9304 *Macromolecules* **2010**, *43*, 9304–9310
DOI: 10.1021/ma101935a

Macromolecules
ARTICLE

Preparation of Side-Chain 18-e Cobaltocenium-Containing Acrylate Monomers and Polymers

Lixia Ren,[†] Christopher G. Hardy,[†] Shanfeng Tang,[†] Deon B. Doxie,[†] Nasrollah Hamidi,[‡] and Chuanbing Tang*,[†]

[†]*Department of Chemistry and Biochemistry and Nanocenter, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208, United States , and* [‡]*Department of Biological and Physical Sciences, South Carolina State University, Orangeburg, South Carolina 29117, United States*

Received August 21, 2010; Revised Manuscript Received October 19, 2010

ABSTRACT: The synthesis and radical polymerization of an 18-e cobaltocenium vinyl monomer, 2-acryloyloxyethyl cobaltoceniumcarboxylate hexafluorophosphate (AECoPF$_6$), are reported. The side-chain cobaltocenium-containing polymer, poly(acryloyloxyethyl cobaltoceniumcarboxylate hexafluorophosphate) (PAECoPF$_6$), is a water-soluble hydrophilic polyelectrolyte. Through an effective ion-exchange process, this polymer was transformed into a hydrophobic poly(acryloyloxyethyl cobaltoceniumcarboxylate tetraphenylborate) (PAECoBPh$_4$) polymer, soluble in strong polar solvents such as dimethylformamide and dimethyl sulfoxide. Electrochemical studies showed that both polymers have reversible redox processes in dimethylformamide. These polymers exhibited high thermal stability.

Introduction

Metallopolymers, a class of polymers with metal atoms either in the backbone or at the side chain, hold many unprecedented properties and functions that conventional organic polymers usually lack.[1−13] Among metallopolymers, metallocene-containing polymers have attracted significant attention due to their unique electrochemical, catalytic, and optical properties.[14−22] Metallocene-containing polymers are widely used for redox active systems as recognition of ions and sugars[22−24] and modification of electrodes.[25] Recently, metallocene-containing polymers have found applications as precursors to prepare magnetic ceramics,[26−28] redox-controlled permeability of microcapsules,[29] templates for fabrication of nanotextured inorganic surfaces,[30,31] catalysts for carbon nanotube growth, and resists for block copolymer nanolithography.[32−35] Among metallocene-containing polymers, ferrocene-containing polymers are widely studied. Synthesis of main-chain and side-chain ferrocene-containing polymers has been achieved by ring-opening polymerization (ROP) and radical polymerization respectively.[13,35−39]

Cobaltocene was first synthesized during the enormous activity following the discovery of ferrocene.[40−42] Similar to ferrocene (18-e), cobaltocene (19-e) has its cobalt(II) sandwiched between two cyclopentadienyl (Cp) rings. Due to the inherent stability of 18 electron species, 19-e cobaltocene can lose one electron readily to form the much more stable 18-e cobaltocenium cation, which is isoelectronic with ferrocene. The ease oxidation of cobaltocene and the inertness of cobaltocenium salts make direct electrophilic substitution almost impossible.[43] Thus, while thousands of substituted ferrocene derivatives have been prepared, only perhaps about 100 substituted cobaltocenes and cobaltocenium salts have been prepared. Substituted derivatives are usually prepared from substituted cyclopentadienes, e.g. methylcyclopentadiene.[44] Particularly after the pioneer work by Sheats et al., methylcyclopentadiene is generally used to prepare methyl- and 1,1′-dimethylcobaltocenium salts, which can be converted to carboxylic acids, esters, amides, amines, and nitro derivatives.[44−48] A large portion of efforts have been devoted to cobaltocenium-containing dendrimer synthesis.[48−54] Among very few reported cobaltocenium polymers, synthesis of main-chain polymers via condensation is dominant,[55−57] probably because the synthesis of 1,1′-disubstituted cobaltocenium is more straightforward. Methylcyclopentadiene can be used as the only substituted cyclopentadiene starting material, circumventing possible contamination of monosubstituted or unsubstituted cobaltocenium. However, most of these polymers have poor solubility and low molecular weight,[56,57] possibly due to poor chemical tunability, inefficient condensation reactions, sensitivity to impurities, and variations in stoichiometry in step-growth polymerization. Recently, Manners' group reported the first ROP to prepare main-chain cobaltocenium polymers.[58]

Herein, we report the first radical polymerization to prepare side-chain cobaltocenium-containing polymers. We have recently prepared side-chain cobaltocenium-containing polymers through postpolymerization modification, in which a templated block copolymer bore suitable functionalities for an esterification reaction with monosubstituted cobaltocenium acyl chloride.[59,60] These block copolymers exhibited unique solubility and self-assembly behaviors. However, nonquantitative yield of postpolymerization modification resulted in a random block with partial side chains decorated with cobaltocenium. On the other hand, direct polymerization of cobaltocenium-containing monomers would allow one to prepare truly side-chain cobaltocenium-containing polymers. To the best of our knowledge, there have been no reports on the preparation and direct polymerization of cobaltocenium vinyl monomers. Specifically, in this work we report the synthesis of the first cobaltocenium acrylate monomer, 2-acryloyloxyethyl cobaltoceniumcarboxylate hexafluorophosphate (AECoPF$_6$), and its free radical polymerization. In addition, we carried out an ion-exchange process to manipulate the solubility of the cationic cobaltocenium-containing polymers and explored how the anions affected the polymer properties.

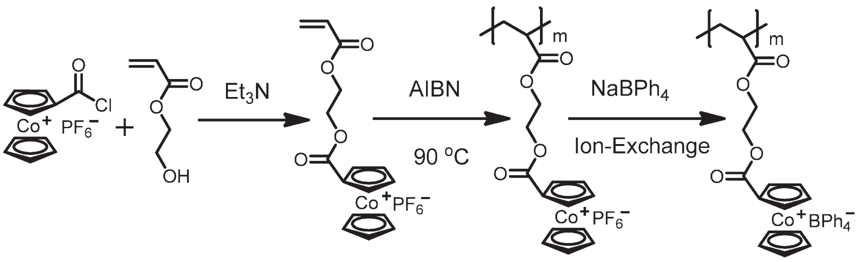
Experimental Section

Materials. 2-Hydroxyethyl acrylate (HEA, 96%, Aldrich) was distilled under vacuum. Monocarboxycobaltocenium was

---

*Corresponding author. E-mail: tang.c@chem.sc.edu.

Scheme 1. Synthesis and Radical Polymerization of $AECoPF_6$ and an Ion-Exchange Process



synthesized according to the earlier reports.[44,57,60] Triethylamine (99%, Aldrich) was dried in molecular sieves. Sodium tetraphenylborate ($NaBPh_4$, 99%, Alfa Aesar), and tetra-*n*-butylammonium hexafluorophosphate (TBAFP, 98%, Acros) were used as received. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. All other reagents were purchased from commercial sources and used as received unless otherwise noted.

Characterization. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. ^{19}F (376 MHz) NMR spectra were recorded on a Varian Mercury 400 spectrometer with CHF_3 as an internal reference. ^{31}P (162 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature. High-resolution mass spectrometry (MS) was conducted on a Waters Micromass quadropole-time of flight (Q-Tof) mass spectrometer, using electrospray ionization in a positive ion mode. The absolute number-average molecular weight (M_n) of polymers was characterized by an osmotic pressure method. The osmotic pressures of various solutions were measured using a membrane osmometer, Osmomat 090 (GONOTEC Gmbh, Berlin). The molecular weight was calculated following the well-known van't Hoff law, $\left(\frac{\pi}{c}\right)_{c \to 0} = \frac{RT}{\langle M_n \rangle}$. Ultaviolet−visible (UV−vis) spectra were recorded on a Shimadzu UV 2450 spectrophotometer. Fourier transform infrared (FT-IR) experiments were operated on a Spectrum 100 FT-IR Spectrometer (Perkin-Elmer). A differential scanning calorimetry (DSC) experiment was conducted on a DSC Q200 instrument (TA Instruments). The enthalpy calibration was based on a run in which a standard metal (indium) is heated through its melting transition. The calculated heat of fusion is compared to the theoretical value. The enthalpy constant is the ratio between these two values, and the temperature calibration was similar to the enthalpy calibration, in which the extrapolated onset of the recorded melting point of this standard is compared to the known melting point. The difference is calculated for temperature calibration. The samples were heated from 25 to 100 °C at a rate of 10 °C/min, maintained at 100 °C for 2 min and then cooled to 25 °C at a rate of 10 °C/min. The data were collected from the second heating scan. The glass transition temperature (T_g) was defined as the mean value of onset and end-point of a peak. Thermogravimetric analysis (TGA) was operated on a SDT Q600 TGA system (TA Instruments) under nitrogen gas at a flow rate of 100 mL/min, ramping from 25 to 1000 °C at a heating rate of 10 °C/min, and maintaining at 1000 °C for 5 min. Cyclic voltammetry (CV) characterization was carried on a BAS CV-50W voltametric analyzer. The samples were dissolved in 0.1 M of TBAFP solution in *N*,*N*′-dimethylformamide (DMF) at a concentration of 0.5 mM or in 0.1 M NaCl aqueous solution. The samples were then purged with nitrogen gas for 10 min before running CV. The samples were scanned at a rate of 100 mV/s at different potential ranges vs Ag/AgCl.

Synthesis of 2-Acryloyloxyethyl Cobaltoceniumcarboxylate Hexafluorophosphate ($AECoPF_6$). HEA (1.0 mL, 9.6 mmol) and triethylamine (3.4 mL, 2.4 mmol) were dissolved in anhydrous tetrahydrofuran (THF) (50 mL) at 0 °C. Monosubstituted cobaltocenium acyl chloride (0.930 g, 2.4 mmol) in THF solution was added into the above mixture slowly. The solution was stirred at room temperature overnight under the protection of nitrogen gas. The solvents were evaporated to yield a viscous liquid, which was then dissolved in 40.0 mL of dichloromethane (DCM). The solution was extracted with $NaPF_6$ aqueous solution (10.0 mL) and water (2 × 10.0 mL). The organic phase was combined and dried over anhydrous $MgSO_4$. The products, which are yellow powder, were obtained by precipitating the crude mixture from diethyl ether three times. Yield: 0.912 g (80%). ^{1}H NMR (CD_3COCD_3, δ, ppm): 6.4 (d, $CH_2{=}CH$, 1H, J = 17.31 Hz); 6.3 (t, Cp, 2H, J = 2.07 Hz); 6.2 (q, $CH_2{=}CH$, 1H, J = 10.36 Hz); 6.1 (t, Cp, 2H, J = 2.07 Hz); 6.05 (s, Cp, 5H); 5.9 (d, $CH_2{=}CH$, 1H, J = 17.30 Hz); 4.6 (m, OCH_2CH_2O, 4H). ^{13}C NMR (CD_3COCD_3, δ, ppm): 166 (CH_2CHCOO); 164 (CpCOO); 132 (CH_2CH); 129 (CH_2CH); 85−90 (Cp ring); 64 (CH_2CH_2); 61 (CH_2CH_2). FTIR (cm^{-1}): 3120, 2980 (CH stretching), 1750 (carboxyl group), 1460, 1410, 1300, 1200, 800−900 (PF_6^-). High resolution MS: calculated value 331.0381, found value 331.0375.

Synthesis of Poly(2-acryloyloxyethyl cobaltoceniumcarboxylate hexafluorophosphate) ($PAECoPF_6$) via free radical polymerization. $AECoPF_6$ (900 mg, 2.0 mmol), AIBN (9 mg, 0.05 mmol), and acetonitrile (2.0 mL) were mixed in a Schlenk flask, followed by purging with nitrogen gas for half hour. The mixture was stirred at 90 °C for 20 h and then poured into acetone. The cobaltocenium-containing polymer was purified by precipitation into acetone three times to remove any unreacted monomers. Yield: 0.300 g (33%), M_n: 6200 g/mol (osmotic pressure method). The polymer is a yellow solid. ^{1}H NMR (D_2O, δ, ppm): 6.15 (broad, Cp, 2H); 5.85 (broad, Cp, 2H); 5.7 (broad, Cp, 5H); 4.4 (d, broad, OCH_2CH_2O, 4H).

Synthesis of Poly(2-acryloyloxyethyl cobaltoceniumcarboxylate tetraphenylborate) ($PAECoBPh_4$). Synthesis of $PAECoBPh_4$ was carried out by an ion exchange with $PAECoPF_6$. $PAECoPF_6$ (M_n: 6200 g/mol, 100 mg, 0.2 mmol of $AECoPF_6$ monomer unit) aqueous solution (2.0 mL) was added into $NaBPh_4$ (342 mg, 1.0 mmol) aqueous solution (10.0 mL) slowly under vigorous stirring. The resultant $PAECoBPh_4$ was precipitated from water to give a brown solid. The product was collected by centrifuge and washed with water several times to remove excess $NaBPh_4$. Yield: 90 mg (80%). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.25 (broad, Ar, 8H); 6.9 (broad, Ar, 8H); 6.7 (broad, Ar, 4H); 6.15 (broad, Cp, 2H); 5.8 (broad, Cp, 7H); 4.4 (broad, OCH_2CH_2O, 4H).

Results and Discussion

Synthesis and Radical Polymerization of $AECoPF_6$. The synthesis of $AECoPF_6$ was carried out with the use of monosubstituted cobaltocenium acyl chloride according to our recent report.[57] Scheme 1 shows the synthetic procedure of $AECoPF_6$ and its polymer $PAECoPF_6$ prepared by free radical polymerization. $AECoPF_6$ was synthesized by adding monosubstituted cobaltocenium acyl chloride into a solution of HEA in the presence of triethylamine. The $AECoPF_6$ monomer is not soluble in water, but is soluble in organic solvents such as acetone, acetonitrile, and DCM. Figure 1 shows the ^{1}H NMR spectrum of the $AECoPF_6$

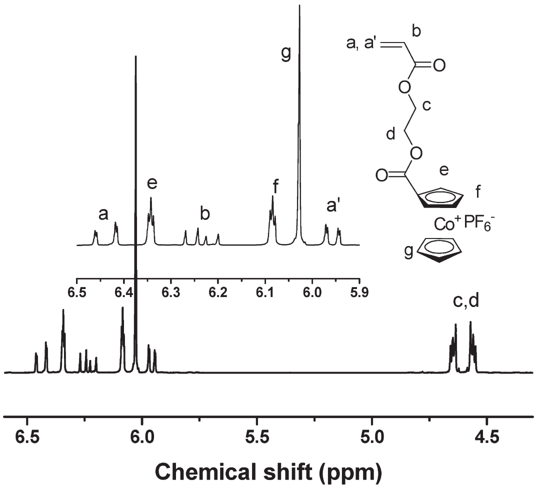


Figure 1. ^{1}H NMR spectrum of AECoPF$_6$ in acetone-d$_6$. The inset is the enlarge region of the spectrum from 5.9 to 6.5 ppm.

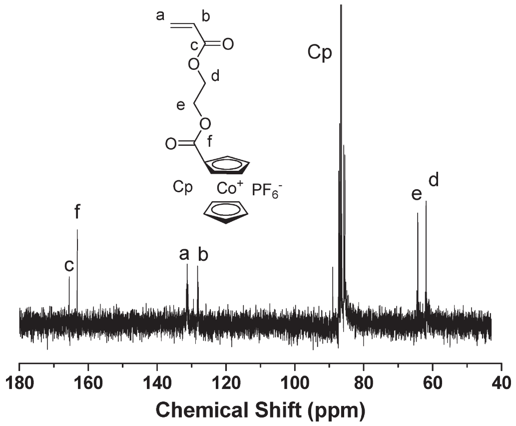


Figure 2. ^{13}C NMR spectrum of AECoPF$_6$ in acetone-d$_6$.

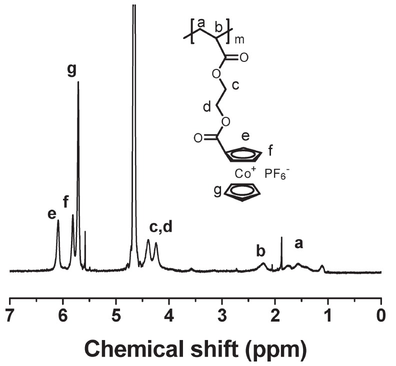


Figure 3. ^{1}H NMR spectrum of PAECoPF$_6$ in D$_2$O.

monomer in acetone-d$_6$. The signals at 5.9 ppm, 6.25 ppm and 6.45 ppm corresponded to the protons from the double bond of acrylate monomer. All vinyl protons were resolved into doublets of doublets. Chemical shifts at ~6.3 ppm, 6.1 ppm and 6.05 ppm were assigned to the protons from Cp rings of cobaltocenium. The two symmetric multipeaks at 4.4 ppm corresponded to the ethyl protons of AECoPF$_6$. The unambiguous assignment and matched integration areas of all protons indicated the successful synthesis of AECoPF$_6$ monomer. ^{13}C NMR analysis further confirmed the monomer structure. As shown in Figure 2, each carbon was clearly assigned. Additional evidence came from high-resolution MS (Figure S1, Supporting Information), which shows a single peak at 331.0375, in good agreement with theoretical mass-to-charge ratio of AECo cations (331.0381), demonstrating high purity of the AECoPF$_6$ monomer.

AECoPF$_6$ monomers were then employed for free radical polymerization to prepare PAECoPF$_6$ polymers. The polymerization was first carried out in water; however, it failed. No polymers were obtained, probably due to poor solubility of the AECoPF$_6$ monomers in water. The polymerization was then carried out in acetonitrile, a good solvent for the monomers. The homopolymers were obtained by precipitation in acetone, in which the AECoPF$_6$ monomers are soluble. Figure 3 shows the ^{1}H NMR spectrum of PAECoPF$_6$ homopolymers. Compared with the AECoPF$_6$ monomers (Figure 1), the characteristic signals of acrylate protons from the monomers disappeared, and broad peaks in the region of 1.0−2.5 ppm that arise from the protons of the polymer backbone appeared, indicating the successful polymerization of the cationic vinyl monomers.

Different from the AECoPF$_6$ monomers, the PAECoPF$_6$ polymers are not soluble in many conventional organic solvents such as DCM and acetone, but only soluble in acetonitrile, methanol, water, and strong polar solvents such as DMF and dimethyl sulfoxide (DMSO), indicating that the PAECoPF$_6$ polymers are a class of hydrophilic cationic polymers. This is in sharp contrast with conventional hydrophobic neutral ferrocene-containing polymers.

After successful synthesis of side-chain cobaltocenium-containing polymers, one of the challenges is to characterize their molecular weight due to their cationic polyelectrolyte nature. We have attempted to use gel permeation chromatography (GPC) to analyze the molecular weight of cationic PAECoPF$_6$ polymers. However, due to strong ionic interactions with the stationary phase of conventional microstyragel columns, most polymers adsorbed onto the columns and did not flow out. Even the use of LiBr-containing DMF as an eluent to minimize electrostatic adsorption also failed.[61,62] We then turned our attention to an Osmotic pressure method, one of the cognitive methods to obtain absolute number-average molecular weight. Cellulose ester (CE) molecular porous dialysis membranes (Spectra, Houston, Texas) with different molecular-weight cutoffs (MWCOs) were used. Figure 4A shows the variation of reduced osmotic pressure versus concentration of PAECoPF$_6$ in fresh deionized distilled water at 303 K using a dialysis membrane with MWCO of 1000 g/mol. At a lower concentration region, the reduced osmotic pressures increased with the increase of concentration, a characteristic nature of polyelectrolytes in diluted aqueous solutions.[63] Additionally, at a higher concentration region, the reduced osmotic pressures decreased as the concentration increased. Figure 4B shows the variation of the inverse of reduced osmotic pressures versus concentration. A straight line fitted the experimental data. From the intercept of the inverse of reduce osmotic pressure at null concentration, the number-average molecular weight was calculated to be $M_n = 6200$ g/mol, according to van't Hoff's law, $\left(\frac{\pi}{c}\right)_{c \to 0} = \frac{RT}{\langle M_n \rangle}$, where π is the osmotic pressure and c is the polymer concentration. When a two-layer membrane with MWCO of 5000 g/mol (Gonote, Germany) was employed, a much higher molecular weight, $M_n = 26\,400$ g/mol, was obtained, perhaps due to the broad molecular weight distribution of PAECoPF$_6$ polymers and the nature of the membrane, which allows the polymers with molar mass under 5000 g/mol to penetrate. Also, the broader molecular weight distribution with the lower molecular weight below the MWCO of the membranes during measurements was

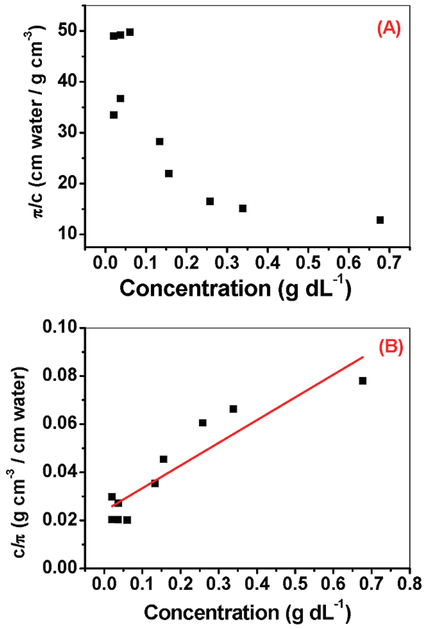


Figure 4. (A) Osmotic reduced pressure versus PAECoPF$_6$ concentration and (B) inverse osmotic reduced pressure versus PAECoPF$_6$ concentration, using a dialysis membrane with MWCO of 1000 g/mol.

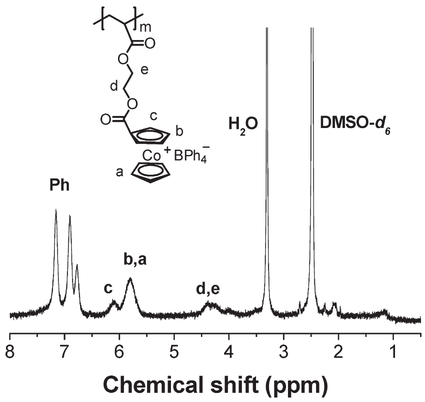


Figure 5. ^{1}H NMR spectrum of PAECoBPh$_4$ in DMSO-d$_6$.

confirmed by setting the baseline at a negative value in both cases. Since the polymers with molecular weight below the MWCO permeating into the lower half of the cell produced osmotic effects, they quickly permeated back after several rinses with water. Such back-and-forth permeation likely produced the above baseline.

Preparation of PAECoBPh$_4$ via Ion-Exchange. Since PAECoPF$_6$ polymers are a class of polyelectrolytes with positive charges at the side chain, change of counterions or anions could tune the physiochemical properties of side-chain cobaltocenium-containing polymers. As the first step, tetraphenylborate was chosen as the counterions to replace hexafluorophosphate ions, expecting to change the hydrophobicity of cobaltocenium polymers. The ion-exchange process was carried out by slowly adding PAECoPF$_6$ polymers to an aqueous solution of NaBPh$_4$. Precipitation of a brown solid was immediately observed, indicating the change of the solubility of the polymers via ion exchange. The obtained PAECoBPh$_4$ polymers were only soluble in strong polar solvents such as DMF and DMSO, but were not soluble in water, THF, DCM, and so forth. Figure 5 shows the ^{1}H NMR spectrum of resulting PAECoBPh$_4$ polymers. Compared with those of PAECoPF$_6$ polymers, new peaks at 6.5−7.2 ppm were assigned to the aromatic protons from the tetraphenylborate group. Integration of all peaks was consistent with the theoretical value of PAECoBPh$_4$ polymers, indicating that PF$_6^-$ ions were quantitatively exchanged to tetraphenylborate ions. In order to further verify the complete ion-exchange, ^{19}F NMR was used to track the amount of fluoride in the polymers. As shown in Figure 6A, before ion-exchange, there was one doublet peak at around −73 ppm, corresponding to the ^{31}P−^{19}F coupling of PF$_6^-$ groups in the PAECoPF$_6$ polymers. After ion-exchange, the peaks at −73 ppm completely disappeared from the ^{19}F NMR spectrum of PAECoBPh$_4$ polymers (Figure 6B), demonstrating the complete removal of PF$_6^-$ ions. ^{31}P NMR spectra also show that the characteristic septuplet peak (due to the ^{19}F−^{31}P coupling in PF$_6^-$) disappeared completely after ion-exchange (Figure 6C,D).

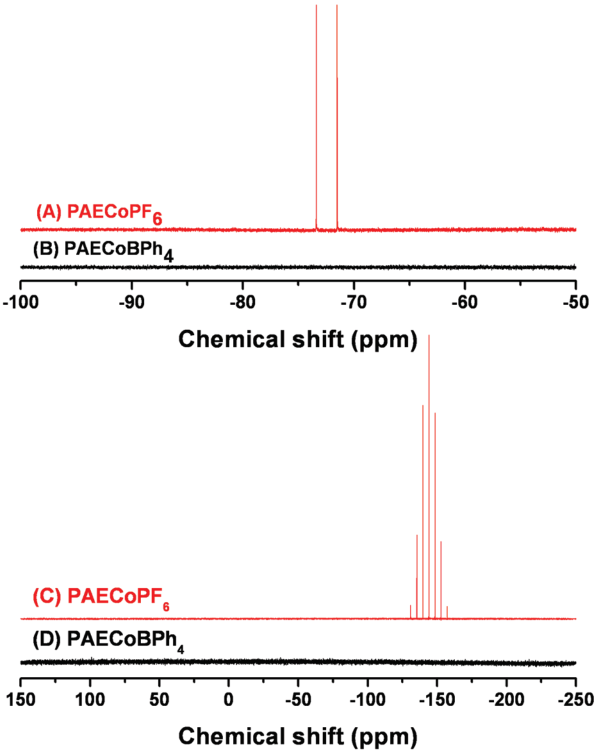


Figure 6. ^{19}F NMR spectra of (A) PAECoPF$_6$ and (B) PAECoBPh$_4$, and ^{31}P NMR spectra of (C) PAECoPF$_6$ and (D) PAECoBPh$_4$ in DMSO-d$_6$.

The cobaltocenium polymers were also characterized with the aid of FT-IR and UV−vis. As shown in Figure S2, the absorption at 860 cm^{-1} originated from the PF$_6^-$ anions. After ion-exchange, a few new sharp peaks at the region of ~700 cm^{-1} appeared, corresponding to the absorption from phenyl groups of tetraphenylborate anions, while the peaks at 860 cm^{-1} disappeared. Figure S3 shows the UV−vis spectra of cobaltocenium polymers before and after ion exchange. The UV−vis absorbance of both polymers in DMF solution was similar: a strong absorbance at 275 nm and a weak broad shoulder at 420 nm. The broad peaks at λ_{max} = ~420 nm for PAECoPF$_6$ and PAECoBPh$_4$ polymers are due to the characteristic forbidden *d*−*d** transition of cobaltocenium.

Electrochemical Properties of Side-Chain Cobaltocenium-Containing Polymers. The electrochemical properties of cobaltocenium vinyl monomers and polymers were studied in different solutions in the presence of electrolytes. As shown in Figure 7A, the CV of AECoPF$_6$ monomers in DMF shows two similar peaks in one cycle: the peak to peak splittings

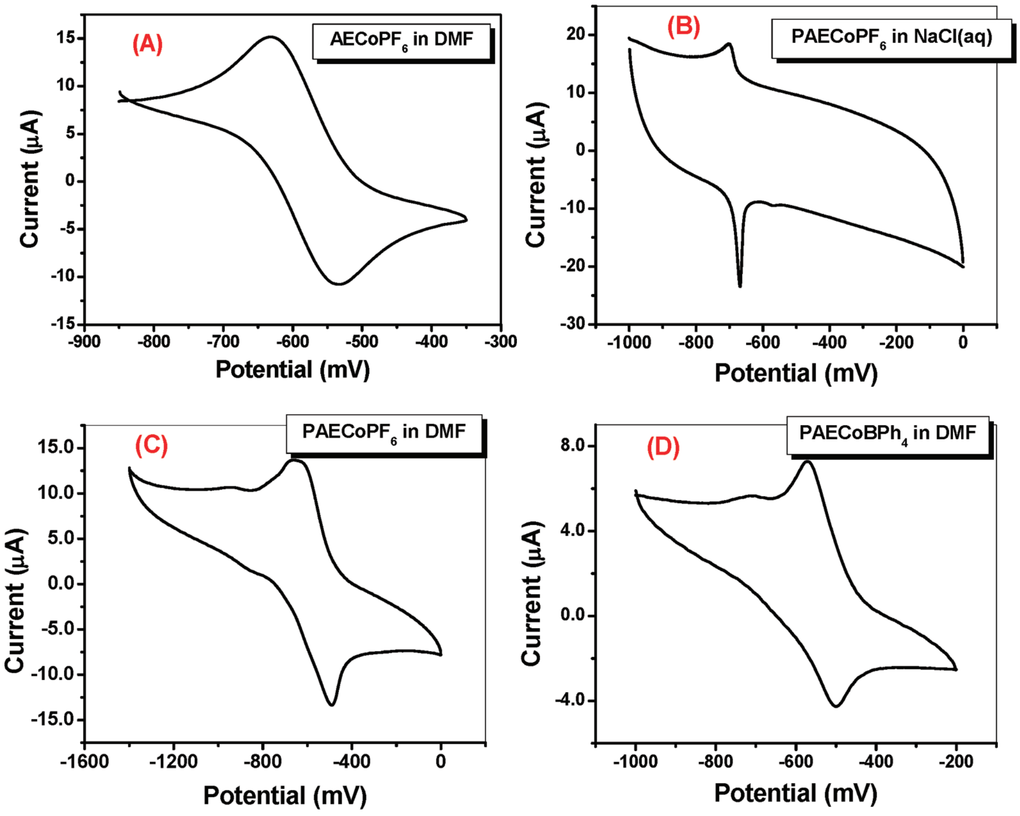


Figure 7. CV curves of (a) $AECoPF_6$ in 0.1 M TBAFP DMF solution, (b) $PAECoPF_6$ in NaCl aqueous solution, and (c) $PAECoPF_6$ and (d) $PAECoBPh_4$ in 0.1 M TBAF DMF solution.

(ΔE_p) of the cathodic and anodic peaks were about 60−70 mV, and the peak currents of the redox process were equal, indicating a reversible one-electron transfer process of $AECoPF_6$ monomers. The CV of $PAECoPF_6$ was first studied in aqueous solution. However, the redox process was not reversible. As shown in Figure 7B, the oxidation peak current was much higher than the reduction peak current. The irreversibility was likely due to the solubility change of $PAECoPF_6$ polymers under redox process. Although $PAECoPF_6$ polymers are soluble in water, the reduced cobaltocenium polymers (cobaltocene-containing polymers) are not soluble in water. This was verified from the observation of some polymers deposited onto the electrode surface after CV experiments. With the change of the solvent to DMF, in which both cobaltocenium and cobaltocene polymers are soluble, the CV shows a reversible redox process as confirmed by equal peak currents (Figure 7C). As shown in Figure 7D, after ion-exchange, $PAECoBPh_4$ polymers show a similar reversible one-electron transfer process in DMF. The redox potential ($E_{1/2}$) vs silver chloride electrode for both polymers were close to each other, about −0.56 V. The CV experiments indicated that the redox process of both cobaltocenium monomers and polymers was reversible in a good solvent. It appeared that change of the counterions had minimal effect on the electrochemical properties. This can be considered an advantage since the solubility of the polymers can be tuned through the ion-exchange process while the characteristic electrochemical and optical properties remained almost unchanged.

Thermal Properties of 2-Acryloyloxyethyl Cobaltoceniumcarboxylate Polymers. The thermal properties of these cobaltocenium polymers were studied by DSC. Figure 8 shows the DSC curves of $PAECoPF_6$ and $PAECoBPh_4$ polymers. The glass transition temperature (T_g) of $PAECoPF_6$ was ca. 52 °C, while the T_g of $PAECoBPh_4$ polymers increased slightly to 55 °C, due to the presence of the more bulky tetraphenylborate group. Compared to the low T_g (~5 °C) of poly(2-hydroxyethyl acrylate), the much higher T_g of $PAECoPF_6$ and $PAECoBPh_4$ polymers indicated that the bulky cobaltocenium group significantly increases the rotation barriers of acrylate polymers.

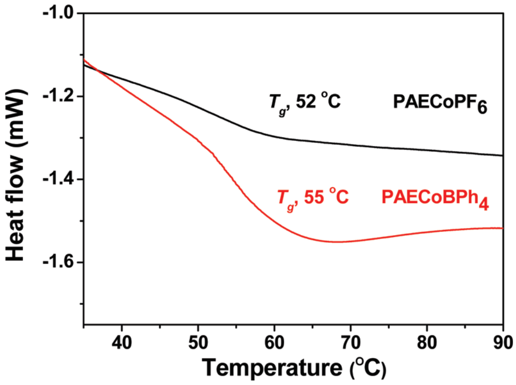


Figure 8. DSC curves of $PAECoPF_6$ and $PAECoBPh_4$.

The thermal stability of both cobaltocenium polymers was studied by TGA. As shown in Figure 9, $PAECoPF_6$ polymers exhibited three stages of weight loss at 210−280 °C (~20%), 300−420 °C (~30%), and 850 °C and above, corresponding to decomposition of PF_6^- ions, complete degradation of the polymer skeleton, and degradation of Cp rings, respectively. Different from conventional organic polymers, the $PAECoPF_6$ polymers still maintained ~50% of total weight at 800 °C, indicating the high thermal stability of the cobaltocenium moiety. Even at 1000 °C there was ~20% materials left. Compared with $PAECoPF_6$ polymers,

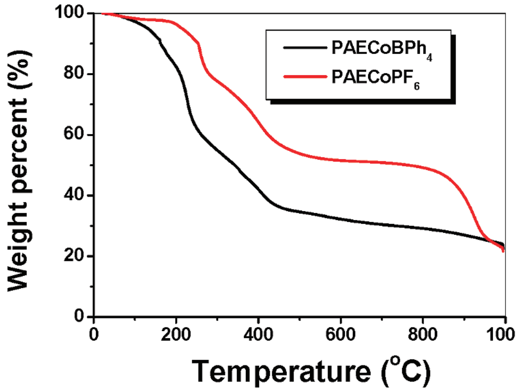


Figure 9. TGA curves of PAECoPF$_6$ and PAECoBPh$_4$.

PAECoBPh$_4$ polymers had ~70% weight loss at temperatures higher than 500 °C (Figure 9) as a result of the decomposition of higher weight fraction of the tetraphenylborate group. After pyrolysis at 1000 °C, both polymers produced a 20% yield of pyrolyzed materials. Although the pyrolyzed materials seemed to be attracted by an axial magnetized disk magnet, detailed analysis and characterization of pyrolyzed materials (e.g., magnetic properties) are currently in progress.

Conclusions

In conclusion, we synthesized the first cobaltocenium acrylate monomer through simple esterification reaction of an organic acrylate with monocarboxycobaltocenium. A free radical polymerization was employed to convert the monomers into side-chain cobaltocenium-containing polymers. These polymers showed tunable solubility through ion-exchange. Polymers with hexafluorophosphate ions are hydrophilic, while polymers with tetraphenylborate ions are hydrophobic. The redox properties depended on the use of solvents. The polymers exhibited reversible redox properties in DMF solution, while exhibiting irreversible properties in aqueous solution. These cobaltocenium polymers showed excellent thermal stability. The successful synthesis of cobaltocenium acrylate polymers has the promise to be extended to other types of polymers such as methacrylic, styrenic, and acrylamide polymers, and potentially block copolymers, which are currently under investigation.

Acknowledgment. We would like to acknowledge the University of South Carolina for providing start-up funds. N.H. acknowledges USDA 1890 Research, and the Minority Leadership Program for financial support.

Supporting Information Available: Mass spectrum of AECoPF$_6$, FT-IR spectra of PAECoPF$_6$ and PAECoBPh$_4$, and UV−vis spectra of PAECoPF$_6$ and PAECoBPh$_4$ in DMF solution. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746.
(2) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892–2926.
(3) Calvert, J. M.; Caspar, J. V.; Binstead, R. A.; Westmoreland, T. D.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6620–6627.
(4) Pickup, P. G. *J. Mater. Chem.* **1999**, *9*, 1641–1653.
(5) Holliday, B. J.; Swager, T. M. *Chem. Commun.* **2005**, *1*, 23–36.
(6) Shunmugam, R.; Gabriel, G. J.; Aamer, K. A.; Tew, G. N. *Macromol. Rapid Commun.* **2010**, *31*, 784–793.
(7) Grubbs, R. B. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4323–4336.
(8) Miinea, L. A.; Sessions, L. B.; Ericson, K. D.; Glueck, D. S.; Grubbs, R. B. *Macromolecules* **2004**, *37*, 8967–8972.
(9) Beck, J. B.; Ineman, J. M.; Rowan, S. J. *Macromolecules* **2005**, *38*, 5060–5068.
(10) Calzia, K. J.; Tew, G. N. *Macromolecules* **2002**, *35*, 6090–6093.
(11) Rawashdeh-Omary, M. A.; Lopez-de-Luzuriaga, J. M.; Rashdan, M. D.; Elbjeirami, O.; Monge, M.; Rodriguez-Castillo, M.; Laguna, A. *J. Am. Chem. Soc.* **2009**, *131*, 3824–3825.
(12) Schubert, U. S.; Newkome, G. R.; Manners, I. *Metal-Containing and Metallosupramolecular Polymers and Materials*; American Chemical Society: Washington, DC, 2006; Vol. *928*.
(13) Manners, I. *Synthetic Metal-Containing Polymers*; Wiley-VCH: Weinheim, Germany, 2004.
(14) Whittell, G. R.; Manners, I. *Adv. Mater.* **2007**, *19*, 3439–3468.
(15) Bellas, V.; Rehahn, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 5082–5104.
(16) Nguyen, P.; Gomez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515–1548.
(17) Abd-El-Aziz, A. S. *Macromol. Rapid Commun.* **2002**, *23*, 995–1031.
(18) Hudson, R. D. *J. Organomet. Chem.* **2001**, *637−639*, 47–69.
(19) Togni, A.; Halterman, R. *Metallocenes: Synthesis - Reactivity - Applications*; Wiley-VCH: Weinheim, Germany, 1998.
(20) Togni, A.; Hayashi, T. *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; VCH Publishers: New York, 1995.
(21) Stepnicka, P. *Ferrocenes: Ligands, Materials and Biomolecules*; John Wiley & Sons: West Sussex, U.K., 2008.
(22) Aranzaes, J. R.; Belin, C.; Astruc, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 132–136.
(23) Ruiz, J.; Medel, M. J. R.; Daniel, M. C.; Blais, J. C.; Astruc, D. *Chem. Commun.* **2003**, 464–465.
(24) Castro, R.; Cuadrado, I.; Alonso, B.; Casado, C. M.; Morn, M.; Kaifer, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5760–5761.
(25) Valerio, C.; Fillaut, J. L.; Ruiz, J.; Guittard, J.; Blais, J. C.; Astruc, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 2588–2589.
(26) MacLachlan, M. J.; Ginzburg, M.; Coombs, N.; Coyle, T. W.; Raju, N. P.; Greedan, J. E.; Ozin, G. A.; Manners, I. *Science* **2000**, *287*, 1460–1463.
(27) Kulbaba, K.; Manners, I. *Macromol. Rapid Commun.* **2001**, *22*, 711–724.
(28) Eloi, J.-C.; Chabanne, L.; Whittell, G. R.; Manners, I. *Mater. Today* **2008**, *11*, 28–36.
(29) Ma, Y. J.; Dong, W. F.; Hempenius, M. A.; Möhwald, H.; Vancso, G. J. *Nat. Mater.* **2006**, *5*, 724–729.
(30) Péter, M.; Lammertink, R. G. H.; Hempenius, M. A.; Vancso, G. J. *Langmuir* **2005**, *21*, 5115–5123.
(31) Lu, J.; Chamberlin, D.; Rider, D. A.; Liu, M. Z.; Manners, I.; Russell, T. P. *Nanotechnology* **2006**, *17*, 5792–5797.
(32) Lastella, S.; Jung, Y. J.; Yang, H. C.; Vajtai, R.; Ajayan, P. M.; Ryu, C. Y.; Rider, D. A.; Manners, I. *J. Mater. Chem.* **2004**, *14*, 1791–1794.
(33) Hinderling, C.; Keles, Y.; Stockli, T.; Knapp, H. E.; de los Arcos, T.; Heinzelmann, H. *Adv. Mater.* **2004**, *16*, 876–879.
(34) Massey, J. A.; Winnik, M. A.; Manners, I.; Chan, V. Z. H.; Ostermann, J. M.; Enchelmainer, R.; Spatz, J. P.; Muller, M. *J. Am. Chem. Soc.* **2001**, *123*, 3147–3148.
(35) Galloway, C. P.; Rauchfuss, T. B. *Angew. Chem., Int. Ed.* **1993**, *32*, 1319–1321.
(36) Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246–6248.
(37) Deschenaux, R.; Turpin, F.; Guillon, D. *Macromolecules* **1997**, *30*, 3759–3765.
(38) Arimoto, F. S.; Haven, A. C. *J. Am. Chem. Soc.* **1955**, *77*, 6295–6297.
(39) Kim, B. Y.; Ratcliff, E. L.; Armstrong, N. R.; Kowalewski, T.; Pyun, J. *Langmuir* **2010**, *26*, 2083–2092.
(40) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6148–6149.
(41) Fischer, E. O.; Jira, R. *Z. Naturforsch.* **1953**, *8b*, 327–328.
(42) Fischer, E. O.; Jira, R. *Z. Naturforsch.* **1953**, *8b*, 1–2.
(43) Laus, G.; Strasser, C. E.; Holzer, M; Wurst, K.; Purstinger, G.; Ongania, K.-H.; Rauch, M.; Bonn, G.; Schottenberger, H. *Organometallics* **2005**, *24*, 6085–6093.
(44) Sheats, J. E.; Rausch, M. D. *J. Org. Chem.* **1970**, *35*, 3245–3249.
(45) Sakai, S; Takayanagi, H.; Sumimoto, N.; Fukuzawa, S.; Fujinami, T.; Saeki, H. *Appl. Organomet. Chem.* **1990**, *4*, 35–42.
(46) Sheats, J. E.; Hlatky, G. *J. Chem. Educ.* **1983**, *60*, 1015–1016.
(47) Simon, R. A.; Mallouk, T. E.; Daube, K. A.; Wrighton, M. S. *Inorg. Chem.* **1985**, *24*, 3119–3126.

(48) Takada, K.; Díaz, D. J.; AbrunÄ, H. D.; Cuadrado, I.; GonzaÂlez, B; Casado, C. M.; Alonso, B.; MoraÂn, M.; Losada, J. *Chem. Eur. J.* **2001**, *7*, 1109–1117.

(49) Astruc, D.; Ornelas, C.; Ruiz, J. *Acc. Chem. Res.* **2008**, *41*, 841–856.

(50) Ornelas, C.; Ruiz, J.; Astruc, D. *Organometallics* **2009**, *28*, 2716–2723.

(51) Casado, C. M.; Gonzalez, B.; Cuadrado, I.; Alonso, B.; Moran, M.; Losada, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2135–2138.

(52) Gonzalez, B.; Casado, C. M.; Alonso, B.; Cuadrado, I.; Moran, M.; Wang, Y.; Kaifer, A. E. *Chem. Commun.* **1998**, 2569–2570.

(53) Sobransingh, D.; Kaifer, A. E. *Langmuir* **2006**, *22*, 10540–10544.

(54) Simon, R. A.; Mallouk, T. E.; Daube, K. A.; Wrighton, M. S. *Inorg. Chem.* **1985**, *24*, 3119–3126.

(55) Kondo, M.; Hayakawa, Y.; Miyazawa, M.; Oyama, A.; Unoura, K.; Kawaguchi, H.; Naito, T.; Maeda, K.; Uchida, F. *Inorg. Chem.* **2004**, *43*, 5801–5803.

(56) Sheats, J. E. *Organomet. Polym.* **1978**, 87–94.

(57) Pittman, C. U., Jr.; Ayers, O. E.; Suryanarayanan, B.; McManus, S. P.; Sheats, J. E. *Macromol. Chem.* **1974**, *175*, 1427–1437.

(58) Mayer, U. F. J.; Gilroy, J. B.; O'Hare, D.; Manners, I. *J. Am. Chem. Soc.* **2009**, *131*, 10382–10383.

(59) Cuadrado, I.; Casado, C. M.; Lobete, F.; Alonso, B.; Gonzalez, B.; Losada, J.; Amador, U. *Organometallics* **1999**, *18*, 4960–4969.

(60) Ren, L.; Hardy, C. G.; Tang, C. *J. Am. Chem. Soc.* **2010**, *132*, 8874–8875.

(61) Domard, A.; Rinaudo, M.; Rochas, C. *J. Polym. Sci., Part B: Polym. Phys.* **1979**, *17*, 673–681.

(62) Rochas, C.; Domard, A.; Rinaudo, M. *Eur. Polym. J.* **1980**, *16*, 135–140.

(63) Cowie, J. M. G. *Polymers: Chemistry & Physics of Modern Materials*, 2nd ed.; Chapman & Hall: London, 1991.