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Reversible Addition−Fragmentation Transfer Polymerization of a Novel Monomer Containing Both Aldehyde and Ferrocene Functional Groups

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ABSTRACT: A new monomer, 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC), containing both aldehyde and ferrocene functional groups was designed and prepared by the reaction of ferrocenecarboxylic acid chloride with 2-hydroxy-5-vinylbenzaldehyde. The controlled radical polymerization of FVFC was achieved using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator and 2-cyanopropyl-2-yl dithiobenzoate (CPDB) as the reversible addition−fragmentation chain transfer (RAFT) agent at 60 °C in tetrahydrofuran (THF). The polymerization nearly followed first-order kinetics, the number-average molecular weight of the obtained polymers increased almost in direct proportion to the monomer conversion, and the molecular weight distribution was narrow (polydispersity index < 1.2). The chain and terminal structures of the obtained polyFVFC were confirmed by ^{1}H NMR and matrix-assisted laser desorption−ionization time-of-flight mass spectrometry analysis. The obtained polyFVFC can be employed as a macro-RAFT agent for styrene polymerization, resulting in polyFVFC-*b*-polystyrene.

Introduction

Synthesis of polymers having reactive groups is among the most significant accomplishments in polymer chemistry. The selection of polymers with particular kinds of reactive groups depends on their intended applications. However, polymers with aldehyde groups are versatile and convenient, particularly for medical and biological applications.[1] Aldehyde groups are able to react under mild conditions with primary amino groups and with hydrazines forming the corresponding Schiff base and hydrazone linkages, respectively. Thus, polymers with aldehyde groups can be used as carriers for covalent immobilization of enzymes, drugs, and many biomolecules such as oligopeptides, proteins, and derivatives of nucleic acids and oligonucleotides.[2−6] Ferrocene-containing polymers have been continually developed for a few decades.[7] The incorporation of transition metal into polymeric framework has resulted in materials with some unusual and attractive characteristics including electrical, magnetic, catalytic, and nonlinear optical properties.[8,9]

In this work, a new styrene monomer, 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC, Scheme 1), was designed for the synthesis of a polymer containing both aldehyde and ferrocene functional groups. This novel polymer may combine the functions of aldehyde- and ferrocene-containing polymers and would thus be of interest due to its potential applications in, for example, the separation, detection, and diagnostics of biomolecules, in which aldehyde groups immobilize the detected compounds while the ferrocene moiety works as a probe for electrochemical detection.[10,11]

“Living”/controlled polymerization process offers many benefits including the ability to control the molecular weight and molecular weight distribution and to prepare block copolymers and other polymers of complex architecture. Reversible addition−fragmentation chain transfer (RAFT) polymerization is one of the techniques employed to obtain “living”/controlled radical polymerization.[12−14] Because of the compatibility with a wide range of monomers and reaction conditions, the RAFT process appears considerably more versatile than other “living”/controlled radical polymerizations such as nitroxide-mediated polymerization[15] and atom transfer radical polymerization.[16,17] The molecular weight control in the RAFT system is based on a dynamic equilibrium between the propagating radical and the dormant species with a dithiocarbonyl group derived from the RAFT agent.

Here we report the first example of the synthesis of a new monomer containing the combination of aldehyde and ferrocene groups, 2-formal-4-vinylphenyl ferrocenecarboxylate, and its conventional and “living”/controlled RAFT radical polymerizations. There are reports on the syntheses of polymers with aldehyde[1] or ferrocene[7] groups; however, to the best of our knowledge, no example of the polymer containing both of them has been reported. This is also true for the “living”/controlled radical polymerization of monomers with either aldehyde or ferrocene group.

Results and Discussion

1. Monomer Synthesis and Its Radical Polymerization with 2,2′-Azobis(isobutyronitrile) (AIBN). The new monomer FVFC containing the combination of aldehyde and ferrocene functional groups was designed and prepared readily by the reaction of ferrocenecarboxylic acid chloride with 2-hydroxy-5-vinylbenzaldehyde (Scheme 1). The structure of FVFC was confirmed on the base of the elemental analysis, MS, and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum exhibits the characteristic resonances corresponding to vinyl (*a*, *b*), aldehyde (*f*), and ferrocene moiety (*g*, *h*, *i*); the other resonances were assigned as shown in Figure 1.

To obtain some insight into the polymerization behavior of the new monomer FVFC, it was polymerized with conventional radical, cationic, and anionic initiators. It is well-known that radical polymerization is more tolerant of polar functionalities than ionic polymerizations. Indeed, a brown and powdery

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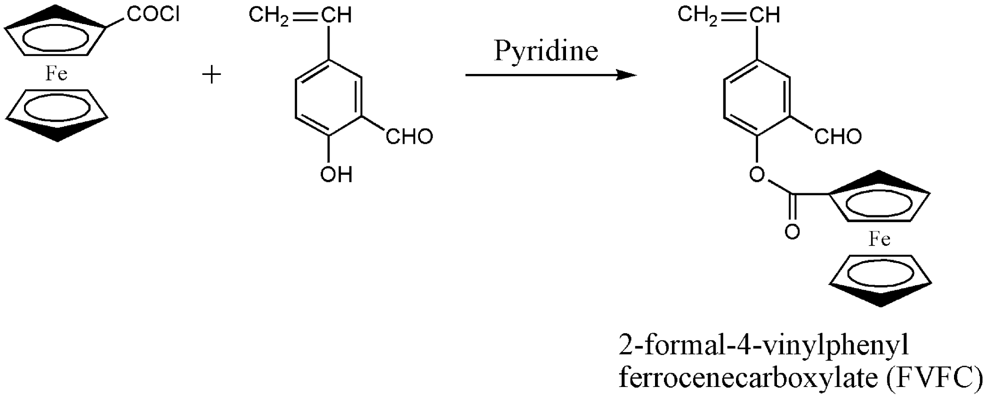
Scheme 1



polymer with number-average molecular weight (M_n) ~ 11 000 and weight-average molecular weight (M_w) ~ 21 780 [measured by GPC (gel permeation chromatography)] was obtained at ~50% conversion when the polymerization was carried out using AIBN at 60 °C in tetrahydrofuran (THF) for 18 h ([FVFC] = 0.57 M, [AIBN] = 5.7 mM). However, a low molecular weight oligomer ($M_n = 770$, $M_w = 880$) was obtained in poor yield (~5%) with anionic initiator *n*BuLi in THF at −40 °C for 18 h ([FVFC] = 0.57 M, [*n*BuLi] = 11.4 mM). Similarly, cationic initiator $BF_3 \cdot OEt_2$ led to a low molecular weight oligomer ($M_n = 1020$, $M_w = 1320$) at ~12% conversion ([FVFC] = 0.57 M, [$BF_3 \cdot OEt_2$] = 11.4 mM, in CH_2Cl_2 at −40 °C for 18 h).

The polymer of FVFC obtained with AIBN is soluble in common organic solvents such as THF, CH_3Cl, acetone, ethyl acetate, etc. Thermogravimetric analysis (Figure 2) indicates that the polymer is thermally stable. The temperature for 5% weight loss is as high as 315 °C, and the weight loss at 900 °C is lower than 50%. Differential scanning calorimetry analysis shows that the glass transition does not occur even at a high temperature up to ~240 °C, at which the weight loss reaches ~1.7%, suggesting the glass transition temperature of the polymer would be higher than its decomposition temperature.

The redox activity of polyFVFC was estimated by cyclic voltammetry in CH_2Cl_2 solution. As shown in Figure 3, the polymer exhibited only a single quasi-reversible oxidation peak at 0.39 V (vs Ag/Ag$^+$) while a corresponding reduction peak occurred at 0.32 V (vs Ag/Ag$^+$). This indicates that all the electroactive ferrocenyl moieties in one polymer possess the same redox potential.

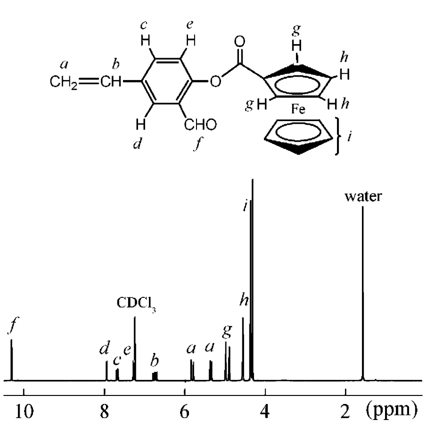


Figure 1. ^1H NMR (300 MHz, $CDCl_3$, room temperature) spectrum of 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC).

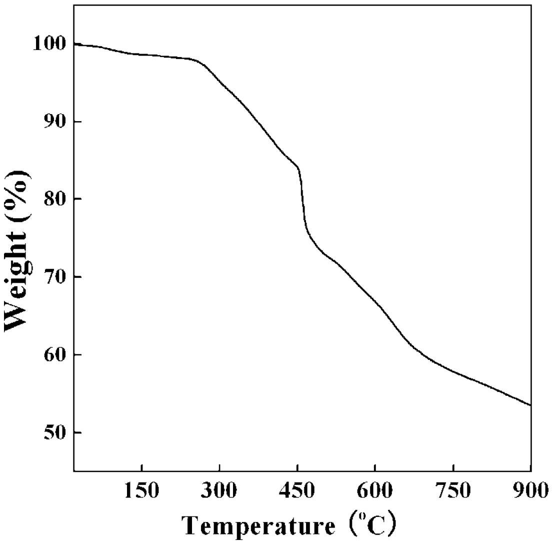


Figure 2. Thermogravimetric analysis thermogram of the polymer of 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC) measured under nitrogen at a heating rate of 20 °C/min. PolyFVFC (M_n = 11 000, M_w = 21 780) was obtained with 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C in tetrahydrofuran for 18 h: [FVFC] = 0.57 M, [AIBN] = 5.7 mM. M_n and M_w are the number- and weight-average molecular weights, respectively.

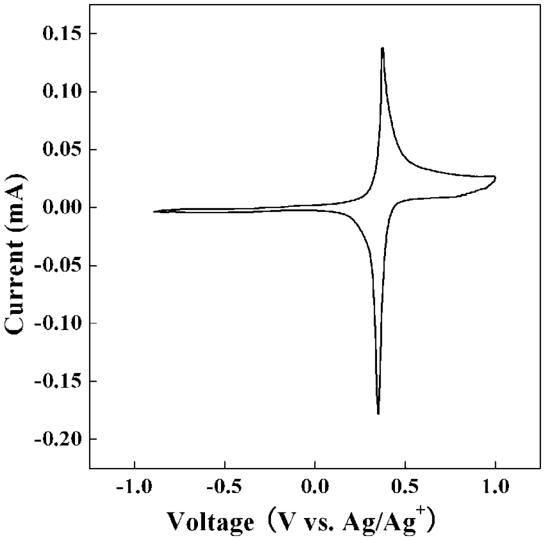


Figure 3. Cyclic voltammogram of the polymer of 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC) in CH_2Cl_2 solution containing polyFVFC (0.4 mg/mL) and [(*n*-Bu)$_4$N]PF_6 (0.1 M) using glassy carbon working electrode and Ag/$AgNO_3$ reference electrode at a scan rate of 50 mV/s. PolyFVFC (M_n = 11 000, M_w = 21 780) was obtained with 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C in tetrahydrofuran for 18 h: [FVFC] = 0.57 M, [AIBN] = 5.7 mM. M_n and M_w are the number- and weight-average molecular weights, respectively.

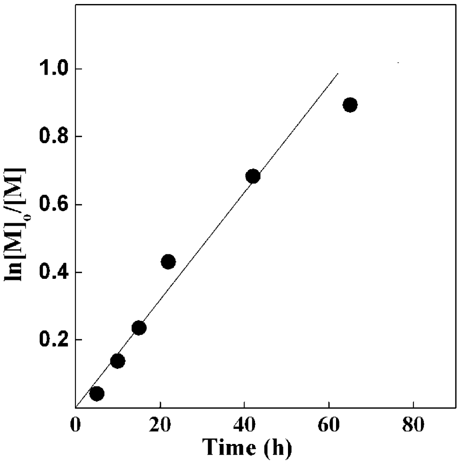


Figure 4. Semilogarithmic kinetic plot for the reversible addition–fragmentation chain transfer (RAFT) polymerization of 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC) with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator and 2-cyanopropyl-2-yl dithiobenzoate (CPDB) as a RAFT agent at 60 °C in tetrahydrofuran: [FVFC] = 0.57 M, [AIBN] = 2.86 mM, [CPDB] = 5.7 mM.

2. RAFT Polymerization of FVFC. (*a*) *Kinetic Behavior of the Polymerization with 2-Cyanopropyl-2-yl Dithiobenzoate (CPDB).* RAFT process is one of the most robust and versatile techniques used to obtain control over the radical polymerization process because it is effective for a wide range of functional monomers and does not require stringent reaction conditions.[12] For a RAFT process, the control operates via the introduction of a specific chain transfer agent (RAFT agent), mostly dithioesters, into the polymerization medium. Thus, the controlled radical polymerization of FVFC was attempted using AIBN as the initiator and CPDB as the RAFT agent at 60 °C in THF. CPDB was selected because of its versatility for a wide range of monomers such as styrene,[18,19] (meth)acrylates,[20] and acrylonitrile.[21]

To demonstrate the "living"/controlled nature of the RAFT polymerization, the polymerization kinetics was investigated. Figure 4 shows the semilogarithmic kinetic plot for the RAFT polymerization. Figure 5 shows the corresponding plots of number-average molecular weights (M_n) and molecular weight distributions (MWDs) of the obtained polymers against the monomer conversions. The polymerization nearly followed first-order kinetics, and M_n increased almost linearly with monomer conversion. The MWDs were narrow (M_w/M_n < 1.2) although they became slightly broader as the polymerization proceeded. These results indicated the "living"/controlled nature of the RAFT polymerization of FVFC.

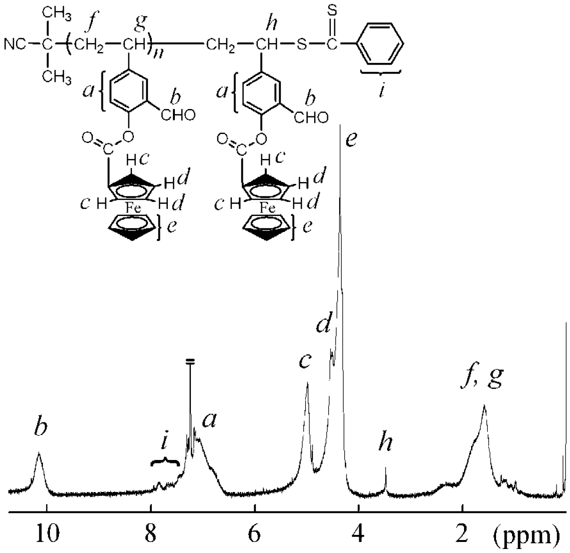


Figure 6. ^{1}H NMR spectrum of the polymer of 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC) [M_n measured by gel permeation chromatography ~ 3200, M_w/M_n ~ 1.10) obtained with 2,2′-azobis(isobutyronitrile) (AIBN)/2-cyanopropyl-2-yl dithiobenzoate (CPDB) at 60 °C in tetrahydrofuran: [FVFC] = 0.57 M, [AIBN] = 2.86 mM, [CPDB] = 5.7 mM. M_n and M_w are the number- and weight-average molecular weights, respectively.

However, the "living" or controlled character could only be observed within ~60% conversion. When the conversion was over 60%, the polymerization seemed to be retarded markedly and therefore deviated from the "living" behavior. Similar behavior was also observed for the other RAFT polymerization systems[22,23] and may be due to irreversible terminations[24−26] and/or other side reactions, resulting in the loss of the RAFT dormant species.[27−30]

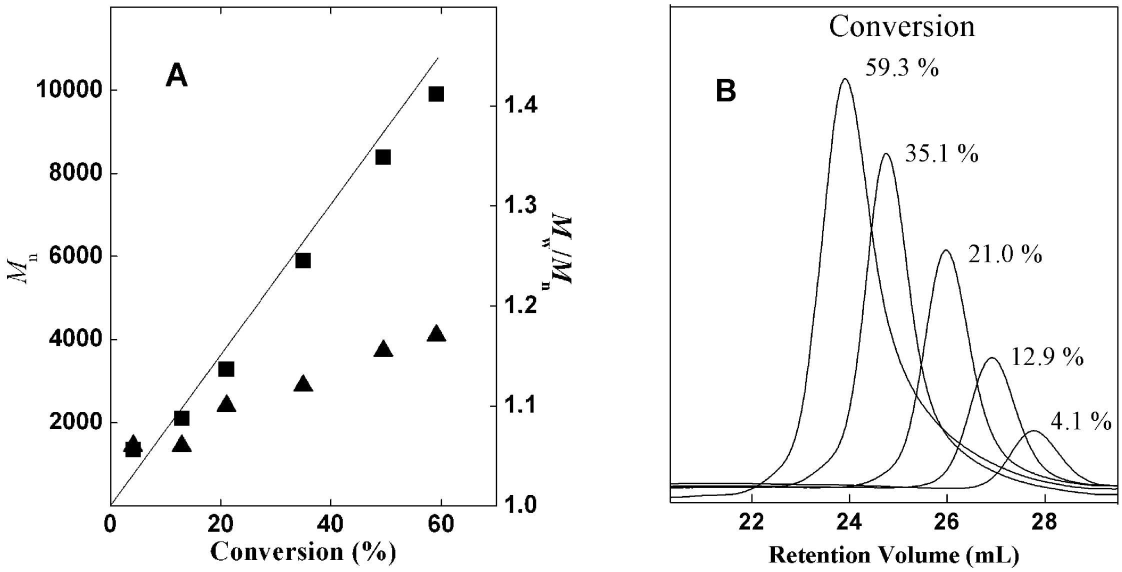


Figure 5. (A) M_n (■) and M_w/M_n (▲) and (B) molecular weight distribution curves of the polymer of 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC) obtained with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator and 2-cyanopropyl-2-yl dithiobenzoate (CPDB) as a RAFT agent at 60 °C in tetrahydrofuran: [FVFC] = 0.57 M, [AIBN] = 2.86 mM, [CPDB] = 5.7 mM. M_n and M_w are the number- and weight-average molecular weights, respectively.

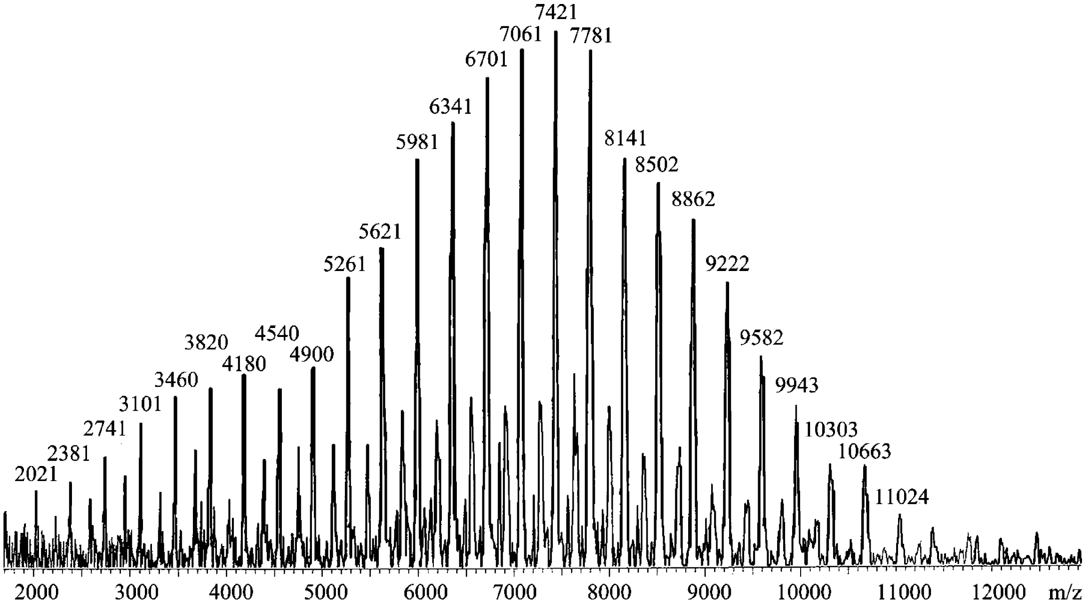


Figure 7. Matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF−MS) spectrum of the polymer of 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC) (M_n measured by gel permeation chromatography ∼ 2100, M_w/M_n ∼ 1.06) obtained with 2,2′-azobis-(isobutyronitrile) (AIBN)/2-cyanopropyl-2-yl dithiobenzoate (CPDB) at 60 °C in tetrahydrofuran: [FVFC] = 0.57 M, [AIBN] = 2.86 mM, [CPDB] = 5.7 mM. M_n and M_w are the number- and weight-average molecular weights, respectively.

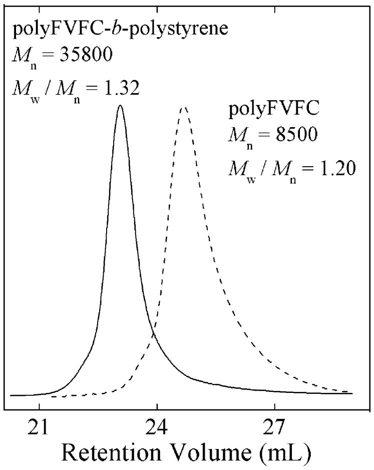


Figure 8. Gel permeation chromatogrphy traces of the polymer of 2-formal-4-vinylphenyl ferrocenecarboxylate (FVFC) and polyFVFC-*b*-polystyrene obtained by chain extension reaction with styrene using polyFVFC as a macro-RAFT (reversible addition−fragmentation chain transfer) agent in bulk at 110 °C for 2 h. M_n and M_w are the number- and weight-average molecular weights, respectively.

(*b*) *Polymer Analysis.* The structure of the obtained polymers was analyzed by ^{1}H NMR spectroscopy. Figure 6 shows the ^{1}H NMR spectrum of a typical sample obtained with AIBN/CPDB in THF after quenching the polymerization at 21% conversion (M_n measured by GPC ∼ 3200, M_w/M_n ∼ 1.10). The spectrum shows the characteristic signals for the main-chain repeating units of FVFC, i.e., the aldehyde protons (*b*), ferrocene protons (*c, d, e*), aromic protons (*a*), and aliphatic protons (*f, g*). In addition to these large absorptions, small signals due to the end groups appeared at 7.3−8.0 ppm. They are attributed to the aromatic (*i*) protons of dithiobenzoate fragment at the ω-chain end derived from the RAFT agent CPDB.[31] Moreover, there appeared an absorption at 3.5 ppm, which corresponds to the end-standing methine proton (*h*) of FVFC unit capped with a CPDB fragment. Therefore, the polymer chain ends were capped with the RAFT agent fragments as expected according to the well-known mechanism of the RAFT process.

The structure of polyFVFC obtained by the RAFT polymerization was further analyzed by matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF MS). As shown in Figure 7, there was a single main series of peaks, each almost separated by an interval of 360 Da, which corresponds to the molecular weight of the FVFC monomer. The absolute value of each peak was very close to the molecular weight expected for the polymer (depending on the degree of polymerization) with CPDB fragments at the α- and ω-chain ends that have a total mass of 221 Da. A minor series of peaks with a 153 Da lower mass was also observed, which suggests the loss of dithiobenzoate fragment at the ω-chain end during the MS analysis.[32]

(*c*) *Block Copolymer of FVFC and Styrene.* The "living"/controlled polymerizations can provide polymers with controlled molecular weight and narrow molecular weight distribution; more importantly, the obtained polymer can be retreated with monomers for chain extension to form block copolymers. The synthesis of a diblock copolymer of FVFC and styrene was then performed using polyFVFC (M_n measured by GPC ∼ 8500, M_w/M_n ∼ 1.20) prepared with CPDB as macro-RAFT agent. The polymerization was performed in bulk at 110 °C for 2 h; the conversion of styrene was 14.9%. The formation of polyFVFC-*b*-polystyrene was demonstrated by clear shift of the GPC trace toward higher molecular weight without visible trace of the macro-RAFT agent polyFVFC, although the MWD became somewhat broadened (Figure 8). Moreover, the block copolymer is insoluble in acetone (solvent for polyFVFC but nonsolvent for polystyrene), indicating almost the absence of polyFVFC macro-RAFT agent. Therefore, it is possible to synthesize the diblock copolymer polyFVFC-*b*-polystyrene via the RAFT process.

Conclusion

In conclusion, the controlled radical polymerization of FVFC, a new monomer containing both aldehyde and ferrocene functional groups, was achieved for the first time using AIBN as the initiator and CPDB as the RAFT agent at 60 °C in THF to afford polymers with controlled molecular weights, narrow MWDs, and well-defined chain end groups. The obtained polyFVFC can be employed as a macro-RAFT agent for styrene polymerization, resulting in polyFVFC-*b*-polystyrene.

Experimental Section

Materials. Ferrocenedicarboxylic acid and oxalyl chloride (both from Aldrich, purity >97%), $[(n\text{-Bu})_4N]PF_6$ and $BF_3{\cdot}OEt_2$ (both from Alfa Aesar, purity >98%), and *n*BuLi (Acros, 2.5 M in *n*-hexane) were all used as received. THF and CH_2Cl_2 (both from China National Medicines Shanghai Corp., purity >99%) were refluxed with sodium chips (for THF) or CaH_2 (for CH_2Cl_2) under N_2 until dry and freshly distilled before use. Pyridine (China National Medicines Shanghai Corp., purity >99%) was reduced pressure over CaH_2 before use. Styrene (China National Medicines Shanghai Corp., purity >99%) was purified by passing through neutral alumina column and distilled twice under reduced pressure over CaH_2 before use. AIBN (China National Medicines Shanghai Corp., purity >99%) was recrystallized twice from methanol. CPDB,[18] ferrocenecarboxylic acid chloride,[33] and 2-hydroxy-5-vinylbenzaldehyde[34] were synthesized according to literature procedures.

Synthesis of 2-Formal-4-vinylphenyl Ferrocenecarboxylate (FVFC). FVFC was prepared by the reaction of ferrocenecarboxylic acid chloride with 2-hydroxy-5-vinylbenzaldehyde, as below. A solution of ferrocenecarboxylic acid chloride (2.35 g, 9.5 mmol) in THF (10 mL) was added dropwise to a mixture of 2-hydroxy-5-vinylbenzaldehyde (0.88 g, 6 mmol) and pyridine (0.3 mL, 3.71 mmol) in THF (30 mL). The reaction mixture was stirred at room temperature overnight and then evaporated to dryness. Purification of the residue by column chromatography with silica gel as the stationary phase and ethyl acetate/*n*-hexane (30:70 v/v) as eluent gave FVFC as a brown solid (1.77 g, 82%); mp = 69−70 °C. ^{1}H NMR ($CDCl_3$), δ (TMS, ppm): 4.38−4.98 (m, 9H, ferrocenyl protons), 5.35 (d, J = 10.8 Hz, 1H, *trans*-CH_2=), 5.81 (d, J = 17.4 Hz, 1H, *cis*-CH_2=), 6.74 (dd, J_1 = 10.8 Hz, J_2 = 17.4 Hz, 1H, =CH−), 7.27 (d, J = 8.4 Hz, 1H, 6-aromtic proton), 7.68 (dd, J_1 = 2.1 Hz, J_2 = 8.4 Hz, 1H, 5-aromtic proton), 7.95 (d, J = 2.1 Hz, 1H, 3-aromtic proton), 10.31 (s,1H, aldehyde proton). FAB MS: *m*/*z* calcd for $C_{20}H_{16}O_3Fe$ 360.19; found 360 (M^+). Anal. Calcd for $C_{20}H_{16}O_3Fe$: C 66.67; H 4.48. Found: C 66.38, H 4.66.

RAFT Polymerization of FVFC. For a typical solution polymerization, a stock solution in THF (35 mL) comprising FVFC (7.2 g, 20 mmol), AIBN (16.4 mg, 0.1 mmol), and CPDB (44.2 mg, 0.2 mmol) was prepared in a N_2-filled dry glovebox. Aliquots (5.0 mL) were removed and transferred to ampules, degassed with three freeze−pump−thaw cycles, sealed, and heated at 60 °C. After the predetermined intervals, the sealed ampules were cooled in an ice bath, and the reaction mixtures were diluted with THF and then poured into a large amount of petroleum ether. The precipitated polymers were washed with petroleum ether and dried to constant weight under vacuum at 40 °C; the overall monomer conversions were determined gravimetrically.

Block Copolymerization with Styrene. A typical example of chain extension experiment is given below. The polyFVFC (0.10 g, $M_n = 8500$, $M_w/M_n = 1.20$) obtained from the polymerization in the presence of CPDB was dissolved in styrene (2.50 g) in a dry ampule; then the solution was degassed by three freeze−pump−thaw cycles, sealed, and heated at 110 °C. After 2 h, the sealed tube was cooled in an ice bath, and the reaction mixture was diluted with THF and then poured into a large amount of methanol. The precipitated polymer was washed with methanol and dried to constant weight under vacuum at 40 °C. The styrene conversion was determined gravimetrically.

Measurements. ^{1}H NMR (300 MHz) spectra were recorded in $CDCl_3$ at room temperature on a Varian Unity Inova 300 spectrometer. Elemental analysis was determined on a CHNS-Vario elemental analyzer. The molecular weights and molecular weight distributions were measured by gel permeation chromatography against polystyrene standard in THF at a flow rate of 1.0 mL/min at 35 °C on three Waters Styragel columns (measurable molecular weight range: 100−5000, 500−30 000, and 5000−600 000) connected to a Waters 1515 pump and a Waters 2414 refractive index detector. Matrix-assisted laser desorption−ionization time-of-flight mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm N_2 laser in the positive linear mode and at a 19 kV accelerating voltage. α-Cyano-4-hydroxycinnamic acid was used as a matrix. Samples were prepared from a THF solution by mixing the matrix (20 mg/mL) and sample (10 mg/mL) in a ratio of 10:1. External mass calibration was performed using a standard peptide mixture. Thermogravimetric analysis was measured on a Netzsch TG/209 under nitrogen at a heating rate of 20 °C/min. Differential scanning calorimetry were performed on a Netzsch DSC/204 at a scan rate of 10 °C/min over a temperature range from 20 to 270 °C. Cyclic voltammograms were recorded on a Princeton Applied Research model 273A potentiostat at ambient temperature in freshly distilled CH_2Cl_2 solution containing polyFVFC (0.4 mg/mL) and supporting electrolyte $[(n\text{-Bu})_4N]PF_6$ (0.1 M) at a scan rate of 50 mV/s. The working and reference electrodes were glassy carbon and $Ag/AgNO_3$ (0.1 M in acetonitrile), respectively.

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