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Self Organization and Redox Behavior of Poly(vinylferrocene)-*block*-Poly(isobutylene)-*block*-Poly(vinylferrocene) Triblock Copolymer†

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Self organization and redox behavior of a ferrocene containing triblock copolymer, poly(vinylferrocene)-*block*-poly(isobutylene)-*block*-poly(vinylferrocene), with narrow molecular weight distribution in solutions and in thin films were investigated. Dynamic light scattering studies of the block copolymer in dilute solutions indicated that the polymer chains aggregated at relatively low concentrations. The aggregations of polymer chains were observed in toluene, as well as in tetrahydrofuran at concentrations as low as 0.014 mg/mL and 0.0045 mg/mL, respectively. Thin films of the copolymer showed reversible single electron redox behavior, similar to that of ferrocene. Morphology and micro-phase separation of the copolymer was analyzed by transmission electron microscopy.

Keywords: Ferrocene, triblock copolymer, aggregation, micro-phase separation

1. Introduction

Since ferrocene was synthesized as an important organometallic compound, ferrocene and its derivatives have attracted substantial interest in fuel additives (1), anticancer ingredients (2–3), photosensitive materials (4), and catalysis (5). Typically, poly(vinylferrocene) (PVFc) shows thermal stability (up to 400°C), high glass transition temperature (190–220°C), low toxicity, and reversible redox activity, which leads to applications in label-free electrochemical sensors for cations (6–7), anions (7), and DNA (8). Block copolymers containing hydrophilic and hydrophobic segments are separated in solid or liquid states. These materials are commonly self-organizing on the nanometer scale and are of considerable current interest for applications in nanolithography (9), electronics (10), and drug delivery systems (11). The ABA triblock copolymers having outer hard (A) and middle soft (B) segments can be controlled to obtain either an elastomer or a thermoplastic by varying the nature and size of the A and B segments (12–14). The triblock copolymers containing A as a glassy thermoplastic and B as an elastomer, will show properties of both plastics and rubbers. They can be molded, extruded and reused like plastics, but they also have typical elastic properties of rubbers like thermosetting characteristics.

Recently, block copolymers comprised of PVFc and poly(isobutylene) (PIB) segments were synthesized using ionic living polymerization (15). These polymers offer advantages of thermoplastic elastomers as well as providing availability of the electro-active ferrocene moiety. Here, we present characterization of an ABA triblock copolymer (where A = PvFc, B = PIB) in solutions and thin films. The triblock copolymer was synthesized by an efficient coupling reaction of α,ω-chlorosilyl di-functional PIB (SiCl-PIB-SiCL) with PVFcLi. This metallocene polymer shows poperties of aggregations in dilute solutions, one electron redox behavior in thin film coating, and micro-phase separation in thin films.

2. Experimental

2.1. *Materials and methods*

Toluene (99.5%) and tetrahydrofuran (THF) (99.9%) used as solvents were purchased from Alfa Aesar and Sigma Aldrich, respectively. Carbon coated copper grid

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†Dedicated to the memory of Professor Sukant K. Tripathy

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(200 mesh) was obtained from Electron Microscopy Sciences. The chemical structure of the ABA triblock copolymer poly(vinylferrocene)-*block*-poly(isobutylene)-*block*-poly(vinylferrocene) (PVFc-*b*-PIB-*b*-PVFc) used for this studying is shown in Figure 1. The molecular weight of the isolated copolymer is 50,600, and the polydispersity index is measured to be 1.09. The weight composition of PIB/PVFc is 70/30.

Dynamic Light Scattering (DLS) measurements in toluene and THF solutions were carried out to determine the aggregation concentration of the polymer. A linearly polarized He-Ne laser (632.8 nm) was utilized. The scattered light was collected at 90°, and detected by an avalanche photodiode. The solutions were first prepared at higher concentrations and then diluted until no aggregation could be detected.

Redox behavior of the polymer was investigated by cyclic voltammetry (CV) using a three-electrode cell with a platinum wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and the copolymer covered ITO coated glass as the working electrode. Cyclic voltammogram was recorded at room temperature in 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The potential scanning range was between −0.30 and +1.00 V. The scanning rate was set at 50 mV/s.

The micro-phase separation of the copolymer thin films was examined by transmission electron microscopy (TEM) at 100 keV. The triblock copolymer in toluene solution (0.01 mg/mL) was deposited on carbon coated copper grids by drop-casting. Out of three samples prepared, two samples were dried in vacuum overnight and annealed at 220°C in a vacuum oven for 1 and 12 h, respectively. It was not required to stain the sample since the iron-rich domains in the copolymer films provide sufficient contrast for TEM.

3. Results and discussion

The aggregation behavior of the triblock copolymer in toluene and THF solutions was studied by DLS. The DLS results showed that the distribution of polymer aggregates was between 10 nm and 200 nm with average size ranging from 55 to 60 nm in dilute solutions, as summarized in Table 1. This large distribution of particle size suggested the further aggregation of polymers to form larger clusters. The aggregations were observed as low as 0.014 mg/mL in toluene solution, and 0.0045 mg/mL in THF solution, respectively.

Table 1. Average aggregate diameter in toluene and THF solutions

Toluene solution		*THF solution*	
Concentration (mg/mL)	*Average aggregate diameter (nm)*	*Concentration (mg/mL)*	*Average aggregate diameter (nm)*
0.25	55	0.1	56
0.1	59	0.033	59
0.033	56	0.01	58

The ferrocene containing triblock copolymer is electrochemically active, and its redox potential was measured by CV. One electron redox activity was detected. Figure 2 shows the cyclic voltammogram of the copolymer, indicating a single, reversible, well-defined redox curve with an oxidation potential (E_{ox}) at 0.496 V and a reduction potential (E_{red}) at 0.445 V. The CV of the ferrocene monomer was also measured, as showed in Figure 2 as a control. Single electron reduction property of ferrocene was observed as reported (16,17). The shift of oxidation and reduction potentials of the ferrocene containing copolymer is due to the fact that the ferrocene units are attached to the polymer backbones, not in solution and different diffusion effects.

It was reported that the copolymer shows two glass transition temperatures at −65°C and 198°C corresponding to PIB and PVFc, respectively (15). This implies that triblock copolymer exhibits micro-phase separation (18–19). The phase separations were observed by TEM in all three samples and are shown in Figure 3. The PVFc region, which is rich in iron, is darker than the PIB region. Before annealing, the triblock copolymer was already micro-phase separated with particle size of about 20–30 nm, as shown in Figure 3(a). Figure 3(b) shows a worm-like phase with a width around 20–30 nm after annealing for 1 h. After annealing for 12 h, the copolymer thin film shows only disordered

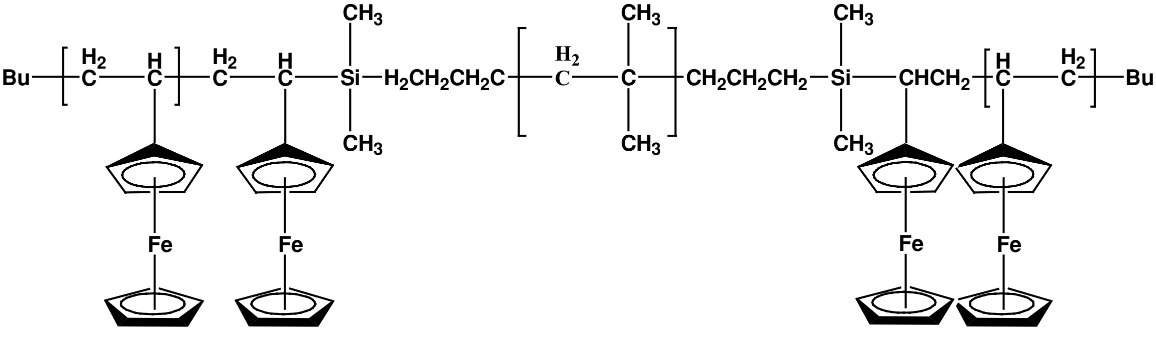


Fig. 1. Chemical structure of the triblock copolymer used in this study.

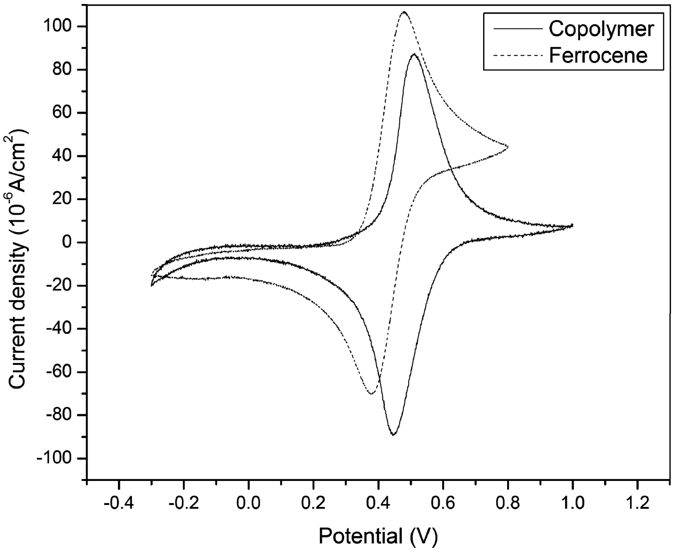
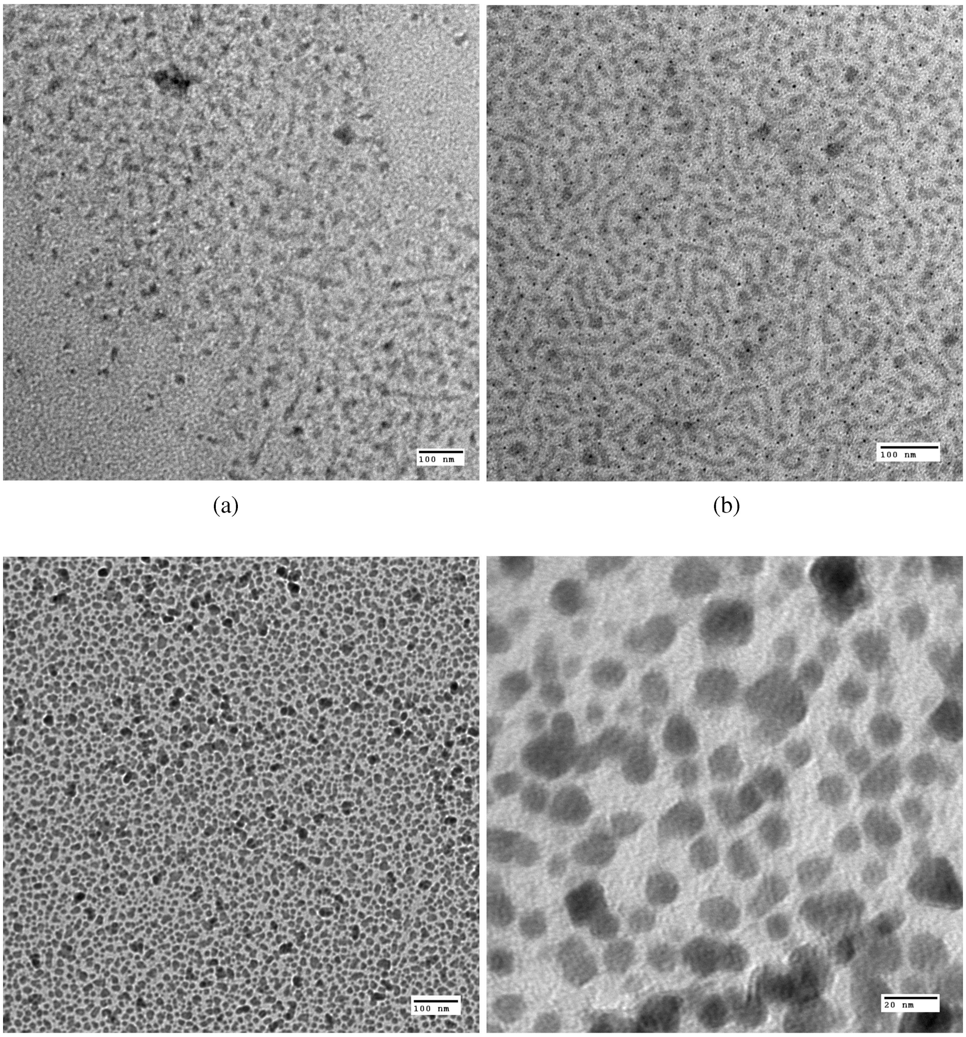


Fig. 2. Cyclic voltammograms of the ferrocene containing copolymer thin film and ferrocene monomer solution.



(a) (b)

(c) (d)

Fig. 3. TEM micrographs of the triblock copolymer thin films: (a) unannealed, (b) annealed for 1 h, (c) and (d) annealed for 12 h.

domains with feature size approximately 8 to 15 nm, as shown in Figure 3(c) and (d).

4. Conclusions

Characterization of the triblock copolymer, PVFc-*b*-PIB-*b*-PVFc was performed. DLS study revealed that this copolymer showed aggregation in common organic solvents at very low concentration. Cyclic voltammograms suggested that the ferrocene containing copolymer exhibits one electron redox behavior, similar to that of ferrocene. TEM analysis indicated that the thin films of this copolymer show interesting micro-phase separation at different temperatures.

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