

# Synthesis of Polyferrocenyldimethylsilane Through Ring-Open Polymerization and Its Electrochemical Properties in Different Mediums

L. WANG,<sup>1</sup> C. Y. YE,<sup>1</sup> P. Y. ZHANG,<sup>1</sup> J. PAN,<sup>1</sup> LINXIAN FENG<sup>1</sup>, S. F. WANG,<sup>2</sup> T. Z. PENG<sup>2</sup>

<sup>1</sup> Department of Polymer Science and Engineering, Zhejiang University, 310027 Hangzhou, People's Republic of China

<sup>2</sup> Department of Chemistry, Zhejiang University, 310027 Hangzhou, People's Republic of China

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**ABSTRACT:** Polyferrocenyldimethylsilanes with different molecular weights were prepared via thermal ring-opening polymerization of the corresponding strained, silicon-bridged ferrocenophanes. The electrochemical behavior of the resultant polymers in different media were investigated by cyclic voltammetry. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3258–3261, 2001

**Key words:** polyferrocenyldimethylsilane; ring-open polymerization; electrochemical properties

## INTRODUCTION

The study of organometallic and inorganic polymers has become an area of considerable interest since such systems can be useful precursors to novel materials unavailable from other sources. Especially, the exploration of processable high molecular weight polymers with skeletal transition-metal atoms has generated increasing interest, both from a fundamental point of view and in terms of their large potential in applications such as materials with novel electrical, optical, or magnetic properties.<sup>1,2</sup> Much of the early work in the field targeted polymetallocene. However, most of synthesizing routes for preparing these polymetallocenes utilized a route of polycondensation reactions. Usually, the resultant products prepared by the route are of low molecular weights, insol-

uble, or poorly characterized. Manners and co-workers reported the discovery of a novel, ring-opening route to organometallic polymers which provides access to the first examples of high molecular weight polyferrocenylsilanes.<sup>3,4</sup> In this article, we report on the synthesis of polyferrocenyldimethylsilanes with different molecular weights, especially with high molecular weight, and the electrochemical properties of the resultant polyferrocenyldimethylsilanes in different electrolytes.

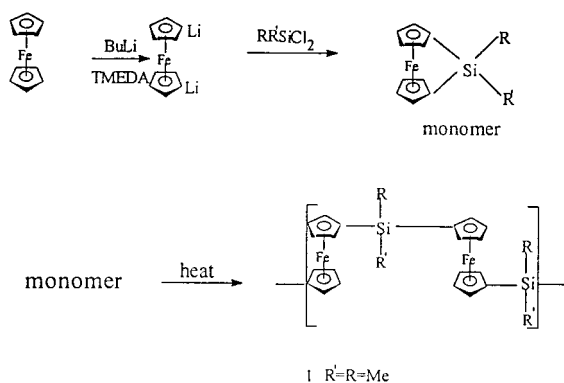
## EXPERIMENTAL

All manipulations were done under an inert, dry atmosphere using standard Schlenk line techniques. Solid transfers were made in a vacuum line. All solvents, chemical reagents, and gases were purchased from commercial sources and purified as required. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was dried before use. Preparation of 1,1'-dilithioferrocene-TMEDA was as follows: *n*-Butyllithium (18.5 mL, 2*M*) in *n*-hex-

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Correspondence to: L. Wang.  
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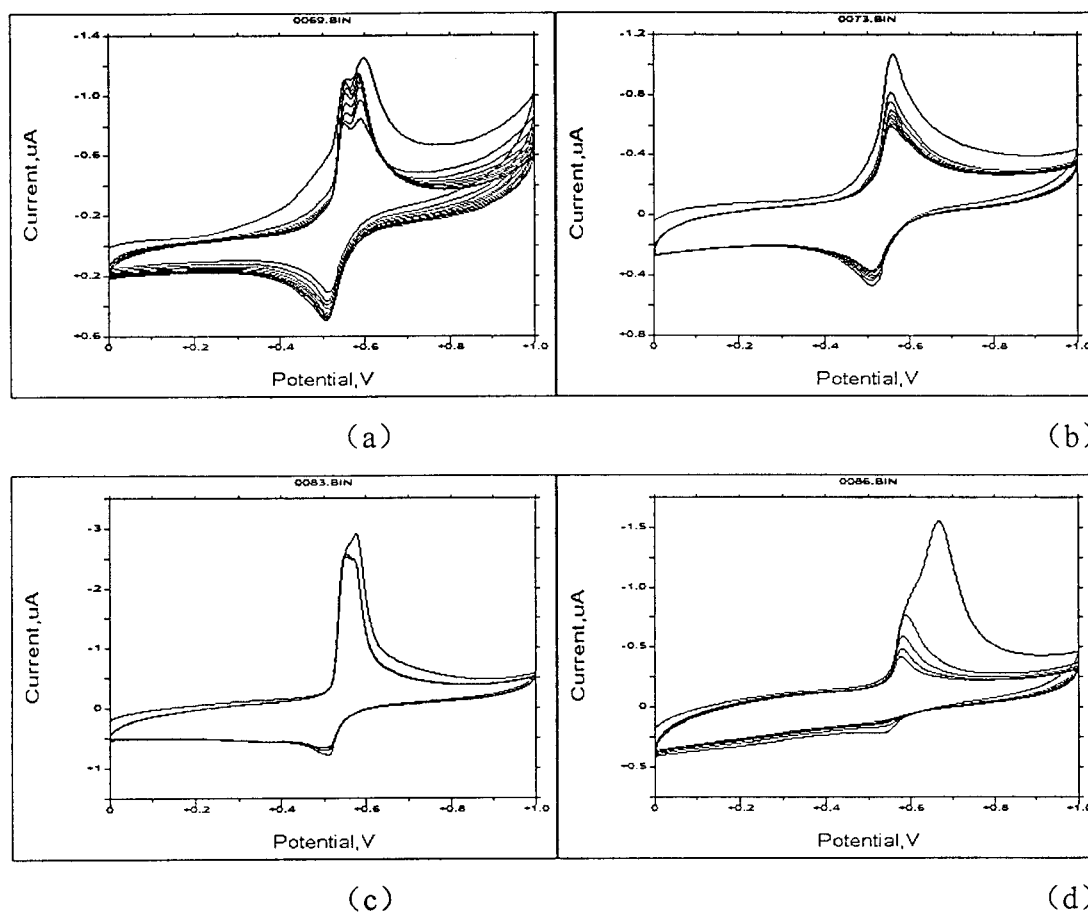
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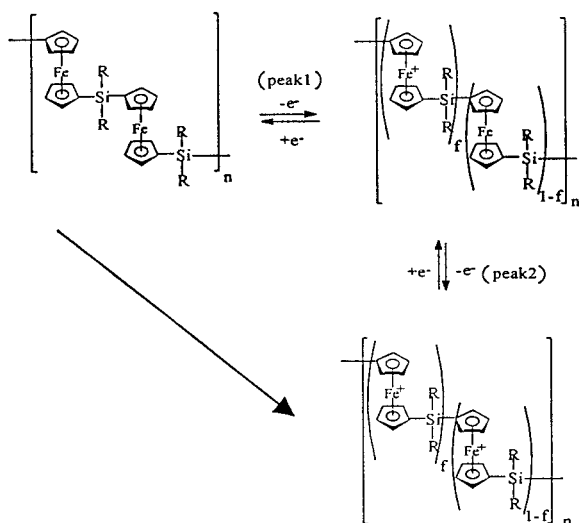
Scheme 1

ane 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  $3 \times 10$  mL of hexane, and dried under a vacuum. This gave about a 90% yield of

an orange, pyrophoric powder. The preparation of 1,1'-ferrocenyldimethylsilane was as follows: Two milliliters of dimethyldichlorosilane 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 a vacuum and the solids were taken up in hexane and filtered to remove LiCl. The solvent was again stripped under a vacuum and the product was extracted from the residue by vacuum sublimation, forming orange platelets; yield about 59%. The preparation of polyferrocenyldimethylsilanes was as follows: 1,1'-Ferrocenyldimethylsilane was sealed in a tube and then the tube was heated at 130°C for different periods. The tube contents were analyzed and  $M_w$ 's (weight-average molecular weight relative to a PS standard) were determined by gel permeation chromatography (GPC). Polymer films on platinum foil electrodes were obtained by casting from



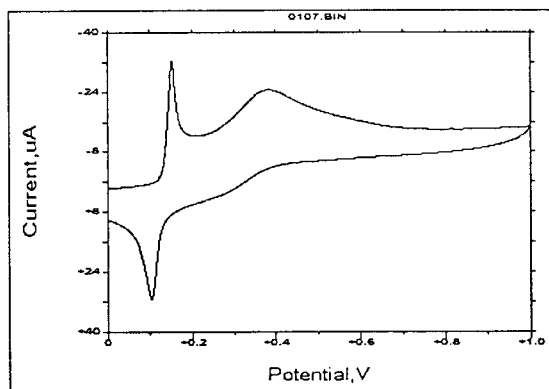
**Figure 1** Cyclic voltammogram of polyferrocenyldimethylsilanes in different electrolytes: (a) 0.1M KCl; (b) 0.1M NaCl; (c) 0.1M HCl; (d) 0.1M H<sub>3</sub>PO<sub>4</sub>.



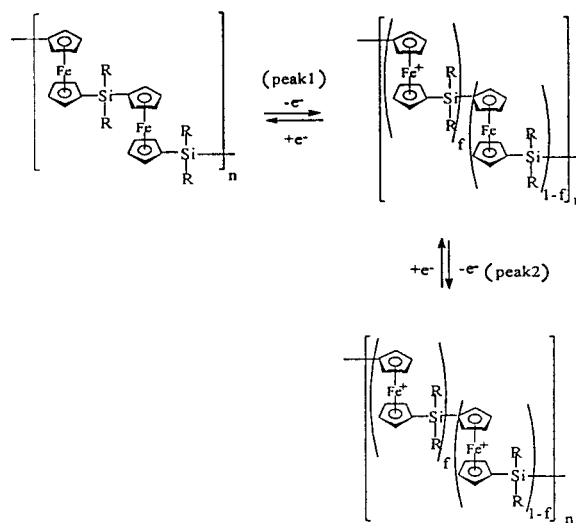
**Scheme 2** Oxidation process of polyferrocenyldimethylsilanes (in 0.1M KCl, 0.1M NaCl, 0.1M HCl, 0.1M H<sub>3</sub>PO<sub>4</sub>).

the tetrahydrofuran polymer solution. The electrochemical measurements of the polyferrocenyldimethylsilane films were performed in a one-compartment cell equipped with a platinum wire counter electrode and a Ag/AgCl reference electrode.

After the (CH<sub>3</sub>)<sub>2</sub>SiCp<sub>2</sub>Fe monomer was sealed into a tube and the tube was heated 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 time at the same temperature. There are signals ( $\delta$  4.2–4.4, 8H in Cp;  $\delta$  0.5, 6H in CH<sub>3</sub>) in the <sup>1</sup>H-NMR spectrum of the resulting product (R = CH<sub>3</sub>) which indicate that the resulting product is pure. GPC demonstrated that



**Figure 2** Cyclic voltammograms of polyferrocenyldimethylsilanes (in 0.1M Et<sub>4</sub>NBF<sub>4</sub>/acetonitrile).



**Scheme 3** Oxidation process of polyferrocenyldimethylsilanes (in 0.1M Et<sub>4</sub>NBF<sub>4</sub>/acetonitrile).

the molecular weight of the polyferrocenyldimethylsilanes depended on the polymerization time. It was found that, by increasing the polymerization time from 5, 10, and 30 min to 60 min, the  $M_w$  increased from  $5.2 \times 10^4$ ,  $5.4 \times 10^4$ , and  $6 \times 10^4$  to  $1.7 \times 10^5$ , respectively.

## RESULTS AND DISCUSSION

Polyferrocenyldimethylsilanes were synthesized according Scheme 1.

The influence of the scanning cycles and electrolyte on the characters of the cyclic voltammograms of polyferrocenyldimethylsilanes in different electrolytes is shown in Figure 1. The voltammograms show a reduction in the size of the peaks with increasing scanning cycles. Previous work confirmed that the reduction in the peak size reflects a loss in electroactivity of polyferrocenyldimethylsilanes and not a loss of material off the electrode.<sup>5</sup> In 0.1M aqueous KCl, 0.1M aqueous NaCl, 0.1M aqueous HCl, and 0.1M aqueous H<sub>3</sub>PO<sub>4</sub>, the neutral films are poorly solvated and highly resistive and not oxidized until the break-in potential (Ebp) is reached and the electrolyte penetrates the film. The oxidation process is as shown in Scheme 2, in which neutral polyferrocenyldimethylsilanes are oxidized directly and completely. Owing to the different permeabilities of the electrolytes, the Ebp's of the polyferrocenyldimethylsilanes were different depending on the kinds of electrolytes.

**Table I Influence of Molecular Weight on  $E_p$** 

Polymer	MW ( $M_w$ )	$^1E_p$ (v)	$^2E_p$ (v)
Polyferrocenyldimethylsilanes	$1.7 \times 10^5$	0.650	0.319
Polyferrocenyldimethylsilanes	$>1.7 \times 10^5$	0.692	0.482
Ferrocene		0.291	0.168

In 0.1M  $\text{Et}_4\text{NBF}_4$ /acetonitrile electrolyte, polyferrocenyldimethylsilanes exhibit two redox couples, as observed in the literature<sup>5</sup> (shown in Fig. 2), which has been proposed to result from the stepwise oxidation of the polymer where alternate ferrocene centers along the chain are oxidized, as shown in Scheme 3.

What is surprising is the influence of the molecular weight on  $E_p$  that was found, as shown in Table I. For comparison, the  $E_p$  of polyferrocenyldimethylsilanes is different from that of ferrocene. It was reported that the oxidation of polyferrocenyldimethylsilanes behaves differently from that of polymers with pendent ferrocene groups.<sup>6</sup> The influence of the molecular weight on  $E_p$  possibly relates to their electronic energy level. Further research is proceeding.

## CONCLUSIONS

In this article, it was found that the electrochemical properties of the resultant polyferrocenyldim-

ethylsilanes was affected by the media and that the oxidation mechanisms in different media were different.

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