

## Synthesis, Characterization and Thermal Stability of Polymers Containing 2,2-Bisferrocenylpropane Group

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The copolymers of 6-vinyl bisferrocenylpropane with vinylbenzene, methyl acrylate and methyl methacrylate, respectively, were obtained from ferrocene and acetone *via* a series of reactions. The monomer and polymers were characterized by elemental analyses, IR spectra and <sup>1</sup>H NMR. The thermal stabilities of the polymers were studied through DTA-TG. The results show that the copolymer of 6-vinyl bisferrocenylpropane with vinylbenzene decompose in higher temperature than the copolymer of 6-vinyl bisferrocenylpropane with methyl acrylate or methyl methacrylate, indicating that the introduction of the phenyl group to the polymer can improve the thermal stability of the polymer. The decomposing temperature of the copolymer of 6-vinyl bisferrocenylpropane with methyl methacrylate is a little higher than the copolymer of 6-vinyl bisferrocenylpropane with methyl acrylate, indicating that the introduction of the methyl group to the polymer can slightly improve the thermal stability of the polymer.

**Keywords:** 6-Vinyl bisferrocenylpropane, Vinylbenzene, Methyl acrylate, Methyl methacrylate, Copolymer, Thermal stability.

### INTRODUCTION

Organometallic polymer chemistry has attracted much attention since Arimoto and Haven<sup>1</sup> reported the vinyl radical polymerization of ferrocene in 1955. The ferrocenyl-containing polymers are not only flexible and easily machined as normal polymers are, but also show high dielectric constant, special catalytic activity, favorable anticancer performance, excellent thermal stability and chemical stability. The ferrocenyl-containing polymers can be used as photosensitizers, catalysts, anticancer drugs, heat-resisting materials and special paints, *etc.*<sup>2-7</sup>. We have reported the synthesis and characterization of the homopolymers of 6-isopropenyl bisferrocenylpropane and 6-( $\alpha$ -benzenevinyl) bisferrocenylpropane<sup>8</sup>. In this paper the copolymer of 6-vinyl bisferrocenylpropane with vinylbenzene, methyl acrylate and methyl methacrylate, respectively, were synthesized and their thermal properties were studied.

### EXPERIMENTAL

Elemental analyses were performed on a Perkin Elmer 2400 microanalyser. Molecular weights of polymers were obtained by GPC method. Infrared spectra were carried out on a NEXUS-670 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were conducted on a Bruker Acance DRX 500 M NMR

spectrometer (CDCl<sub>3</sub> as solvent, TMS as internal standard). Thermogravimetric analyses were measured on a DTG-50 thermal analyzer.

The synthetic routes of 6-vinyl bisferrocenylpropane (monomer I), copolymer of 6-vinyl bisferrocenylpropane with vinylbenzene (polymer I), copolymer of 6-vinyl bisferrocenylpropane with methyl acrylate (polymer II) and copolymer of 6-vinyl bisferrocenylpropane with methyl methacrylate (polymer III) are shown in Fig. 1.

2,2-Bisferrocenylpropane was synthesized according to the literature<sup>9</sup>, 6- $\alpha$ -hydroxyethyl-2,2-bisferrocenylpropane were synthesized according to the literature<sup>10</sup>.

6-Vinyl bisferrocenylpropane was synthesized by the reaction of 6- $\alpha$ -hydroxyethyl-2,2-bisferrocenylpropane and acid Al<sub>2</sub>O<sub>3</sub> in refluxing benzene. The product was purified with column chromatography, petroleum ether as mobile phase. Elemental analysis (%) (Calc.): C 68.78 (68.49), H 6.11 (5.94).

Polymer I was synthesized by the reaction of 6-vinyl bisferrocenylpropane and vinylbenzene in the presence of azodiisobutyronitrile (AIBN, weight fraction 10 %) and purified with benzene-petroleum ether mixture. Same synthetic method is also be used in the syntheses of polymer II and polymer III.

The molecular weight and elemental analyses data are listed in Table-1.

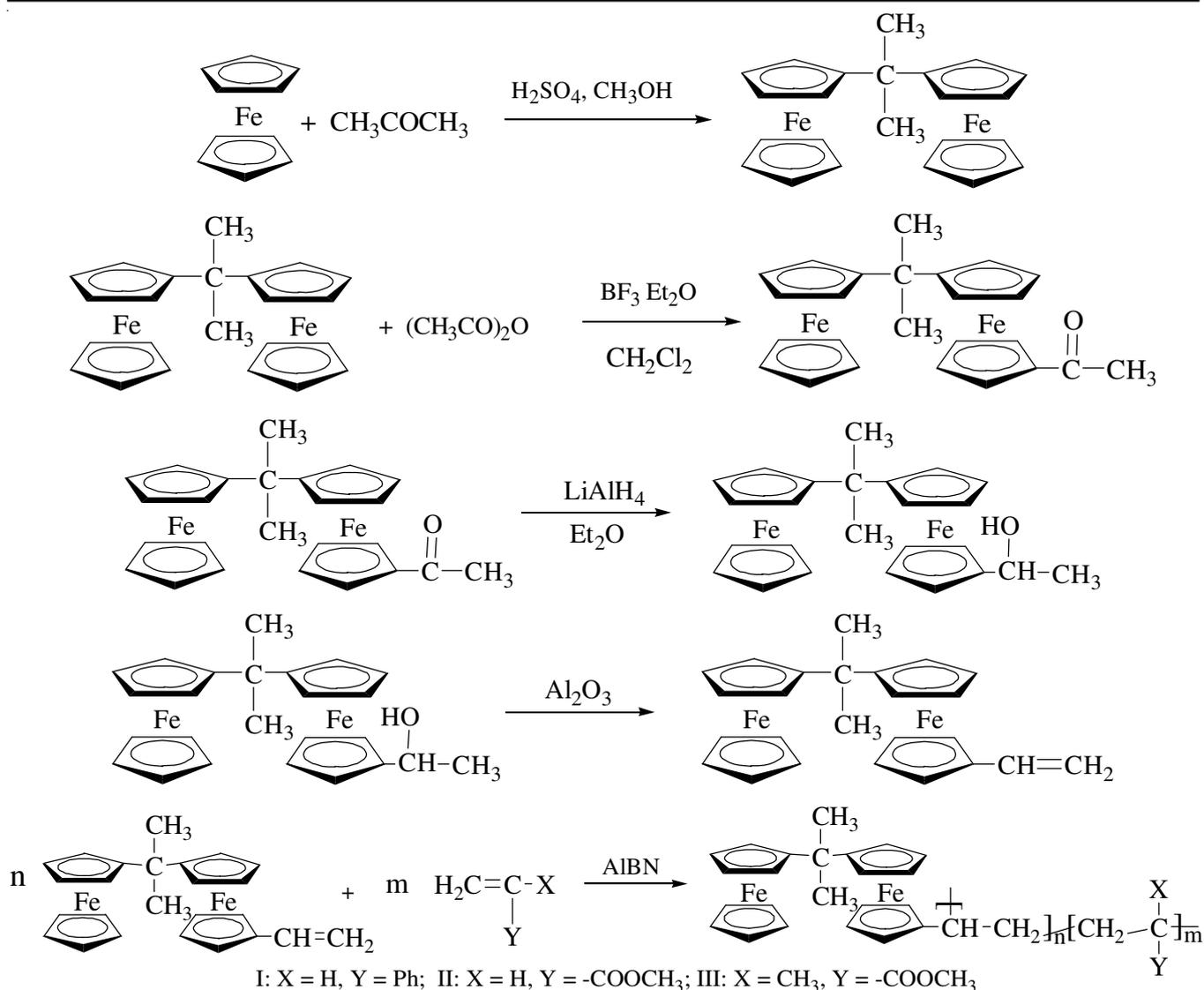


Fig. 1. Synthetic routes of the monomer and polymers

TABLE-1  
MOLECULAR WEIGHT AND  
ELEMENTAL ANALYSES OF COPOLYMERS

Polymers	Number-average molecular weight	Weight-average molecular weight	D	Found (%)	
				C	H
I	894	1490	1.67	72.27	6.42
II	8550	9080	1.06	67.48	6.28
III	8090	8290	1.02	65.90	6.54

## RESULTS AND DISCUSSION

The IR spectra data of the monomer I and polymers and the ascription of the absorption peaks are listed in Table-2.

TABLE-2  
IR DATA OF THE MONOMER AND POLYMERS (cm<sup>-1</sup>)

Compounds	Functional groups									
	$\nu_{C-H}$ (Fc)	$\nu_{Ar-H}$	$\nu_{asC-H}$ (CH <sub>3</sub> )	$\nu_{asC-H}$ (CH <sub>2</sub> )	$\nu_{sC-H}$ (CH <sub>3</sub> )	$\nu_{C=C}$	$\nu_{C=O}$	$\nu_{asC-H}$	$\nu_{sC-H}$ (CH <sub>3</sub> )	$\nu_{C-H}$ (Fc)
Monomer I	3092	—	2971	2931	2868	1629	—	1471	1356	816
Polymer I	3089	3026	2969	2925	2863	—	—	1451	1356	817
Polymer II	3092	—	2968	2923	2867	—	1734	1469	1353	818
Polymer III	3089	—	2970	2951	2867	—	1729	1468	1354	817

Fc: ferrocenyl

Monomer I shows strong absorption peaks for C=C stretching vibration at 1629 cm<sup>-1</sup> in the IR spectra. No corresponding absorption can be observed in the IR spectrum of polymers, indicating completely conversion of the C=C double bands.

**<sup>1</sup>H NMR spectra:** <sup>1</sup>H NMR data of the monomer I and polymers and ascription of peaks are listed in Table-3.

Because the space environments of protons with similar structures in polymers are just slightly different, the absorption peaks with similar chemical shifts overlay each other and form broad multiple peaks. Chemical shifts of ferrocenyl protons are between 3.89 and 4.29 ppm. Chemical shifts of methyl

TABLE-3  
<sup>1</sup>H NMR DATA OF THE MONOMER AND POLYMERS (ppm)

Compounds	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{CH}_3 \\   \end{array}$	Fc-H	CH <sub>2</sub> =	-CH=	-CH <sub>2</sub> -	$\begin{array}{c}   \\ -\text{CH}- \\   \end{array}$	Ar-H	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}- \\   \end{array}$	-OCH <sub>3</sub>
Monomer I	1.61 (6H) (s)	3.89-4.29 (17H) (m)	4.99 (1H) (d) 5.29 (1H) (d)	6.40 (1H) (t)	—	—	—	—	—
Polymer I	1.53-1.63	3.92-4.13	—	—	1.21-1.34	1.76-1.95	7.08-7.29	—	—
Polymer II	1.58-1.62	4.08-4.15	—	—	1.23-1.28	1.76	—	—	3.73
Polymer III	1.58-1.62	4.09-4.15	—	—	1.18-1.28	1.53	—	0.81-0.92	3.68

Fc: ferrocenyl

protons connecting to the bridge carbon are between 1.53 and 1.63 ppm. Chemical shifts of protons connecting to the C=C double band in the monomer I are 4.99 and 5.29 for CH<sub>2</sub>= and 6.40 for -CH=, but shift to 1.18-1.34 and 1.53-1.95 after polymerization, respectively.

**Thermal properties of the polymers:** The DTA-TG diagrams of the polymers are shown in Figs. 2-4.

Polymer I begins to decompose at about 330 °C and shows two exothermic peaks at 442 and 450 °C in its DTA curve, respectively. The corresponding weight loss is 85.24 % altogether in its TG curve.

Polymer II starts to decompose at about 280 °C and shows an exothermic peak at 443 °C in its DTA curve. The corresponding weight loss is 71.58 % in its TG curve.

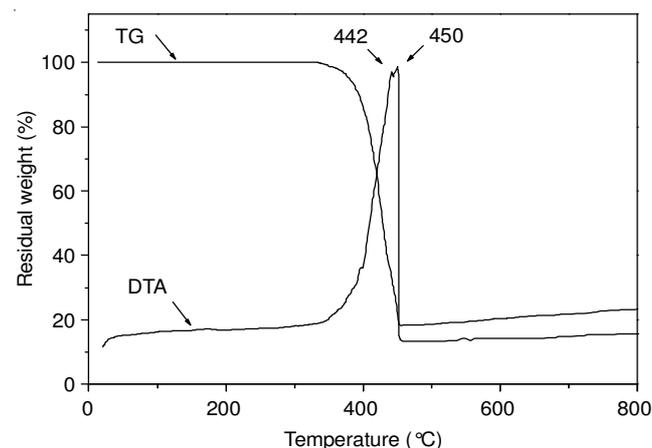


Fig. 2. DTA-TG diagram of polymer I

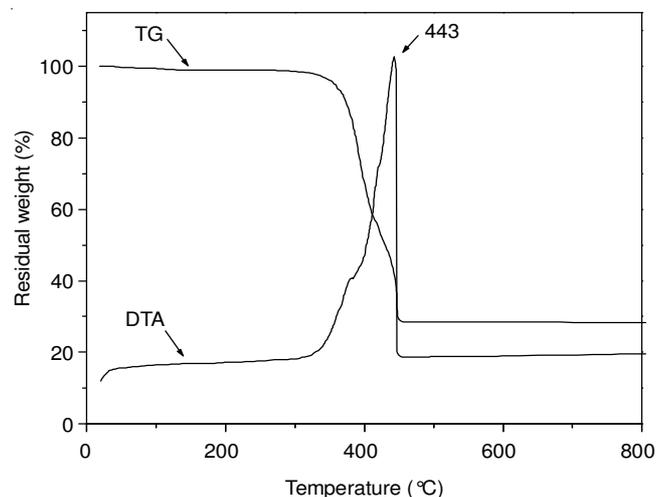


Fig. 3. DTA-TG diagram of polymer II

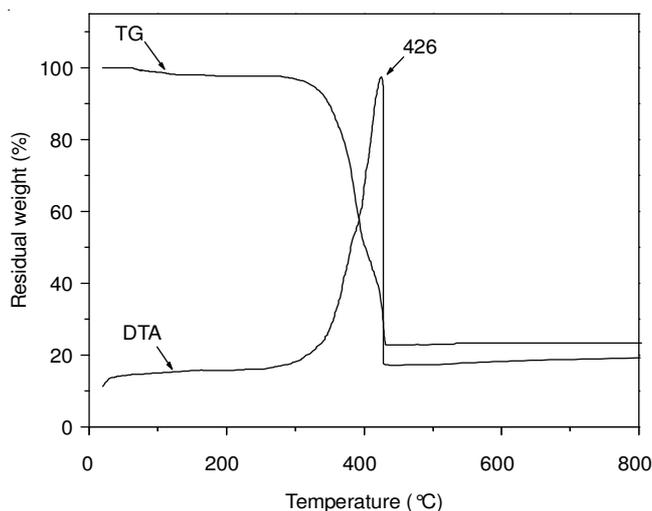


Fig. 4. DTA-TG diagram of polymer III

Polymer III begins to decompose at about 300 °C and shows an exothermic peak at 426 °C in its DTA curve. The corresponding weight loss is 76.75 % in its TG curve.

The decomposition temperatures of the three polymers are not obviously different because the structures of them are similar. Polymer I starts to decompose at about 330 °C, higher than that of the polymer II and polymer III (at about 280 and 300 °C) due to the existence of the phenyl group in the polymer. This phenomenon indicates that the introduction of the phenyl group to the polymer can improve the thermal stability, which is in accordance with the literature<sup>11</sup>. Polymer III decomposes in a little higher temperature than the polymer II, indicating that the introduction of the methyl group to the polymer can slightly improve the thermal stability of the polymer.

## Conclusion

The copolymer of 6-vinyl bisferrocenylpropane with vinylbenzene decomposes in higher temperature than the copolymer of 6-vinyl bisferrocenylpropane with methyl acrylate or methyl methacrylate, indicating that the introduction of the phenyl group to the polymer can improve the thermal stability of the polymer. The decomposing temperature of the copolymer of 6-vinyl bisferrocenylpropane with methyl methacrylate is a little higher than the copolymer of 6-vinyl bisferrocenylpropane with methyl acrylate, indicating that the introduction of the methyl group to the polymer can slightly improve the thermal stability of the polymer.

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