

Synthesis and Electrochemical Characterization of Polyurethane with Fixed Redox-Active Units in Hard Segments

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ABSTRACT: Electrochemically active polyurethanes containing ferrocene units in hard segments (PU-H-Fc) have been synthesized and identified by $^1\text{H-NMR}$ spectra. Electrochemical properties of PU-H-Fc blending with lithium perchlorates were investigated by cyclic voltammetry (CV) and compared with that of polyurethane with ferrocene units in polyether soft segments (PU-S-Fc) and of ordinary polyurethane blending with ferrocene (PU-B-Fc). The apparent formal potentials were found to be similar. The results illustrated that the original redox property of ferrocene was maintained when it was covalently linked to the hard segment as well as to the soft polyether main chain. The peak separation in PU-S-Fc was much greater than in PU-H-Fc, demonstrating that the softness and flexibility of the PEO chain was maintained by fixing the redox units on the

hard segments instead of on the soft segments, and the diffusion rate of redox units was increased because the migration of the active substance was enforced by the motion of the polymer chain. The peak position and peak separation of PU-H-Fc were similar to those of ordinary polyurethane blending with ferrocene. In the PU-H-Fc system the physical loss of admix redox molecules by migration can be avoided and the diffusion rate of redox units maintained. This is highly desirable in many electrochemical systems. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1555–1561, 2003

Key words: polyurethane; ferrocene; redox-active electrolyte; cyclic voltammetry; electrochemical response

INTRODUCTION

Redox-active polymers have attracted a great deal of attention because of their advantages in applications of electrochemical systems, which mutually convert chemical energy and electrical energy, and play an important role in artificial and biological systems.^{1–3} Ion-containing electrolytes that provide the reaction fields of electron transfer and electroactive species that can be electrochemically reduced and/or oxidized are essential to building an electrochemical system. Compared with liquid electrolytes, polymer solid electrolytes that allow fast and selective transport of ions in the solid state have certain advantages. They can readily incorporate many electroactive molecules to fabricate an electrochemically active polymer system without the problem of leakage, which usually exists in a system using liquid electrolytes. Moreover, an electrochemically active polymer system can be easily processed as thin films and can confine active species near the electrode surface. Therefore, solid-state cells can be readily miniaturized for attractive applications as all-solid-state sensors,¹ microelectronics and me-

chanical systems (MEMS), batteries,⁴ and electrode materials for enzyme.⁵ In the past two decades successful applications in electrochemistry and biomaterials have been shown. Ferrocene-pyrrole conjugates were found to be efficient oxidants in anode polymerization form redox-active films.⁶ Carbon-paste electrodes modified with ferrocene-containing polysiloxane were more stable than those modified with monomeric dimethylferrocene and appeared to be suitable for the measurement of crude samples.⁷ Electrodes modified by ferrocene-containing poly(ethylene oxide) respond rapidly, with larger steady-state response currents.⁸ An enzyme electrode with a redox polymer (ferrocene-containing crosslinked polyallylamine) was able to determine glucose concentrations up to 7 mM.⁹

Redox-active polymers can be prepared by two methods: blending small redox-active molecules with polymers and chemically fixing redox species to the side or end of a polymer chain. The difficulty of dispersion stability or insufficient solubility of redox materials with polymers may be avoided by the latter method. Such polymers as poly(3-methylthiophene)/ferrocene,¹⁰ ferrocene-pyrrole conjugates⁶, ferrocene-containing siloxane polymer,¹¹ ferrocene-amylose,¹² poly(*N*-ethylacrylamide-*co*-vinylferrocene) and poly(*N,N*-diethylacrylamide-*co*-vinylferrocene)¹³ have been prepared and show good electroactive proper-

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ties. However, the ionic conductivity and mechanical strength of these polymers have to be improved for practical use. In recent years we have synthesized a series of polyurethane electrolytes that have good mechanical behavior and high ionic conductivity at ambient temperature¹⁴ and have studied the solid-state electrochemical properties of redox-active solutes in electrolyte media.¹⁵ We also have prepared redox-active polyurethanes containing ferrocene units in polyether soft segments.¹⁶ The results show that incorporating ferrocene units into PEO main chains can avoid the physical loss of admix redox molecules by migration. The advantages of using polyurethane are related to its solubility in organic solvents for thin-film coating, good durability, excellent mechanical strength, and strong attachment to the electrode. The polyurethane matrix acts as a binder as well as an electrolyte.

In this article we report a novel redox-active polyurethane with covalently linked ferrocene units in the hard segment (PU-H-Fc). It is well known that polyurethane elastomers are composed of the urethane linkage of hard segment alternating with polyether or polyester soft segments. The ion conduction of polyurethane electrolyte is from the migration of ions, and such migration is enforced by the motion of the polymer chain, that is, the polyether soft segment in polyurethane. The softness and flexibility of the PEO chain would be maintained by fixing the redox units on the hard segments instead of on the soft segments, thus both the ionic conductivity and diffusion rate of redox units would be increased, improving the performance of the electrochemical system. Also important is that polyether polyurethane electrolytes with ionic conduction species either in a hard domain¹⁴ or in a soft domain¹⁷ have high ionic conductivities at ambient temperature.

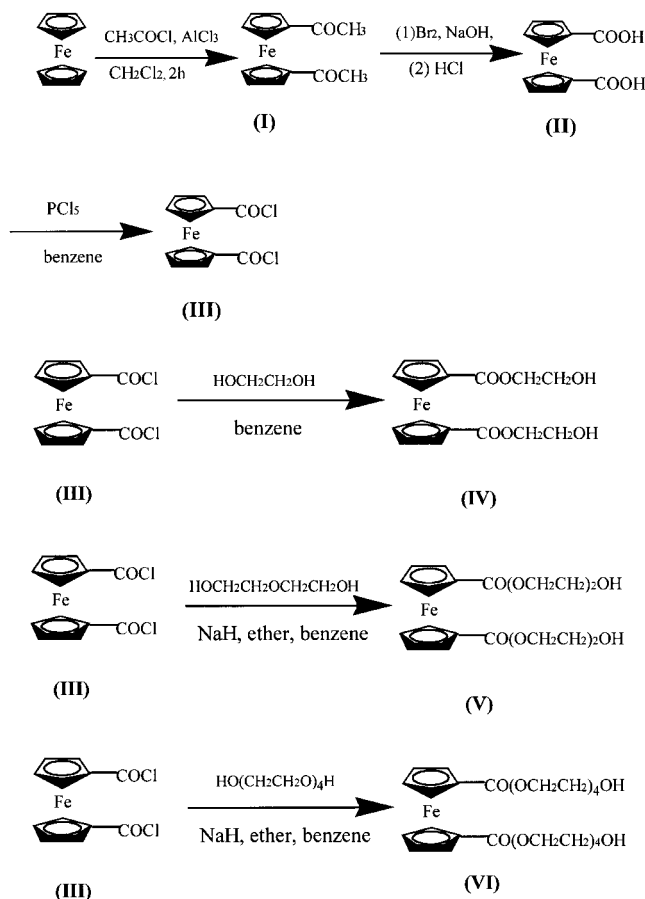
We will demonstrate that in the PU-H-Fc system, the physical loss of admix redox molecules by migration can be avoided and that the diffusion rate of redox units maintained. This is highly desirable in many electrochemical systems.

EXPERIMENTAL

Materials

Ferrocene was purified by steam distillation before use. Sodium hydride (NaH; SERVA Company) was washed with anhydrous petroleum ether. 4,4'-methylenebis(phenyl isocyanate) (MDI; Aldrich Chemical Co.) was used as received. Poly(ethylene oxide) (PEO; $M_w = 1000$) was washed by anhydrous benzene and then dried in a vacuum over 48 h at 65°C. *N,N'*-Dimethylformamide (DMF) was dried by anhydrous CaH₂ and purified through vacuum distillation.

1,1'-Diacetylferrocene [Scheme 1(I)], ferrocene-1,1'-dicarboxylic acid [Scheme 1(II)], and 1,1'-ferrocenedi-



Scheme 1

carbonyl chloride [Scheme 1(III)] were synthesized as reported in a previous article.¹⁶

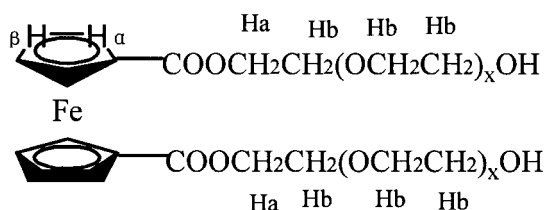
Dihydroxyethyl 1,1'-ferrocenedicarboxylate [Scheme 1(IV)] was synthesized by the reaction of 1,1'-ferrocenedicarbonyl chloride [Scheme 1(III)] with ethylene glycol. A 1,1'-ferrocenedicarbonyl chloride [Scheme 1(III)]/benzene solution was added dropwise over a period of 24 h to a benzene solution of ethylene glycol under a nitrogen atmosphere and refluxed for 48 h. The product was separated by column chromatography on neutral aluminum oxide. The second fraction eluted with chloroform was dihydroxyethyl 1,1'-ferrocenedicarboxylate [Scheme 1(IV)].

¹H-NMR: $\delta = 4.77$ ppm for Ha (4H), 4.45 ppm for Fc-H α , and Fc-H β (8H), 3.87 ppm for Hb (4H); FTIR: 3469 (ν_{OH}), 3111 (ν_{C-H}), 2956 (ν_{CH_2}), and 1712 ($\nu_{C=O}$) cm⁻¹. Yield: 25.4%.

The synthesis of Fc(COO(CH₂CH₂O)₂H)₂ [Scheme 1(V)] and Fc(COO(CH₂CH₂O)₄H)₂ [Scheme 1(VI)] followed this procedure: 1,1'-ferrocenedicarbonyl chloride [Scheme 1(III)] was mixed with sodium condensed ethylene glycol, which were prepared by mixing NaH and condensed ethylene glycol in anhydrous

ether in a salt-ice bath. Methanol was added to remove the residual NaH. Column chromatography of silica was used to separate the crude product, using benzene, ether, and ether/acetone (1:1) as the developing solvents.

$^1\text{H-NMR}$: for substance V— $\delta = 4.88$ ppm for Ha (4H), 4.5 ppm for Fc-H α and Fc-H β (8H), 3.78 ppm for Hb (12H); Yield: 67.4%; for substance VI— $\delta = 4.88$ ppm for Ha (4H), 4.4 ppm for Fc-H α and Fc-H β (8H); 3.78 ppm for Hb (28H); Yield: 82.2%.



Here, $x=0, 1, 3$ for IV, V, and VI, respectively

Sample preparation

PU synthesis

Polyurethane with ferrocene units in hard segments (PU-H-Fc) was prepared by a two-step condensation reaction. PU-H-Fc [Scheme 2(A)] was obtained from the reaction of MDI, PEO ($FW = 1000$), dihydroxyethyl 1,1'-ferrocenedicarboxylate [Scheme 1(IV)] and 1,4-butanediol (BD) with a molar ratio

3:1.2:0.9:0.9, as shown in Scheme 2(A). The PEO/DMF solution was added dropwise into the MDI/DMF solution containing 0.05% dibutyltin dilaurate at 55°C . After being kept 1.5 h at 65°C , the solution was cooled down to 55°C , and the mixture of dihydroxyethyl 1,1'-ferrocenedicarboxylate [Scheme 1(IV)] and BD/DMF solution was added dropwise. The reaction was kept for 2 h at 65°C and then 4 h at 85°C for the chain extension. The product was precipitated from distilled water and then washed by ethanol. After centrifugation the polyurethane was dried under vacuum at 65°C for 72 h. A similar procedure was followed for PU-H-Fc [Scheme 2(B)] and PU-H-Fc [Scheme 2(C)], except that the chain extender BD was not used. The molar ratio of the reactants was 3:1:1 for MDI/PEO ($FW = 1000$)/[Scheme I(V)] or [Scheme 1(VI)]. The synthetic route is outlined in Scheme 2(B,C).

Yield: 76.9% for PU-H-Fc [Scheme 2(A)], 54.8% for PU-H-Fc [Scheme 2(B)], and 65.2% for PU-H-Fc [Scheme 2(C)].

Sample preparation for electrochemical characterization

Polyurethanes with redox and ionic species were obtained by mixing PU-H-Fc with lithium perchlorate. The molar ratio of ethylene oxide/ Li^+ varied; they were 20:1, 10:1, 4:1, and 1:1. A sample of the nomenclature is: PU-H-Fc/ Li^+ 4:1 represents polyurethane with an ethylene oxide/ Li^+ molar ratio of 4:1.

CHARACTERIZATION

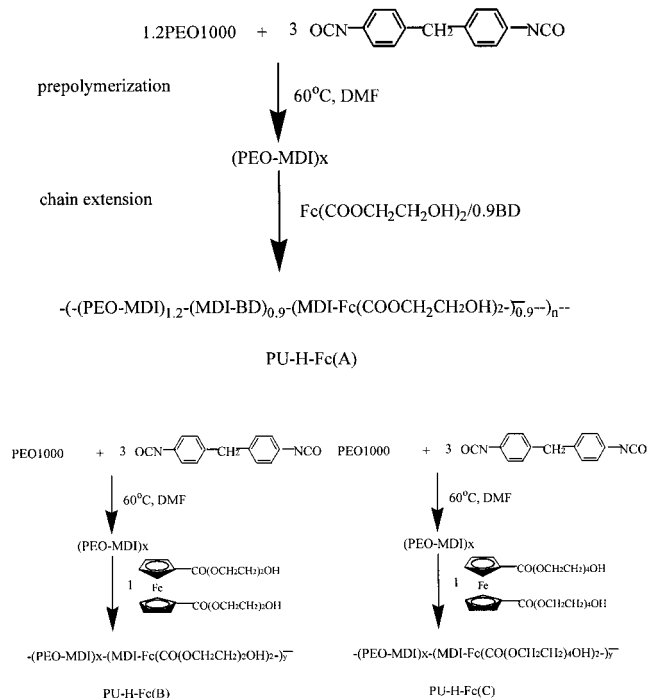
FTIR spectra were recorded by a Bruker IFS66V vacuum spectrometer. $^1\text{H-NMR}$ spectra were recorded on a Bruker AM-300 spectrometer, with CDCl_3 or d-DMSO as the solvent and internal standard.

A three-electrode system was used in electrochemical characterization. Redox potentials of ferrocene in DMF were recorded and compared with the literature to prove the validity of the electrode system. The experiments were carried out on an EG&G Princeton Applied Research Potentiostat Model 273. Working and auxiliary electrodes were Pt wires (geometric areas were $4 \times 10^{-3} \text{ cm}^2$), and the reference electrode was saturated calomel electrode (SCE). Lithium perchlorate was used as the supporting electrolyte and DMF as the solvent. Absence of any peak in the range of -1.0 V to 1.0 V means that DMF is a suitable solvent for electrochemical analysis of the present system.

RESULTS AND DISCUSSION

Sample identification

Proton magnetic response spectra of PU-H-Fc [Scheme 2(A)], PU-H-Fc [Scheme 2(B)] and PU-H-Fc



Scheme 2

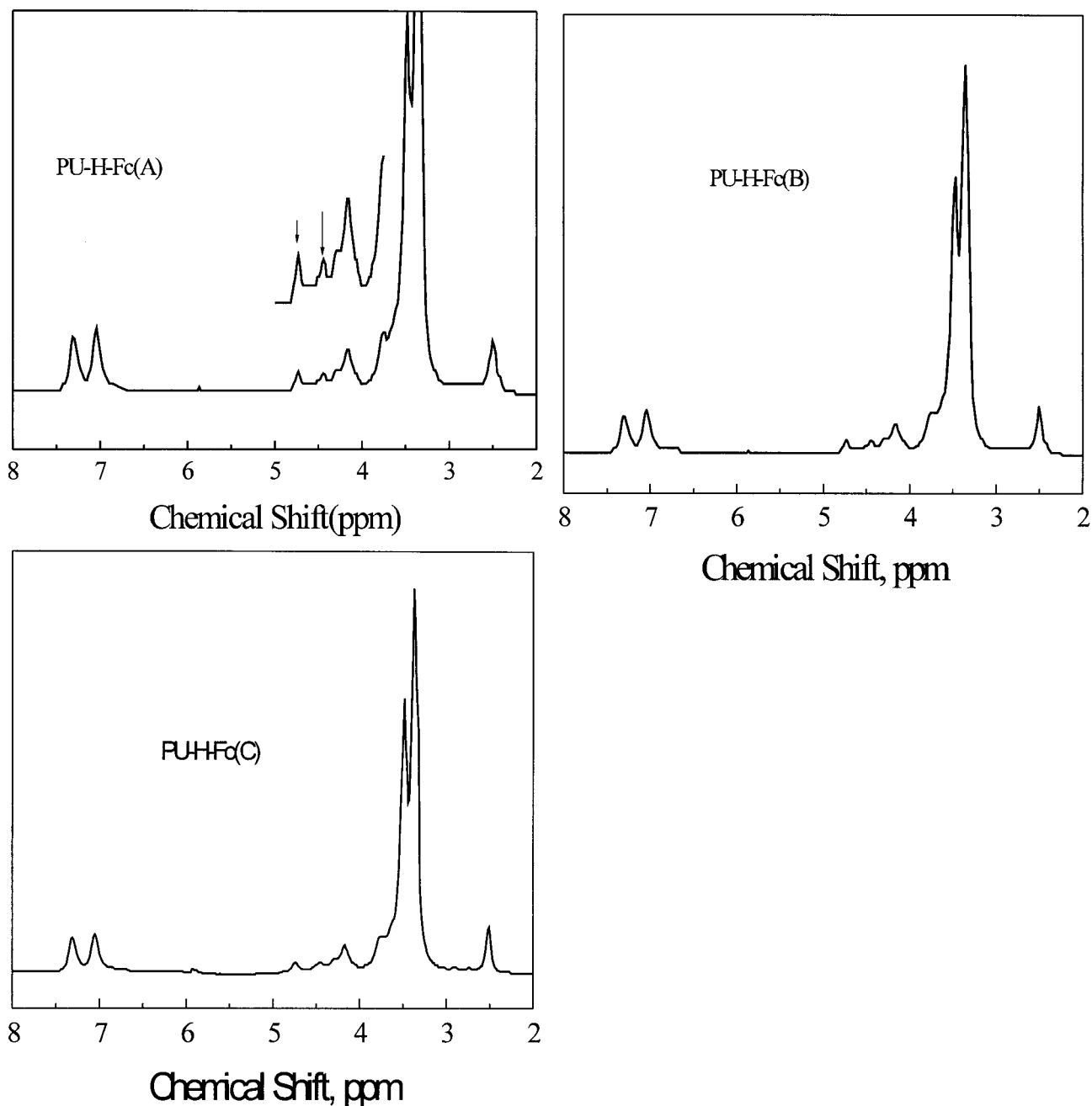


Figure 1 (a) $^1\text{H-NMR}$ of PU-H-Fc [Scheme 2(A)]; (b) $^1\text{H-NMR}$ of PU-H-Fc [Scheme 2(B)]; (c) $^1\text{H-NMR}$ of PU-H-Fc [Scheme 2(C)].

[Scheme 2(C)] in d-DMSO were shown in Figure 1. The chemical shifts for Fc-H α and Fc-H β of PU-H-Fc are 4.7 ppm and 4.5 ppm, respectively. The results are unanimous with that observed in polyurethanes with ferrocene units in soft segments.¹⁶

Electrochemical analysis

Cyclic voltammograms for the DMF solution of PU-H-Fc (A), PU-H-Fc (B) and PU-H-Fc (C) containing LiClO₄ supporting electrolytes are shown in Figure

2. Electrochemical process of ferrocene, dissolved in ordinary polyether polyurethane (PU-B-Fc), was also studied as control system. The cathodic and anodic potentials (E_p^c and E_p^a) of the ferrocene/ferrocinium (Fc/Fc⁺) couple in polyurethane with fixed ferrocene group in hard segments were around 500 and 310 mV (scan rate 20mV/s), respectively. Table I shows the cathodic and anodic peaks of different systems. For comparison the electrochemical data of PU-B-Fc and PU-S-Fc were also listed. Compared with the results of PU-B-Fc and PU-S-Fc, the ap-

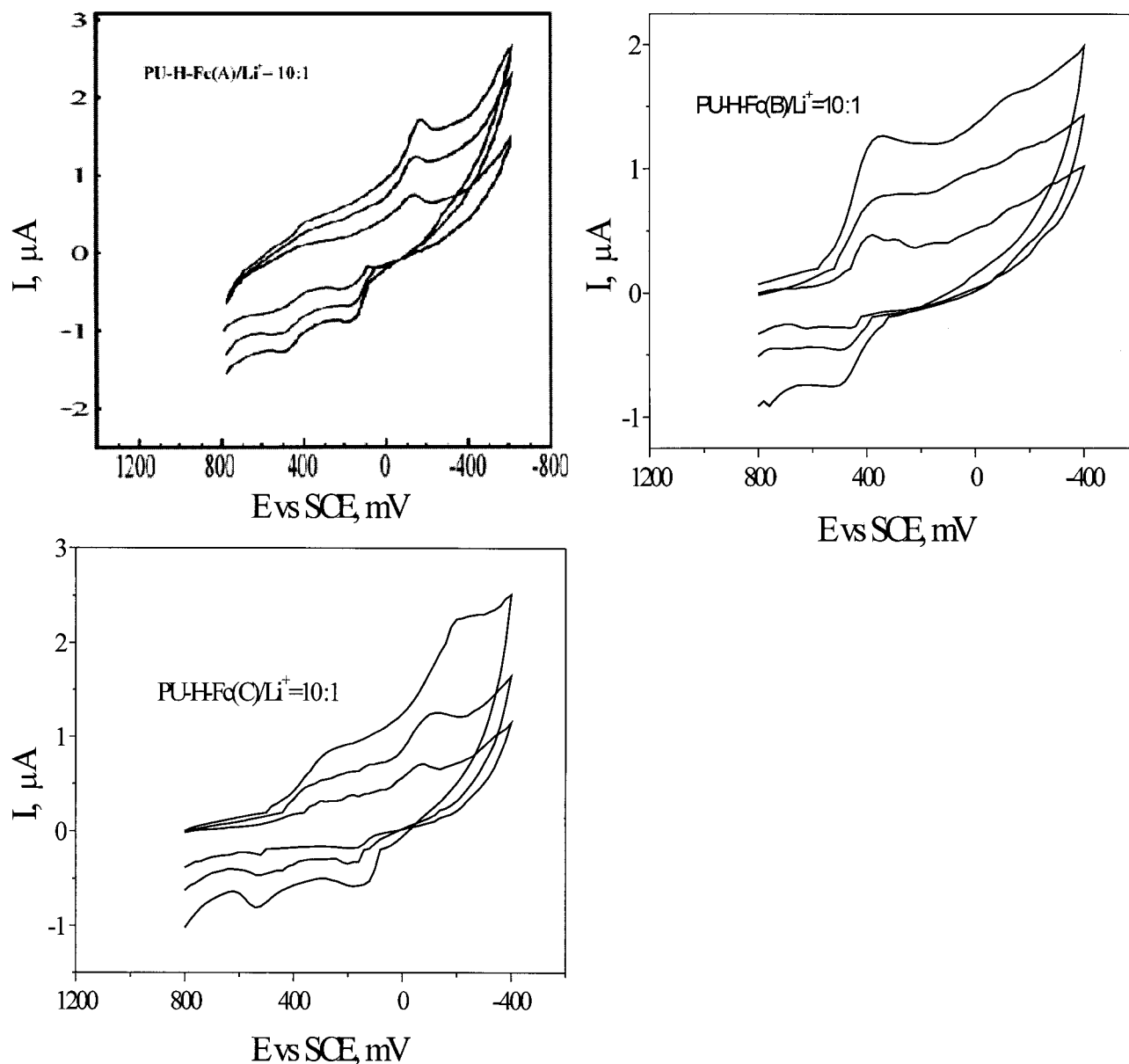


Figure 2 (a) Cyclic voltammograms of PU-H-Fc [Scheme 2(A)]/DMF solution with LiClO_4 as supporting electrolytes (scan rate: 200, 100, 50 mV/s, from up to down); (b) cyclic voltammograms of PU-H-Fc [Scheme 2(B)]/DMF solution with LiClO_4 as supporting electrolytes (scan rate: 200, 100, 50 mV/s, from up to down); and (c) cyclic voltammograms of PU-H-Fc [Scheme 2(C)]/DMF solution with LiClO_4 as supporting electrolytes (scan rate: 200, 100, 50 mV/s, from up to down).

parent formal potentials, which were defined as the average of cathodic and anodic peak potentials, were found to be similar and almost independent of

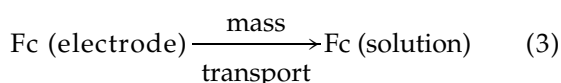
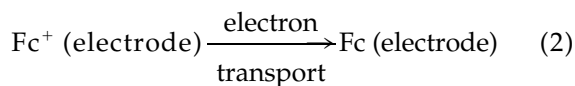
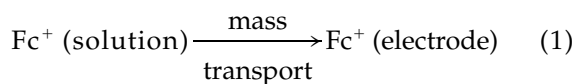
the scan rate, although PU-S-Fc gave greater peak separation and broader peaks, which will be discussed in the next section. This illustrated that the

TABLE I
Electrochemical Data of Ferrocene-Containing Polyurethanes

System	Anodic E_a (mV)	Cathodic E_c (mV)	$(E_c + E_a)/2$ (mV)	$\Delta E_p = (E_a - E_c)$ (mV)
PU-H-Fc(A)	500	330	415	170
PU-H-Fc(B)	501	318	409	183
PU-H-Fc(C)	500	305	403	195
PU-B-Fc	496	338	417	158
PU-S-Fc	674	116	395	558

original redox property of ferrocene would be maintained to a great extent when covalently linked to the hard segment as well as to the soft polyether main chain.

As discussed in a previous article,¹⁶ in a typical cyclic voltammetry process when ferricinium (Fc^+) is reduced to ferrocene, there are at least three steps:



During the electrode reaction, if the electron transfer rate is significantly greater than the mass transfer rate, the cathodic peak potential and peak separation are independent of the scan rate. However, if the mass transfer rate becomes comparable to the electron transfer rate, the peak separation will increase.¹⁸ For the polyurethanes with fixed ferrocene in soft or hard segments, the mobility of ferrocene species on the surface of the electrode was restricted by the polymer chain, so the electrochemical redox reaction of ferrocene units was more difficult than that in PU-B-Fc; a greater peak separation was found in polyurethanes with fixed ferrocene, both in the soft and hard domains, than in the polyurethane with blending ferrocene.

One notable result was that the peak separation in PU-S-Fc was much greater than in PU-H-Fc. It is well known that polyurethane elastomers are composed of the urethane linkage of a hard segment alternating with polyether or polyester soft segments. The migration of the active substance is enforced by the motion of polymer chain, that is, the polyether soft segment in polyurethane. The softness and flexibility of the PEO chain would be maintained by fixing the redox units on the hard segments instead of on the soft segments, and the diffusion rate of redox units will be increased because the mobility of ferrocene species on the electrode depends mainly on the motion of the domain in which they locate. The peak position and peak separation of PU-H-Fc are similar to that of the polyurethane blending system with ferrocene. In the PU-H-Fc system the physical loss of admix redox molecules by migration can be avoided and the diffusion rate of redox units maintained. This is highly desirable in many electrochemical systems.

There is a notable pair of postpeaks around -158 mV and 200 mV on the cyclic voltammograms of PU-H-Fc. It might be ascribed to the existence of adsorption of sample on the electrode surface.

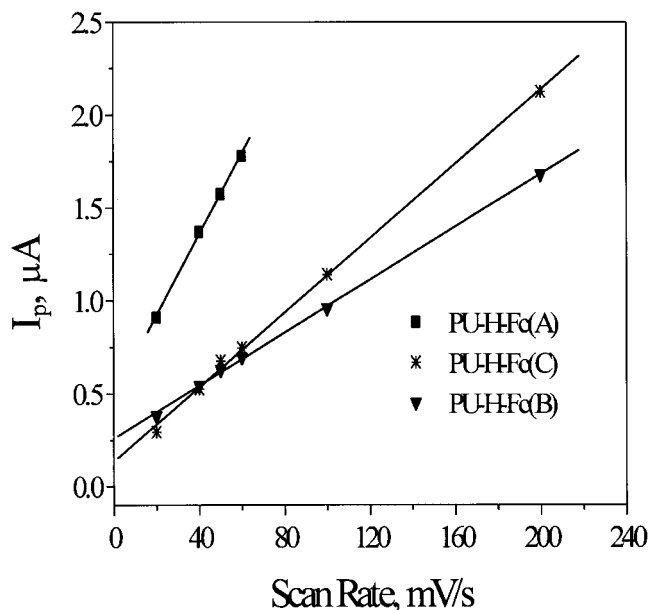
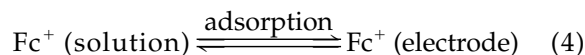


Figure 3 I_p of adsorption peak versus scan rate.



If the adsorption of the Fc^+/Fc couple were different from each other, the adsorption prepeak or postpeak would be found.¹⁸ Figure 3 illustrates the linear relationship between the I_p and scan rate (SR). The result demonstrated that the postpeak was an adsorption peak¹⁹ and also illustrated that polyurethane with fixed ferrocene in the hard domain has stronger adsorption and better adhesion than polyurethane with fixed ferrocene in the soft segment.

The influence of the length of hard segments was also investigated. As shown in Table I, there is no obvious difference for peak position, whereas peak separation becomes broader with the increase of the length of hard segments.

Figure 4 shows the effect of the concentration of the supporting electrolyte LiClO_4 on the peak current and potential. The concentration of LiClO_4 has little effect on the peak current. However, the concentration of LiClO_4 affects the potential value significantly. The solution, with a stoichiometry of 10:1, has the most positive cathodic peak potential, which corresponds to our previous result.¹⁶

CONCLUSION

Polyurethanes with ferrocene groups in different lengths of hard segments were synthesized based on the polycondensation reaction of MDI, PEO, and Fc-glycol with a molar ratio of 3:2:1. Substituted cyclopentadienyl ring proton signals can be seen in the $^1\text{H-NMR}$ spectra of PU-H-Fc.

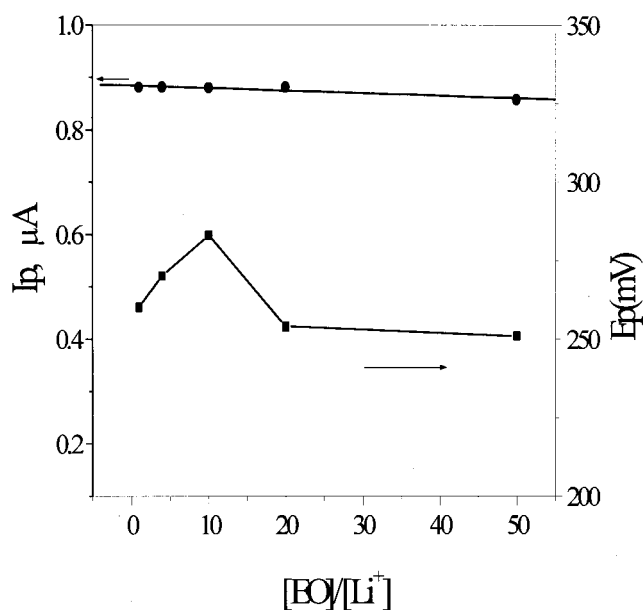


Figure 4 I_p and E_p of diffusion peak versus the molar ratio of EO to Li^+ .

1. PU-H-Fc exhibited normal cathodic and anodic peaks of ferrocene/ferricinium (Fc/Fc^+) coupled in DMF solution, with lithium perchlorate as the supporting electrolyte. The apparent formal potentials of PU-H-Fc, PU-S-Fc, and PU-B-Fc were found to be similar, which illustrated that the original redox property of ferrocene was maintained when it was covalently linked to the hard segment as well as to the soft polyether main chain.
2. The peak separation in PU-H-Fc was close to that in PU-B-Fc and much smaller than that in PU-S-Fc. It demonstrated that the softness and flexibility of PEO chain was maintained by fixing the redox units on the hard segments instead of on the soft segments. In the PU-H-Fc system the physical loss of admix redox molecules by migra-

tion can be avoided and the diffusion rate of redox units maintained. The PU-H-Fc system also showed better adhesion with the electrode. These are highly desirable in many electrochemical systems.

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