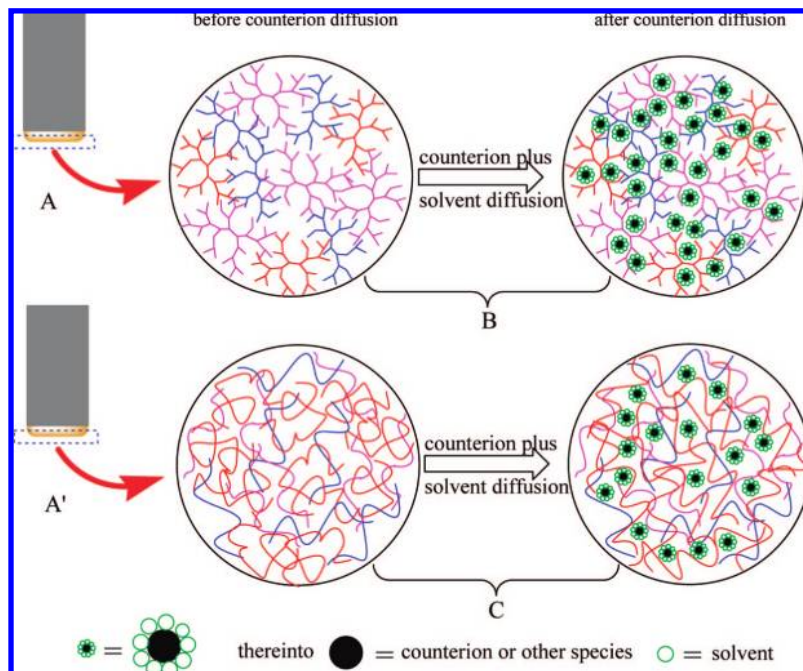
TABLE 2: Electrochemical Data of the HPFMS Film in Different Solvents[a]

solvent	E_{pc} (mV)	i_{pc} (μA)	E_{pa} (mV)	i_{pa} (μA)	ΔE_p^b (mV)
water	392	171.6	734	−126.0	342
methanol	384	410.7	809	−385.8	425
ethanol	331	184.7	934	−197.7	603
isopropanol	208	75.50	950	−84.67	742
n-butanol	101	77.69	1009	−84.73	908
ethyl acetate	49.0	18.32	1260	−27.88	1171
acetonitrile	511	19.70	666	−19.97	155
glycol	313	39.33	922	−38.89	609

[a] Coverage $\Gamma = 1.4 \times 10^{-6}$ mol/cm^2 of ferrocene site; scan rate = 100 mV/s; concentration of electrolyte = 0.1 M LiClO$_4$ solution. [b] $\Delta E_p = E_{pa} - E_{pc}$.

solvent effect to explore the electrochemical behavior and potential application of polymer films. As discussed above, HPFMS films possessed higher charge transport efficiency relative to LOFS: larger peak current and charge transport rate. Hereby, the HPFMS film modified electrode was chosen to investigate the influence of solvent on its electrochemical behavior. Water and seven organic solvents, methanol, ethanol, isopropanol, n-butanol and ethyl acetate, acetonitrile, and glycol, were selected to study the solvent effect on electrochemical behaviors of HPFMS films. The typical cyclic voltammograms of HPFMS films in different solvents are shown in Figure S2 (Supporting Information), and their electrochemical data are listed in Table 2.

As shown in Figure 3A and Figure S2 (Supporting Information), one pair of symmetric redox peaks are observed in cyclic voltammograms of HPFMS films in various solvents, which indicates that almost all ferrocene groups are situated in a similar chemical environment in the hyperbranched structure.[29] However, electrochemical behaviors of HPFMS films in different solvents have the particular peak shape, peak current (i_p), peak potential (E_{pa} and E_{pc}), and difference of redox peak potentials (ΔE_p). Among the eight solvents, peak shape in water, methanol, or ethanol is relatively narrower, and that in ethyl acetate is the broadest one; with the increase of the carbon chain of the

solvent, E_{pa} shifts toward the positive direction and E_{pc} toward the negative direction, and thus, ΔE_p increases (see Figure S2 (Supporting Information) and Table 2). The differences in i_p, E_p, and ΔE_p reflect the remarkable influences of the physical parameters of solvent on the charge transport through polymer film.

Similar to the kinetic performance of HPFMS film in water, i_p of HPFMS films in seven organic solvents is linear with the square root of scan rate at high polymer coverage, thus the electrode process in organic solvent is also controlled by the flowing of counterion into polymer film and solvent swelling.[30−38] Therefore, the parameters of the solvent, which affect the ion motion and electron transfer within the film, impacts the electrochemical behavior of the HPFMS film. As for a solvent, its viscosity determines the situation of substrate flow, solubility parameter and polarity influence the interaction between solvent and polymer and thus the swelling degree of polymer, and the dielectric constant has an effect on the conductivity of the film system.[38] Therefore, four main physical parameters, including viscosity (v), solubility parameter (δ), polarity and dielectric constant (ε), were chosen to investigate the influence of solvent on charge transport through the HPFMS films. These physical parameters of all solvents are listed in Table S2 (Supporting Information).

Then, we discussed the influences of physical parameters on charge transport through HPFMS films, that is, the apparent diffusion coefficient, D_{app}. D_{app}, of HPFMS films in different solvents could be calculated from their chronocoulometric responses, and the relationships between D_{app} and different physical parameters are sketched out in Figure 7.

As we know, the better swollen the polymer film, the easier the ion diffusion and charge transport through the film. The maximum degree of swelling can be reached when the polymer and solvent have the same solubility parameter.[49] Figure 7A shows the dependence of D_{app} on δ of the solvent, and one peak can be observed at 14.5 for methanol. Interestingly, when we just consider D_{app} in the solvents with different solubility parameters but similar values of the other three parameters, it
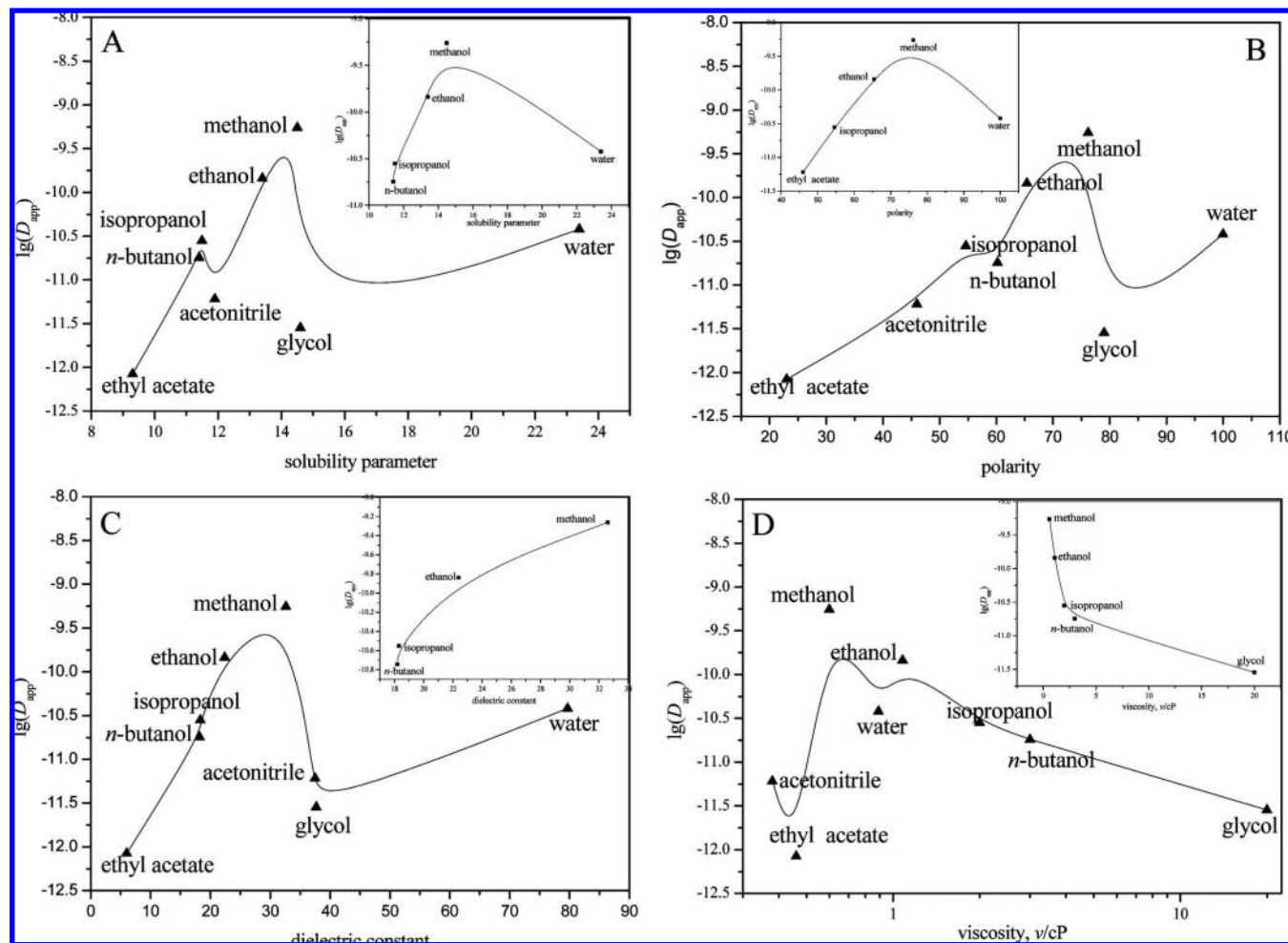
Figure 7. Influences of solubility parameter (A), polarity (B), dielectric constant (C), and viscosity (D) of solvents on D_{app} of HPFMS film; the inset of each figure represents the dependence of D_{app} on one physical parameter with three other similar parameters. Coverage $\Gamma = 1.4 \times 10^{-6}$ mol/cm^2 of ferrocene site; 0.1 M LiClO$_4$ solution.

is found that the relationship between D_{app} and the solubility parameter of solvent is approximately a normal distribution function, and D_{app} reaches a maximum at a solubility parameter of 14.5 for methanol (inset of Figure 7A), which is consistent with the relationship between the swelling degree of ferrocenyl polymer and the solubility parameter of the solvent.[49] The dependence of D_{app} on solvent polarity (Figure 7B) is similar to that on D_{app} and the solubility parameter, possibly because both parameters reflect the interaction between polymer film and solvent and thus the swelling degree of the polymer film. It is well known that the electrode process is affected by ion flow, more specifically, the dissociation of electrolytes, which can be controlled by the solvent with different dielectric constants. Therefore, the dielectric constant is also an important factor influencing charge transport through polymer films. One peak is also observed in the plots of D_{app} versus ε (Figure 7C); however, when we sketched out the plot of D_{app} in the solvents with different dielectric constants but similar values of other three parameters versus the dielectric constant, it was found that D_{app} increases with the increase of the dielectric constant (inset of Figure 7C), suggesting that the higher dielectric constant is in favor of charge transport through the polymer film. Lower D_{app} for water, glycol, and acetonitrile with higher dielectric constant is probably ascribed to their lower swelling degree and higher viscosity (see Figure 7A and D). Figure 7D indicates that the viscosity of solvent or the resistance of ion flow through HPFMS films remarkably influences charge transport through

the film. It is observed that D_{app} decreases with increasing viscosity of the solvent, with the exception of water, ethyl acetate, and acetonitrile, indicating that the high resistance of ion flow decreases the rate of charge transport through the polymer film (inset of Figure 7D). The exception possibly results from the low swelling capacity of water, ethyl acetate, and acetonitrile (Figure 7A).

The discussions above imply that the solvent evidently influences charge transport through the film, and a proper solvent is very important to increase the charge transport efficiency of the sensor system. For example, D_{app} of the HPFMS film in methanol (5.5×10^{-10}) greatly exceeds that in glycol (8.4×10^{-13}) and is even about 14 times greater than that in water (3.8×10^{-11}). As a result, a solvent with appropriate solubility and polarity, higher dielectric constant, and lower viscosity is able to enhance the charge transport efficiency within the polymer film. These conclusions are also consistent with the proposed models above that the low resistance of counterion flow through the film is helpful for charge transport within the polymer film.

4. Conclusions and Outlook

The electrochemical behaviors and thus the charge transport through HPFMS and LOFS films were studied systematically by cyclic voltammetry and chronocoulometry under different conditions: polymer coverage and solvent. Both poly(ferroce-

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nylsilanes) show stable cyclic voltammographs in LiClO$_4$ solutions. However, compared with the LOFS film, the HPFMS film exhibits higher charge transport efficiency due to its hyperbranched structure: peak current (i_p) and apparent diffusion coefficient (D_{app}) for HPFMS films are larger than those for LOFS films, especially at high polymer coverage. The effect of solvents on the electrochemical behaviors of HPFMS films indicates that the solvent with the appropriate solubility parameter and polarity, lower viscosity, and higher dielectric constant is in favor of charge transport through polymer film. The results indicate that, compared with their linear analogues, the hyperbranched ferrocenyl polymers have the potential to be excellent chemical sensor materials with convenient synthesis and high sensitivity. Further research in this area is in progress in our laboratory.

Supporting Information Available: Cyclic voltammograms of HPFMS and LOFS films in 0.1 M LiClO$_4$ aqueous solution; some physical parameters of eight solvent; cyclic voltammograms of HPFMS films in methanol, ethanol, isopropanol, *n*-butanol, water, ethyl acetate, acetonitrile, and glycol in 0.1 M LiClO$_4$ solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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