

Ferrocene-containing Polymers Synthesized by Acyclic Diene Metathesis (ADMET) Polymerization*

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Abstract Herein we reported that ferrocene-containing polymers could be synthesized *via* acyclic diene metathesis (ADMET) polymerization of ferrocene-containing bis-styryl monomers. The all-*trans*-configured vinylene bonds of stilbene segment were proven by means of ¹³C-NMR, ¹H-NMR, MALDI-TOF mass spectrometry and FTIR. Poly(**1**) showed maxima for absorption at 320 nm and emission at 430 nm which are structurally very similar to *trans*-stilbene, but 24 and 16 nm red shifted respectively. CIE chromaticity diagram shows that emission color could be adjusted by controlling the molecular weight. The polymer showed excellent solubility in common organic solvents and good thermal stability evidenced by TGA and DSC. The results of CV suggested the polymer possessed noninteracting metal centers which was confirmed by a reversible one-electron redox wave observed for the polymer.

Keywords: Ferrocene; Polymers; Acyclic diene metathesis polymerization (ADMET).

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INTRODUCTION

Transition metal containing polymers have received much attention because of their novel physical properties and have emerged applications in magnetic, electronic, optical and catalytic properties^[1–19]. The incorporation of transition metals into polymers can lead to processable materials such as fibers, ceramic films and coatings in addition to significant enhancement of the electronic properties of the polymers themselves^[1–19]. Poly(ferrocene)s represent one of the most important transition metal-containing polymers^[7–23]. The first polymerization of ferrocene-based derivatives were reported by Arimoto and Haven in 1955 which was prepared by the radical-initiated polymerization of vinyl ferrocene (Fig. 1)^[20]. Common main-chain poly(ferrocene)s which are typically prepared using ring-opening polymerization (ROP) of bridged (and often strained) metallocenes were discovered by Brandt and Rauchfuss^[21] and subsequently systematically developed by Manners and other researchers^[22–39]. Ring-opening metathesis polymerization (ROMP) of ferrocenophanes was the another method to prepare the main-chain poly(ferrocene)s-containing polymers. For example, Tilley^[40], Grubbs^[41], Lee^[42, 43], Manners^[44] and co-workers have used ROMP of ferrocenophanes bridged by unsaturated alkyl chains such as ethylene and butadiene to obtain highly conjugated poly(ferrocene)s. However, main-chain poly(ferrocene)s-containing polymers has been rarely reported by researchers using acyclic diene metathesis

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(ADMET)^[45–48] polymerization method in particular. Up to now, only two reports dealing with the ADMET polymerization of main-chain poly(ferrocene)s-containing polymers have been published (Fig. 2)^[49, 50]. Boncella^[49] and coworker reported that the metathesis of 1,1'-divinylferrocene gave oligomers with an average of four repeating units and a trans/cis ratio of 2:5. Recently, Plenio's^[50] group demonstrated that polymerization of monomer 1,1'-di(4-vinylphenyl)-3,3',4,4'-tetramethylferrocene by using ADMET technology was not succeeded. On the other hand, macromolecules featuring alternating conjugated aromatic segments in the backbone are of fundamental interest in both academic and industrial research^[51–60]. They often represent valuable candidates as electronic or photonic materials in advanced applications. Recently, Peetz^[61] and coworker demonstrated that silylene functionalized conjugated polymers can be accessed *via* ADMET. In addition, polycarbosilane containing conjugated segments was reported by Interrante^[62–64] and coworkers using ADMET technology. Li and Nomura have also synthesized the electroactive and photoreactive polymers through ADMET polymerization^[65–68]. In the present work, we report the synthesis of ferrocene-containing polymers by ADMET and characterization of the resulting polymers. The properties of these materials were further investigated.

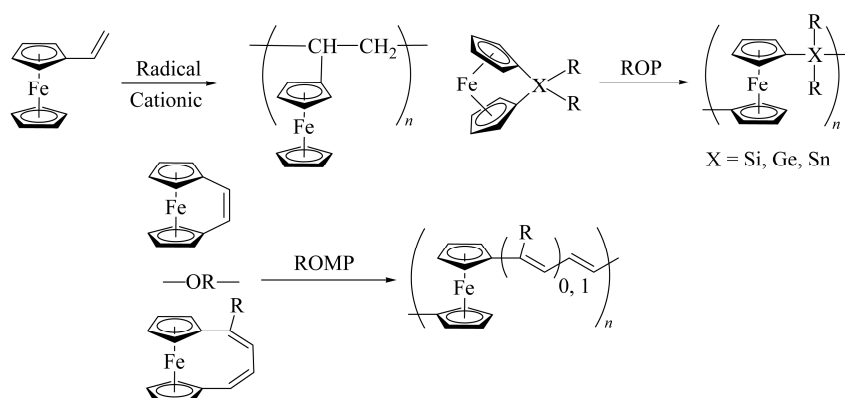


Fig. 1 General polymerization method for synthesizing poly(ferrocene)s

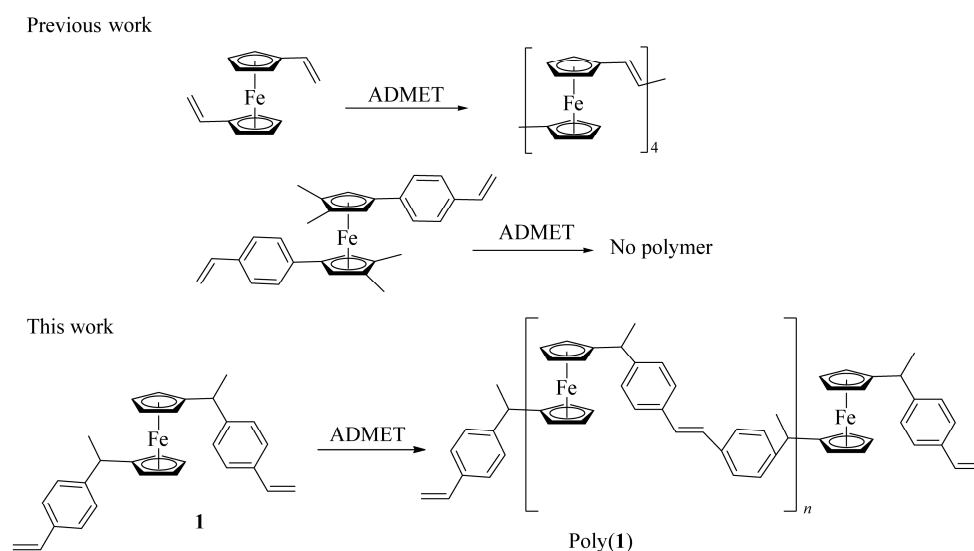


Fig. 2 Ferrocene-containing polymers synthesized by acyclic diene metathesis (ADMET) polymerization

EXPERIMENTAL

All experiments were carried out under a nitrogen atmosphere in a drybox and conventional Schlenk line techniques unless otherwise specified. All ether and hydrocarbon solvents were distilled before use from their purple sodium/ benzophenone solutions. All the chemicals were purchased from Aldrich Chemical Co., and the Grubbs type catalysts were prepared according to the literature. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker 500 spectrometer (499.65 MHz, ^1H). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are referenced to Me_4Si . ^{13}C -NMR spectra for monomer and polymers were recorded on a Bruker 500 spectrometer (125.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 s, the acquisition time was 0.8 sec, the pulse angle was 90° , and the number of transients accumulated was ~ 6000 . The polymer samples for analysis were prepared by dissolving the polymers in CDCl_3 solution, and the spectra were measured at 25°C . GPC analysis was carried out on a Waters 2545. Number- (M_n) and weight- (M_w) averaged molecular weights and polydispersity indices (M_w/M_n) of the polymers were estimated by a Waters 2545 instrument equipped with four Waters Styragel HR columns, *i.e.* HR-1, HR-3, HR-4, and HR-5E. HPLC grade THF was used as eluent at a flow rate of 1.0 mL/min at 40°C . A set of linear polystyrenes was used for the molecular weight calibration. Measurements are relative to a calibration with polystyrene standards and third order relative calibration curve was used to measure the molecular weight of unknown samples. IR spectra were recorded on a Nicolet nexus 670 FTIR spectrophotometer. UV spectra were measured on an FLS 920 spectrophotometer. Thermogravimetric analysis (TGA) measurements were carried out under nitrogen on a Perkin-Elmer TGA 7 analyzer at a heating rate of 20 K/min. DSC measurements were performed on a Mettler-Toledo S1 at a scan rate of 10 K/min under a nitrogen atmosphere. Cyclic voltammetry (CV) analyses were recorded on a autolab-pgstat (model 302). All the measurements were carried out at room temperature using a conventional three-electrode configuration, and Bu_4NPF_6 (0.1 mol/L) was used as supporting electrode. The working and reference electrodes were glassy carbon and Ag/AgNO_3 (0.1 mol/L in acetonitrile), respectively. The reference electrode was checked versus ferrocene as recommended by IUPAC. All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to electrochemical measurements. The samples for electron microscopy were prepared by drop casting 1 drop of suspension of the sample onto a carbon coated copper grid which was placed on a piece of filter paper to remove excess solvent. Bright field transmission electron micrographs were obtained both on JEOL1200EX TEM Mk1 and Mk2 microscopes operating at 120 kV.

Procedure for the Synthesis of Monomer

A reaction tube was charged with potassium carbonate (2.1 g, 15.2 mmol), 4-vinylbenzylboronic acid (2.2 g, 14.9 mmol), ferrocenyltosylhydrazone (1.5 g, 2.5 mmol) and dioxane (30 mL). The system was heated at 110°C with stirring and reflux. When the reaction was completed after 20 h, the crude reaction mixture was allowed to reach room temperature, the solvent was eliminated under vacuum pump, and a saturated solution of NaHCO_3 and dichloromethane were added and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with two portions of a saturated solution of NaHCO_3 , then dried over MgSO_4 and filtered. Solvent was removed under reduced pressure. Product was purified by chromatography on neutral Al_2O_3 .

Monomer **1**: yellow oil, 0.54 g (50% yield); R_f (petroleum ether/ethyl acetate 25:1) = 0.58. ^1H -NMR (500 MHz, CDCl_3) δ 7.29 (d, J = 8.0 Hz, 4H), 7.14 – 6.96 (m, 4H), 6.78 – 6.55 (m, 2H), 5.67 (d, J = 17.5 Hz, 2H), 5.17 (d, J = 11.0 Hz, 2H), 4.13 (d, J = 16.5 Hz, 2H), 4.03 (d, J = 17.5 Hz, 4H), 3.90 (d, J = 17.5 Hz, 2H), 3.77 (dq, J = 30.5, 7.0 Hz, 2H), 1.53 (dd, J = 7.0, 4.5 Hz, 6H). ^{13}C -NMR (126 MHz, CDCl_3) δ 147.3, 147.3, 136.7, 135.4, 127.4, 127.3, 126.2, 113.1, 94.2, 68.9, 68.7, 68.6, 67.9, 67.8, 67.0, 66.6, 39.5, 39.5, 22.7, 22.6. HRMS (ESI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{30}\text{H}_{30}\text{Fe}$ 446.1697; Found: 446.1732.

Procedure for the Synthesis of Homopolymer and Copolymer

A 100 mL reaction tube was charged with monomer **1** (0.1g, 0.22 mmol, 0.22 mol/L) and 1 mL toluene in

glovebox. The catalyst solution of Grubbs 2nd catalyst (1.9 mg, 2.2 μ mol, 100 μ L, 0.02 mol/L) was injected into the reaction tube. The reaction took place under vacuum and 80 °C. After 12 h, the polymerization was quenched by adding ethyl vinyl ether in excess amount. The reaction mixture was then stirred for 1 h for completion. 100 mL methanol was added into the reaction solution to end the reaction. The yellow solid polymer was collected by filtration and was then dried in vacuo.

Poly(**1**): yellow solids, 47.0 mg (64% yield); ¹H-NMR (500 MHz, CDCl₃) δ 7.37 (d, J = 7.5 Hz, 4H), 7.11 (d, J = 7.5 Hz, 4H), 7.00 (s, 2H), 4.15 (d, J = 16.5 Hz, 2H), 4.05 (d, J = 15.5 Hz, 4H), 3.92 (d, J = 18.0 Hz, 2H), 3.80 (dq, J = 29.0, 7.0 Hz, 2H), 1.55 (m, 6H). ¹³C-NMR (126 MHz, CDCl₃) δ 147.0, 135.4, 127.9, 127.5, 126.4, 94.3, 68.9, 68.6, 67.9, 67.8, 67.0, 66.7, 39.6, 22.7, 22.6.

A 100 mL reaction tube was charged with monomer **1** (0.1g, 0.22 mmol, 0.22 mol/L), *cis*-cyclooctene (0.25g, 0.22 mmol, 0.22 mol/L) and 1 mL toluene in Glovebox. The catalyst solution of Grubbs 2nd catalyst (1.9 mg, 2.2 μ mol, 100 μ L, 0.02 mol/L) was injected into the reaction tube. The reaction took place under vacuum and 80 °C. After 12 h, the polymerization was quenched by adding ethyl vinyl ether in excess amount. The reaction mixture was then stirred for 1 h for completion. 100 mL methanol was added into the reaction solution to end the reaction. The sticky yellow polymer was collected by filtration and was then dried in vacuo.

Copolymer (feed ratio of **1** with COE = 1/1): sticky yellow polymer, 68.2 mg (62% yield); ¹H-NMR (500 MHz, CDCl₃) δ 7.37 (d, J = 7.6 Hz, 4H), 7.22 (d, J = 7.7 Hz, 3H), 7.11 (d, J = 7.5 Hz, 4H), 7.06 (d, J = 7.6 Hz, 3H), 7.00 (s, 2H), 6.32 (d, J = 15.6 Hz, 2H), 6.25–5.89 (m, 2H), 5.38 (s, 2H), 4.15 (d, J = 15.6 Hz, 5H), 4.04 (d, J = 12.8 Hz, 8H), 3.91 (d, J = 13.2 Hz, 4H), 3.78 (dd, J = 19.8, 11.2 Hz, 4H), 2.17 (d, J = 6.7 Hz, 4H), 1.98 (d, J = 21.7 Hz, 4H), 1.61–1.47 (m, 13H), 1.43 (s, 4H), 1.29 (d, J = 23.2 Hz, 12H). ¹³C-NMR (126 MHz, CDCl₃) δ 147.0, 146.2, 135.8, 135.3, 130.4, 129.6, 129.1, 128.9, 128.3, 128.1, 127.9, 127.5, 127.3, 126.4, 125.8, 125.4, 94.4, 94.3, 68.9, 68.6, 67.8, 67.0, 66.6, 39.5, 39.4, 33.1, 32.6, 29.7, 29.4, 29.1, 22.7, 22.6, 22.6.

RESULTS AND DISCUSSION

Acyclic Diene Metathesis (ADMET) Polymerization of Ferrocene Containing Bis-styryl Monomer **1** Using Various Grubbs-type Catalysts

The monomer **1** was synthesized by the route outlined in Fig. 3. Acetylferrocene was prepared by typical procedure of Friedel-Crafts acetylation of ferrocene^[69]. Then, the ferrocenyl carbonyl compound was added to the solution of tosylhydrazine to form the ferrocenyl methyl ketone-derived tosylhydrazones. In the second step, efficient coupling reaction between ferrocenyl methyl ketone-derived tosylhydrazones and boronic acids was used to prepare the corresponding ferrocene containing bis-styryl monomer **1** according to the established method^[70]. Typical yields after purification were 50%. The monomer **1** was fully characterized by ¹H-NMR,

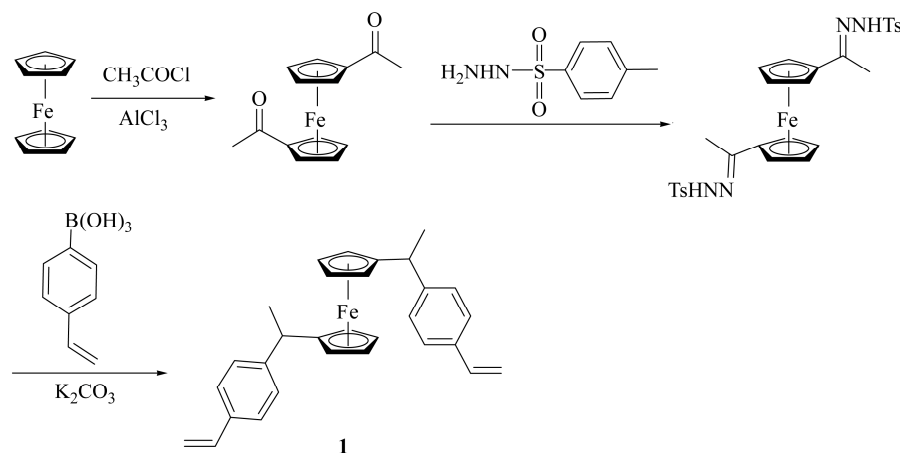
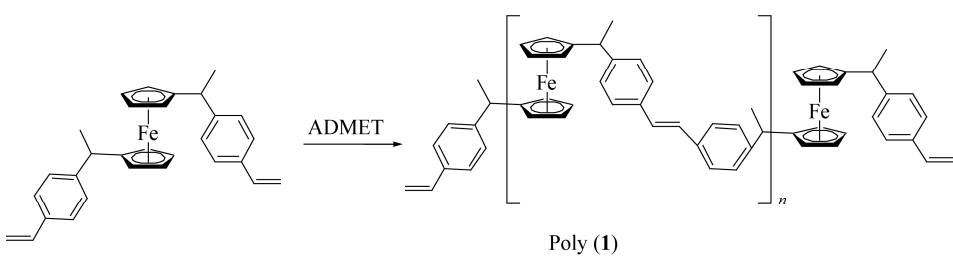


Fig. 3 Synthetic route for ferrocene-containing bis-styryl monomer **1**

^{13}C -NMR and HRMS. The synthetic scheme for poly(**1**) is shown in Fig. 2. Representative results of these polycondensations are summarized in Table 1. For the preliminary study, we intended to synthesize poly(**1**) by using the Grubbs 1st generation catalyst (Table 1, entry 1), but we did not obtain the desired product. Successful ADMET of monomer **1** was carried out in the presence of Grubbs 2nd, Grubbs 3rd generation catalyst and Hoveyda-Grubbs 2nd generation catalyst in neat at 40 °C for 12 h under intermittent vacuum (Table 1, entries 2–4). It can be seen that the Grubbs 2nd generation catalyst and Hoveyda-Grubbs 2nd generation catalyst give higher yield with high molecular weight under the same condition. In order to find the optimal conditions, a small screening of temperature and several solvents were performed for acyclic diene metathesis (ADMET) of ferrocene-containing bis-styryl monomer **1** (Table 1, entries 5–15). Finally, it was concluded that under the following reaction conditions the highest molecular weight poly(**1**) could be obtained in good yield which were similar to previously report^[49, 50]: Grubbs 2nd generation catalyst as catalyst in 1,2-dichlorobenzene at 80 °C for 12 h (Table 1, entries 15).

Table 1. ADMET of monomer **1** by using Grubbs-type catalyst ^a



Entry	Catalyst	Solvent (mL)	<i>T</i> (°C)	<i>M_n</i> ^b	<i>M_n</i> ^c	<i>M_w</i> / <i>M_n</i> ^c	Yield ^d (%)
1	G1	CH ₂ Cl ₂ (0.3)	40	—	—	—	—
2	G2	CH ₂ Cl ₂ (0.3)	40	—	3400	1.40	63
3	G3	CH ₂ Cl ₂ (0.3)	40	—	1970	1.11	31
4	H-G2	CH ₂ Cl ₂ (0.3)	40	—	3400	1.50	59
5	G2	CH ₂ Cl ₂ (3)	40	—	2400	1.19	62
6	G2	THF(3)	40	2100	2300	1.17	53
7	G2	Toluene(3)	40	2500	2700	1.26	55
8	G2	Toluene(3)	60	—	4200	1.56	64
9	G2	Toluene(3)	80	4600	4700	1.73	70
10	H-G2	Toluene(3)	80	—	4200	1.47	68
11	Ind 2	Toluene(3)	80	—	4400	1.63	61
12	G2	Toluene(1)	80	—	4800	1.56	54
13	H-G2	Toluene(1)	100	—	4600	1.61	58
14	G2	DCB(3)	80	—	4100	1.68	64
15	G2	DCB(1)	80	5000	5100	1.92	47

^a Conditions: Initial monomer concentration is 67 μmol/mL, molar ratio of monomer/catalyst = 100:1; G1 = Ru(CHPh)(Cl)₂(PCy₃)(PCy₃); G2 = Ru(CHPh)(Cl)₂(IMesH₂)(PCy₃), IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene; G3 = Ru(CHPh)(Cl)₂(IMesH₂)(C₅H₄N)₂; H-G2 = Ru(2-*i*-PrO-CHPh)(Cl)₂(IMesH₂); Ind 2 = Ru(3-phenyl-1H-inden-1-ylidene)(Cl)₂(IMesH₂)(PCy₃); ^b Molecular weight estimated by ¹H-NMR; ^c GPC data in THF versus polystyrene standards; ^d Isolated yields

The structure of both the monomer and the polymer was determined by ¹H- and ¹³C-NMR spectroscopy as shown in Fig. 4. Two doublets at δ = 5.18 (*cis*, **H_a**, *J* = 11 Hz) and 5.68 (*trans*, **H_b**, *J* = 18 Hz) were assigned to the proton resonances from the terminal vinyl group (—CH_c=CH₂) of the monomer respectively. A doublet of doublets at δ = 6.70 was assigned to the —CH_c=CH₂, (*J* = 11 Hz) proton resonance from the terminal vinyl group (—CH_c=CH₂) of the monomer. The resonances from the aromatic protons (**H_d** and **H_e**) are centered around δ = 7.25 as two doublets. The chemical shifts of the Cp ring protons are observed around δ = 3.89–4.16. After the formation of poly(**1**) by ADMET, the resonances from the terminal vinyl groups in monomer **1** disappeared. The new internal *trans*-vinylene protons (—CH_{a'}=CH_{a'}—) appear as a new singlet resonance at

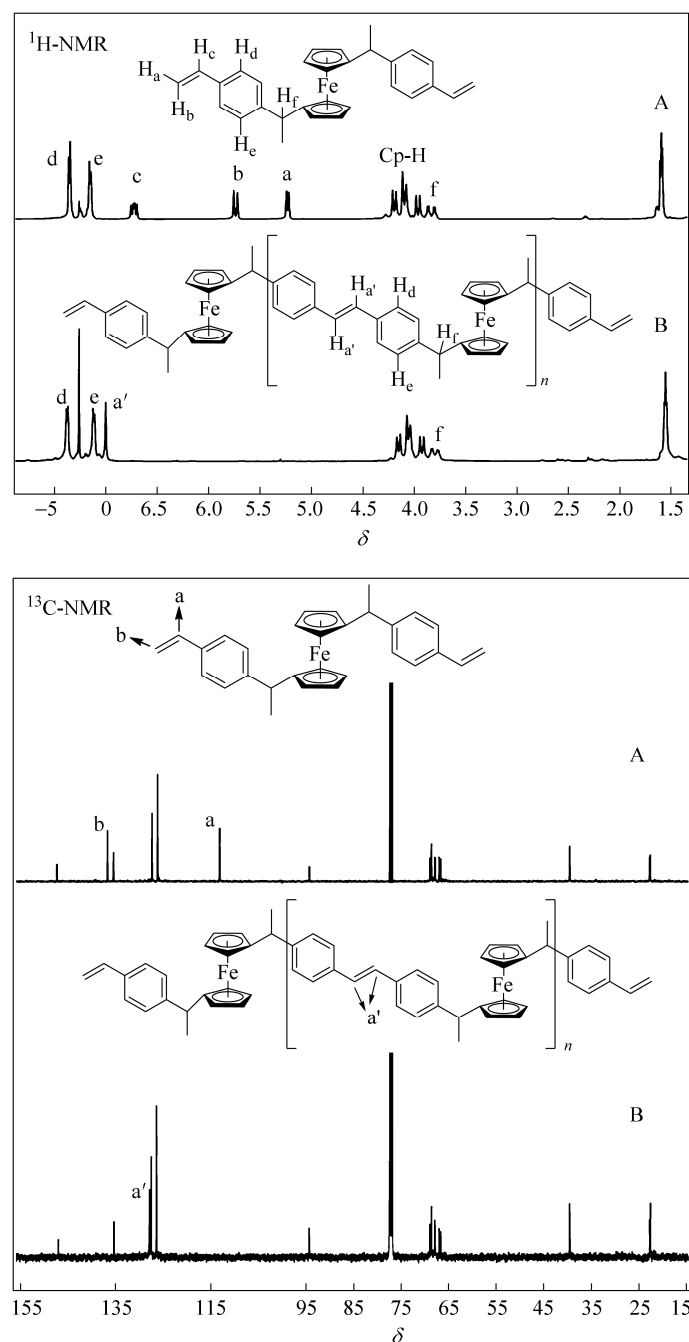


Fig. 4 ^1H -NMR (500 MHz, CDCl_3) and ^{13}C -NMR (125 MHz, CDCl_3) spectra of (A) monomer **1**, (B) Poly(**1**) ($M_n = 2300$, PDI = 1.17, Table 1, run 6)

$\delta = 7.00$. No resonances for a *cis*-configured double bond were observed. The aromatic protons appear as a resonance at $\delta = 7.11$ and 7.38. The down field shift of the aromatic protons in poly(**1**) relative to monomer **1** might be due to the extended electron conjugation in the larger aromatic segments of the polymer compared to the monomer. Moreover, after ADMET, the carbon resonances of the terminal vinyl group ($-\text{C}_a\text{H}=\text{C}_b\text{H}_2$) at $\delta = 113.1$ and 136.7 disappeared and a new resonance around $\delta = 129.2$ was observed, corresponding to the internal vinylenic carbons ($-\text{C}_a\text{H}=\text{C}_a\text{H}-$). FTIR spectroscopy showed the distinct differences between

monomer **1** and poly(**1**). Figure S2 illustrates this for a select region of the FTIR spectra of monomer **1** and poly(**1**). The most characteristic change observed in the bending at 998 and 908 cm^{-1} in the monomers of C=C stretching disappeared after ADMET reaction and a new signal appeared at 966 cm^{-1} , strongly indicating *oop* bending of the newly formed internal *trans*-vinylene bond. Analysis of the resulting polymer by matrix-assisted laser desorption time of flight (MALDI-TOF MS) (Fig. 5) revealed ions corresponding to the different oligomers with n values between 2 and 12 repetitive individual monomer units which are highly in good agreement with the data of GPC, ^1H -NMR and the calculated. (Figs. S3, S4 and S5). Based on the above results, we can conclude that exclusively *trans* configured vinylene bonds of stilbene were formed by acyclic diene metathesis (ADMET) polymerization of monomer **1**.

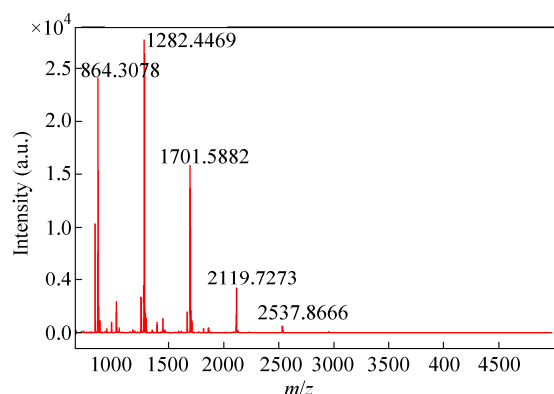


Fig. 5 MALDI-TOF spectrum of selected poly(**1**) ($M_n = 2700$, PDI = 1.26, Table 1, run 7)

Optical Characterization (Solution)

UV/Vis absorption and emission spectra of dichloromethane solutions of monomer **1**, poly(**1**), and *trans*-stilbene are shown in Figs. 6(a) and 6(b). As expected, the absorptions of all poly(**1**)s are red-shifted compared to that of the monomer **1**. Monomer **1** and poly(**1**) show maxima for absorption at 256 nm and 320 nm and emission at 350 nm and 430 nm respectively. The red shift of the poly(**1**) relative to monomer **1** is expected and due to the extended conjugation. The absorption spectrum of poly(**1**) features two major components with maxima at 230 nm and 320 nm. Absorption and emission of poly(**1**) with different molecular weight are structurally very similar to *trans*-stilbene, but 24 and 80 nm red shifted respectively. Figure 6(c) shows the CIE chromaticity diagram of the poly(**1**) with different molecular weight under 390 nm excitation. It can be seen that poly(**1**) with different molecular weight ($M_n = 2400, 4100$ and 5100) leads to chromaticity coordinates of (0.179, 0.193), (0.184, 0.201) and (0.194, 0.231), respectively. Moreover, the emission color varies from blue to green with increasing the molecular weight, which may indicate that the emission color could be adjusted by controlling the molecular weight.

Thermal and Electrochemical Properties

The thermal characteristics of the polymers were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Thermogravimetric analysis was performed under inert atmosphere (N_2) with a heating rate of 10 K/min. The trend of thermal decomposition behavior of the different molecular weight polymers is similar. The polymer showed good stability up to $\sim 444^\circ\text{C}$ under nitrogen, indicative of their strong resistance to thermolysis. However it starts degrading rapidly above that temperature (Fig. 7). In the case of poly(**1**)₅₁₁₃, the average repeat unit weight is 418 g/mol. The rapid degradation of the polymeric backbone started at 444°C resulted in a weight loss of 57% that corresponds to the fragmentation of ferrocene moiety (Fc group) whose exact mass is 186 g/mol. Moreover, TGA analysis of poly(**1**) showed no appreciable weight loss up to $\sim 566^\circ\text{C}$, with a significantly higher char yield ($\sim 81\%$) on pyrolysis to 1000°C in air as compared to the char yield under N_2 ($\sim 57\%$) (Fig. 7). Furthermore, it can be seen that a slowly degradation was observed even after heating to 1000°C under nitrogen atmosphere. Poly(**1**) shows a glass transition temperature (T_g) of 104°C . However, we were not able to observe a clear T_m . (Fig. S6)

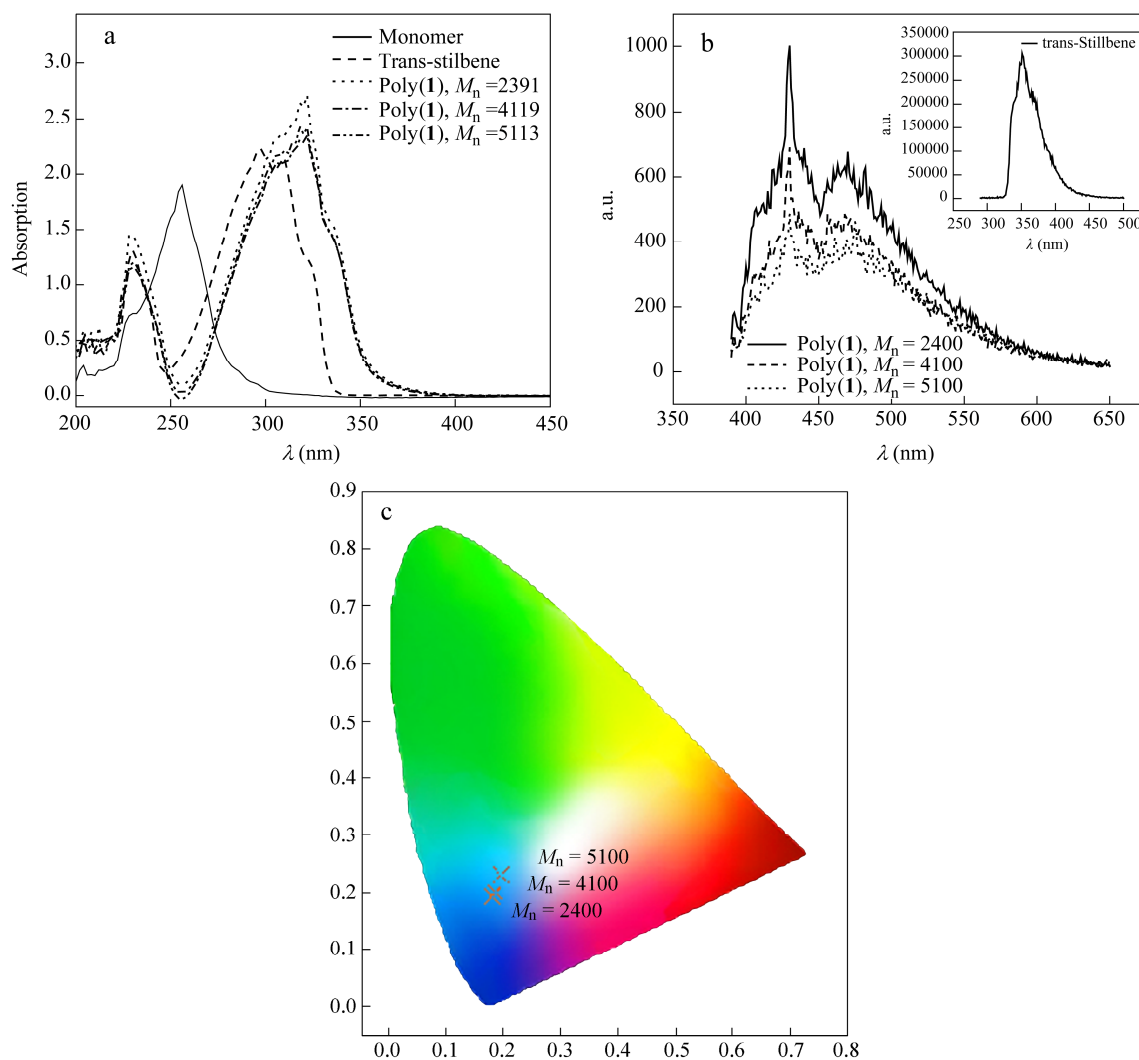


Fig. 6 (a) Comparison of absorption spectra of monomer **1**, *trans*-stilbene and poly(**1**)s in CH_2Cl_2 ; (b) Comparison of emission spectra of monomer **1**, *trans*-stilbene and poly(**1**)s in CH_2Cl_2 ; (c) CIE chromaticity diagram for poly(**1**) with different molecular weight $\{([\text{Poly}(\mathbf{1})] = [\text{monomer } \mathbf{1}] = [\text{trans-stilbene}] = 6.0 \times 10^{-6} \text{ mol/L})\}$

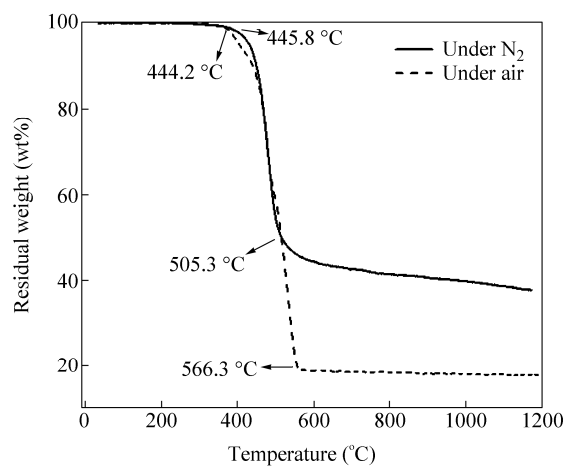


Fig. 7 TGA curves for poly(**1**) ($M_n = 5100$) under N_2 and air

The electrochemical properties of monomer **1** and poly(**1**) were probed using CV. The voltammogram obtained in a CH₂Cl₂ solution of monomer **1** at a scan rate of 100 mV/s showed a reversible one-electron redox wave with a half-wave potential, $E_{1/2}$, of + 0.35 V versus the ferrocene/ferrocenium ion couple with $i_{\text{red}}/i_{\text{ox}} = 0.99$. The cyclic voltammogram of poly(**1**) acquired under identical conditions showed a half-wave $E_{1/2}$ value of +0.33 V versus ferrocene/ferrocenium couple (Fig. 8). These values along with a reversible one-electron redox wave suggest that the polymer chain of poly(**1**) possesses noninteracting metal centers. Sample preparation for TEM imaging of polymer **1** consisted of dissolution in toluene and addition of methanol until precipitation occurred. The TEM images obtained showed homopolymer arranged as ball structures with a typical width of about 300 nm (see Fig. S7).

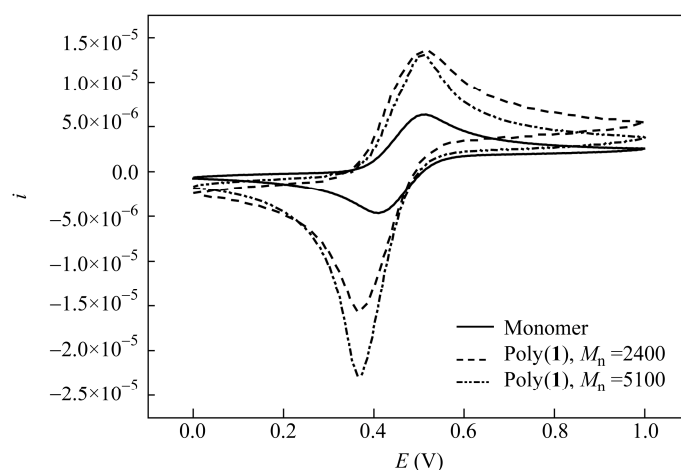
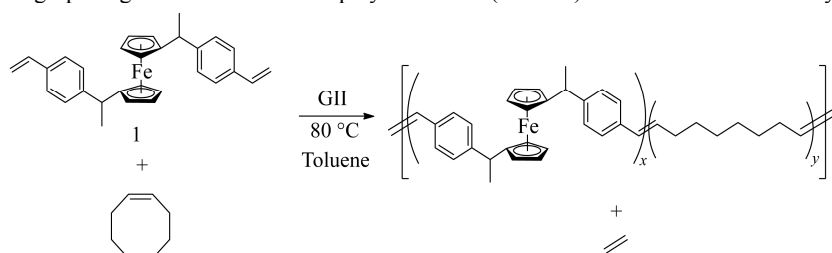


Fig. 8 Cyclic voltammograms of CH₂Cl₂ solutions of monomer **1** and poly(**1**) referenced to Fe(C₅H₅)₂/Fe(C₅H₅)₂⁺ (scan rate = 100 mV/s; 0.1 mol/L [*n*Bu₄N][PF₆], 1 mmol/L analyte)

In order to obtain relative high molecular weight polymers containing ferrocene group in the main chain, we carry out the ring-opening-insertion-metathesis polymerization (ROIMP)^[71] of *cis*-cyclooctene with monomer **1** under optimal condition. The results were summarized in Table 2. Notably, multiblock copolymers were obtained which was confirmed by ¹H-NMR and ¹³C-NMR (see Figs. S8 and S9). It can be seen that the ratio of incorporation of ferrocene group could be adjusted by simple variation of monomer feed ratio.

Table 2. Ring-opening-insertion-metathesis polymerization (ROIMP) of monomer **1** with *cis*-cyclooctene ^a



Entry	1 /COE ^b	Yield ^d (%)	M_n ^c (Da)	M_w ^c (Da)	PDI ^c	x ^e	y ^e
1	3:1	72	4000	5500	1.37	8	1
2	2:1	73	4900	7200	1.46	6	1
3	1:1	76	5100	8000	1.56	2	2
4	1:3	70	5600	9500	1.70	2	4
5	1:5	65	6100	10600	1.73	2	6

^a Conditions: toluene as solvent (1.0 mL), 80 °C, 1 mol% G2, G2 = Ru(CHPh)(Cl)₂(IMesH₂) (PCy₃), IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene, 12 h; ^b Monomer **1** to COE ratio; ^c GPC data in THF versus polystyrene standards;

^d Isolated yields; ^e Determined by ¹H-NMR

CONCLUSIONS

In summary, ferrocene-functional polymers could be prepared *via* ADMET polymerization of ferrocenyl-containing bis-styryl monomers. The microstructure of polymer was determined by means of ^{13}C -NMR, ^1H -NMR, FTIR and MALDI-TOF MS. These results clearly showed the organic conjugated segment formed was stilbene with only *trans*-configured vinylene bonds. Photophysical characterization of the products showed 24 and 16 nm red shifts respectively. CIE chromaticity diagram showed that emission color could be adjusted by controlling the molecular weight. Future work will target the design of precisely controlled block copolymers with a poly(ferrocene)s block, which are desirable for studies of the properties of these materials.

SUPPORTING INFORMATION

Detailed experimental procedures and characterization data for new compounds and polymer are included. These materials are available free of charge *via* internet.

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