

# Modification of Styrene–Divinylbenzene Copolymer by Anchoring Ferric–Dipyridylamine Complex

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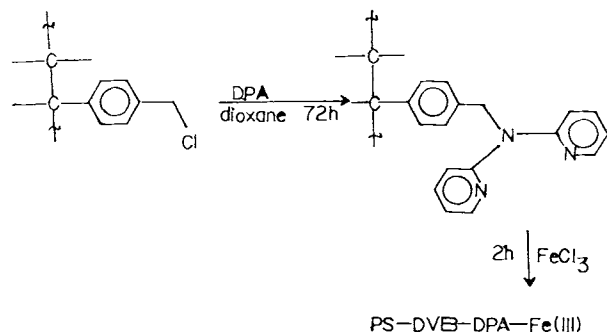
## SYNOPSIS

Polystyrene–divinylbenzene (PS–DVB) copolymer was modified by anchoring dipyridylamine (DPA) on it followed by complexation with Fe(III). Under the experimental conditions followed, 9% incorporation of Fe(III) was achieved. PS–DVB–DPA and PS–DVB–DPA–Fe(III) were characterized by IR spectra. Diffuse reflectance spectra for PS–DVB–DPA–Fe(III) and DPA–Fe(III) revealed  $\lambda_{\max}$  at  $\sim 360$  and  $\sim 310$ , respectively. This difference could be due to a difference in the nature of the coordinating moieties complexing with Fe(III) in these two systems. Scanning electron micrographs of PS–DVB, PS–DVB–DPA–Fe(III), and heat-treated PS–DVB–DPA–Fe(III) revealed some typical surface features. Thermal stability varied in the order PS–DVB–DPA–Fe(III) > PS–DVB–DPA  $\cong$  PS–DVB, and DTA showed characteristic exotherms. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

Increasing research attention<sup>1</sup> has been paid of late to explore novel metal-containing polymer systems in regard to a structure–property correlation of these polymers vis-à-vis their specific applications. In course of our continuing research<sup>2–8</sup> on the preparation and property evaluation of metal-containing polymers, we report now the preparation and structural, morphological, and thermal stability characteristics of styrene–divinylbenzene (S–DVB) resin modified by anchoring ferric–dipyridylamine (Fe–DPA) complex.

The preparation of polystyrene–divinylbenzene (PS–DVB) bound 2–2′-dipyridylamine (DPA) was done by a slightly modified procedure used by Hendricker<sup>9</sup> schematically shown below:



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## EXPERIMENTAL

### Materials

Chloromethylated PS–DVB (1%) beads (Cl<sup>+</sup> content = 1.34 meq/g, Aldrich), 2–2′-DPA (Aldrich), and anhydrous FeCl<sub>3</sub> (Merck) were used directly as supplied. All other chemicals and solvents were reagent-grade materials and used after purification by recommended procedures.

### Preparation of PS–DVB–DPA

Chloromethylated PS–DVB and a fivefold excess of 2–2′-DPA were refluxed in dioxane for 72 h. The resulting yellow beads were collected by filtration, washed with copious amounts of dioxane, dioxane–water, water, THF, and THF–H<sub>2</sub>O and extracted with THF in a Soxhlet extractor for 24 h, and finally dried in vacuum.

### Preparation of PS–DVB–DPA–Fe(III)

A solution of FeCl<sub>3</sub> in THF ( $5 \times 10^{-3}$  M) was added to a weighed amount of PS–DVB–DPA in a round-bottomed Pyrex flask (100 mL/g) and the mixture was stirred for 2 h at room temperature. The metal complex was collected by filtration, repeatedly washed with THF, and, finally, heated at 60°C in vacuum for 24 h. Two batches were prepared under similar conditions for a reproducibility check.

## Characterization

### Spectra

IR spectra were taken on a Perkin-Elmer Model 889 spectrophotometer in KBr pellets. Diffuse reflectance spectra of the solid PS-DVB-DPA-Fe(III) were taken on a Shimadzu UV-VIS-NIR MPC 3100 spectrophotometer.

### Estimation of Iron

Fe(III) was extracted from PS-DVB-DPA-Fe(III) by leaching it with 6NHCl in THF. The extract was evaporated nearly to dryness, and to the residue 40 mL, 1 mL, and 1 drop of water, concentrated HCl, and concentrated HNO<sub>3</sub> were added, respectively. The solution was once again diluted to 60 mL. Ten milliliters of this solution was mixed with 2.5 mL of KCNS (2M) and 1.4 mL of 4NHNO<sub>3</sub> and the volume was made up to 25 mL. The absorbance of this solution was determined spectrophotometrically and the concentration of Fe(III) was determined from a calibration curve.<sup>10</sup>

### Scanning Electron Micrography

Scanning electron micrographs of the various polymers were obtained on a CAM SCAN, Series 2 scanning electron microscope.

### Thermal Stability

TGA and DTA of the polymers were done on a Shimadzu DT-40 thermal analyzer in air at a heating rate of 10°C/min.

### Magnetic Characteristics

A Gouy magnetic balance was used to determine the magnetic characteristics of PS-DVB-DPA-Fe(III).

## RESULTS AND DISCUSSION

The attachment of a number of polydentate amines and of 2,2'-DPA to chloromethylated PS-DVB has been established.<sup>11</sup> In light of these observations, the scheme indicating the mode of anchoring of Fe(III) to PS-DVB-DPA appears plausible. However, evidence in support of the attachment of Fe(III) to PS-DVB-DPA may now be discussed.

Two batches of PS-DVB-DPA-Fe(III) were prepared (Table I). The color of the whitish PS-DVB resin changed to yellow and reddish yellow following the introduction of DVB and of Fe(III), respectively. The diffuse reflectance spectra of PS-

**Table I Preparation of PS-DVB-DPA-Fe(III)**

PS-DVB	DPA	PS-DVB-DPA (isolated)	PS-DVB-DPA-Fe(III) % Fe(III) <sup>a</sup> color
1 g	5.0 g	1.038 g	8.8
1 g	5.04 g	1.041 g	8.9

<sup>a</sup> Fe(III) estimated spectrophotometrically.

DVB-DPA-Fe(III) revealed a  $\lambda_{\max}$  at 360 nm, while the same for the DPA-Fe(III) complex appeared at 310 nm. This might be due to the environmental difference experienced by the Fe(III) ions complexing with the DPA units in the Fe(III)-DPA complex and those attached to the PS-DVB matrix. In the latter case, the availability of the required DPA moieties for coordination with Fe(III) would be restricted unlike in Fe(III)-DPA. It is likely that the necessary coordination number of Fe(III) in PS-DVB-DPA-Fe would be satisfied by other adventitious moieties such as THF or H<sub>2</sub>O. This is because the availability of DPA moieties attached to various segments of PS-DVB would require considerable rearrangement of the polymer chains, which would be indeed difficult in such a cross-linked network. The fact that  $\lambda_{\max}$  in PS-DVB-DPA-Fe(III) appears at a higher wavelength than that in DPA-Fe(III) appears consistent with the larger stabilization energy of DPA compared to H<sub>2</sub>O or to other oxygenated species (THF) in the spectrochemical series.<sup>12</sup>

Direct analysis of Fe(III) attached to PS-DVB-DPA after quantitative stripping of Fe(III) from the polymers revealed 9% metal loading in the matrix. Although the conditions of optimum metal ion loading were not explored, this intake compared well with other reports available with somewhat different experimental conditions.<sup>9</sup>

### IR Spectra

Table II compares the IR absorption characteristics of the polymers with probable assignments. The attachment of DPA to PS-DVB is well endorsed by these data.<sup>9</sup> The IR absorptions vary with temperatures and this feature will be of relevance in connection with discussions on thermal stability of these polymers.

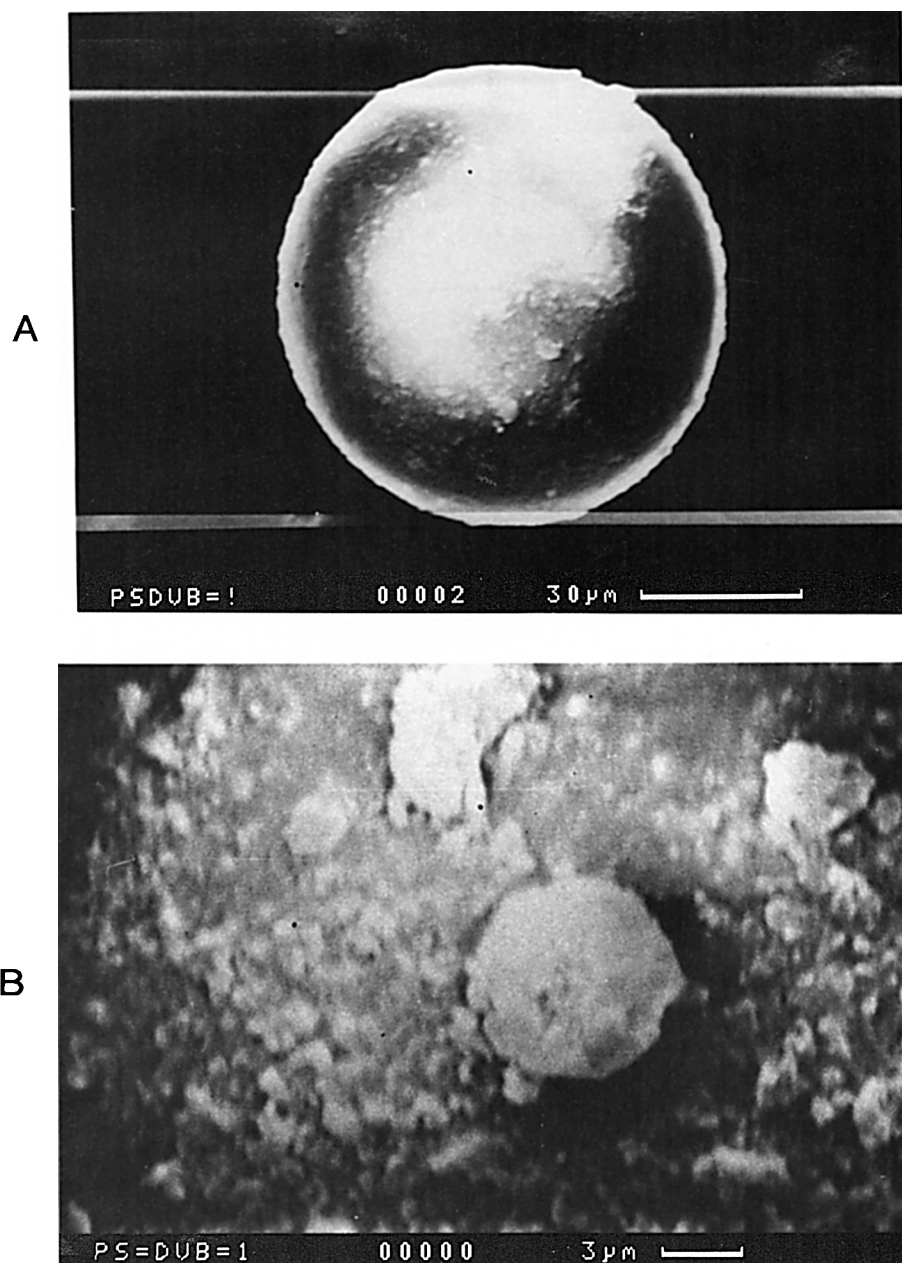
### Surface Morphology

Scanning electron micrographs of PS-DVB (A, B), of PS-DVB-DPA-Fe(III) (C, D), and of the latter

Table II Characteristic (IR) Peaks<sup>a</sup> of PS-DVB, PS-DVB-DPA, and PS-DVB-DPA-Fe(III) at Ambient and Elevated Temperatures (°C)

PS RT	Polymers								Probable Assignments (cm <sup>-1</sup> )
	PS-DVB		PS-DVB-DPA		PS-DVB-DPA-Fe(III)				
	RT (1)	298 (2)	RT (3)	308 (4)	416 (5)	RT (6)	288 (7)	379 (8)	
3060	3021 (s)	3021 (rw-1)	3021 (rw-1)	3025 (rw-1)	3025 (rw-3)	3025 (rw-1)	3025	3025 (w)	Aromatic C—H Str
2923	2923 (s)	2923 (rw-1)	2923 (rw-1)	2923 (rw-1)	2851 (rw-1)	2851 (rw-1)	2923	2924 (w)	Aliphatic C—H Str
2851	2851 (s)	2851 (rw-1)	2851 (rw-1)	2851 (rw-1)		2923 (rw-1)	2851		
1601	1598 (s)	1598 (rw-1)	1598 (rw-1)	1598 (rw-1)	1598 (rw-3)	1598 (rw-1)	1601	1601 (w)	In-plane bond Str phenyl ring
1492	1500 (s)	1500 (rw-1)	1500 (rw-1)	1500 (rw-1)	1452 (rw-3)	1500 (rw-1)	1485	1495 (w)	
1450	1452 (s)	1452 (rw-1)		1452 (rw-1)		1450 (rw-1)	1450	1452 (w)	
756	756 (s)	756 (rs-1)	756 (rw-1)	756 (rw-1)		756 (rw-1)	756	756 (w)	Out-of-plane hydrogen
700	700 (s)	700 (rs-1)	700 (rw-1)	700 (rw-1)		700 (rw-1)	700	700 (w)	Out-of-plane phenyl ring
			1620	1620 (vw)		1620 (rw-3)	1620 (rw-3)	1620 (vw)	DPA attachment indicating peaks
			1530	1530 (vw)		1530 (rw-3)	1530 (rw-3)	1530 (vw)	
			1470	1470 (vw)		1470 (rw-3)	1470 (rw-3)	1470 (vw)	
			1150	1150 (vw)		1150 (rw-3)	1150 (rw-3)	1150 (vw)	
								(all rw-1)	

<sup>a</sup> s = strong; w = weak; rw = relatively weak (relative to 1, 2, 3 . . . , etc.); vw = very weak.



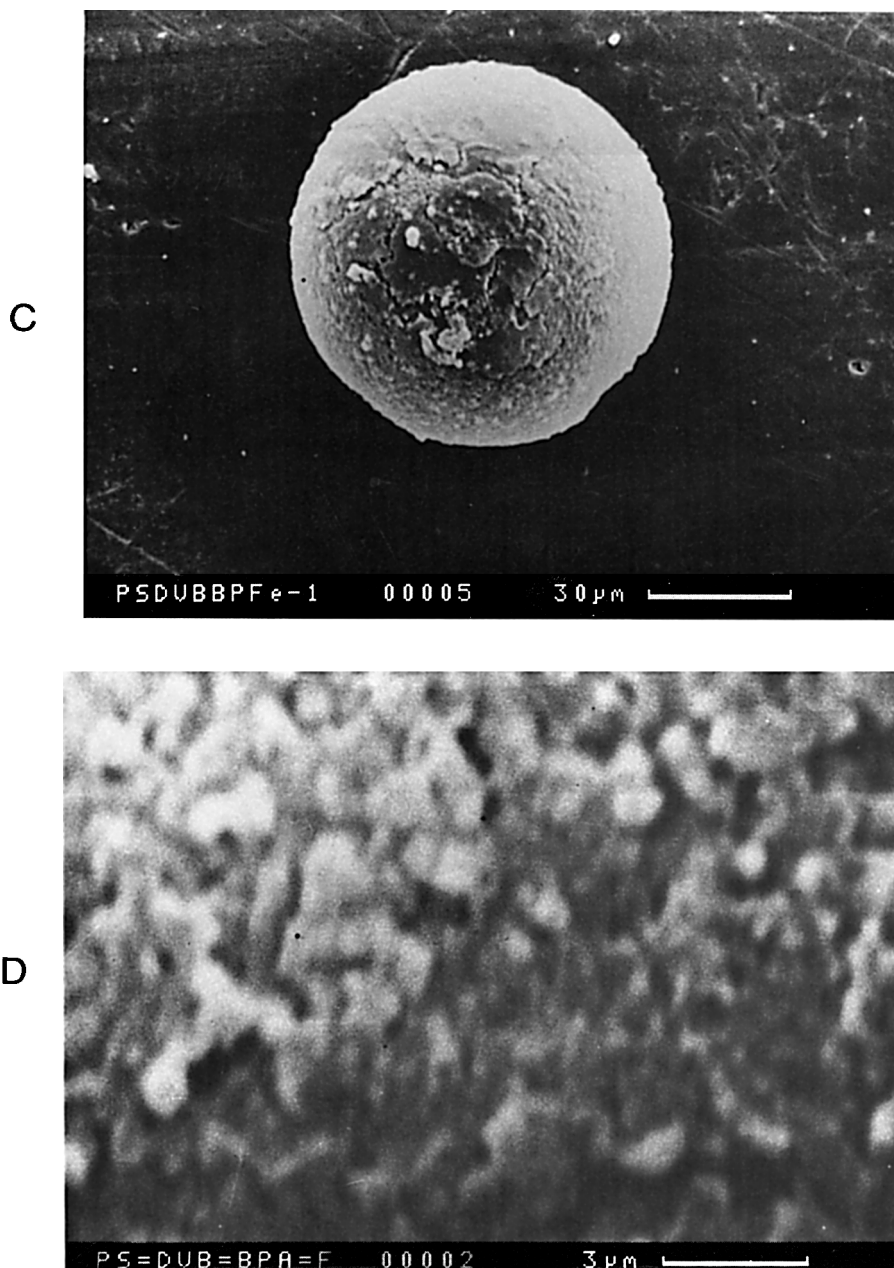
**Figure 1** Scanning electron micrographs for (A, B) PS-DVB, (C, D) PS-DVB-DPA-Fe, and (E, F) PS-DVB-DPA-Fe (288°C).

preheated to 288°C (E, F, G) are presented in Figure 1. (A) shows the spherical structure of PS-DVB beads, whereas (B) reveals a magnified section of the same surface. It shows some irregular agglomerates. (C) shows that anchoring of DPA-Fe(III) on PS-DVB does not affect the spherical bead structure, whereas (D), presenting a closer view, reveals a marked tendency to formation of clusters and agglomerates. However, no crystalline pattern can be discerned. (E) and (F) show the development

of prominent and sharp cracks on the bead structure upon heat treatment to 288°C. (G) reveals a magnified view of the heat-treated surface with cracks and breaking of aggregates.

#### Thermal Stability

Figure 2 clearly indicates that the overall thermogravimetric stability of PS-DVB-DPA-Fe(III) is appreciably higher than that for PS-DVB or PS-



**Figure 1** (Continued from the previous page)

DVB-DPA. A similar trend was already reported by Biswas and Moitra<sup>2</sup> in the case of 3d-metal-ion-loaded PVC-dimethylglyoxime. The difference in stability between PS-DVB and PS-DVB-DPA is not appreciable, which implies that attachment of DPA as a pendant moiety does not involve any major structural change in the matrix. However, on coordination with Fe(III), the polymer anchoring the DPA-Fe complex will require additional thermal energy to break the complex as well as the network. Relevantly, Biswas and Moitra<sup>2</sup> reported that the

thermal stability trend in the PVC-dimethylglyoxime-M(III) 3d metal system is parallel to the crystal-field stabilization energy of the dimethylglyoxime-3d metal complexes. However, no claim can be made on the basis of the present results that this is the sole factor enhancing the stability of PS-DVB-DPA-Fe(III). If the Fe(III) ion could coordinate with more than one DPA unit anchored on different chains of the PS-DVB network, the polymer would become more cross-linked and thus exhibit enhanced stability. However, as discussed earlier, sufficient

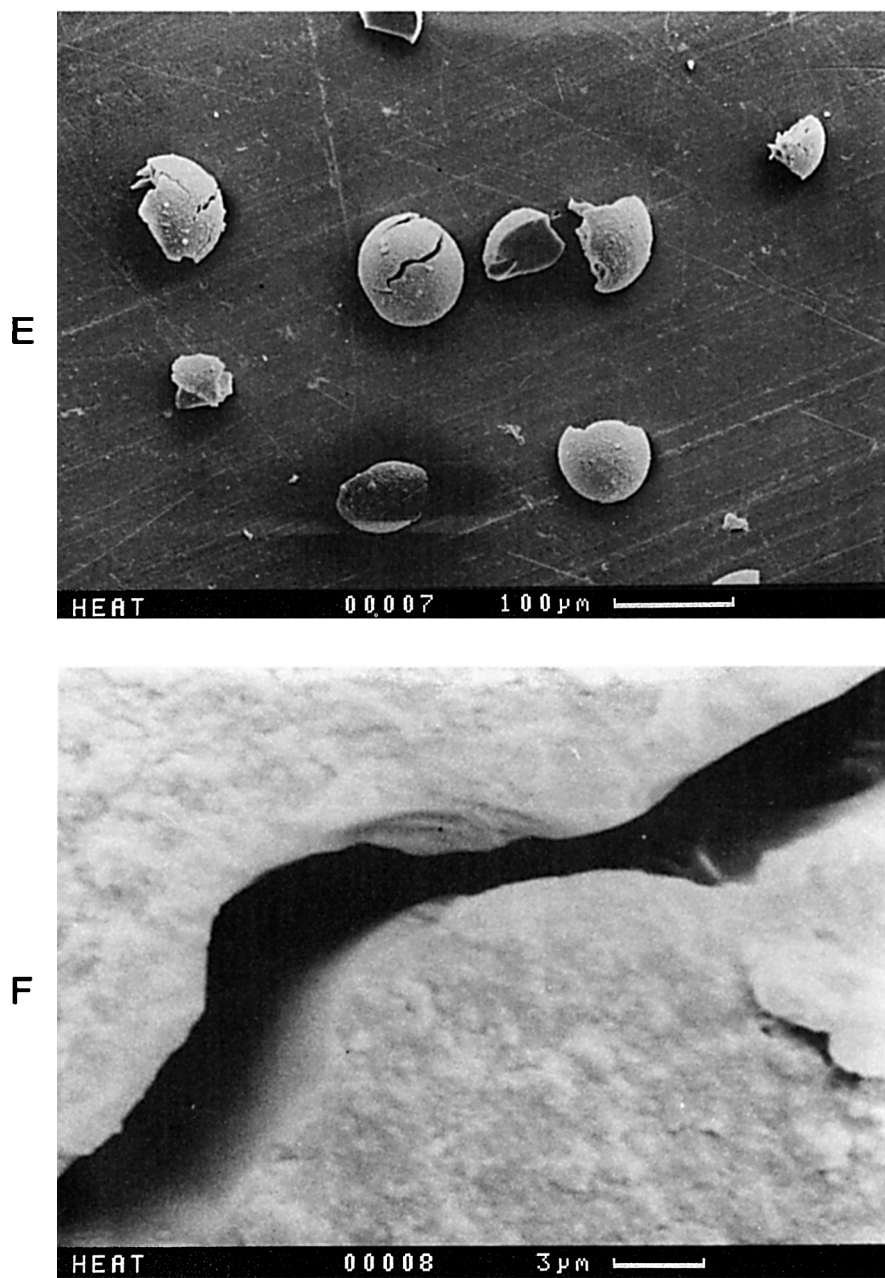


Figure 1 (Continued from the previous page)

evidence is lacking as to the exact coordination mechanism in these cases.

DTA of the polymers reveals some interesting features (Fig. 3 and Table III). PS-DVB is characterized by two, PS-DVB-DPA by three, and PS-DVB-DPA-Fe(III) by four exothermic peaks. The first peak in the region 288–308°C corresponds to degradation of aromatic C—H bonds and the IR absorptions corresponding to C—H are seen to decrease progressively with temperature (Table II). In the light of abundant information on thermal degradation in PS systems,<sup>13,14</sup> the region corre-

sponding to the temperature range 360–420°C concerns degradation of the PS-DVB network to monomeric products and lesser amounts of aromatic hydrocarbons vis-à-vis thermooxidation of these decomposition products.

With inclusion of DPA in PS-DVB, a third peak manifests at ca. 431–438°C (Fig. 3(B) and (C) and Table II). IR data (Table II) indicate the virtual loss of DPA absorptions in this temperature range, implying oxidative degradation of the DPA moieties in the presence of oxygen.

Finally, the sharp exotherm common to all three

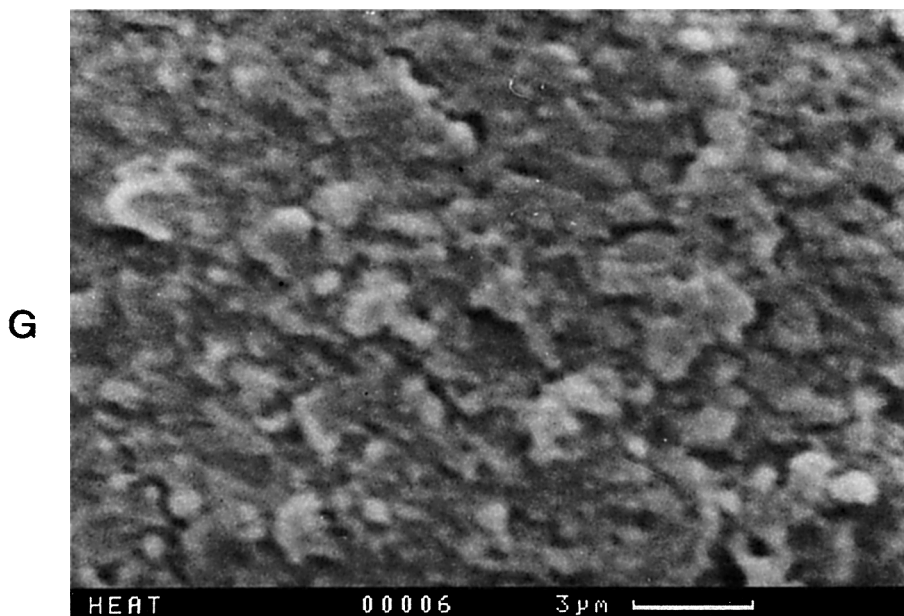


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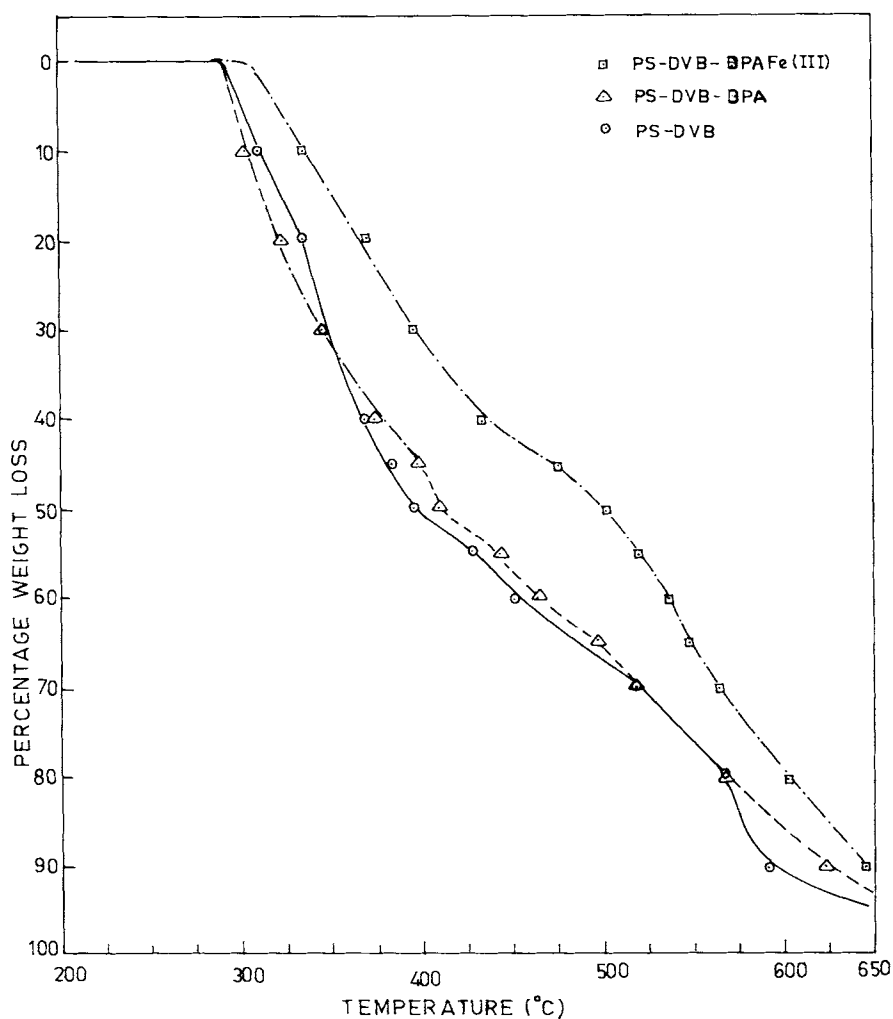


Figure 2 TG curves for (○) PS-DVB, (△) PS-DVB-DPA, and (□) PS-DVB-DPA-Fe.

polymer systems and manifesting at 560°C appears to reflect the oxidative breakdown of the network as a whole. Significantly, a reddish brown residue, probably iron oxide, was detected in the case of PS-DVB-DPA-Fe(III) after heating to 1000°C.

### CONCLUDING REMARKS

The results presented in this research endorse that incorporation of Fe(III) to a polystyrene-divinylbenzene network through the anchoring of a complexing ligand dipyridylamine significantly improves the overall thermal stability of the base polymer. It would be of interest to compare the effect of 3d ions other than Fe(III) on the thermal stability. Like the PVC-anchored dimethylglyoxime-3d metal complexes, these polymers may also possess catalytic

**Table III** DTA Characteristic Peaks of Polymers

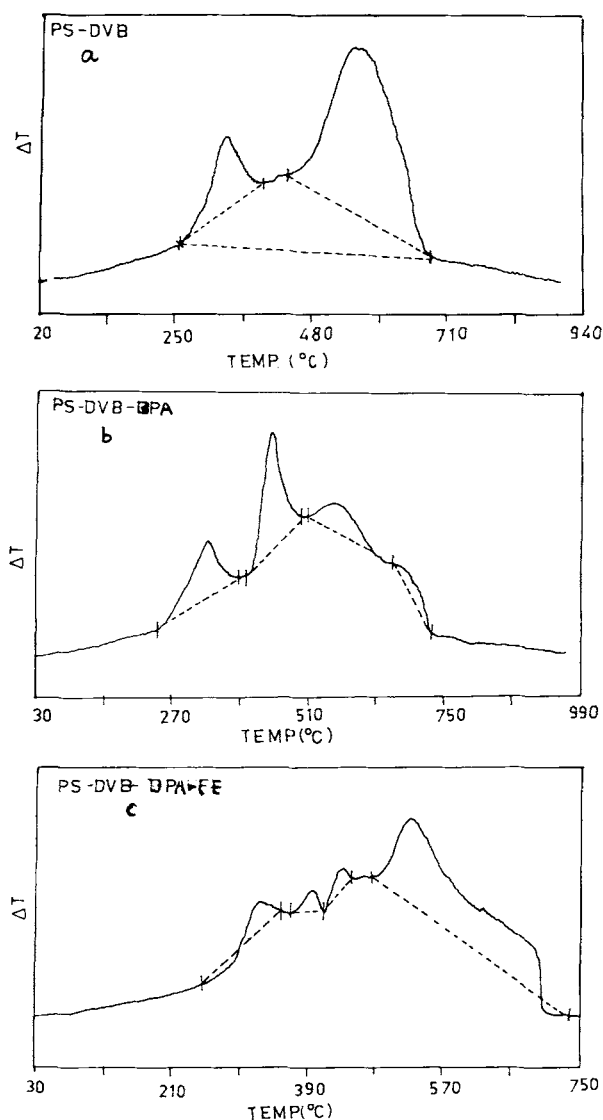
Polymer	Peak	Peak Nature
PS-DVB	339	Exothermic
	560	Exothermic
PS-DVB-DPA	375	Exothermic
	438	Exothermic
	550	Exothermic
PS-DVB-DPA-Fe(III)	375	Exothermic
	393	Exothermic
	431	Exothermic
	521	Exothermic

activity toward polymerization or other processes. These features are receiving closer attention.

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**Figure 3** DTA curves for (a) PS-DVB, (b) PS-DVB-DPA, and (c) PS-DVB-DPA-Fe.

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