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Cyclic voltammetry properties of ferrocene-modified block copolyurethanes

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1. Introduction

Molecular and macromolecular materials that contain atoms of transition elements in close proximity are attracting increasing attention because of their potentially interesting electrical, redox, optical, and magnetic characteristics [1].

The ferrocene unit has proved to be a versatile building block with excellent thermal and photochemical stability, which displays a reversible redox reaction in organic solutions. Ferrocenyl-based polymers have been used in the chemical modification of electrodes, in the construction of amperometric biosensors and, more recently, in the area of nonlinear optical (NLO) materials [2].

In our previous paper, a series of new ferrocene urethane block copolymers were synthesized and their fire retardancy was reported [3]. The purpose of this study is to analyze the electrochemistry of ferrocene-modified block copolyurethanes and the effect of different molecular weight diisocyanate prepolymers on the reversibility of the oxidation–reduction process. Polyurethanes are highly soluble in organic solvents and therefore suitable for thin-film coatings. In addition, they possess excellent mechanical properties and strong attachments to the electrode surface. Therefore, polyurethane with ionic conductivity properties may be a suitable medium for redox of the electroactive solute [4,5,6].

The extent of the interaction between ferrocenyl units can be measured by the difference in redox potentials. It has been shown that the presence of an insulating CH_2 unit between the ferrocene groups leads to a decrease in redox potential difference. Moreover, for species with more than one CH_2 unit between the ferrocenyl groups, only one oxidation wave is detected [7,8,9,10].

2. Experimental

Ferrocene-modified polyurethane materials investigated in this work, as well as their physical characteristics, have been published [3]. Therefore, only basic information concerning sample preparation is presented here. Cyclic Voltammetric Analysis was performed using a BAS CV-50W voltammetric analyzer with Pt working and auxiliary electrodes and Ag reference electrode with ferrocene (0.001 M) as an internal reference and 0.1 M (n-Bu)$_4$NPF$_6$/CH$_2$Cl$_2$ solution.

2.1. Ferrocene-containing hydroxyl-terminated (FcOH) prepolymer synthesis

To the solution of 4.0 g (0.013 mole) 1,1′-di(chlorocarbonyl)ferrocene in dry benzene (95 ml), 1.82 g (0.0154 mole) 1,6-hexanediol and pyridine (1.1 ml) was added. The mixture was stirred at 70–75°C under an inert atmosphere (N_2 gas) for 4 h. The pyridinium chloride salt, being insoluble in benzene was precipitated from the reaction phase. The mixture was filtered and the solvent was evaporated under reduced pressure. The residue was extracted with CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4) and evaporated to give 4.3 g (88%) of ferrocene-containing hydroxyl-terminated prepolymer, FcOH (Scheme 1). ^{1}H NMR of this compound showed an average molecular weight of ~3600.

2.2. Polymer synthesis using FcOH

Block copolymers were prepared using the prepolymer method. The diisocyanate-terminated prepolymer (Baytec® ME-050, ME-080, or ME-090 with NCO content of 5.51, 8.64, and 9.93%, respectively) was heated at 100–110°C for about 30 min; for example, 11.55 g (0.012 mole) of ME-080. To this, 2.25 g (6.65×10^{-4}mole) FcOH dissolved in 5 ml THF and several drops of T-12 catalyst solution

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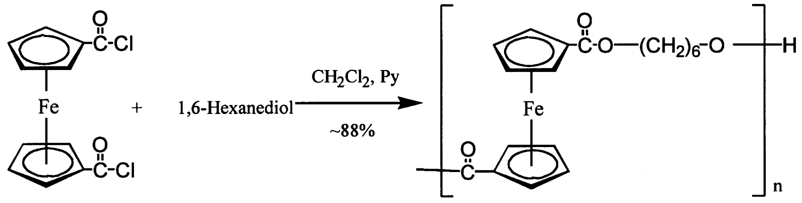

Scheme 1. Hydroxyl-terminated polyester prepolymer (FcOH).

(dibutyltin dilaurate) were added. The mixture was mechanically stirred under nitrogen for 20 min, and then 1.1 g (9.3×10^{-3}mole) HDO was added and stirred for one minute. The viscous mixture was then poured into a $4''\times4''\times1/8''$ preheated mold. The specimen was cured under vacuum and at 80 °C for 6 h to give A6 polymer with 15% FcOH prepolymer. Table 1 shows the other compositions of synthesized polymers.

3. Results and discussion

Cyclovoltammetric studies were carried out in CH_2Cl_2 solution with Bu_4NPF_6 (0.1 M) as the supporting electrolyte and ferrocene (0.001 M) as an internal reference. The data $E^0=(E_{pa}+E_{pc})/2$, $\Delta E_p=E_{pc}-E_{pa}$, and i_{pa}/i_{pc} are presented in Table 2.

The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current(i_{pa}) and cathodic peak current (i_{pc}), and the anodic peak potential (E_{pa}) and cathodic peak potential(E_{pc}). For the forward sweep of the first cycle, the voltammetric peak current (i_{pc}) is directly proportional to $\nu^{1/2}$ and is given by the Randales–Sevcik equation, which also describes i_p for species dissolved in solution and diffusing to the electrode [11]

$$i_{pc}=2.69\times10^5 n^{3/2}A(D^{1/2}C)\nu^{1/2},$$

where A is the electrode surface area, n the electron stoichiometry, D the diffusion coefficient, C the concentration, and ν is the scan rate [12]. For diffusion-controlled processes $i_p/\nu^{1/2}$ must be constant and for fully reversible redox couple in solution, the i_{pa}/i_{pc} ratio should be 1.

Table 1
Composition of ferrocene-modified copolymers

Sample	NCO terminated prepolymer	FcOH (%wt)
A1	ME-050	5
A2	ME-050	10
A3	ME-050	15
A4	ME-080	5
A5	ME-080	10
A6	ME-080	15
A7	ME-090	5
A8	ME-090	10
A9	ME-090	15

Fig. 1 shows a representative Cyclic Voltagramm for A1 Block Copolymer. In all cases, only one oxidation wave was detected, which is due to the influence of six insulating CH_2 groups between the ferrocene groups. Apparent formal potentials, E^0, were almost independent of the scan rate. The separation between voltammetric peaks (ΔE_p) ranges from a low of 0.046 V at a 20 mV/s scan rate for A9 polymer to a high of 0.175 V at 120 mV/s for A3 polymer. The peak potential difference and broadening of the peaks at higher scan rates suggests the slow electron transfer to the redox center and the interaction between the redox

Table 2
Cyclic voltammetry data

	Sample	ν (mVs^{-1})					
		20	40	60	80	100	120
A1	E^0 (mV)	794	785	785	787	796	785
	ΔE_p (mV)	81	96	103	115	128	134
	i_{pa}/i_{pc}	0.96	0.95	0.97	0.99	1.03	1.01
A2	E^0 (mV)	828	827	827	827	852	834
	ΔE_p (mV)	113	131	136	144	153	161
	i_{pa}/i_{pc}	0.94	0.92	0.96	0.97	0.99	1.02
A3	E^0 (mV)	795	796	798	796	803	798
	ΔE_p (mV)	95	123	137	150	166	175
	i_{pa}/i_{pc}	0.89	0.95	0.98	0.99	1.11	1.04
A4	E^0 (mV)	789	789	789	790	797	792
	ΔE_p (mV)	88	105	111	120	126	136
	i_{pa}/i_{pc}	0.83	0.87	0.89	0.91	0.97	0.94
A5	E^0 (mV)	785	781	778	777	771	775
	ΔE_p (mV)	76	94	101	112	120	133
	i_{pa}/i_{pc}	0.77	0.81	0.83	0.85	0.84	0.86
A6	E^0 (mV)	783	783	784	787	793	777
	ΔE_p (mV)	93	113	127	139	151	163
	i_{pa}/i_{pc}	0.73	0.79	0.83	0.87	0.88	0.86
A7	E^0 (mV)	852	812	810	812	812	815
	ΔE_p (mV)	78	91	94	103	106	113
	i_{pa}/i_{pc}	0.95	0.97	0.96	0.99	1.00	1.03
A8	E^0 (mV)	807	804	806	807	809	815
	ΔE_p (mV)	81	96	99	107	117	124
	i_{pa}/i_{pc}	0.96	0.98	1.00	1.02	1.03	1.07
A9	E^0 (mV)	797	794	788	787	789	785
	ΔE_p (mV)	46	59	58	67	73	76
	i_{pa}/i_{pc}	0.93	0.95	0.93	0.95	0.96	0.96

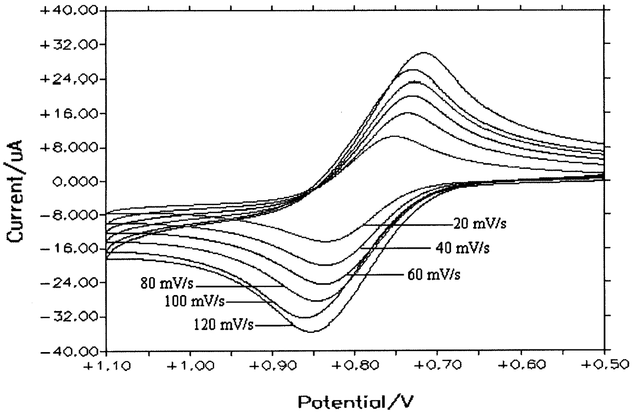

Fig. 1. Cyclic voltagramm for A1 block copolymer at 20, 40, 60, 80, 100, and 120 mV/s scan rate.

metal centers along the polymer chain. Recently, a peak broadening of about 0.558 V for polyurethane with ferrocene units in their backbone was reported [13]. This difference, between the published value and values in this study, suggests that the redox property of ferrocene was maintained to a greater extent when incorporated in the form of a block in the backbone structure of the polymer rather than as an individual unit. Plots of i_{pc} versus square root of scan rate ($\nu^{1/2}$) were linear for values between the examined scan rates, indicating that the electron transfer is essentially diffusion-controlled. Fig. 2 shows representative plots for A1, A2, and A3 samples.

In addition, the cyclovoltammograms of the polymers show that the ferrocene moieties, which can be reversibly ($i_{pa}/i_{pc} \approx 1$) oxidized at $E^0 \approx 0.77$–0.852 V (vs. Ferrocene $E^0 = 0.321$ V) and higher scan rates, are equivalent. Higher potentials for the ferrocene-modified polyurethanes are due to the electron-withdrawing ester functional group attached to ferrocene.

Moreover, the data reported in Table 2 suggest that molecular weight of diisocyanate prepolymers has no apparent effect on the electrochemistry of ferrocene-modified polyurethanes.

4. Conclusions

The ferrocene-modified block copolyurethanes, A1–A9, exhibited normal cathodic and anodic peaks for ferrocene/ferricinium (Fc/Fc$^+$) except for the broadening of the peaks at higher scan rates due to slow electron transfer to the redox center and interaction between the redox metal centers along the polymer chain. In addition, plots of cathodic peak current versus square root of scan rate were linear for values between the examined scan rates (20, 40, 60, 80, 100, 120 mV/s). This indicated that the electron transfer was diffusion controlled and the effect of other means of mass transport such as convection and migration is minimal. It is demonstrated that the original redox properties of ferrocene are maintained to a greater extent when it is covalently linked to the polyether polyurethane main chain as a block copolymer.

The main difference between these studies and those of others is that the present study deals with high molecular weight block copolyurethanes that contain small percentages of ferrocene blocks. In other work the main focus has been on ferrocenic polymers with much lower molecular weight and much higher ferrocene levels. The main goal was to see whether ferrocene blocks keep their electrochemistry properties when incorporated into high molecular weight copolyurethane elastomers. It is known that electron transfer to the redox center and interaction between the redox metal centers along the polymer chain can be significantly diminished, due to high molecular weight and not having an accessible ferrocene center, to the extent that no oxidation–reduction peaks might be detected.

In this work we were hoping to see that the ferrocene blocks have kept their electrochemistry integrity within the polymer chain. The results show that not only is there good interaction between ferrocene units but also much better than when ferrocene is incorporated individually. We also wanted to know if the molecular weight of the diisocyanate prepolymer would have any effect on this electrochemistry. Our extensive CV analysis at different ferrocene percentages and scan rates showed that the

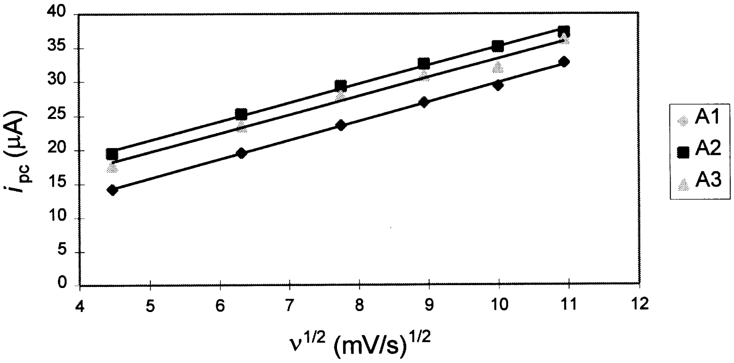

Fig. 2. Plots of i_{pc} vs. the square root of the scan rate for the oxidation peaks observed for A1, A2, and A3 polymers.

electrochemistry of these polymers was unaffected by the molecular weight of diisocyanate prepolymer.

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References

[1] Nguyen T, Diaz AF. Chem Mater 1994;6:952.
[2] Casado CM, Moran M, Losada J, Cuadrado I. Inorg Chem 1995;34:1668.
[3] Najafi-Mohajeri N, Nelson GL, Benrashid R. J Appl Polym Sci 2000;76:1847.
[4] Xu HS, Yang CZ. J Polym Sci Polym Phys 1995;33:745.
[5] Wei X, Yu XH. J Polym Sci Polym Phys 1997;35:225.
[6] Xu H-S, Zhu J-J, Cheng HC, Yang C-Z. Phys Stat Sol 1996;156:59.
[7] Muller-Westerhoff UT. Angew Chem Int Ed Engl 1986;25:702.
[8] Dong TY, Hwang MY, Wen Y, Hwang WS. J Organomet Chem 1990;391:377.
[9] Dement'ev VV, Cervantes-Lee F, Pakanyi L, Sharma H, Pannell KH, Nguyen MTK, Diaz AF. Organometallics 1993;12:1983.
[10] Foucher D, Honeyman CH, Nelson JM, Zhong Tang B, Manners I. Angew Chem Int Ed Engl 1993;32:1709.
[11] Murray RW. In: Bard AJ, editor. Electroanalytical chemistry, Vol. 13. New York: Marcel Dekker, 1984. p. 191.
[12] Bu H, English AM, Mikkelsen SR. J Phys Chem B 1997;101:9593.
[13] Qun-Dong S, Suo-Long N, Hai-Sheng X, Chang-Zheng Y. J Appl Polym Sci 1999;74:2674.