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ARTICLE

RAFT Polymerization of Styrene Mediated by Ferrocenyl-Containing RAFT Agent and Properties of the Polymer Derived from Ferrocene

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ABSTRACT: Two novel reversible addition−fragmentation chain transfer (RAFT) agents, (ferrocen-1-yl) ethyl benzodithioate (FEB) bearing ferrocenyl moiety in the R group, and benzyl ferrocenecarbodithioxylate (BFEC) bearing ferrocenyl moiety in the Z group, were designed and synthesized, respectively. The FEB and BFEC were then used as the RAFT agents for the controllable polymerization of styrene and their performance in the controllability was investigated respectively. Obtained polystyrenes were labeled as FEB−PS and BFEC−PS respectively. The results indicated that FEB and BFEC could make the polymerization of styrene very controllable, such as, the number-average molecular weight measured by gel permeation chromatography ($M_{n,GPC}$) increases linearly with the monomer conversion, the $M_{n,GPC}$s were close to the predicted values ($M_{n,th}$), the polydispersity index (PDI) values were less than 1.25, and the chain-extension experiments of the obtained polymer with styrene were successfully carried out etc. The UV−vis absorption, electrochemical behavior and the stability in common organic solvents of the polystyrene with ferrocenyl group attached at the chain ends mediated by two RAFT agents, were further investigated. UV−vis absorption spectra of FEB−PS and BFEC−PS showed typical spectrum of ferrocene with a red shift from 440 to 475 nm and 560 nm, respectively. The electrochemical behaviors of FEB−PS and BFEC−PS were similar to that of ferrocene. $E_{1/2}$ ($E_{1/2} = (E_{p1} + E_{p2})/2$) of FEB−PS was a negative shift, and $E_{1/2}$ of BFEC−PS was a large positive shift compared with that of ferrocene. The peak currents of FEB−PS and BFEC−PS gradually dropped with the increase of molecular weight of the polymers. The stability of BFEC−PS and FEB−PS in common organic solvents was in the order of CH_2Cl_2 > THF > acetone > $CHCl_3$ > DMF. FEB−PS showed better stability than that of BFEC−PS in these solutions. The concentration of the polymers end-capped with ferrocenyl was calculated by the examination of iron contents using atomic absorption spectrometry and nuclear magnetic resonance (^{1}H NMR) measurement, respectively. The results showed that the percentage of polystyrene end-capped with ferrocenyl in BFEC−PS and FEB−PS was about 80% and 70%.

Introduction

Reversible addition−fragmentation chain transfer (RAFT) polymerization, which was developed in 1998,[1,2] assimilated the advantages of the radical polymerization and living polymerization. By using the RAFT polymerization technique, the architectures of the polymer can be well-designed and constructed. RAFT polymerization can also be used to polymerize monomers in an aqueous environment at a low temperature with nonrigorous reactions. Furthermore, the wide range of monomers used in RAFT polymerization make it predominant over other "living"/controlled free radical polymerizations, such as atom transfer radical polymerization (ATRP),[3−5] and stable free radical polymerization (SFRP).[6,7] RAFT polymerization is expected to be one of the most promising methods among the "living"/controlled free radical polymerization in the practical application. The key in the RAFT process is the thiocarbonylthio compounds used as the RAFT agents, which have common structures such as ZC(=S)SR. The repeated reversible transfer events of the RAFT agents during the polymerization induce equilibria between the dormant and living chains, which result in the "living"/controlled behavior of the polymerization.[8] According to the RAFT mechanism, most of the polymer chains from the RAFT polymerization are end-capped by the Z and R groups at the respective ω and α chain ends. Hereby, the RAFT polymerization provides a means of introducing functional group into polymer chain ends by selecting appropriate RAFT agents.[9,10] The application of RAFT polymerization in the synthesis of functionalized polymers has a promising future.

Ferrocene is a versatile molecule with important properties, such as high electron density, aromaticity, thermal stability and redox reversibility.[11] Ferrocene has interested a number of scientists and research groups worldwide because of its applications in material science.[12,13] Various materials containing ferrocenyl moieties have been prepared in past decades.[14−17] Among them, polymers incorporated with ferrocenyl moieties have brought some unusual and attractive characteristics, such as electrochemical, magnetic, catalytic, redoxactive and nonlinear optical properties etc.[18−21] Polymers containing ferrocene are superior candidates as redox catalysts in electrochemical assays, due to high chemical stability, decrease in interferences, good antifouling property, and good characteristic electrochemical responses.[22−28] Over the last several years, various polymers containing ferrocene moieties have been prepared. Hempenius research group synthesized poly(ferrocenylsilane) polyelectrolyte hydrogels with redox controlled swelling.[29] Lee Yook Heng and co-worker obtained a photocurable polymer film containing

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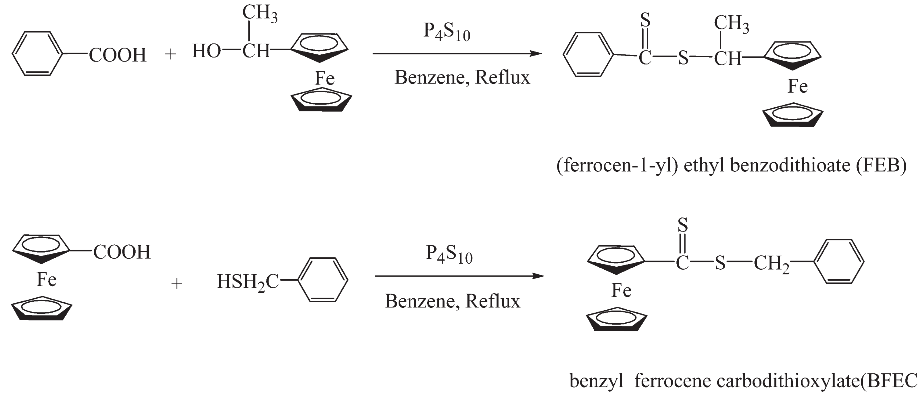
Scheme 1. Synthesis Routes of (Ferrocene-1-yl)ethyl Benzodithioate (FEB) and Benzyl Ferrocenecarbodithioxylate (BFEC)



ferrocene as a glucose biosensor.[30] The ferrocenyl moiety can be embedded into a polymer chain network either as a side group or as a chain backbone unit.[17−19,31] Until now, the incorporation of ferrocenyl moiety into the polymer chain ends has not yet been reported because of the limitations of the conventional polymerization methods. In this article, two new RAFT agents, (ferrocen-1-yl)ethyl benzodithioate (FEB) containing ferrocenyl moiety in the R group and benzyl ferrocenecarbodithioxylate (BFEC) containing ferrocenyl moietiy in the Z group, were designed and synthesized, respectively. By using FEB and BFEC in the RAFT polymerization of styrene, a well-defined polystyrene bearing ferrocenyl moieties at the chain ends was obtained. UV−vis absorption and electrochemical properties of the polystyrene reinforced by ferrocenyl groups were explored. The stability of the polystyrene end-capped by ferrocenyl moiety was also investigated.

Experimental Part

Materials. 1-(Ferrocene-1-yl) ethanol (97%) was purchased from Acros Co. Ltd. Benzyl mercaptan (99%), phosphorus pentasulfide (P, 27%; S, 72%) were purchased from Sigma-Aldrich Co. Ltd. Ferrocene carboxylic acid (98%), benzoic acid (99%) and other chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents Co. Ltd. (China). Styrene was washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, styrene was distilled under reduced pressure and kept in a refrigerator under 0 °C. 2,2′-Azoisobutyronitrile (AIBN, 98%) was recrystallized from ethanol and kept in a refrigerator under 4 °C. Benzene, chloroform, and dichloromethane were dried by a 4 Å molecular sieve and distilled before use. Other chemicals were used as received.

Typical Procedure for the Synthesis of Reversible Addition−Fragmentation Chain Transfer (RAFT) Agents. FEB and BFEC were synthesized by a similar method as described in the literature.[32−34] The chemical structures and synthetic routes of the FEB and BFEC are shown in Scheme 1. Typical procedures for the synthesis of FEB were as follows: benzoic acid (2.50 mmol, 0.305 g), 1-(ferrocene-1-yl)ethanol (2.50 mmol, 0.575 g), P_4S_{10} (1.25 mmol, 0.555 g), sodium hydrogen carbonate (6.00 mmol, 0.500 g), and benzene (25 mL) were added to a 50 mL of three-neck-round flask with magnetic stirring. The solution was then heated and refluxed for about 20 h under argon atmosphere. The reaction solution was filtrated after cooling. The solvent in the filtrate layer was removed by rotation evaporation. The crude product was purified by column chromatograph on silica oxide with petroleum ether/benzene (v:v = 8:1) and then with petroleum ether/benzene (v:v = 20:1) as the eluents. Purified FEB, an orange-red solid, was stored at −18 °C under argon atmosphere (0.11−0.12 g, yield = 12−13%). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.80 (d, 3H, (ferrocenyl) $CHCH_3$), 4.10−4.30 (m, 9H, ferrocenyl), 5.20 (q, 1H, (ferrocenyl) $CHCH_3$), 7.30−8.09 (m, 5H, phenyl). Anal. Calcd (%): C, 62.30; H, 4.95. Found (%): C, 62.56; H, 5.06. Mp: 62.6−65.9 °C. The synthesis of BFEC was similar to that of FEB with 23−25% (0.20−0.22 g) yield. The violet-black solid BFEC was stored at −18 °C under argon atmosphere. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.10−4.20 (m, 5H, ferrocenyl), 4.50−4.60 (m, 4H, ferrocenyl connected with dithioester group), 5.10−5.20 ppm (s, 2H, methylene neighboring phenyl), 7.20−7.40 ppm (m, 5H, phenyl).

Typical Reversible Addition−Fragmentation Chain Ttransfer (RAFT) Polymerization of Styrene. A dry 2 mL ampule was filled with styrene (8.70 mmol, 1.0 mL), (ferrocen-1-yl)ethyl benzodithioate (FEB) (8.70×10^{-2} mmol, 31.8 mg) and 2,2′-azoisobutyronitrile (AIBN) (0.0174 mmol, 2.86 mg). The contents were purged with argon for approximately 10 min to eliminate oxygen. Then, the ampule was flame-sealed and placed in an oil bath held by a thermostat at the desired temperature to polymerize. At timed intervals, the ampule was immersed in ice water and then opened. The contents were dissolved in 2 mL of tetrahydrofuran (THF) and then precipitated into 200 mL of methanol. The polymer was obtained by filtration and dried at room temperature under vacuum to constant weight. Conversion of styrene was determined gravimetrically. The RAFT polymerization of styrene using benzyl ferrocenecarbodithioxylate (BFEC) was similar to that of FEB. The polymerization time, conversion and number-average molecular weight (M_n) measured by gel permeation chromatographer (GPC) were shown in Figure 1 and Figure 2, respectively. The polystyrene mediated by FEB and BFEC was characterized by ^{1}H NMR and shown in Figure 3.

Typical Chain Extension with Polystyrene as the Macro-RAFT Agent. The procedure of chain extension experiment was similar to those described above except the RAFT agents were replaced by the polystyrene synthesized via RAFT polymerization of styrene.

Characterization. The number-average molecular weight (M_n) and polydispersity (PDI) of the synthesized polymer was determined by a Waters 1515 gel permeation chromatographer (GPC) equipped with a refractive index detector (model 494), using a HR1, a HR3, and a HR4 column with the molecular weight range of 100−500 000. The molecular weight was calibrated with polystyrene standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 $mL \cdot min^{-1}$ operated at 30 °C. Matrix assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry measurement was performed using a Bruker Autoflex III (MALDI−TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Both matrice 4-hydroxy-α-cyanocinnamic acid and sample were dissolved in 1:1 (v/v) acetonitrile: water with 1% trifuoroacetic acid. 0.5 μL of this mixture solution was placed on a metal sample plate. The sample was air-dried at ambient temperature. ^{1}H NMR (400 HMz) spectra of the polymers were recorded on

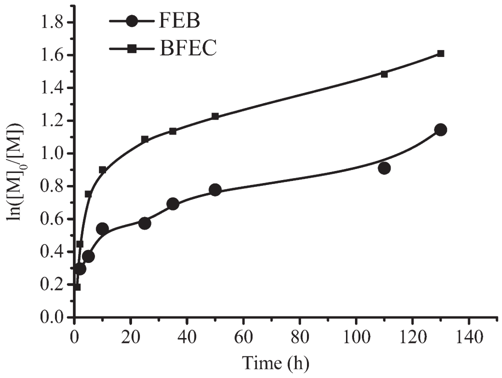


Figure 1. $\ln([M]_0/[M])$ versus polymerization time for reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene with (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) as RAFT agents, respectively. $[\text{styrene}]_0$:$[\text{RAFT agent}]_0$:$[\text{AIBN}]_0$ = 500:5:1, 80 °C, $[\text{styrene}]_0$ = 8.74 mol/L, AIBN refers to 2,2′-azoisobutyronitrile, [M] is the styrene concentration at time of t, $[M]_0$ is the initial styrene concentration.

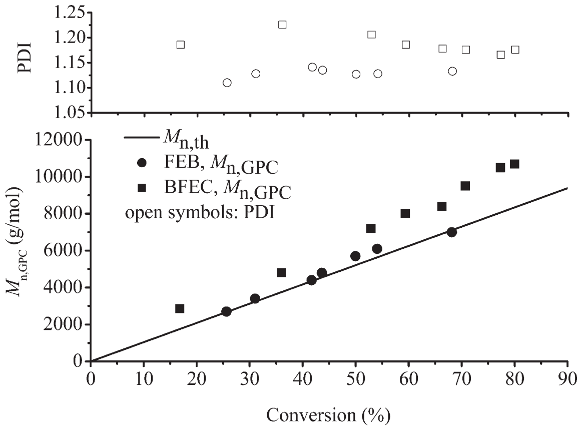


Figure 2. Dependence of number-average molecular weight (M_n) and polydispersity index (PDI) on conversion for reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene using (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) as RAFT agents, respectively (The reaction conditions are the same as Figure 1).

an INOVA400 nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. Elemental analyses (EA) of C, H and N were measured by the EA1110 CHND-S. The UV−vis absorption spectra of the polymers in CH_2Cl_2 solutions were determined on a Shimadzu RF540 spectrophotometer. Cyclic voltammograms (CV) were carried out with an electrochemical analyzer (CHI630B, Shanghai Chenghua instrument Co. China) using tetraethyl ammonium perchlorate [$(n\text{-Et})_4NH_4ClO_4$] or tetrabutyl ammonium perchlorate [$(n\text{-Bu})_4NH_4ClO_4$] (0.1 M) as the supporting electrolyte at a scan rate of 0.1 V/s in CH_2Cl_2 solution. The measurement was conducted at room temperature under an oxygen-free atmosphere. The atomic absorption spectroscopy of the iron content was determined by Varian Spectra AA 220 FS (Varian Inc.).

Results and Discussion

Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization of Styrene. The RAFT polymerizations of styrene mediated by FEB and BFEC were carried out at 80 °C in bulk. Figure 1 showed the plots of $\ln([M]_0/[M])$ versus polymerization time for the polymerizations of styrene using FEB and BFEC as RAFT agents, respectively.

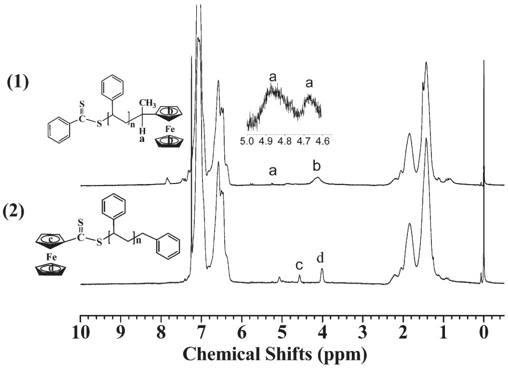


Figure 3. ^{1}H NMR spectra of polystyrene mediated by (ferrocene-1-yl) ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC), respectively. $[\text{styrene}]_0$:$[\text{RAFT agent}]_0$:$[\text{AIBN}]_0$ = 500:5:1, temperature = 80 °C, $[\text{styrene}]_0$ = 8.74 mol/L. $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) as the internal standard. (1) polystyrene mediated by FEB: conversion = 49.9%, reaction time = 24 h, number-average molecular weight by GPC ($M_{n,GPC}$) = 5560 g/mol, polydispersity index (PDI) = 1.13; (2) polystyrene mediated by BFEC: conversion = 60.1%, reaction time = 9 h, number-average molecular weight by GPC ($M_{n,GPC}$) = 6600, polydispersity index (PDI) = 1.18.

2,2′-Azoisobutyronitrile (AIBN) was used as the initiator with a molar ratio of $[\text{styrene}]_0$:$[\text{RAFT agent}]_0$:$[\text{AIBN}]_0$ = 500:5:1. It can be found from Figure 1 that the polymerization rate mediated by BFEC was significantly higher than that by FEB under the same experimental conditions. Meanwhile, the kinetic plots of the polymerization mediated by FEB and BFEC did not show the classic pseudo first-order plots but degressive plots after about 10 h under the reaction conditions. As for the "living"/controlled radical polymerization, the kinetics show decelerated plots instead of pseudo first-order plots, which is due to some side reactions[35] or the exhaustion of the initiator.[36] In our work, the decrease of the polymerization rate is probably due to the exhaustion of AIBN after 10 h of polymerization.[36]

Figure 2 exhibited the evolutions of number-average molecular weight (M_n) and polydispersity index (PDI) value versus the monomer conversion when FEB and BFEC were used as the RAFT agent, respectively. The number-average molecular weight measured by GPC ($M_{n,GPC}$) increased linearly with the monomer conversion. Furthermore, the $M_{n,GPC}$s were close to the predicted values ($M_{n,th}$) ($M_{n,th}$ = $[\text{styrene}]_0/[\text{RAFT agent }]_0 \times$ conversion + molecular weight of RAFT agent), and the PDI values of the polystyrene were lower than 1.25. The $M_{n,GPC}$ of polystyrene obtained by FEB was closer to the predicted value ($M_{n,th}$), and with lower PDI values (<1.15) than that obtained by BFEC. These results indicated that FEB and BFEC can perform as effective RAFT agents in the polymerizations of styrene. The controllability of FEB was a little better than that of BFEC. The reason may be that the phenyl can stabilize the intermediate radical better in the RAFT process than ferrocenyl.[9,10] That is, the phenyl group should be a more effective Z group than the ferrocenyl.

The chain ends of polystyrene prepared by the RAFT polymerization using FEB and BFEC as the RAFT agent were analyzed by ^{1}H NMR spectroscopy as shown in Figure 3(1) and Figure 3(2), respectively. In Figure 3(1), the signals at about δ = 0.9−2.4 ppm (3H, integration = $I_{0.9-2.4}$ = 210.61) were ascribed to the protons of the ethenyl from styrene units. The signals at δ = 4.6−5.0 ppm (a,1H) correspond to the proton neighboring at the ferrocene moiety. The signals at δ = 3.9−4.2 ppm (b, 9H, intergration = $I_{3.9-4.2}$ = 9) were ascribed to aromatic protons of ferrocenyl rings. In Figure 3(2), the signals at about

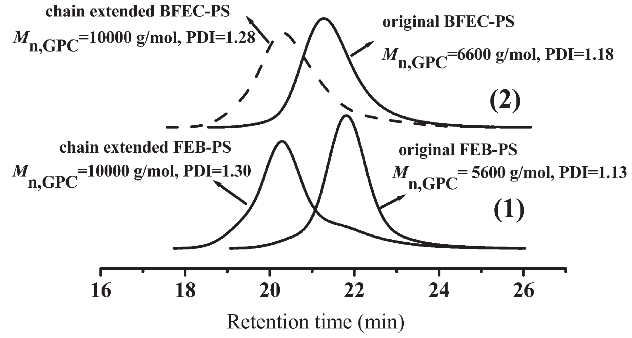


Figure 4. GPC traces of the original polystyrene and the chain-extended polymers with styrene as the second monomer. Temperature = 80 °C, [styrene]$_0$:[macro-RAFT agent]$_0$:[AIBN]$_0$ = 1000:10:5. (1) FEB−PS as the macro-RAFT agent. (2) BFEC−PS as the macro-RAFT agent. FEB−PS and BFEC−PS refer to the polystyrene obtained from (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization, respectively. AIBN refers to 2,2′-azoisobutyronitrile. GPC is gel permeation chromatography.

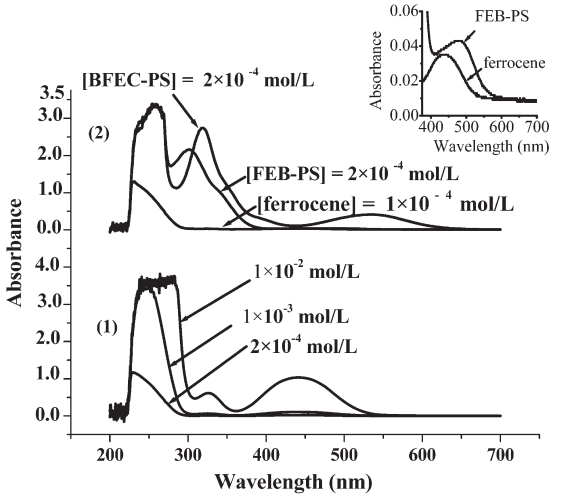


Figure 5. UV−vis spectra in CH_2Cl_2 solution at room temperature. (1) ferrocene with different concentrations. (2) ferrocene, FEB−PS and BFEC−PS, [ferrocene]$_0$ = 10^{-4} mol/L, [FEB−PS]$_0$, [BFEC−PS]$_0$ = 2×10^{-4} mol/L. FEB−PS and BFEC−PS refer to the polystyrene obtained from (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization, respectively.

δ = 0.9−2.4 ppm (3H, integration = $I_{0.9-2.4}$ = 229.48) can be ascribed to the protons of the ethenyl from styrene units. The signals at about δ = 4.5−4.7 ppm (c, 4H) corresponded to the protons of ferrocenyl rings incorporated with thiocarbonyl. The signals at about δ = 3.8−4.2 ppm (d, 5H, intergration = $I_{3.8-4.2}$ = 5) were ascribed to the protons of other ferrocenyl rings in BFEC. These results indicated that the moieties of FEB and BFEC were attached to the corresponding polymer chain ends, confirming that the polymerization was accordant with the RAFT mechanism.

For convenience, polystyrene obtained by FEB and BFEC mediated polymerization were termed as FEB−PS and BFEC−PS, respectively. Assuming that each polymer chain was captured by a ferrocenyl ring moiety, the molecular weight ($M_{n,\,NMR}$) of FEB−PS and BFEC−PS can be respectively calculated from the integrations in ^{1}H NMR, according to eqs 1 and 2

$$M_{n,\,NMR}(g/mol) = (I_{0.9-2.4}/3) \times 104/(I_{3.9-4.2}/9) + 366 \quad (1)$$

$$M_{n,\,NMR}(g/mol) = (I_{0.9-2.4}/3) \times 104/(I_{3.8-4.2}/5) + 352 \quad (2)$$

where 104 g/mol, 366 g/mol, and 352 g/mol are the molecular weights of styrene, FEB, and BFEC, respectively. The molecular weights ($M_{n,NMR}$) of FEB−PS and BFEC−PS calculated from the ^{1}H NMR spectra (Figure 3) were 7540 g/mol and 8300 g/mol, respectively. The molecular weights ($M_{n,GPC}$) of FEB−PS and BFEC−PS from gel permeation chromatography (GPC) were 5560 g/mol and 6600 g/mol, respectively, which were lower than the corresponding $M_{n,NMR}$. The deviation of the $M_{n,NMR}$ from $M_{n,GPC}$ indicated that not every polymer chain end was labeled by the ferrocenyl moiety. The percentage of polymer chains with ferrocenyl groups (C_{psfc} (%)) can be calculated by the equation: C_{psfc} (%) = $M_{n,GPC}/M_{n,NMR}$. The calculated C_{psfc} (%) of FEB−PS and BFEC−PS was about 74% and 80%, respectively.

The concentration of the polymer end-capped with ferrocenyl may also be calculated by iron contents detected by atomic absorption spectrometry (AAS). Assuming each polymer chain was captured by a ferrocenyl moiety, the theoretical percentage of iron ($C_{Fe,th}$ (%)) can be calculated by the equation: $C_{Fe,th}$ (%) = $56/M_{n,\,GPC}$. The percentage of polystyrene end-capped with ferrocenyl (C_{psfc} (%)) can be calculated with the equation: C_{psfc} (%) = $C_{Fe,ac}/C_{Fe,th}$. The $C_{Fe,ac}$ refers to the iron content from AAS analysis. The FEB−PS and BFEC−PS samples used in AAS were the same as those used for ^{1}H NMR detection (Figure 3). The C_{psfc} (%) of FEB−PS and BFEC−PS calculated from AAS was about 70% and 85%, respectively. These values were close to those from the ^{1}H NMR measurement.

On the basis of the RAFT mechanism, the polymer obtained via RAFT polymerization should be end-labeled with the dithio-groups at the chain ends. However, various kinds of side reactions, such as the reactions between intermediate radicals and other radical species etc., can potentially complicate the RAFT mechanism, causing retardation in the reaction, formation of byproduct and anomalies in the molecular weight distributions etc. As a result, the percentage of polymer functionalized with the dithio-groups decreased with the conversion. As for FEB−PS, C_{psfc} (%) was lower than that of BFEC−PS, which may be due to that the ferrocenyl group in FEB was located at the R group, while it was located at the Z in BFEC. According to the RAFT polymerization mechanism, most of the polymer chains should be α-terminated with the R group. However, there will inevitably be a small fraction of the polymer chains which are α-end-capped by the moieties from the initiator derivation.[8] Therefore, the C_{psfc} (%) of FEB−PS was lower than that of BFEC−PS.

Alternatively, the investigation of "livingness" of polystyrene obtained by the RAFT polymerization can also be validated from the chain extension reaction using the polystyrene obtained by the RAFT polymerization as the macro-RAFT agent. A typical chain extension reaction was carried out by the addition of fresh styrene to polystyrene with AIBN as the initiator at 80 °C. Figure 4 showed the respective GPC curves of FEB−PS and BFEC−PS before and after the chain extensions. There was an obvious peak shift from the macro-RAFT agent to the chain-extended product. The molecular weight increased from 5600 g/mol (PDI = 1.13) to 10000 g/mol (PDI = 1.30, time = 2.0 h, conversion = 16.2%) for FEB−PS, and from 6600 g/mol (PDI = 1.18) to 10000 g/mol (PDI = 1.28, time = 1.5 h, conversion = 16.2%) for

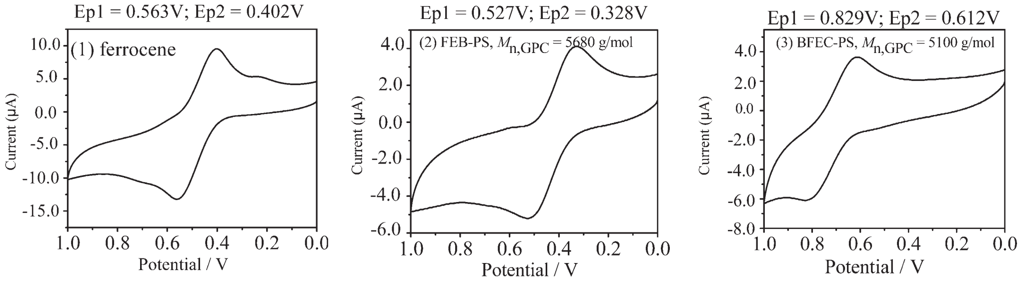


Figure 6. Cyclic voltammogram of ferrocene (1), FEB−PS (2), and BFEC−PS (3) in CH_2Cl_2 solution with concentration of 5 × 10^{-4} mol/L and Et_4NClO_4 (0.1 M) using platinum working electrode and saturated calomel reference electrode at a scan rate of 0.1 V/s. FEB−PS and BFEC−PS refer to the polystyrene obtained from (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization, respectively.

BFEC−PS. Both PDI values of the chain extension products were a little larger than that of the original polymer, which may be caused by a fraction of the dead polymer chains in the original polymer and the side reactions during the chain-extension. It can be concluded from above results that most chains of FEB−PS and BFEC−PS were still "living", and the polymerizations complied with the classical RAFT polymerization mechanism.

Properties of Polystyrene Derived from Ferrocene. In this work, the ferrocenyl moiety was designed and incorporated into the R group or Z group of the RAFT agent. As a result, most of the polymer chains were end-capped by ferrocenyl moieties, which was confirmed by ^{1}H NMR spectra of FEB−PS and BFEC−PS (Figure 3). On the basis of the high sensitivity of the ferrocenyl moiety to ultraviolet (UV) light, UV−vis spectroscopy of ferrocene, FEB−PS and BFEC−PS in CH_2Cl_2 solution were investigated, respectively. It can be noticed from Figure 5(1) that the ferrocene in CH_2Cl_2 solution exhibits three absorption peaks around 230 nm, 325 and 440 nm, respectively. The highest absorption occurred at 230 nm and the lowest absorption occurred at 325 nm. The result was basically consistent with the reference.[37,38] After the ferrocenyl was incorporated into the polymer chain ends, the UV−vis absorptions of FEB−PS and BFEC−PS (Figure 5(2)) showed a red shift from 440 to 475 nm and 560 nm, respectively. Furthermore, it can be found from Figure 5(2) that there was a strong absorption peak around 250 nm for both FEB−PS and BFEC−PS, which was attributed to the absorption peak of benzene ring together with that of ferrocene around 230 nm. Two strong absorptions around 300 and 330 nm in FEB−PS and BFEC−PS, were attributed to the absorption peaks of thiocarbonyl groups together with that of ferrocene around 325 nm.

Figure 5 demonstrated that UV−vis absorption intensity of the BFEC−PS and the FEB−PS were stronger than that of ferrocene and showed a red-shift under the same experimental conditions, especially for BFEC−PS. This was because chain-ends of ferrocenyl moieties in FEB−PS and BFEC−PS were connected with an alkyl group and a thiocarbonyl group, respectively. The interaction between thiocarbonyl group or alkyl group and ferrocene rings induced strong absorption and red-shift under UV−vis radiation. In particular, the strong $\pi-\pi$ conjugation between the thiocarbonyl group and ferrocenyl moiety produced by BFEC−PS resulted in a strong absorption and red shift.

It has been reported that polymers containing the ferrocene exhibit a redox response. The reversible redox activities of FEB−PS and BFEC−PS were estimated by cyclic voltammetry (CV) in CH_2Cl_2 solution. For comparison purpose, the CV of ferrocene (97%) was also measured. The redox peaks and CV data of ferrocene, FEB−PS and BFEC−PS were shown in Figure 6 and Table 1, respectively. The results indicated that the electrochemical behavior of FEB−PS and BFEC−PS were similar to ferrocene. The difference (ΔE_p, $\Delta E_p = E_{p1} - E_{p2}$) between anodic ($E_{p1}$) and cathodic ($E_{p2}$) peak potential of FEB−PS and BFEC−PS increased slightly compared with that of ferrocene (Table 1). The reason may be due to the influence of polymer on the electron-transfer process of the electrode surface. From $E_{1/2}$ ($E_{1/2} = (E_{p1} + E_{p2})/2$) of ferrocene, FEB−PS and BFEC−PS in Table 1, it can be found that $E_{1/2}$ of FEB−PS was a negative shift, and $E_{1/2}$ of BFEC−PS was a large positive shift compared with that of ferrocene, which was due to the different chemical environment of ferrocenyl moiety in FEB−PS and BFEC−PS. The substituent group connected on ferrocenyl ring in FEB−PS was a weak electron-donating alkyl group resulting in the $E_{1/2}$ negative shift, and the substituent group connected on ferrocenyl ring in BFEC−PS was a dithioester group, which was a strong electron-withdrawing group resulting in the large positive shift.

Table 1. Data of Cyclic Voltammograms of Ferrocene, FEB−PS and BFEC−PS Corresponding to those in Figure 6[a]

item	E_{p1} (V)	E_{p2} (V)	ΔE_p (mV)	$E_{1/2}$ (V)
ferrocene	0.563	0.402	161	0.483
FEB−PS	0.527	0.328	199	0.428
BFEC−PS	0.829	0.612	217	0.721

[a] FEB−PS and BFEC−PS refer to the polystyrene obtained from (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization, respectively. E_{p1} (V) and E_{p2} (V) refer to the anodic peak potential and cathodic peak potential, $\Delta Ep = E_{p1} - E_{p2}$, $E_{1/2} = (E_{p1} + E_{p2})/2$.

The effect of molecular weight ($M_{n,GPC}$) of the polymers on CV performance was investigated. Figure 7 and Table 2 showed that the peak currents of FEB−PS and BFEC−PS gradually dropped with the increase of the polymers molecular weight ($M_{n,GPC}$) . Using the peak current of ferrocene as reference, the peak current of FEB−PS dropped from 70% to 30% when the molecular weight ($M_{n,GPC}$) increased from 4420 to 46400. The peak current of BFEC−PS dropped from about 63% to 25% as molecular weight ($M_{n,GPC}$) increased from 4500 to 38950. Factors resulting in a drop of peak current could be as follows: (1) The amount of ferrocene attached to the polymer gradually declined as molecular weight ($M_{n,GPC}$) of the polymer increased. This is caused by growing side reactions in RAFT polymerization as molecular weight ($M_{n,GPC}$) of the polymer increases, such as the reactions between intermediate radicals and other radical species etc. (2) It should be harder for electron transfer to take place on the elctrode as the molecular weight ($M_{n,GPC}$) of the polymer increases. Figure 7 and Table 2 showed that with similar molecular weight ($M_{n,GPC}$), the peak current of BFEC−PS was lower than that of FEB−PS.

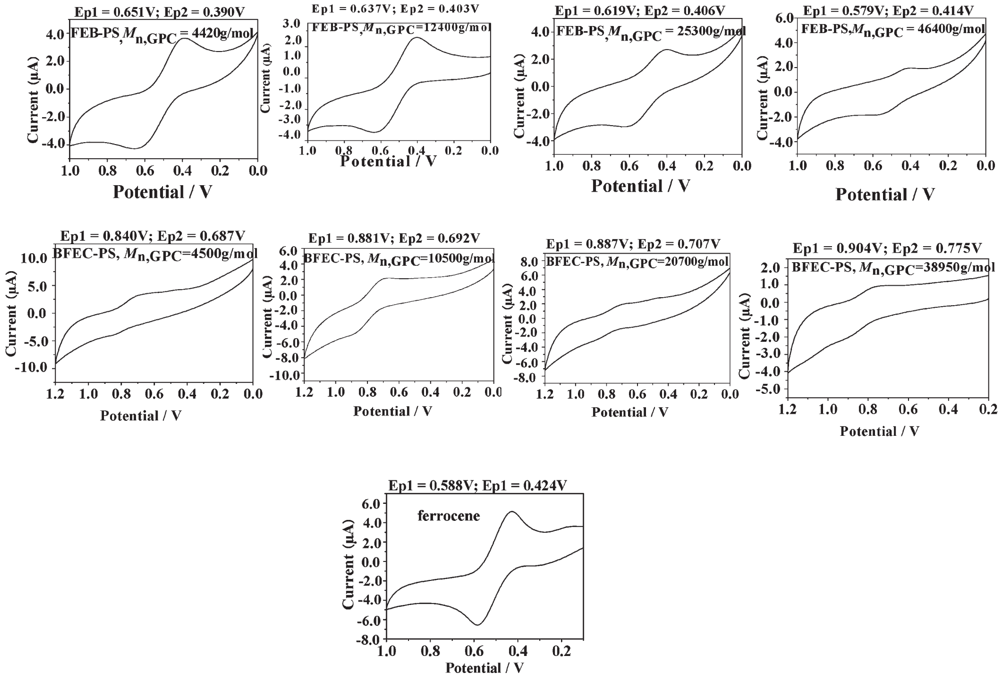


Figure 7. Cyclic voltammogram of ferrocene, FEB−PS and BFEC−PS with different molecular weight ($M_{n,GPC}$) in CH_2Cl_2 solution with concentration of 5×10^{-4} mol/L and $(n\text{-}Bu)_4NClO_4$ (0.1 M) using platinum working electrode and saturated calomel reference electrode at a scan rate of 0.1 V/s. FEB−PS and BFEC−PS refer to the polystyrene obtained from (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization, respectively. $M_{n,GPC}$: number-average molecular weight by gel permeation chromatography (GPC).

Table 2. Peak Current Data of Ferrocene, FEB−PS, and BFEC−PS with Different Molecular Weights Corresponding to Those in Figure 7[a]

item	$M_{n,GPC}$, g/mol	I_{pa} (μA)	I_{pc} (μA)
ferrocene		−5.135	6.546
FEB−PS	4420	−3.672	4.267
	12400	−2.593	3.463
	25300	−2.715	2.954
	46400	−1.951	1.825
BFEC−PS	4500	−3.250	3.897
	10500	−2.144	4.921
	20700	−1.917	3.168
	38950	−0.886	2.060

[a] FEB−PS and BFEC−PS refer to the polystyrene obtained from (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization. I_{pa} and I_{pc} refer to the anodic peak current and cathodic peak current. $M_{n,GPC}$ refers to the number-average molecular weight by gel permeation chromatography (GPC).

This could be due to different chemical environments the ferrocene group was in. The ferrocene group in BFEC−PS is directly bonded to dithioester group which is likely to affect the electron transfer process during redox reaction.

To further prove the reversible redox activities of the polymers end-capped by ferrocenyl moieties, some control experiments were concucted. The cyclic voltammograms of the pure polystyrene obtained at 110 °C with thermal initiation ($M_{n,GPC}$ = 160000 g/mol, PDI = 2.0), and the polystyrene (NDB−PS) obtained using 1-menaphthyl dithiobenzoate (NDB) as RAFT agent (without ferrocene) and AIBN as the initiator ($M_{n,GPC}$ = 6400 g/mol, PDI = 1.12), respectively. The results showed that both pure polystyrene and NDB−PS had no redox response under the similar CV measurement conditions (refer to the Supporting Information).

Investigation of the Stability of Polystyrene. Dithiobenzoate usually shows a yellow or red color. The FEB synthesized in this work was orange-yellow, and BFEC was blue-violet. The color of BFEC was deepened due to the conjugation between dithioester group and ferrocenyl ring. In the polymer, the thiocarbonyl group and R group of FEB or BFEC connected to α and ω chain-ends, respectively. Thus, colorful polymers can be obtained. The colors of ferrocene, FEB−PS and BFEC−PS in CH_2Cl_2 solution with concentration of 2×10^{-4} mol/L were shown in Figure 8.

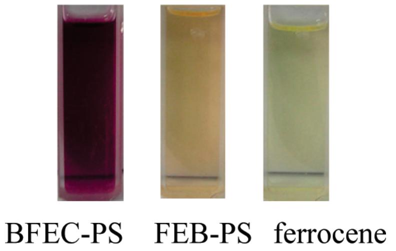


Figure 8. Colors of ferrocene, FEB−PS, and BFEC−PS in CH_2Cl_2 solution with a concentration of 2×10^{-4} mol/L. FEB−PS and BFEC−PS refer to the polystyrene obtained from (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization, respectively.

Generally, a compound with thiocarbonyl-thio group is of less stability, such as being easily hydrolyzed, oxidized, etc. Effects of common organic solvents, such as tetrahydrofuran (THF), $CHCl_3$, acetone, *N*,*N*-dimethylformamide (DMF), and CH_2Cl_2, on the stability of BFEC−PS and FEB−PS were also investigated in this work. The results showed that FEB−PS had better stability than BFEC−PS, e.g., FEB−PS was little affected but BFEC−PS was affected at different degree by some organic solvents. The stability was in the order of CH_2Cl_2 > THF > acetone > $CHCl_3$ > DMF. After the BFEC−PS solution in CH_2Cl_2 with the concentration of 2×10^{-4} mol·L^{-1} was placed for 1 month, the color was almost invariant. However, under the same condition, the color of DMF solution rapidly changed into yellow,

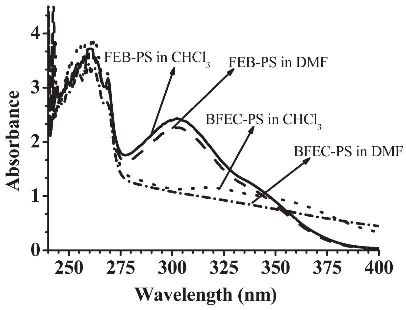


Figure 9. UV−vis spectra of BFEC−PS, FEB−PS in N,N-dimethylformamide (DMF) and stored in $CHCl_3$ for 48 h, at room temperature, respectively. All concentrations were 2×10^{-4} mol/L. FEB−PS and BFEC−PS refer to the polystyrene obtained from (ferrocene-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization, respectively.

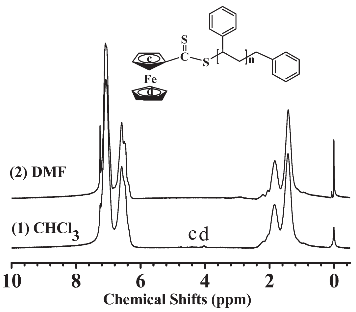


Figure 10. ^1H NMR spectra of BFEC−PS in *N,N*-dimethylformamide (DMF) and after being stored in $CHCl_3$ for 48 h at room temperature, respectively: (1) after being stored in $CHCl_3$ for 48 h; (2) in DMF. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) as internal standard. BFEC−PS refers to the polystyrene obtained from benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization.

which was similar to that of ferrocene. After the polymer solution in $CHCl_3$ was placed for 48 h, the color gradually changed into yellow. The change of the color showed that thiocarbonylthio group had been detached from the polymer chain-end, which had been further confirmed by ^1H NMR spectra and UV−vis spectra, shown in Figure 9 and Figure 10, respectively.

It can be seen from Figure 9 that after BFEC−PS dissolved in DMF or stored in $CHCl_3$ for 48 h at room temperature, the strong absorption peak around 320 nm arising from the thiocarbonyl group had disappeared. However, the absorption profile of FEB−PS treated by DMF or $CHCl_3$ was basically the same as that of the original FEB−PS. The ^1H NMR spectra shown in Figure 10 confirmed that the signals at about $\delta = 4.5-4.7$ ppm and 3.8−4.2 ppm, corresponding to the proton of ferrocenyl group of BFEC−PS, became extremely weak after dissolving in $CHCl_3$ for 48 h, and indecipherable after dissolving in DMF. The difference of the stability between BFEC−PS and FEB−PS in above solvents was caused by whether the thiocarbonyl group was connected with ferrocenyl moiety or not. In the case of the solution of BFEC−PS in $CHCl_3$, the charge-transfer complex between ferrocene (as donor) and $CHCl_3$ (as acceptor) can be obtained,[39] which prompted the detachment of thiocarbonyl−thio group from chain-ends of BFEC−PS. Mallik et al. had found that after photoexcitation of ferrocene-doped PMMA film containing $CHCl_3$ molecules, appeared the characteristic absorption band of ferricenium cation (FcH^+) dissociated by charge-transfer complex.[41] Actually, it was also found in our work, that the hydrolysis of BFEC−PS was more sensitive to acid than base, which may be related to the formation of ferricenium cation (FcH^+) under acidic condition. As for the DMF solution of BFEC−PS, the detachment of thiocarbonyl group at chain-ends of polymer may be caused by interaction between active aldehyde group in DMF and ferrocenyl moieties in BFEC−PS.

Conclusions

In this article, two new RAFT agents, (ferrocen-1-yl)ethyl benzodithioate (FEB) and benzyl ferrocenecarbodithioxylate (BFEC) were successfully synthesized. The results proved that FEB and BFEC are two effective reversible addition−fragmentation chain transfer (RAFT) agents for the polymerization of styrene. FEB−PS and BFEC−PS obtained by ((ferrocen-1-yl) ethyl benzodithioate (FEB)) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization had similar electrochemical behavior as ferrocene. $E_{1/2}$ ($E_{1/2} = (E_{p1} + E_{p2})/2$) of FEB−PS was a negative shift, and $E_{1/2}$ of BFEC−PS was a large positive shift compared with that of ferrocene. The peak currents of FEB−PS and BFEC−PS gradually dropped with the increase of molecular weight ($M_{n,GPC}$) of the polymers. FEB−PS had better stability in the common organic solvent than that of BFEC−PS.

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Supporting Information Available: Text discussing and figures showing the MALDI−TOF mass spectrometry of FEB−PS and BFEC−PS obtained by ((ferrocen-1-yl)ethyl benzodithioate (FEB)) and benzyl ferrocenecarbodithioxylate (BFEC) mediated polymerization and cyclic voltammograms of control samples in CH_2Cl_2 solution [(1) ferrocene, pure-PS and sample mixed homo-PS with ferrocene and (2) ferrocene, NDB−PS and sample mixed NDB−PS with ferrocene], where pure-PS refers to the polystyrene obtained at 110 °C with thermal initiation and NDB−PS refers to the polystyrene obtained using 1-menaphthyl dithiobenzoate (NDB) as RAFT agent and AIBN as the initiator. This material is available free of charge via the Internet at http://pubs.acs.org.

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