A novel photoreversible poly(ferrocenylsilane) with coumarin side group: synthesis, characterization, and electrochemical activities

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A novel poly(ferrocenylsilane) with a coumarin side group was synthesized. This photoreversible polymer exhibits interesting electrochemical activities, which change with photodimerization and photoscission reactions of the coumarin moieties.

Since the discovery of high molecular weight poly(ferrocenylsilane) (PFS) consisting of alternating ferrocenyl units and silicon atoms in the main chain by Manners *et al.* through thermal ring-opening polymerization (ROP) of silaferrocenoplane in 1992,[1] this new class of well-defined organometallic polymers has received considerable attention in the past decade due to its interesting optical and unique electronic, magnetic, and chemical properties. These polymers promise to be used in many fields such as semiconductors, sensors, optical crystals, etching resists, redox-active gels, liquid crystals, and nonlinear optic devices.[2] A lot of PFS polymers with different side groups have been prepared for different applications already.[3] However, most reported PFS polymers just have alkyl or aryl groups attached to the silicon atoms.

In recent years, considerable interest has been turned to the synthesis of new functional PFS polymers for special purposes.[4] Recently, Manners *et al.* first reported the synthesis of a photo cross-linkable PFS, which has potential use as an etching resist.[5] On the other hand, polymers with coumarin moieties are very useful in many fields, such as laser dyes, photoresists, energy-transfer materials, and alignment agents for liquid crystals because of the photodimerization ability of the coumarin unit through the [2-2] cyclization of the double bond.[6] The photoreversible moieties in PFS will endow these polymers with some interesting and controllable optical properties for special applications. At the same time, the thermal stability and mechanical properties of these PFS polymers will be enhanced with cross-linking. However, to our knowledge, no photoreversible PFS have been reported to date.

In this study, we first reported the synthesis of a photoreversible PFS with coumarin side groups and the influence of photodimerization and photoscission reactions of the coumarin groups on its physicochemical, especially electrochemical property. This new photoreversible PFS possesses some useful photochemical properties with redox activity and may be used in photomemory materials, redox-active gels, redox drug controlled-release carriers, and the redox switching of optical devices.

The synthetic route of poly(ferrocenylsilane) with coumarin side groups is represented in Scheme 1a. The monomer **1** was prepared by added dichloro(3-choropropyl)methylsilane dropwise into

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dilithioferrocene–TMEDA according to Manners *et al.*[1] Polymer **2** was synthesized by transition metal-catalyzed ring-opening polymerization of monomer **1**,[1,7] which was followed by side group exchange reaction with iodoethane to produce polymer **3**. Then, 7-hydroxycoumarin was successfully introduced into **3** by macromolecular nucleophilic substitution reaction to produce poly(ferrocenyl(3-(7-hydroxycoumarin) propyl)methylsilane) (**4**). Fig. 1 displays the 400 MHz ^{1}H NMR spectrum and the
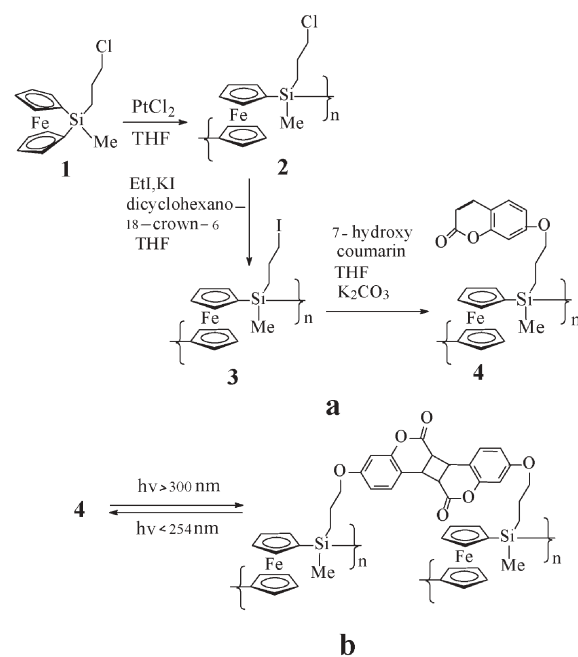
Scheme 1 Synthesis (a) and photodimerization and photoscission reactions (b) of poly(ferrocenyl(3-(7-hydroxycoumarin) propyl)methyl-silane) (**4**).
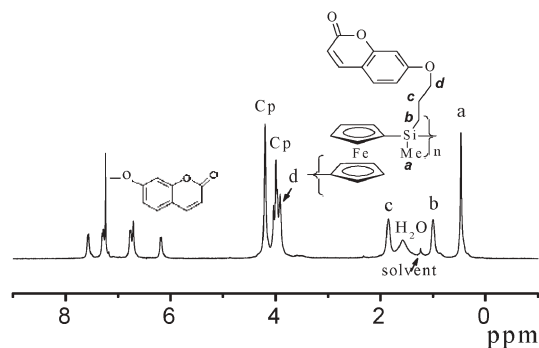

Fig. 1 ^{1}H NMR spectrum of **4** in CD$_3$Cl.

assignments of **4** in CDCl₃. The signal at 3.18 ppm (3-CH$_2$I) shifted to 4.0 ppm (3-CH$_2$O–), indicative of the complete conversion of **3** into **4**. Elemental analysis showed a good agreement between calculated and measured compositions for **4**. C$_{23}$H$_{22}$O$_3$Si (430.36): calcd C 63.32 H 5.15; found C 62.43 H 5.25. The molecular weight $M_w = 1.97 \times 10^5$ g mol^{-1} and polydispersity $M_w/M_n = 1.97$ of polymer **4** were estimated by GPC using narrowly distributed polystyrene as standard. Polymer **4** in THF shows two main absorptions at 237 and 320 nm in the UV-vis spectrum, which are attributed to the maximum absorption of ferrocenyl and coumarin moieties, respectively. The grafting of 7-oxycoumarin groups to **3** can also be confirmed by the FTIR and emission spectra. Polymer **4** exhibits the absorption of C=C bonds at 1626 cm^{-1} and the stretch absorption of C=O group at 1733 cm^{-1}, which are the characteristic bands of coumarin residues. Furthermore, the maximum emission λ_{em} of polymer **4** in THF only slightly blue-shifts to 371 nm from $\lambda_{em} = 383$ nm for free 7-oxycoumarin. These results indicate that the polymer **4** is obtained by the macromolecular nucleophilic substitution reaction of polymer **3** with 7-oxycoumarin.

The thermal properties of polymer **4** were characterized using TG and DSC. The measured T_g value of **4** is 76 °C, which is higher by 34 °C than that of **3**. As previously suggested by Manners *et al.*, side residues attached to silicon atoms can strongly influence the T_g of PFS polymers.[2b] The higher T_g of **4** may be attributed to the bulky coumarin side groups, which reduces the polymer mobility effectively. No melting transition is observed from the DSC curves of both **3** and **4** over the range from −60 °C up to the decomposition temperature, for commonly symmetric substituents on PFS favor crystallization, while asymmetric substituted PFS is usually amorphous.[5] Furthermore, TG thermograms show that the degradation temperature T_d corresponding to the maximum weight-loss rate is 285 and 301 °C for **3** and **4**, respectively, indicating that **4** has only a slightly higher thermal stability than **3**.

The photo cross-linking of **4** can be performed through the dimerization addition of coumarin by light irradiation.[6] The photoreaction process of polymer **4** is denoted in Scheme 1b. As shown in the Fig. 2a, the absorbance of **4** at 320 nm decreases with elongating the irradiation time due to the dimerization of the coumarin groups. As the coumarin dimerizes, the level of unsaturation decreases due to the formation of cyclobutane cross-linking junctions.[6] The photodimerization reaction seems to
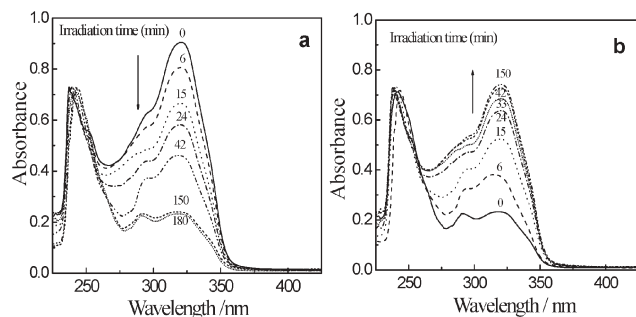
become difficult after irradiated for about 150 min. The degree of cross-linking of **4** can be approximately estimated by the equation: $D = (a - b)/a$, where D is the degree of cross-linking, and a is the absorbance of **4** at 320 nm, and b is the absorbance of **4** at 320 nm after UV irradiation, because the absorbance at 320 nm decreases with cross-linking of **4**. The maximum cross-linking degree of **4** is determined to be 81.5%. On the other hand, UV irradiation also significantly improves the thermal stability of **4**, for the degradation temperature T_d of **4** after irradiated for 180 min increases from 301 to 350 °C. The enhanced thermal stability should be due to the photo cross-linking of coumarin moieties.

The cyclobutane ring in the photodimer of coumarin can be cleaved to regenerate coumarin by irradiation of light with wavelength shorter than 300 nm.[6] The photoscission reaction of the photo cross-linked **4** is performed at room temperature by irradiation under a 254 nm UV lamp. The absorbance at 320 nm increases with increasing irradiation time, because the cyclobutane ring in the cross-linked **4** is cleaved gradually to regenerate coumarin. As known from Fig. 2b, however, the absorbance of **4** after irradiation for 180 min is slightly lower than that of the original **4** before cross-linking. According to the UV absorbance, only 80.7% of cross-linked **4** can be recovered by the photoscission due to the partial reversibility of the dimerized coumarin.

The electrochemical activities of these polymers were studied by cyclic voltammetry (CV). As shown in the Fig. 3a, **4** just shows one
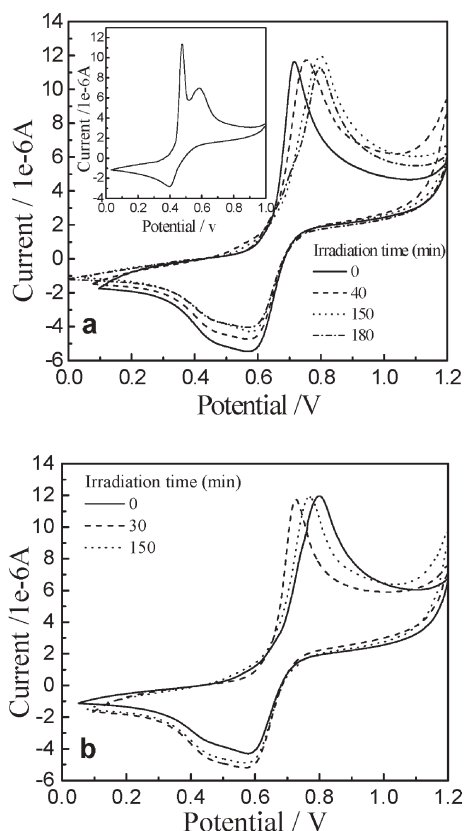
Fig. 3 (a) Cyclic voltammogram of the film of **4** on a glassy carbon electrode in 0.1 M NaCl solution at different irradiation time with a 450-W high-pressure Hg lamp and (b) with a 254 nm low-pressure Hg lamp. Insert: Cyclic voltammogram of the film of **3** on a glassy carbon electrode in 0.1 M NaCl solution. The potential scan rate v is 0.01 V s^{-1}.

Fig. 2 (a) UV absorption spectra of **4** in THF (2.7×10^{-4} g ml^{-1}) changing with irradiation time with a 450-W high-pressure Hg lamp. (b) UV absorption spectra of **4** in THF (2.7×10^{-4} g ml^{-1}) that has been irradiated for 180 min changing with irradiation time at 254 nm with a low-pressure Hg lamp.
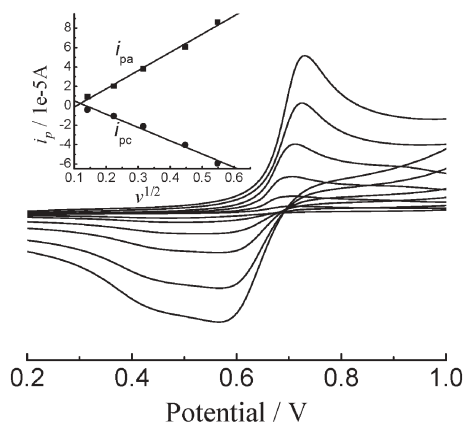
Fig. 4 Cyclic voltammogram of the film of **4** on a glassy carbon electrode in 0.1 M NaCl solution at different potential scan rate: 0.02, 0.05, 0.1, 0.2, 0.3 V s^{-1}. The liner relationships between i_p and $v^{1/2}$ are i_{pa} = $-20.12 + 187.79$ $v^{1/2}$ ($r = 0.995$), i_{pc} = 18.68–136.89 $v^{1/2}$ ($r = -0.991$).

couple of redox peak, while **3** has two oxidation peaks and one reduction peak, indicating the existence of communication between the iron centers along the PFS main chains of **3**.[8] Generally, the oxidation potential E_{pa} will change if the substitution at the silicon atom of PFS is altered. It is found that the oxidation potential E_{pa} of **4** (0.72 V *vs.* Ag/AgCl) is higher than that of **3** (0.51 V *vs.* Ag/AgCl), indicating that **4** is more difficult to be oxidized than **3**. The potential difference ΔE ($E_{pa} - E_{pc}$) of **4** is 0.13 V, higher by 0.10 V than that of **3** (calculated from the first oxidation peak). The reason for this may be that the bulky coumarin moiety baffles the rotation of the polymer chains and makes the charge transfer between the neighboring active sites in **4** much more difficult. As a result, the ΔE of **4** is slightly higher than that of **3**. Therefore, the electrochemical activity of PFS has been altered by the introduction of the electron-rich coumarin substituent into PFS side chain. In addition, the ΔE and the redox peak current of **4** increase with the potential scan rate and a linear relationship between the redox peak current value i_p and the square root of potential scan rate $v^{1/2}$ is observed (Fig. 4), which agrees well with Randle–Sevick equation. Thus, the electrode processes of the films of polymer **4** are diffusion control and exhibit quasi-reversible features.[9]

In order to reveal the influence of the photo cross-linking on the electrochemical behavior of PFS films, the CV measurement was performed with the polymer film coating on a glassy carbon electrode after irradiation for different times at 25 °C. From Fig. 3a, we can see that only oxidation potential E_{pa} of **4** increases with the irradiation time until 150 min and the shape of the CV curves is similar. Thus, **4** after UV irradiation becomes more difficult to be oxidized. It is most likely that the movement of the polymer chains is further restricted in the photo cross-linked **4**, which makes the charge transfer between the active sites more difficult. But the reduction potential E_{pc} of **4** is unvaried with the irradiation time. It is possible that it is easy for the redox active site to access electrons during the reduction process due to the

existence of electron-rich coumarin side groups, because the electron donating group favors the reduction process.[10] As a result, the ΔE of **4** increases with irradiation time. Furthermore, the ΔE of **4** reaches the maximum value of 0.22 V after irradiated for about 150 min. This is consistent with the maximum degree of cross-linking of **4** estimated from data in Fig. 2a. It is particularly worth noting that the oxidation potential E_{pa} of **4** gradually decreases after irradiated with 254 nm UV lamp due to photoscission of cyclobutane ring and reaches the minimum value after irradiated for 150 min (Fig. 3b). The minimum E_{pa} of **4** is 0.73 V, which is only slightly higher by 0.01 V than 0.72 V of original **4** before irradiation. This is due to the partial photoscission of photo-induced cyclobutane rings in the cross-linking **4**, similar to what is reflected by Fig. 2b. We also find that the corresponding reduction peak current value i_{pc} decreases with the photodimerization reaction from Fig. 3a. The possible reason may be that the dimerization reaction of C=C bands weakens the electron donating capability of coumarin in polymer **4** for the electron donating group favors the reduction process. On the contrary, the reduction peak current value i_{pc} increases during the process of photoscission (Fig. 3b).

In conclusion, a new photoreversible poly(ferrocenyl(3-(7-hydroxycoumarin) propyl)methylsilane) was synthesized by introducing 7-hydroxycoumarin into PFS *via* macromolecular nucleophilic substitution reactions. The photoreversible PFS exhibits interesting electrochemical activities with almost reversible photodimerization and photoscission. The photo cross-linking polymer exhibits a better thermal stability. If the percent of coumarin moiety can be controlled, and then the unsubstituted reaction-active 3-iodopropyl will be engaged for other functional groups. Further study is in progress.

Notes and references

1 D. A. Foucher, B. Z. Tang and I. Manners, *J. Am. Chem. Soc.*, 1992, **114**, 6246.
2 (*a*) I. Manners, *Science*, 2001, **294**, 1664; (*b*) K. N. Power-Billard and I. Manners, *Macromolecules*, 2000, **33**, 26.
3 I. Manners, *Adv. Organomet. Chem.*, 1995, **37**, 131.
4 K. Kulbaba and I. Manners, *Macromol. Rapid Commun.*, 2001, **22**, 711.
5 P. W. Cyr, D. A. Rider, K. Kulbaba and I. Manners, *Macromolecules*, 2004, **37**, 3959.
6 S. R. Trenor, A. R. Shultz, B. J. Love and T. E. Long, *Chem. Rev.*, 2004, **104**, 3059.
7 P. Gómez-Elipe, R. Resendes, P. M. Meadonald and I. Manners, *J. Am. Chem. Soc.*, 1998, **120**, 8348.
8 (*a*) D. A. Foucher, C. H. Honeyman, J. M. Nelson, B. Z. Tang and I. Manners, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1709; (*b*) R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant and W. E. Geiger, *J. Am. Chem. Soc.*, 1996, **118**, 12683.
9 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons: New York, 1980, ch. 6.
10 X. J. Wang, L. Wang, J. J. Wang and T. Chen, *J. Phys. Chem. B*, 2004, **108**, 5627.