Study on ESR Spectra of Poly(ferrocenyldimethylsilane)/ TCNE and Spin-Probed Poly(ferrocenyldimethylsilane)

L. Wang, X. J. Wang, J. Pan, L. X. Feng

Department of Polymer Science and Engineering, Zhejiang University, 310027 Hangzhou, People's Republic of China

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ABSTRACT: Poly(ferrocenyldimethylsilanes) with different molecular weights, especially with high molecular weight, have been synthesized. It is found by using the ESR technique that the formation of charge transfer complexes (CTC) between poly(ferrocenyldimethylsilanes) with different molecular weights and tetracyanoethylene (TCNE) is possible. Using 2,2,6,6-Tetramethyl-piperidone-1 as a spin probe, the segment motion of resultant polymers was investigated. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3508–3511, 2002

Key words: ESR; poly(ferrocenyldimethylsilone); spin probe

INTRODUCTION

The exploration and investigation of novel polymer magnetic materials has generated increasing interest, both from a fundamental point of view and in terms of their large potential in applications of audio equipment and communication equipment.[1–3] Recently, polymers containing transition metal in their skeletons and having magnetic properties are attracting growing attention as processable materials. In 1992, Manners and coworkers reported the discovery of a novel, ring-opening route to organometallic polymers that provide access to the first examples of high molecular weight poly(ferrocenylsilanes).[4] This is vital as high molecular weight is required to realize the chain entanglement needed to access the advantageous properties of macromolecules such as ease of fabrication into films with magnetic properties.[5–9] Previous work has shown the formation of a charge transfer complex between metallocene and reagents such as tetracyanoethylene (TCNE),[10,11] but did not discuss ESR spectra in detail. The charge transfer complexes provide materials that exhibit low-temperature magnetic behavior.[12–15]

With these considerations, in this articles, we would like to report a synthesis of poly(ferrocenyl dimethylsilanes) with different molecular weights, especially with high molecular weight, and the ESR spectra of charge transfer complexes (CTC) between poly(ferrocenyl dimethylsilanes) and tetracyanoethylene (TCNE) and ESR spectra of spin probed-resultant polymers.

EXPERIMENTAL

All manipulations were done under inert, dry atmosphere using standard Schlenk line techniques. Solid transfers were made in a vacuum line.[9] All solvents, chemical reagents, and gases were purchased from commercial sources and purified as required. *N,N,N′,N′*-Tetramethyl ethylenediamine (TMEDA) was dried before use. Preparation of 1,1′-Dilithioferrocene-TMEDA is as following: *n*-Butyllithium (18.5 mL, 2 *M*) in *n*-hexane was added to 3 g (0.016 mol) of ferrocene dissolved in 20 mL of hexane, followed by 3 mL (0.02 mol of TMEDA). The reaction was allowed to proceed overnight. The product was filtered off, washed with 3 × 10 mL of hexane and dried under vacuum. This gave ca. 90% yield of orange, pyrophoric powder. Preparation of 1,1′-Ferrocenediyldimethylsilane was as follows: 2 mL of dimethydichlorosilane in 50 mL of hexane was added over 1 h to above resultant 1,1′-dilithioferrocene-TMEDA in a slurry with 20 mL of hexane. The reaction mixture was allowed to stir overnight. Hexane and excess silane were removed under vacuum and the solid were

TABLE I
Effect of Polymerization Time on M_w

	Sample 1	Sample 2	Sample 3	Sample 4
Polymerization time	5 min	10 min	30 min	60 min
M_w	5.2×10^4	5.4×10^4	6×10^4	1.7×10^5
Polydispensity (PD)	3.0	2.3	2.0	2.7

Correspondence to: L. Wang.

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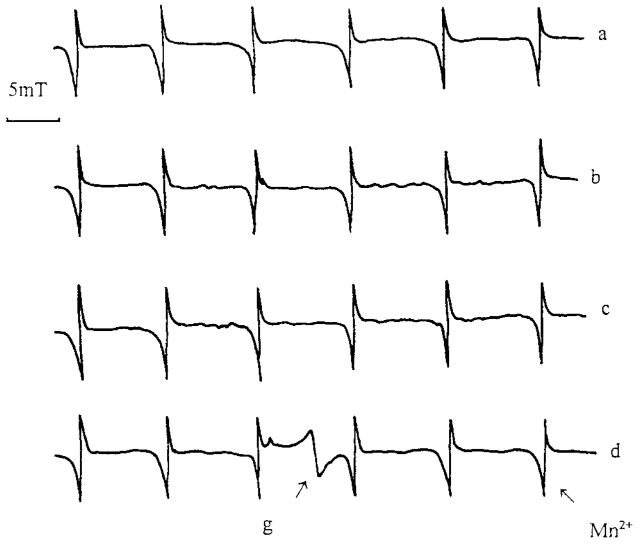


Figure 1 ESR spectra of ferrocene/TCNE. (a) Empty tube; (b) *TCNE*; (c) ferrocene; (d) ferrocene/TCNE.

taken up in hexane and filtered to remove LiCl. The solvent was again stripped under vacuum and the product was extracted from the residue by vacuum sublimation, forming orange platelets. The yield was ca. 59%. Preparation of Poly(ferrocenyldimethylsilanes) was as follows: 1,1′-Ferrocenediyldimethylsilane was heated in an evacuated, sealed tube at 130°C and for different periods. The tube contents were analyzed by GPC. Preparation of the Charge Transfer Complex between Poly(ferrocenyldimethylsilanes) and TCNE was as follows: a solution of 34 mg of TCNE in 20 mL of dichloromethane was added dropwise to a solution of 59 mg of poly(ferrocenyldimethylsilanes). After 18 h, the solvent was removed *in vacuo* and the resultant solids were analyzed by ESR. The ^{1}H-NMR spectrum of poly(ferrocenyldimethylsilanes) was obtained on a Bruker 500 MHz spectrometer. Molecular weights of poly(ferrocenyldimethylsilanes) were measured on a Waters 208-GPC instrument using PS as standard. ESR spectra of spin-probed poly(ferrocenyldimethylsilanes) were recorded on a JEOL JES-FEIXG ESR instrument using *Mn* as standard.

RESULTS AND DISCUSSION

The preparation of poly(ferrocenyldimethylsilanes) can be described as follows:

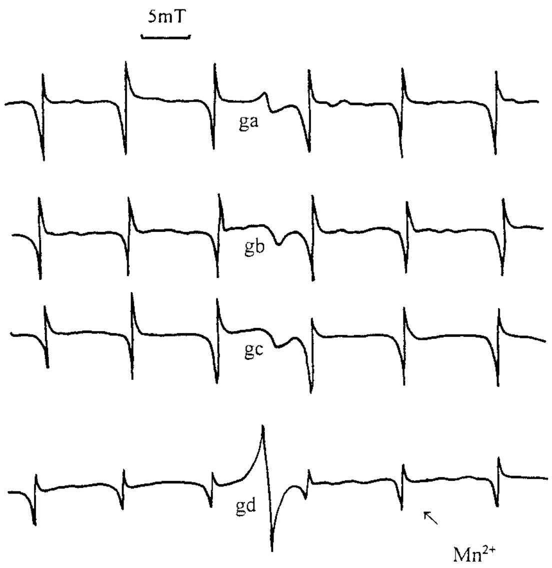
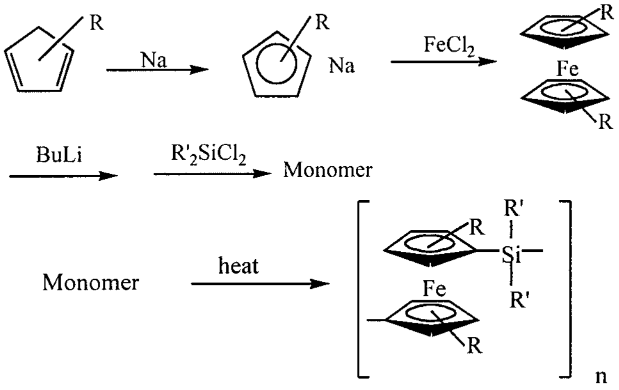


Figure 2 ESR spectra of poly(ferrocenyldimethylsilane)/TCNE. (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4.



When (CH3)2SiCp2Fe monomer was heated in an evacuated, sealed tube at 130°C, the tube contents became molten and then rapidly more viscous. After 10 min the tube contents were completely immobile. Heating was continued for an additional 50 min at the same temperature. The 1H-NMR spectrum of the resulting product(R = H, R′ = CH3), indicated that the resulting product was pure.[9] Gel permeation chromatography demonstrated that molecular weight of poly(ferrocenyl dimethylsilanes) depended on the polymerization time as shown in Table I. As shown in the Table I, it was found that with increasing polymerization time from 5 min to 60 min, *Mw* increased from 5.2×10^4 to 1.7×10^5.

TABLE II
Gram Value of Poly(ferrocenyldimethylsilane)/TCNE

Number of sample (same as Table I)	Sample 1	Sample 2	Sample 3	Sample 4
Polymerization time (min)	5	10	30	60
g [poly(ferrocenyldimethylsilane)/TCNE]	ga = 2.003	gb = 2.003	gc = 2.002	gd = 2.003

To confirm the formation between poly(ferrocenyldimethysilanes) and TCNE, for comparison, the ESR spectra of an empty tube, TCNE, ferrocene, and ferrocene/TCNE were recorded as shown in Figure 1. No appreciable ESR signals were detected in empty tube, TCNE, and ferrocene respectively [see Fig. 1 (a), (b) and (c)]. It was obvious that there was a ESR signal with g ≈ 2 in resulting ferrocene/TCNE.

A solution of TCNE in dichloromethane was added dropwise to a solution of poly(ferrocenyldimethylsilanes) with different MW. After 18 h, the solvent was removed *in vacuo* and the resultant dark green solids was analyzed by ESR (see Fig. 2 and Table II). An ESR signal was detected after poly(ferrocenyldimethylsilanes) with high molecular weight reacted with TCNE, which demonstrated the possibility of preparing CTC paramagnetic film.

Usually, the segmental motion of a polymer is an important property for polymer processing.

However, information on the segment motion of polymer can be obtained indirectly by observing the ESR signals of spin-probed polymers.

ESR spectra of spin-probed resultant polymers with different molecular weights are shown in Figure 3, which indicates that the polymer chain with lower molecular weight (sample A) is more flexible than the higher molecular weight (sample B).

ESR spectra of spin-probed resultant polymers recorded at different temperatures are shown in Figure 4. It is obvious that, with decreasing temperature from 290 to 100 K, the segment motion of resultant polymer was frozen gradually. It also is found that the segment motion of resultant polymer with higher molecular weight was frozen earlier with decreasing temperature.

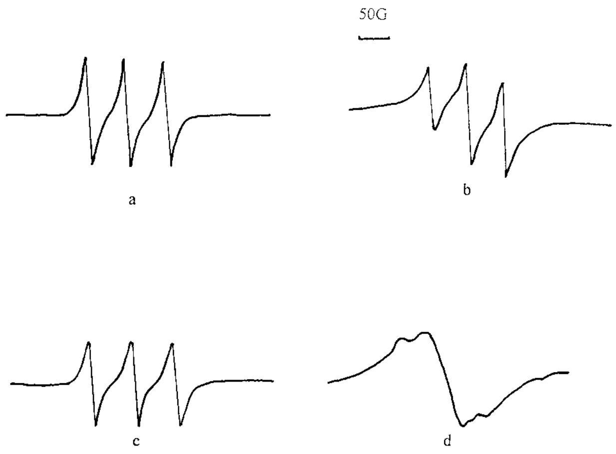


Figure 3 ESR spectra of spin-probed resultant polymers. (a) Sample A measured at room temperature; (b) sample A measured at low temperature; (c) sample B measured at room temperature; (d) sample B measured at low temperature; sample A: WM = 8.5×10^4; sample B: MW = 10.1×10^4.

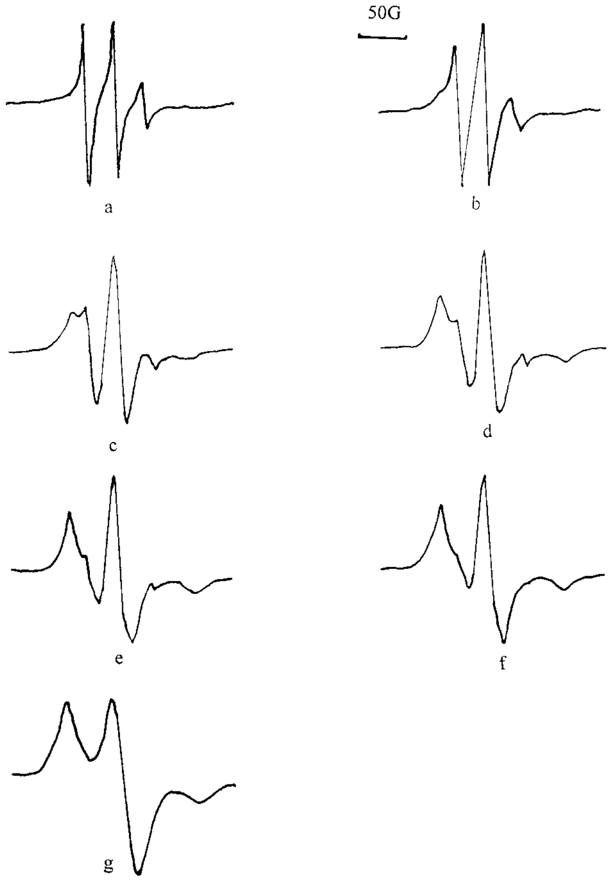


Figure 4 ESR spectra of spin-probed resultant polymers. (a) Recorded at 290 K; (b) recorded at 280 K; (c) recorded at 270 K; (d) recorded at 260 K; (e) recorded at 250 K; (f) recorded at 240 K; (g) recorded at 100 K.

CONCLUSION

This preparative route provides a means to make a series of new polymetallocene charge transfer complexes and CTC paramagnetic films.

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