

## Novel Synthesis and Characterization of Side-Chain Ferrocene-Containing Polymers

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**ABSTRACT:** A convenient and economic one-step synthesis of 2-ferrocenylethyl alcohol was developed, which led to the high yield monomer synthesis of 2-ferrocenylethyl acrylate, 2-ferrocenylethyl methacrylate, 2-ferrocenylethylacrylamide, and 2-ferrocenylethylmethacrylamide. Using AIBN as initiator, the homopolymerization or copolymerization of these monomers with *N*-isopropylacrylamide in toluene or THF under various conditions resulted in high molar mass homopolymers or thermally sensitive copolymers. They were characterized by <sup>1</sup>H NMR and IR spectroscopies as well as by a combination of static and dynamic laser light scattering. Our results showed that for poly(2-ferrocenylethyl acrylate) and poly(2-ferrocenylethyl methacrylate) homopolymers the *z*-average translational diffusion coefficient (*D*) can be scaled to the weight-average molar mass (*M<sub>w</sub>*) as  $\langle D \rangle = 1.3 \times 10^5 M_w^{-0.57}$  and  $\langle D \rangle = 1.9 \times 10^5 M_w^{-0.52}$ , respectively, indicating that these polymer chains are flexible and have a coil conformation in toluene. The collapse and swelling of poly[(*N*-2-ferrocenylethylacrylamide)-*co*-(*N*-isopropylacrylamide)] copolymers in water led to a convenient way to alternate the average interdistance between ferrocene groups.

### Introduction

Ferrocene-based polymers have been continually developed for a few decades.<sup>1</sup> The incorporation of transition metals into polymeric structures has resulted in materials with some unusual and attractive characteristics including electrical, magnetic, preceramic, catalytic, and nonlinear optical properties.<sup>2,3</sup> A number of ferrocene derivatives with various functional groups have been prepared. The metallocene unit can be incorporated into polymers either as a side group or as a chain backbone unit.<sup>1–3</sup> It is a challenge to synthesize polymeric systems which include organometallic moiety as a main-chain element using traditional synthetic methods such as addition polymerization because the preparation of metal compounds with suitably reactive multiple bonds is difficult.<sup>3</sup> In the 1960s and 1970s, much attention was directed to polycondensation of bifunctional monomers.<sup>4</sup> Since the purification of these monomers is difficult, the reaction stoichiometry could not be precisely maintained, and often only low molar mass oligomers were produced.<sup>5</sup>

Recently, some novel ring-opening approaches have basically solved this problem. For example, Rauchfuss synthesized ferrocene-based polymers via atom-abstraction-induced ring-opening polymerization.<sup>6</sup> Later, Manners prepared poly(ferrocenylsilanes) with a molar mass as high as  $\sim 10^6$  g/mol by thermal ring-opening polymerization.<sup>7,8</sup> On the other hand, it is relatively easy to introduce metal moieties as side groups as long as they are stable under polymerization conditions.<sup>9</sup> Poly(vinylferrocene) as a typical example has been prepared by both cationic and free-radical polymerization.<sup>10–15</sup> The modification of side groups could also introduce transition metals into polymer chains such as the derivation of poly(*p*-bromostyrene) followed by complexation. The

potential applications of such modified polymers in product separation and catalyst recovery have been addressed.<sup>9</sup>

Poly(2-ferrocenylethyl acrylate) can be converted to its electron-transfer polymer salt upon treatment with dichlorodicyanoquinone.<sup>16</sup> In the preparation of poly(2-ferrocenylethyl acrylate), Pittman et al. showed a multistep and low yield tedious process of synthesizing 2-ferrocenylethyl acrylate monomers.<sup>16,17</sup> Recently, we have developed a convenient and economic one-step synthesis of 2-ferrocenylethyl alcohol and 2-ferrocenylethylamine as well as a subsequent polymerization or copolymerization of their (meth)acrylates and amides. This paper reports the synthesis and characterization of these homo- and copolymers.

### Experimental Section

**General Procedures.** All experiments were performed under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques. All chemicals, except otherwise mentioned, were purchased from Aldrich Chemical Co. HPLC grade hexane, pentane, ether, and THF and toluene (99%) were refluxed several hours and freshly distilled from sodium benzophenone ketyl immediately prior to use. HPLC grade CH<sub>2</sub>Cl<sub>2</sub> was freshly distilled from CaH<sub>2</sub> prior to use. HPLC grade DMF was first stirred over CaH<sub>2</sub> for 2 h and then distilled twice under reduced pressure into a flask containing MgSO<sub>4</sub>. AIBN (97%) was recrystallized three times from MeOH. *N*-Isopropylacrylamide (97%) was recrystallized twice from a solution of hexane/toluene (1:1). Ethylene oxide (99.5%) was distilled over NaOH and stored at  $-15$  °C. Acryloyl chloride (96%) was freshly distilled before use. Methacryloyl chloride and *t*-BuLi were prepared according to literature methods.<sup>18,19</sup> Sodium azide (99%), LiAlH<sub>4</sub> (powder, 95%), silica gel (200–400 mesh), and *p*-toluenesulfonyl chloride (99%) were used as received. Infrared spectra were obtained from KBr pellets on a BIO-RAD FTS-185 Fourier transform spectrometer. Mass spectra were recorded on a HP5989A spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AM-300 spectrometer. All chemical shifts are reported in  $\delta$  units with reference to internal or external TMS (0.00 ppm) or with respect to the residual

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protons of the deuterated solvent for proton chemical shifts. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry. Low critical solution temperature (LCST) was measured from the temperature dependence of the relative scattering ( $I_s/I_0$ ) of the polymer aqueous solution.

**2-Ferrocenylethyl Alcohol.** *t*-BuLi (42.0 mL of 1.00 M in pentane, 42.0 mmol) was slowly added to a THF solution (42 mL) of ferrocene (8.40 g, 45.1 mmol) at 0 °C, and the reaction mixture was stirred for ca. 15 min. Ethylene oxide (1.50 mL, 33.1 mmol) was then added dropwise at 0 °C. The mixture was stirred for 1.5 h at room temperature. The resulting solution was hydrolyzed with a 5% hydrochloric acid (20 mL) and then extracted with ether (3 × 50 mL). The ether portions were combined, washed with water, and dried over MgSO<sub>4</sub>. The solvent was removed to give the crude product that was purified by fast column chromatography (SiO<sub>2</sub>) using a mixture of hexane/ether (7:3) as an eluent, affording 2-ferrocenylethyl alcohol as an orange solid (5.10 g, 73%); mp 39–40 °C (lit.<sup>20</sup> 41–42 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.18 (br s, 9H, Cp), 3.72 (m, 2H, OCH<sub>2</sub>), 2.59 (t, *J* = 6.5 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): ν 3310 (br), 2933 (s), 2850 (s), 1410 (m), 1105 (m), 1039 (m), 1025 (m), 1001 (s), 819 (m). MS (EI), *m/z* (relative abundance): 230 (M<sup>+</sup>, 100%).

**2-Ferrocenylethyl Acrylate (FEA).** *n*-BuLi (5.00 mL of 2.16 M in cyclohexane, 10.8 mmol) was slowly added to a THF solution (20.0 mL) of 2-ferrocenylethyl alcohol (2.27 g, 9.90 mmol), and the mixture was stirred at 0 °C for 30 min. A THF solution (10.0 mL) of acryloyl chloride (2.00 mL, 24.6 mmol) was then added dropwise. The reaction mixture was refluxed for 1 h. The resulting solution was cooled to 0 °C by an ice bath, hydrolyzed with water (20 mL), and extracted with ether (3 × 30 mL). The ether portions were combined and dried over MgSO<sub>4</sub>. The solvent was removed to give the crude product that was purified by fast column chromatography (SiO<sub>2</sub>) using a hexane/ether (20:1) mixture as an eluent, giving FEA as an orange solid (2.36 g, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.42 (dd, *J* = 1.5 and 17.3 Hz, 1H, vinyl *H*), 6.13 (dd, *J* = 10.4 and 17.3 Hz, 1H, vinyl *H*), 5.83 (dd, *J* = 1.5 and 10.4 Hz, 1H, vinyl *H*), 4.29 (t, *J* = 6.7 Hz, 2H, OCH<sub>2</sub>), 4.16 (m, 9H, Cp), 2.67 (t, *J* = 6.7 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): ν 3110 (w), 2980 (m), 2860 (m), 1715 (s), 1639 (s), 1625 (m), 1411 (m), 1292 (m), 1104 (s), 1045 (m), 995 (m), 976 (m). MS (EI), *m/z* (relative abundance): 284 (M<sup>+</sup>, 85%). Anal. Calcd for C<sub>15</sub>H<sub>16</sub>FeO<sub>2</sub>: C, 63.41; H, 5.68. Found: C, 63.69; H, 5.78.

**2-Ferrocenylethyl Methacrylate (FEMA).** This compound was prepared as an orange solid from 2-ferrocenylethyl alcohol (2.28 g, 9.91 mmol), *n*-BuLi (5.00 mL of 2.16 M in cyclohexane, 10.8 mmol), and methacryloyl chloride (2.15 g, 20.6 mmol) in THF using the procedures used above for FEA. Yield: 2.76 g (93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.12 (s, 1H, vinyl *H*), 5.57 (s, 1H, vinyl *H*), 4.25 (t, *J* = 6.7 Hz, 2H, OCH<sub>2</sub>), 4.19 (m, 9H, Cp), 2.64 (t, *J* = 6.7 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.95 (s, 3H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): ν 3094 (w), 2998 (s), 2875 (s), 1730 (s), 1637 (s), 1473 (m), 1453 (m), 1167 (m), 1102 (s), 1040 (m), 1017 (m), 997 (m), 810 (m). MS (EI), *m/z* (relative abundance): 298 (M<sup>+</sup>, 78%). Anal. Calcd for C<sub>16</sub>H<sub>18</sub>FeO<sub>2</sub>: C, 64.45; H, 6.08. Found: C, 64.31; H, 5.82.

**Poly(2-ferrocenylethyl acrylate) (PFEA).** A mixture of *N*-(2-ferrocenylethyl) acrylate (FEA) (450 mg, 1.58 mmol) and AIBN (22.5 mg, 0.137 mmol) in toluene (2.25 g, 2.60 mL) was heated at 60 °C for 48 h. The flask was then cooled with an ice bath, and the polymerization was terminated by methanol addition (~1 mL). The polymer was isolated by precipitation in hexane (~10 mL), purified by three times precipitation from toluene (~5 mL) into hexane (~15 mL), and dried overnight in vacuo (1 mmHg) at approximately 50 °C to give PFEA-1 as an orange-red powder (0.41 g, 90%). LLS:  $M_w = 0.29 \times 10^5$  ( $M_w/M_n = 2.48$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.15 (m, 11H, Cp and -OCH<sub>2</sub>), 2.65 (br, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.64–1.27 (br, 3H, CH<sub>2</sub>CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): ν 3092 (w), 2953 (m), 2860 (m), 1732 (vs), 1447 (m), 1410 (m), 1160 (s), 1105 (s), 817 (m).

**Poly(2-ferrocenylethyl methacrylate) (PFEMA).** Poly-mer (PFEMA-1) was prepared as an orange-red powder from

*N*-(2-ferrocenylethyl) methacrylate (FEMA) (450 mg, 1.51 mmol) and AIBN (22.5 mg, 0.137 mmol) in toluene (2.60 mL) using procedures similar to those used in the synthesis of PFEA-1: yield 0.43 g (93%). LLS:  $M_w = 0.68 \times 10^5$  ( $M_w/M_n = 1.64$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.24 (m, 11H, Cp and OCH<sub>2</sub>), 2.63 (br, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.94–1.26 (br, 6H, CH<sub>2</sub>CHCH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): ν 3092 (w), 2970 (m), 2860 (m), 1727 (vs), 1474 (m), 1388 (m), 1150 (s), 1106 (s), 819 (s).

**2-Ferrocenylethyl Tosylate.** A CH<sub>2</sub>Cl<sub>2</sub> solution (15 mL) of *p*-toluenesulfonyl chloride (6.94 g, 36.4 mmol) was slowly added to an ice-cooled CH<sub>2</sub>Cl<sub>2</sub> solution (20.0 mL) of 2-ferrocenylethyl alcohol (4.19 g, 18.2 mmol) and triethylamine (10.0 mL), and the reaction mixture was stirred at room temperature overnight. The resulting solution was quenched by water (10 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The CH<sub>2</sub>Cl<sub>2</sub> portions were combined and dried over MgSO<sub>4</sub>. The solvent was removed to give the crude product that was purified by fast column chromatography (SiO<sub>2</sub>) using a hexane/ethyl acetate (5:1) mixture as an eluent, producing 2-ferrocenylethyl tosylate as a redish solid (6.17 g, 88%); mp 75–76 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.76 (dd, *J* = 8.2 and 2.2 Hz, 2H, aromatic *H*), 7.34 (dd, *J* = 8.2 and 2.2 Hz, 2H, aromatic *H*), 4.11 (m, 11H, Cp and OCH<sub>2</sub>), 2.66 (t, *J* = 6.7 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 2.44 (s, 3H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): ν 3082 (s), 2965 (s), 2900 (s), 1596 (s), 1342 (m), 1173 (m), 1096 (m), 1042 (s), 1001 (s), 828 (m), 812 (m), 774 (m). MS (EI), *m/z* (relative abundance): 384 (M<sup>+</sup>, 100%).

**2-Ferrocenylethylamine.** A DMF solution (20 mL) of 2-ferrocenylethyl tosylate (2.40 g, 6.30 mmol) and sodium azide (810 mg, 12.5 mmol) was heated at 80 °C for 6 h and then cooled with an ice bath. Ether (150 mL) was added to the reaction mixture. The organic layer was separated and washed with water (5 × 50 mL) and a saturated aqueous solution of NaCl (5 × 50 mL), respectively, and then dried over MgSO<sub>4</sub>. Removal of the solvents gave 2-ferrocenylethyl azide as a yellow solid (1.57 g). A THF solution (10 mL) of LiAlH<sub>4</sub> (0.80 g, 21.1 mmol) was refluxed for several minutes before adding a THF solution (20 mL) of 2-ferrocenylethyl azide (1.57 g, 6.15 mmol) dropwise. The reaction mixture was then refluxed for 1 h. The resulting solution was cooled with an ice bath before slowly adding water (1 mL), ether (200 mL), anhydrous Na<sub>2</sub>SO<sub>4</sub> (3.50 g), and NaOH (2.50 g). The mixture was stirred for another 1 h. The precipitates were filtered off and washed with ether (3 × 100 mL). The ether portions were combined, washed with water, and dried over MgSO<sub>4</sub>. The solvent was removed to give a crude product that was purified by fast column chromatography (SiO<sub>2</sub>) using a CH<sub>2</sub>Cl<sub>2</sub>/methanol (8:1) mixture as an eluent, affording 2-ferrocenylethylamine as an orange solid (1.34 g, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.10 (m, 9H, Cp), 2.79 (t, *J* = 7.9 Hz, 2H, CH<sub>2</sub> NH<sub>2</sub>), 2.55 (t, *J* = 7.9 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 1.13 (br s, 2H, NH<sub>2</sub>) (this peak disappeared after adding D<sub>2</sub>O). IR (KBr, cm<sup>-1</sup>): ν 3363 (m), 3295 (m), 3092 (s), 2931 (s), 1581 (s), 1472 (s), 1323 (s), 1105 (vs), 1039 (s), 1001 (s), 819 (vs). MS (EI), *m/z* (relative abundance): 229 (M<sup>+</sup>, 100%).

***N*-(2-Ferrocenylethyl) Acrylamide (FEAA).** A THF solution (10.0 mL) of acryloyl chloride (1.70 mL, 17.6 mmol) was added to a THF solution (20.0 mL) of 2-ferrocenylethylamine (2.12 g, 9.25 mmol) and triethylamine (6.00 mL, 43.0 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 5 h before quenching with water (20 mL). The resulting solution was extracted with ether (5 × 20 mL). The ether portions were combined and dried over MgSO<sub>4</sub>. The solvent was removed to give a crude product that was purified by fast column chromatography (SiO<sub>2</sub>) using a hexane/ethyl acetate (4:1) mixture as an eluent, affording FEAA as an orange solid (1.87 g, 71%); mp 133–134 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.28 (dd, *J* = 1.5 and 16.9 Hz, 1H, vinyl *H*), 6.06 (dd, *J* = 10.3 and 16.9 Hz, 1H, vinyl *H*), 5.75 (s, 1H, NH), 5.64 (dd, *J* = 1.5 and 10.3 Hz, 1H, vinyl *H*), 4.18 (m, 9H, Cp), 3.45 (t, *J* = 6.5 Hz, 2H, NHCH<sub>2</sub>CH<sub>2</sub>), 2.57 (t, *J* = 6.5 Hz, 2H, NHCH<sub>2</sub>CH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): ν 3023 (s), 3080 (w), 2967 (w), 2862 (w), 1675 (m), 1652 (s), 1622 (m), 1563 (s), 1407 (m), 1306 (m), 1253 (m), 1104 (m), 1038 (m), 1001 (w), 986 (w), 948 (m), 825 (m), 808 (m). MS (EI), *m/z* (relative abundance): 283 (M<sup>+</sup>, 100%). Anal.



Calcd for  $C_{15}H_{17}FeNO$ : C, 63.63; H, 6.05; N, 4.95. Found: C, 63.90; H, 6.12; N, 4.98.

***N*-(2-Ferrocenylethyl) Methacrylamide (FEMAA).** This compound was prepared as an orange solid from 2-ferrocenylethylamine (880 mg, 3.84 mmol), triethylamine (2.20 mL, 15.8 mmol), and methacryloyl chloride (700  $\mu$ L, 7.24 mmol) in THF using procedures used for FEAA. Yield: 0.85 g (75%); mp 77–78 °C.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.88 (s, 1H, *NH*), 5.65 (s, 1H, vinyl *H*), 5.30 (s, 1H, vinyl *H*), 4.12 (m, 9H, Cp), 3.43 (t, *J* = 6.9 Hz, 2H,  $NHCH_2CH_2$ ), 2.59 (t, *J* = 6.9 Hz, 2H,  $NHCH_2CH_2$ ), 1.94 (s, 3H,  $CH_3$ ). IR (KBr,  $cm^{-1}$ ):  $\nu$  3360 (s), 3105 (w), 2978 (w), 2873 (w), 1653 (m), 1610 (s), 1538 (m), 1448 (w), 1434 (m), 1410 (w), 1301 (w), 1265 (w), 1104 (m), 1043 (w), 1000 (w), 968 (w), 935 (m), 822 (m), 810 (m). MS (EI), *m/z* (relative abundance): 297 ( $M^+$ , 100%). Anal. Calcd for  $C_{16}H_{19}FeNO$ : C, 64.67; H, 6.44; N, 4.71. Found: C, 64.64; H, 6.47; N, 4.69.

**Poly(*N*-2-ferrocenylethylacrylamide) (PFEEA).** A mixture of *N*-(2-ferrocenylethyl) acrylamide (FEAA) (300 mg, 1.06 mmol) and AIBN (0.60 mL of 5.00 mg/mL in THF, 0.02 mmol) in THF (2.46 g, 2.77 mL) was heated at 60 °C for 24 h. The flask was then cooled with an ice bath, and the polymerization was terminated by methanol addition (~1 mL). The polymer was isolated by precipitation in hexane (~18 mL), purified by three times precipitation from THF (~4 mL) into hexane (~15 mL), and dried overnight in vacuo (1 mmHg) at approximately 50 °C to give PFEEA-1 as an orange-red powder (0.186 g, 62%). LLS:  $M_w = 6.5 \times 10^3$  g/mol.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.36 (br, 1H, *NH*), 4.13 (m, 9H, Cp), 3.33 (br s, 2H,  $NHCH_2$ ), 2.52 (br s, 2H,  $NHCH_2CH_2$ ), 2.13–1.35 (br, 3H,  $CH_2CH$ ). IR (KBr,  $cm^{-1}$ ):  $\nu$  3399 (m), 3313 (w), 3088 (w), 2928 (w), 1654 (vs), 1527 (s), 1436 (w), 1411 (w), 1237 (w), 1105 (m), 819 (m).

**Poly(*N*-2-ferrocenylethyl methacrylamide) (PFEMAA).** Polymer (PFEMAA-2) was prepared as an orange-red powder from *N*-(2-ferrocenylethyl) methacrylamide (FEMAA) (300 mg, 1.00 mmol) and AIBN (0.60 mL of 5.00 mg/mL in THF, 0.02 mmol) in THF (970 mg, 1.09 mL) using procedures similar to those used in the synthesis of PFEEA-1: yield 0.291 g (97%). LLS:  $M_w = 9.62 \times 10^4$  g/mol.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  5.79 (br, 1H, *NH*), 4.13 (m, 9H, Cp), 3.25 (br s, 2H,  $NHCH_2$ ), 2.50 (br s, 2H,  $NHCH_2CH_2$ ), 1.94–0.88 (br, 6H,  $CH_2CHCH_3$ ). IR (KBr,  $cm^{-1}$ ):  $\nu$  3442 (m), 3370 (w), 3090 (w), 2928 (m), 1659 (vs), 1515 (s), 1436 (m), 1411 (w), 1264 (w), 1105 (m), 819 (m).

**Poly[*N*-(2-ferrocenylethylacrylamide)-*co*-(*N*-isopropylacrylamide)] (Poly(FEAA-*co*-NIPAM)).** A THF solution (10.6 mL) of *N*-(2-ferrocenylethyl) acrylamide (FEAA) (10.1 mg, 0.036 mmol), *N*-isopropylacrylamide (NIPAM) (814 mg, 7.20 mmol), and AIBN (8 mg, 0.06 mmol) was heated at 60 °C for 24 h. The flask was then cooled with an ice bath, and the polymerization was terminated by methanol addition (~1 mL). The polymer was isolated by precipitation in hexane (~30 mL), purified by three times precipitation from THF (~8 mL) into hexane (~30 mL), and dried overnight in vacuo (1 mmHg) at approximately 50 °C to give copolymer-1 as pale yellow powder (0.820 g, 99%). LLS:  $M_w = 8.4 \times 10^4$ . IR (KBr,  $cm^{-1}$ ):  $\nu$  3499 (m), 3312 (m), 3077 (w), 2975 (m), 1653 (vs), 1545 (s), 1459 (m), 1388 (m), 1368 (m), 1269 (w), 1173 (m), 1131 (m), 1106 (w).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.08–6.56 (br, *NH*), 4.12 (s, Cp), 4.03 (br,  $CHMe_2$ ), 3.34 (s,  $NHCH_2$ ), 2.61–1.63 (br m,  $CH_2CH$ ), 1.14 (s,  $^iPr$ ). Atomic absorption spectrometer: Fe%, 0.23. For copolymer-2:  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.88–6.64 (br, *NH*), 4.12 (s, Cp), 3.99 (br,  $CHMe_2$ ), 3.26 (s,  $NHCH_2$ ), 3.01–1.63 (br m,  $CH_2CH$ ), 1.13 (s,  $^iPr$ ). Atomic absorption spectrometer: Fe%, 0.48. For copolymer-3:  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.88–6.51 (br, *NH*), 4.12 (s, Cp), 4.03 (br,  $CHMe_2$ ), 3.34 (s,  $NHCH_2$ ), 2.55–1.63 (br m,  $CH_2CH$ ), 1.14 (s,  $^iPr$ ). Atomic absorption spectrometer: Fe%, 0.97.

**Laser Light Scattering.** A commercial LLS spectrometer (ALV/SP-150 equipped with an ALV-5000 multi- $\tau$  digital time correlator) and a solid-state laser (ADLAS DPY 425 II, output power is 400 MW at  $\lambda = 532$  nm) as the light source was used. The primary beam is vertically polarized with respect to the scattering plane. The details of the LLS instrumentation and theory can be found elsewhere.<sup>21–23</sup> All solutions for LLS were clarified by 0.5  $\mu$ m filter and carried out at  $25 \pm 0.1$  °C. At 25 °C and  $\lambda = 532$  nm, the specific refractive index increments

( $dn/dc$ ) of PFEA and PFEMA in toluene are 0.051 and 0.055 mL/g, respectively, and for PFEMAA in THF,  $dn/dc = 0.153$  mL/g, determined by a precise and novel differential refractometer which was incorporated as part of the LLS spectrometer. The refractometer and LLS spectrometer shared the same laser so that the wavelength correction was not necessary. The position of the refracted laser beam was recorded using a position sensitive detector with a precision of 0.3  $\mu$ m. The detail of the refractometer can be found elsewhere.<sup>24</sup>

In static LLS,<sup>21</sup> the angular dependence of the absolute time-average scattered intensity, known as the excess Rayleigh ratio,  $R_v(q)$ , of a dilute polymer solution at concentration  $C$  (g/mL) and scattering angle  $q$  was measured.  $R_v(q)$  is related to the weight-averaged molar mass  $M_w$ , the scattering vector  $q$ , and  $C$  as

$$\frac{KC}{R_v(q)} \approx \frac{1}{M_w} \left( 1 + \frac{1}{3} \langle R_g^2 \rangle q^2 \right) + 2A_2C \quad (1)$$

where  $K = 4\pi(dn/dc)^2 r^2 / (N_A \lambda_0^4)$  and  $q = (4\pi n / \lambda_0) \sin(\theta/2)$  with  $N_A$ ,  $n$ , and  $\lambda_0$  being Avogadro's number, the solvent refractive index, and the wavelength of light in vacuo, respectively.  $A_2$  is the second virial coefficient, and  $\langle R_g^2 \rangle^{1/2}$  (or written as  $\langle R_g \rangle$ ) is the root-mean square  $z$ -average radius of gyration of the polymer. By measuring  $R_v(q)$  at different  $C$  and  $q$ , we are able to determine  $M_w$ ,  $R_g$ , and  $A_2$  from a Zimm plot which incorporates both the  $q$  and  $C$  extrapolation on a single grid.

In dynamic LLS,<sup>22</sup> the intensity–intensity time correlation function  $G^{(2)}(t)$  in the self-beating mode was measured, and  $G^{(2)}(t)$  is related to the normalized first-order electric field–electric field time correlation function  $g^{(1)}(t)$  as  $G^{(2)}(t) = A[1 + \beta |g^{(1)}(t)|^2]$

$$G^{(2)}(t) = A[1 + \beta |g^{(1)}(t)|^2] \quad (2)$$

where  $A$  is a measured baseline,  $\beta$  is a parameter depending on the detection coherence, and  $t$  is the delay time. For a polydisperse sample,  $g^{(1)}(t)$  is related to the line width distribution  $G(\Gamma)$  by eq 3.

$$|g^{(1)}(t)| = \int G(\Gamma) e^{-\Gamma t} d\Gamma \quad (3)$$

The Laplace inversion of  $|g^{(1)}(t)|$  can result in  $G(\Gamma)$ . For a pure diffusive relaxation,  $\Gamma$  is further related to the translational diffusion coefficient  $D$  by  $\Gamma = Dq^2$  or the hydrodynamic radius  $R_h$  by the Stokes–Einstein equation  $D = k_B T / (6\pi\eta R_h)$ , where  $k_B$ ,  $T$ , and  $\eta$  are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

## Results and Discussion

**Poly(2-ferrocenylethyl acrylate) and Poly(2-ferrocenylethyl methacrylate).** A novel synthetic route for 2-ferrocenylethyl alcohol is shown in Scheme 1. To the best of our knowledge, this is the most convenient and economic way to synthesize 2-ferrocenylethyl alcohol and its related monomers.<sup>16</sup> The results of the syntheses of poly(2-ferrocenylethyl acrylate) (PFEA) and poly(2-ferrocenylethyl methacrylate) (PFEMA) with different initiator/monomer ratios are summarized in Table 1. Unlike those prepared in benzene solution,<sup>16b</sup> the resulting polymers were completely soluble in toluene. As expected, the conversion rate is directly proportional to the AIBN/monomer ratio. The IR spectra of PFEA and PFEMA exhibit no C=C double-bond stretching absorption at about 1638  $cm^{-1}$  in comparison with the corresponding monomers. No vinyl proton resonances were observed in the  $^1H$  NMR spectra of the polymers. It is difficult to measure the ratio of syndiotactic, isotactic, and atactic isomers presumably due to the effects of the ferrocene units.<sup>14</sup>

**Table 1.** Light Scattering Characterization of Poly(2-ferrocenylethyl acrylate) (PFEA) and Poly(2-ferrocenylethyl methacrylate) (PFEMA) Prepared by Solution Polymerization in Toluene at 60 °C

sample	monomer/ solvent (wt %)	initiator/ monomer (wt %)	yield (%)	$M_w$ /(g/mol)	$\langle D \rangle$ /(cm <sup>2</sup> /s)	$\langle R_h \rangle$ /nm	$M_w/M_n$
PFEA-1	20	5	90	$2.9 \times 10^4$	$9.3 \times 10^{-7}$	5.1	2.48
PFEA-2	20	2	93	$3.5 \times 10^4$	$8.4 \times 10^{-7}$	5.7	2.08
PFEA-3	20	0.5	85	$5.3 \times 10^4$	$8.1 \times 10^{-7}$	5.9	2.12
PFEA-4	20	0.2	30	$2.0 \times 10^5$	$5.9 \times 10^{-7}$	7.8	1.88
PFEA-5	20	0.1	27	$3.9 \times 10^5$	$4.7 \times 10^{-7}$	10	2.28
PFEA-6	20	0	trace				
PFEMA-1	20	5	93	$6.8 \times 10^4$	$8.3 \times 10^{-7}$	5.7	1.64
PFEMA-2	20	2	95	$2.1 \times 10^5$	$6.6 \times 10^{-7}$	7.2	1.76
PFEMA-3	20	0.5	96	$3.6 \times 10^5$	$5.4 \times 10^{-7}$	8.9	1.68
PFEMA-4	20	0.2	54	$5.3 \times 10^5$	$5.1 \times 10^{-7}$	9.3	1.40
PFEMA-5	20	0.05	47	$8.7 \times 10^5$	$4.0 \times 10^{-7}$	129	1.56
PFEMA-6	20	0	trace				

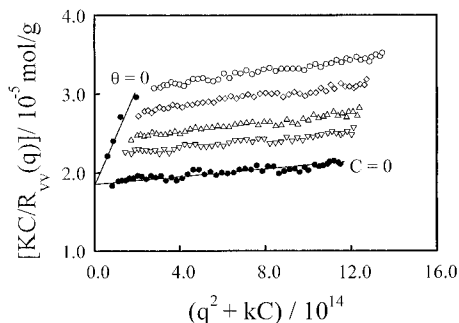
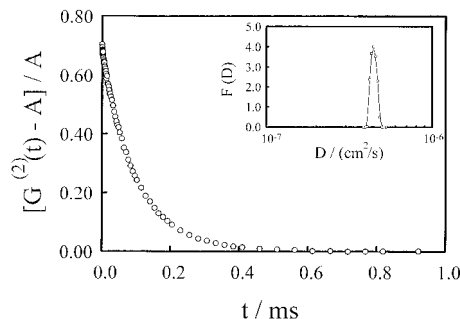
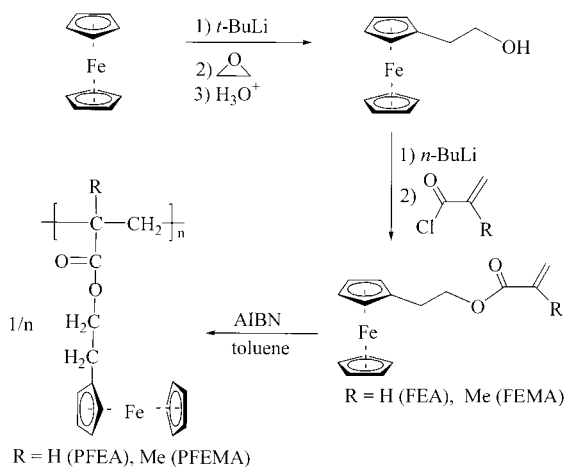
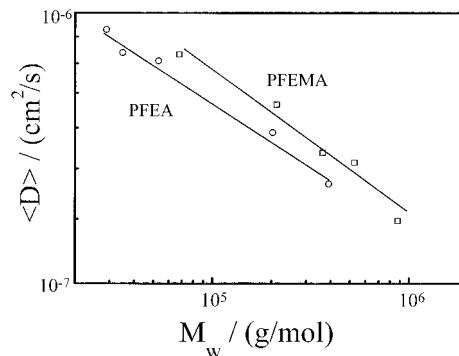
**Figure 1.** Typical Zimm plot of PFEMA-3 in toluene at 25 °C, where the concentrations are  $3.92 \times 10^{-3}$  (hollow circles),  $2.45 \times 10^{-3}$  (diamonds),  $1.76 \times 10^{-3}$  (triangles), and  $1.22 \times 10^{-3}$  g/mL (inverted triangles) and  $k = 5 \times 10^{16}$  mL/g.**Figure 2.** Typical mean time correlation fraction  $[G^{(2)}(t) - A]/A$  of PFEMA-3 fractions in toluene at 25 °C and  $\theta = 15^\circ$ . The inset shows a corresponding translational diffusion coefficient distributions  $G(D)$ .**Scheme 1. Synthesis of FEA, FEMA, and Their Homopolymers**

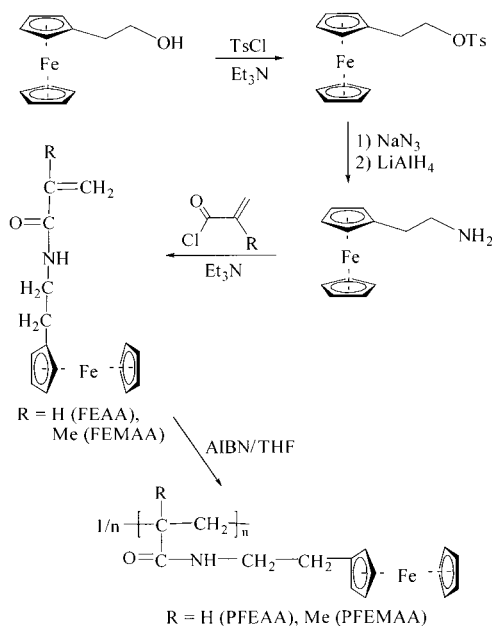
Figure 1 shows a typical Zimm plot of PFEMA in toluene at 25 °C. The values of  $M_w$ ,  $\langle R_g \rangle$ , and  $A_2$  were calculated from the extrapolation of  $[KC/R_v(q)]_{q \rightarrow 0, C \rightarrow 0}$ , the slopes of  $KC/R_v(q)_{C \rightarrow 0}$  vs  $q^2$  and  $C$ , respectively, on the basis of eq 1. Table 1 summarizes the static LLS results for different PFEA and PFEMA samples. The slightly positive values of  $A_2$  indicate that toluene is a marginal solvent for PFEA and PFEMA at 25 °C.  $\langle R_g \rangle$  is too small to be accurately determined for most of them.

Figure 2 shows a typical measured time correlation fraction of PFEMA at  $q = 15^\circ$  and 25 °C in toluene. The inset shows a corresponding translational diffusion coefficient distribution  $G(D)$ . The monomodal distribution is expected for free radical homopolymerization.<sup>25</sup> The relative distribution width of  $\mu_2/\langle D \rangle^2 \sim 0.3$ , where  $\mu_2$  and  $\langle D \rangle$  are respectively defined as  $\int_0^\infty G(D)(D - \langle D \rangle)^2$

**Figure 3.** Double-logarithmic plots of  $\langle D \rangle$  vs  $M_w$  for PFEA and PFEMA in toluene at 25 °C, where the lines respond the least-squares fitting of  $\langle D \rangle = k_D M_w^{-\alpha_D}$ .

$dD$  and  $\int_0^\infty G(D)D dD$ . The distribution is not too broad for a free-radical polymerization. The polydispersity index ( $M_w/M_n$ ) estimated from  $M_w/M_n \sim 1 + \mu_2/\langle D \rangle^2$  is  $\sim 2.2$ , where  $M_n$  is the number-average molar mass.<sup>26</sup>  $\langle R_h \rangle$  calculated from  $\langle D \rangle$  by using the Stokes–Einstein equation is 9.3 nm. The dynamic LLS results of  $\langle D \rangle$  and  $\langle R_h \rangle$  as well as the estimates of  $M_w/M_n$  of different PFEA and PFEMA samples are also listed in Table 1.

Figure 3 shows double-logarithmic plots of the average translational diffusion coefficient ( $\langle D \rangle$ ) vs the weight-average molar mass ( $M_w$ ), where each line represents a least-squares fitting of  $D$  (cm<sup>2</sup>/s) =  $k_D M_w^{-\alpha_D}$ , where  $k_D = (1.9 \pm 0.2) \times 10^{-5}$  and  $\alpha_D = 0.52 \pm 0.03$  for PFEMA and  $k_D = (1.3 \pm 0.1) \times 10^{-5}$  and  $\alpha_D = 0.57 \pm 0.02$  for PFEA. For linear chains, at the Flory  $\Theta$ -condition,  $\alpha_D \sim 0.5$ ,<sup>25</sup> while in the range  $0.5 < \alpha_D < 0.6$ , the solvent is good.<sup>25</sup> Therefore, toluene at 25 °C is a  $\Theta$ -solvent for PFEMA but a fairly good solvent for PFEA. Figure 3 also shows that for a given molar mass  $M_w$  PFEA chains have a small  $\langle D \rangle$ , i.e., a larger  $\langle R_h \rangle$ , indicating that PFEA

**Scheme 2. Synthesis of FEAA, FEMAA, and Their Homopolymers**

**Table 2. Poly(*N*-2-ferrocenylethylacrylamide) (PFEAA) and Poly(*N*-2-ferrocenylethylmethacrylamide) (PFEMAA) Prepared in THF at 60 °C**

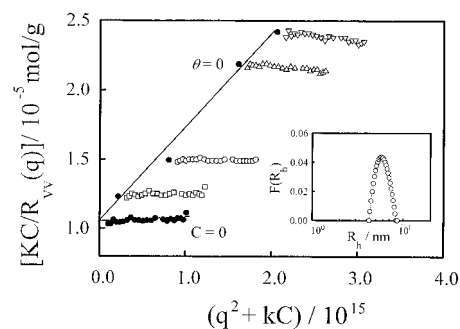
sample	monomer/ solvent (wt %)	initiator/ monomer (wt %)	yield (%)	$M_w$ (g/mol) <sup>a</sup>	$M_w/M_n$
PFEAA	10	1.0	62	$6.5 \times 10^3$	2.3
PFEMAA-1	10	1.0	46	$4.3 \times 10^4$	1.8
PFEMAA-2	20	1.0	97	$9.6 \times 10^4$	2.0

<sup>a</sup> By LLS.

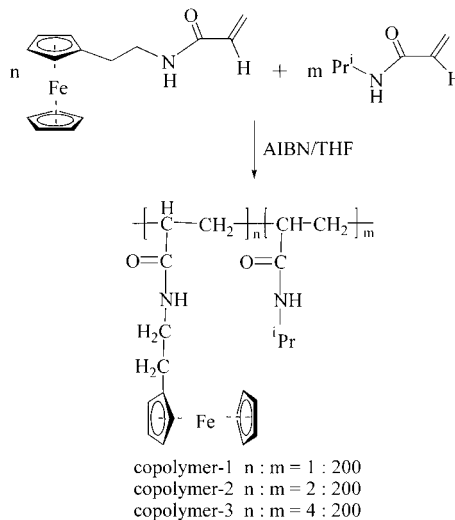
chains in toluene at 25 °C are more swollen than the PFEMA chains even though only one proton is replaced by one methyl group. This further indicates that toluene at 25 °C is a better solvent for PFEA.

**Poly(*N*-2-ferrocenylethylacrylamide) and Poly(*N*-2-ferrocenylethylmethacrylamide).** The synthetic routes for the preparation of new monomers, poly(*N*-2-ferrocenylethylacrylamide) and poly(*N*-2-ferrocenylethylmethacrylamide), are shown in Scheme 2. Table 2 summarizes the polymerization results. The two new monomers can be readily polymerized in dry THF solution using AIBN as initiator, resulting in poly(*N*-2-ferrocenylethylacrylate) and poly(*N*-2-ferrocenylethyl methacrylate), respectively. No vinyl proton resonances were observed in the <sup>1</sup>H NMR spectra of the polymers. The IR spectra of the homopolymers exhibited no C=C double-bond stretching absorption at about 1622 or 1610 cm<sup>-1</sup> in comparison with those of monomers. The carbonyl stretch frequency at about 1659 cm<sup>-1</sup> was very strong. The IR spectra also showed the presence of the N-H bonds in the polymers.

Figure 4 shows a typical Zimm plot of poly(*N*-2-ferrocenylethyl methacrylamide) (PFEMAA) in THF at 25 °C, where the concentration ranges from  $0.42 \times 10^{-3}$  to  $4.12 \times 10^{-3}$  g/mL. The values of  $M_w$  and  $A_2$  calculated on the basis of Figure 4 are  $9.62 \times 10^4$  g/mol and  $1.7 \times 10^{-3}$  mol mL/g, respectively. The positive  $A_2$  reveals that THF is a good solvent for PFEMAA at 25 °C. The inset in Figure 4 shows a corresponding hydrodynamic radius distribution  $F(R_h)$ , which indicates that PFEMAA chains were narrowly distributed.



**Figure 4.** Typical Zimm plot of poly(*N*-2-ferrocenylethyl methacrylamide) in THF at 25 °C, where the concentrations are  $4.30 \times 10^{-4}$  (squares),  $1.61 \times 10^{-3}$  (hollow circles),  $3.23 \times 10^{-3}$  (triangles), and  $4.12 \times 10^{-3}$  g/mL (inverted triangles) and  $k = 5 \times 10^{17}$  mL/g. The inset shows a corresponding hydrodynamic radius distribution  $F(R_h)$ .

**Scheme 3. Synthesis of Poly(FEAA-*co*-NIPAM)**


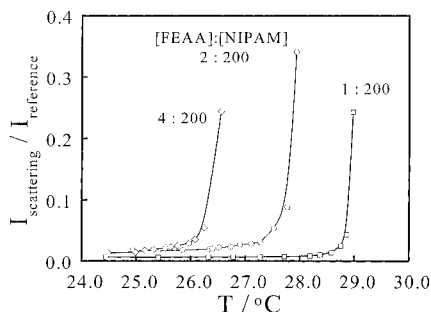
**Poly[(*N*-2-ferrocenylethylacrylamide)-*co*-(*N*-isopropylacrylamide)].** The copolymers were prepared by free-radical random copolymerization in THF using AIBN as initiator, as shown in Scheme 3. Table 3 summarizes the characteristics of poly[(*N*-2-ferrocenylethylacrylamide)-*co*-(*N*-isopropylacrylamide)] copolymers with different *N*-2-ferrocenylethylacrylamide contents. The weight-average molar masses were characterized using LLS. The final chemical composition was determined from the IR, <sup>1</sup>H NMR spectroscopy, and iron analyses. The <sup>1</sup>H NMR spectra of the polymers showed a broad peak at ~7.0–6.5 ppm (protons of the NHR groups), a singlet at ~4.1 ppm (protons of the Cp ring), a broad peak at ~4.0 ppm (CH proton of the isopropyl group), a singlet at ~3.3 ppm (α-protons of NHCH<sub>2</sub>CH<sub>2</sub> unit), several broad peaks at ~2.6–1.6 ppm (protons of backbone chain CH<sub>2</sub>CH + β-protons of NHCH<sub>2</sub>CH<sub>2</sub>), and a singlet at ~1.1 ppm (CH<sub>3</sub> protons of the isopropyl group). The FEAA-to-NIPAM ratio in the copolymers was calculated from the peak areas of two singlets at ~3.3 and ~1.1 ppm. This ratio was confirmed by the iron content measured by atomic absorption spectroscopy. The IR spectra showed the disappearance of the C=C double-bond stretching absorption at ~1622 cm<sup>-1</sup> in comparison with those of the monomers. The carbonyl stretching frequency at about 1653 cm<sup>-1</sup> was strong. The copolymers also exhibited a characteristic N-H stretching band at ~3499 cm<sup>-1</sup>.



**Table 3.** Characterization of Poly[(*N*-2-ferrocenylethylacrylamide)-*co*-(*N*-isopropylacrylamide)] Copolymers Prepared by Solution Polymerization in THF at 60 °C

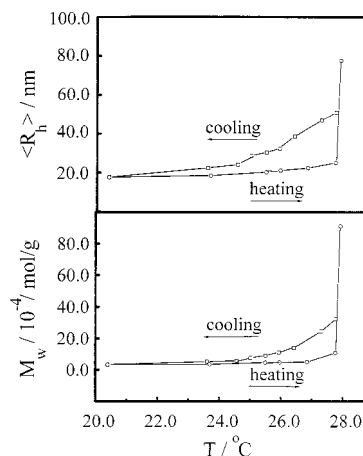
copolymer	[FEAA]/[NIPAM]			$M_w$ (g/mol) <sup>c</sup>	$M_w/M_n$	LCST (°C) <sup>d</sup>
	theory	by <sup>1</sup> H NMR <sup>a</sup>	by Fe content <sup>b</sup>			
1	1:200	1:201	1:207	$8.4 \times 10^4$	2.1	28.6
2	2:200	2:198	2:201	$3.4 \times 10^4$	2.0	27.2
3	4:200	4:196	4:194	$4.2 \times 10^4$	2.3	26.0

<sup>a</sup> Calculated from the peak areas at 3.3 and 1.1 ppm. <sup>b</sup> Calculated from the Fe content measured by atomic absorption spectroscopy. <sup>c</sup> By LLS. <sup>d</sup> LCST was estimated from the temperature at which the scattered light intensity started to sharply increase.

**Figure 5.** Temperature dependence of relative scattered light intensity ( $I_{\text{scattering}}/I_{\text{reference}}$ ) in water for poly(FEAA-*co*-NIPAM), where the scattering angle is 60°.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a thermally sensitive polymer with a low critical solution temperature (LCST) of ~32 °C;<sup>27–30</sup> namely, it is hydrophilic and soluble in water at temperatures lower than 32 °C but becomes hydrophobic and insoluble at higher temperatures.<sup>31–33</sup> The incorporation of PFEMAA into PNIPAM enables us to adjust the average interdistance between ferrocene groups by a simple temperature variation. All three copolymers were soluble in water at room temperature because of a low content of PFEMAA. The aqueous solution became turbid at higher temperatures, indicating the formation of large interchain aggregates. Figure 5 shows a typical temperature dependence of the relative scattering intensity ( $I_{\text{scattering}}/I_{\text{reference}}$ ) of different copolymer aqueous solutions. It shows that before the temperature reaches a critical temperature  $I_{\text{scattering}}/I_{\text{reference}}$  remains constant, revealing no significant interchain aggregation in this temperature range. The temperature at which the scattering intensity starts to sharply increase was defined as the LCST. Note that the scattering intensity is proportional to the square of molar mass of the scattering object so that a small amount of interchain aggregates can lead to a significant increase in the scattered light intensity. Therefore, the present method is more sensitive than the conventional turbidity measurement. As expected, the LCST of the copolymers decreases as the hydrophobicity of the polymer chain increases.

Figure 6 shows the temperature dependence of the average hydrodynamic radius ( $\langle R_h \rangle$ ) and the weight-average molar mass  $M_w$  of the copolymer-2 in water in a cooling-and-heating cycle, where  $C = 7.6 \times 10^{-4}$  g/mL. In the heating-and-cooling cycle, the solution was slowly heated and cooled to a desired temperature. The LLS measurement was only conducted after the equilibrium was reached at each temperature. The solution was prepared at ~25 °C. Before the cooling experiment, the solution was first quickly heated to its LCST. After the solution was cooled to 20 °C, the solution was then gradually heated in the heating experiment. Figure 6 shows that in the cooling both  $\langle R_h \rangle$  and  $M_w$  decrease as the temperature decreases, indicating the dissolution of the interchain aggregates formed at the LCST. This

**Figure 6.** Temperature dependence of average hydrodynamic radius ( $\langle R_h \rangle$ ) and weight-average molar mass  $M_w$  of poly(FEAA-*co*-NIPAM) with [FEAA]/[NIPAM] = 2:200 in water, where the concentration was kept at  $7.6 \times 10^{-4}$  g/mL.

is expected since water is a better solvent for PNIPAM at a lower temperature. Contrarily, both  $\langle R_h \rangle$  and  $M_w$  in the heating only increase slightly until the temperature reaches the LCST. In comparison, PNIPAM homopolymer in a similar cooling-and-heating cycle showed a much less hysteresis in  $\langle R_h \rangle$  and  $M_w$ .<sup>34–36</sup> The large hysteresis in Figure 6 clearly reveals the formation of interchain association in the collapsed state at higher temperatures, presumably via the hydrophobic attraction between the PFEMA monomers. Such interchain association is so strong that it can only be destroyed when water becomes a good solvent at ~20 °C.

## Conclusion

A convenient and economic one-step synthesis of 2-ferrocenylethyl alcohol was developed, which leads to a high yield of 2-ferrocenylethyl acrylate and 2-ferrocenylethyl methacrylate monomers. The polymerization of these monomers results in toluene-soluble high molar mass ferrocene-containing polyesters poly(2-ferrocenylethyl acrylate) (PFEA) and poly(2-ferrocenylethyl methacrylate) (PFEMA). A combination of static and dynamic laser light scattering (LLS) studies shows that the average translational diffusion coefficient ( $D$ ) is scaled to the weight-average molar mass ( $M_w$ ) as  $\langle D \rangle = 1.3 \times 10^{-5} M_w^{-0.57}$  for PFEA and  $\langle D \rangle = 1.9 \times 10^{-5} M_w^{-0.52}$  for PFEMA, indicating that both PFEA and PFEMA have a flexible coil conformation in toluene. On the basis of the synthesis of 2-ferrocenyl alcohol, two new ferrocene-containing monomers and *N*-2-ferrocenylacrylamide, as well as *N*-2-ferrocenyl methacrylamide, and their corresponding homopolymers were also prepared. The copolymerization of these ferrocene-containing monomers with *N*-isopropylacrylamide resulted in a series of copolymers, poly[(*N*-2-ferrocenylethylacrylamide)-*co*-(*N*-isopropylacrylamide)] with different monomer ratios.

The thermal sensitivity of PNIPAM leads to an easy way to manipulate the average interdistance of ferrocene groups by a simple temperature variation.

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