

# Thermal Characteristics of Iron(III), Cobalt(II), and Copper(II) Complexes of Dipyriddyamine Anchored on Polystyrene–Divinylbenzene Copolymer

AMIT MUKHERJEE and MUKUL BISWAS\*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

## SYNOPSIS

Polystyrene–divinylbenzene (PS–DVB) (partially chloromethylated) has been modified by anchoring dipyriddyamine (DPA) followed by subsequent complexation with Fe(III), Co(II), and Cu(II). Analytical and spectroscopic evidence has been presented to confirm the attachment of the metal–dipyriddy complex on the PS–DVB matrix. All the metal-loaded polymers exhibit appreciable improvement in thermal stability relative to the base polymer, the initial decomposition temperature and stability order being PS–DVB–DPA–Cu (315°C) > PS–DVB–DPA–Fe(II) (310°C) > PS–DVB–DPA–Co (300°C) > PS–DVB–DPA (280°C) = PS–DVB. DTA studies reveal exothermic peaks between 300 and 380°C, 420 and 440°C, and 500 and 700°C, which are ascribable to the exothermic cleavage of the PS–DVB–DPA matrix. The glass transition temperatures of the modified polymers do not reveal any characteristic difference from the corresponding value for the base polymer.

© 1993 John Wiley & Sons, Inc.

## INTRODUCTION

A good deal of research attention is being paid, of late, to chemical modification of polymers and their properties by metal-ion loading. The diversity of the research already accumulated on this topic and the enormous scope of the field have been highlighted in a recent review on metal-containing polymers by Biswas and Mukherjee.<sup>1</sup>

Earlier research<sup>2–5</sup> from this laboratory in this field indicated that 3*d*-metal complexes of dimethylglyoxime (DMG) can be anchored on poly(vinyl chloride) (PVC), and the resultant PVC–DMG–M(II) complexes exhibit overall improvement in bulk properties such as thermal stability, dielectricity, and conductivity depending upon the nature of the 3*d*-metal center.

It is of relevance to know to what extent such changes are related to the nature of the base polymer, nature of the anchored ligand, and the corresponding metal ions being loaded. To this end, a

different base polymer, a partially chloromethylated polystyrene–divinylbenzene matrix (PS–DVB) has been chosen to which a ligand dipyriddyamine (DPA) has been anchored by a Cl-displacement method.<sup>6</sup> Fe(III),<sup>7</sup> Cu(II), and Co(II) complexes of PS–DVB–DPA have been prepared and characterized in regard to structure, morphology, and thermal stability. Salient features of the results are highlighted in this article.

## EXPERIMENTAL

### Materials

Chloromethylated PS–DVB (1%) beads (Cl' content 1.34 meq/g, Aldrich) 2-2' DPA (Aldrich), and anhydrous FeCl<sub>3</sub>, CuCl<sub>2</sub>, and CoCl<sub>2</sub> (Merck) were used directly as supplied. Dioxan and tetrahydrofuran (THF) were dried and purified by recommended methods.<sup>8</sup>

### Preparation of PS–DVB–DPA

Chloromethylated PS–DVB and a fivefold excess of 2,2'-DPA were refluxed in dioxane for 72 h. The re-

\* To whom correspondence should be addressed.

sulting yellow beads were collected by filtration, washed with copious amounts of dioxane, dioxane-water, water, tetrahydrofuran (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-M

A solution of FeCl<sub>3</sub>, CuCl<sub>2</sub>, and CoCl<sub>2</sub> each in THF 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 polymer-metal complex was collected by filtration, repeatedly washed with THF, and finally heated at 60°C in vacuum for 24 h.

### Preparation of Metal-DPA Complexes

#### Iron(III)-DPA Complex

Anhydrous iron(III) chloride (0.3 g) in dry ethanol and DPA (0.5 g) was refluxed for 30 min.<sup>9</sup> A dark brown material was obtained that was filtered and washed with sufficient ethanol until the FeCl<sub>3</sub> was completely removed.

#### Cobalt(II)-DPA Complex

Anhydrous Co(II) chloride (0.3 g) was dissolved in 15 mL reagent-quality acetone and the solution was filtered to remove any undissolved material. To the filtrate was added with vigorous stirring a solution

containing 0.5 g of DPA in 10 mL acetone. A blue precipitate was obtained that was then freed from the mother liquor by filtration (without suction) and was washed with four successive 5 mL portions of acetone.<sup>10</sup>

### Copper(II)-DPA Complex

A solution of 0.785 g of anhydrous Cu(II) chloride in 3 mL absolute ethanol was filtered and washed with absolute alcohol. The filtrate was then added slowly with vigorous stirring to a solution of 2,2'-DPA (0.5 g) dissolved in 10 mL reagent-grade acetone. The resulting bright green precipitate was removed by filtration washed with four successive 5 mL portion of acetone.<sup>11</sup>

### Characterization

#### Spectra

IR spectra were taken on a Perkin-Elmer Model 889 spectrophotometer in KBr pellets. However, for identification of metal-nitrogen IR peaks, Nujol pellets were used.

#### Estimation of Metal Ions in Polymers

The metal-ion intake in the polymers was estimated by inductive coupled plasma emission spectroscopy (ARL FISSIONS 3410, ICP-ES). The spectrometer was provided with a 1 m monochromator in a Czerny /

**Table I** Analytical and Spectroscopic Characterization of PS-DVB-DPA-M Complexes

Polymer	Color	Metal-ion Loading <sup>a</sup> mmol/g of PS-DVB-DPA by ICP-ES Technique <sup>b</sup>	IR	
			Characteristics Observed (cm <sup>-1</sup> )	M—N Band from Literature (cm <sup>-1</sup> )
PS-DVB	Whitish	—	—	—
PS-DVB-DPA	Yellow	—	—	—
PS-DVB-DPA-Co(II)	Green	0.18 <sup>c</sup> 0.16 <sup>d</sup>	260	266 <sup>16</sup>
PS-DVB-DPA-Cu(II)	Dark yellow	0.23 <sup>c</sup> 0.20 <sup>d</sup>	270	268 <sup>16</sup>
PS-DVB-DPA-Fe(III)	Reddish yellow	0.38 <sup>b</sup>	362	367 <sup>17</sup>

<sup>a</sup> Hendricker and co-workers<sup>6</sup> reported a higher loading of Fe<sup>3+</sup>, Co<sup>2+</sup>, and Cu<sup>2+</sup> with PS-DVB-DPA prepared with the PS-DVB ratio equal to 1 : 30 as against 1 : 5 used in this work. Significantly, the trend reported by them is Fe<sup>3+</sup> > Cu<sup>2+</sup> > Co<sup>2+</sup>, which is similar to that observed in the present analysis.

<sup>b</sup> Accuracy of the technique is ±1%.

<sup>c</sup> Even after repeated leaching with acids, all the metal-loaded polymers retained some residual color, indicating bound metal ions; this implies that actual loading may be somewhat higher than observed.

<sup>d</sup> Results for extraction by 90 min leaching.

Turner optical mount, vacuum version; holographic gratings = 2400 grooves/nm; resolution = 0.007 nm; coolant argon flow = 7.5 L/min, and carrier flow and plasma flow 0.8 L/min. The instrument was calibrated with single-element standard of Cu and Co (Spex Industries Inc., U.S.A.) and deionized in (16M- $\Omega$ ) acidic water.

The sample preparation was done as follows: A solution of PS-DVB-DPA-M (M = Co, Cu, Fe) in 6N HCl solution in THF was heated in a water bath for 45 min to leach out the metal. The solution was filtered off and the filtrate evaporated to 5 mL. A few drops of N/10HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> were added and the solution further diluted to 100 mL using double-distilled water. A clear solution was obtained, the prescribed aliquot of which was fed into the spectrometer for ICP-ES analyses. Two individual extraction processes conducted for 45 and 90 min yielded reproducible results that indicated (Table I) completion of the extraction.

### Thermal Studies

Thermogravimetry (TG) and differential thermal analyses (DTA) were done on a Shimadzu DT-40 thermal analyzer in air at a heating rate of 10°C/min. The glass transition temperature ( $T_g$ ) of the various metal-loaded polymer samples were obtained on a thermomechanical analyzer, Shimadzu TMA-30, with the following experimental conditions: heating rate, 10°C/min, and applied load, 28 cN.

### Scanning Electron Micrography

Scanning electron micrographs of the base polymer and the metal-loaded polymers were obtained on a CAM SCAN Series 2 scanning electron microscope.

## RESULTS AND DISCUSSION

The copolymer PS-DVB reportedly<sup>12</sup> swells several times its original volume in organic solvents such as dichloromethane, dimethylformamide, and THF. Maximum expansion of the beads can be as large as 200-fold.<sup>13</sup> Previous research has confirmed that even after derivatizing the chloromethyl groups with very large organic molecules the beads do not become filled up and, therefore, there is sufficient room for inserting bulky groups into the beads. Consequently, the inclusion of bulky groups like DPA appears feasible in principle. Furthermore, the attachment of a number of polydentate amines to chloromethylated PS-DVB has been established.<sup>14</sup> In the light of these

observations, the attachment of DPA to PS-DVB and subsequent complexation of PS-DVB-DPA by metal ions appear plausible.

Some experimental evidence may now be presented to endorse the attachment of M-DPA units to the PS-DVB matrix. The IR spectrum of PS-DVB-DPA shows in addition to PS absorptions<sup>15</sup> new bands at 1620, 1530, 1470, and 1150 cm<sup>-1</sup> (Fig. 1), which are indicative of the attachment of DPA.<sup>6</sup>

There is a distinct change of color in the various metal-loaded polymer samples. Thus, the color of whitish PS-DVB resin changed to yellow following the incorporation of DPA and, subsequently, to reddish yellow, green, and dark yellow upon complexation with Fe(III), Co(II), and Cu(II), respectively. Furthermore, results of estimation of metal ions corroborate their inclusion in the PS-DVB-DPA matrix (Table I).

The far-infrared spectra of all the three metal-loaded polymer samples also reveal several characteristic metal-nitrogen vibrations (Fig. 2) that agree well with the literature data (Table I).

### Scanning Electron Micrography

Figure 3 presents the scanning electron micrographs of the Fe(III), Co(II), and Cu(II) loaded PS-DVB-

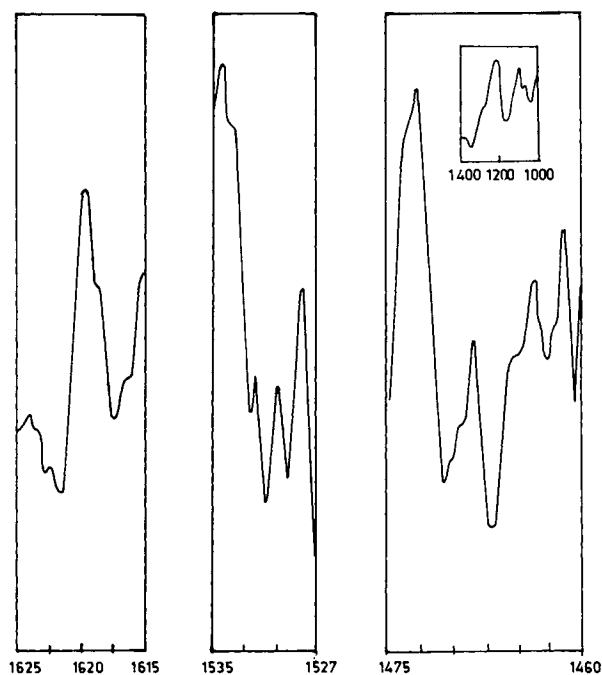


Figure 1 IR bands indicating attachment of DPA to PS-DVB.

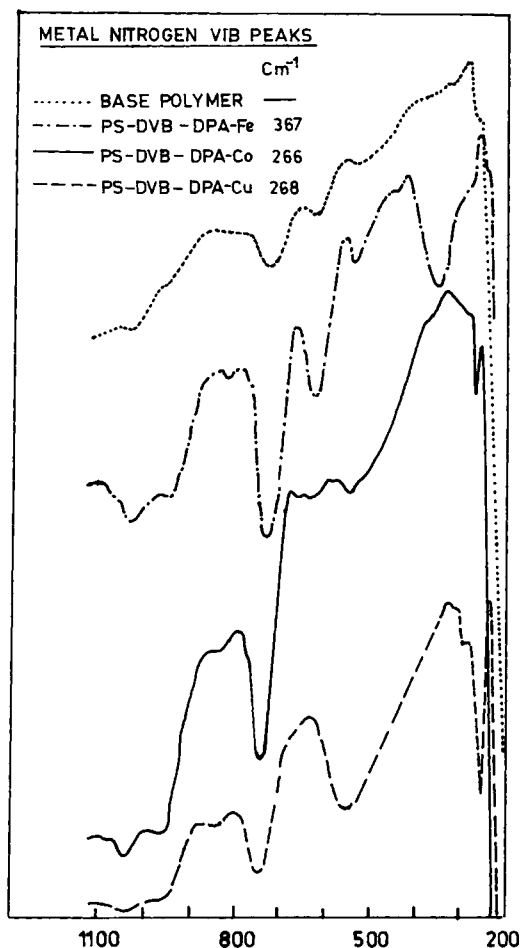


Figure 2 IR metal-nitrogen vibration peaks.

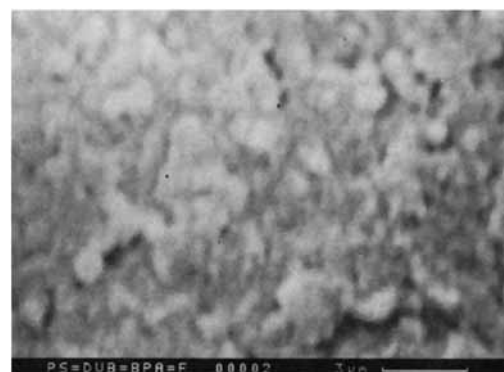
DPA complexes. They are not much different from one another and reveal, in general, agglomerates of particles. The cracks developed in the heat-treated polymers are clearly visible in Figure 4 (a) and (b).

### Thermal Stability Characteristics

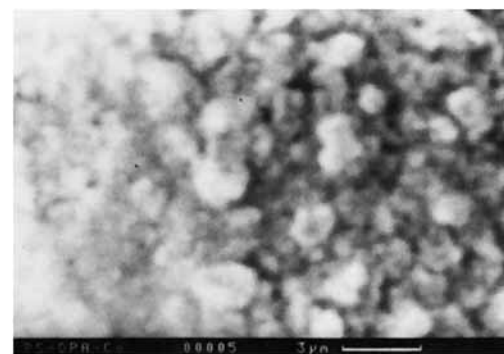
A comparative evaluation of the thermogravimetric curves of PS-DVB, PS-DVB-DPA, and the corresponding Fe-, Cu-, and Co-loaded polymers (Fig. 5) reveals the following features of interest: (i) The initial decomposition temperatures obey the trend PS-DVB = PS-DVB-DPA (280°C) < PS-DVB-DPA-Co (300°C) < PS-DVB-DPA-Fe (310°C) < PS-DVB-DPA-Cu (315°C). (ii) PS-DVB-DPA-Cu exhibits the highest overall stability in the range (300–700°C; 0–83% decomposition). Between Fe- and Co-loaded PS-DVB-DPA, the former is thermally more stable than the latter up to ca. 575°C (60% decomposition). Beyond this temperature and

in the range 500–700°C, they do not differ appreciably in stability, although Co-DPA-anchored polymer tends to reveal somewhat higher stability than does the Fe-DPA anchored PS-DVB. (iii) The metal-loaded PS-DVB polymer retains about 10–20% residues beyond 700°C, whereas the base polymer retains very low residues (<5%) in the same range.

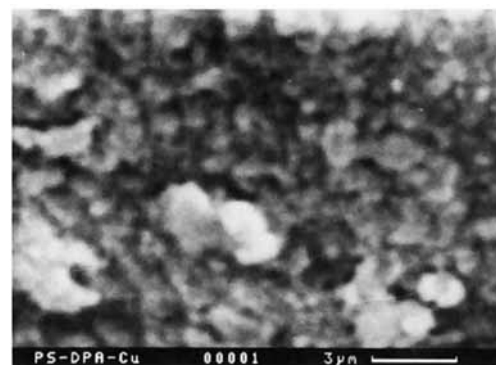
The stability difference between PS-DVB and PS-DVB-DPA is not appreciable, which may imply that the attachment of DPA as a pendant moiety to



(a)

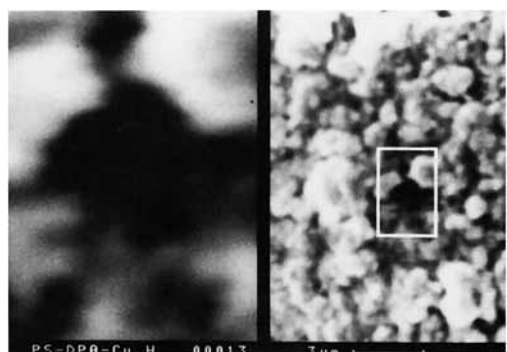


(b)

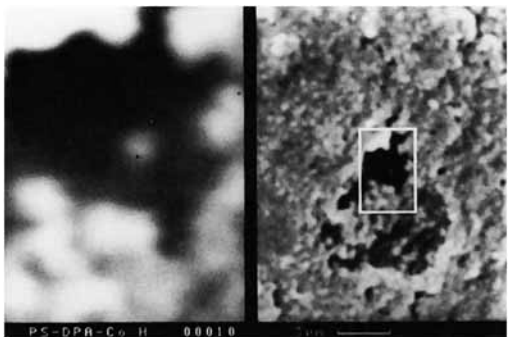


(c)

Figure 3 Scanning electron micrographs of (a) PS-DVB-DPA-Fe(III), (b) PS-DVB-DPA-Co(II), and (c) PS-DVB-DPA-Cu(II).



(a)

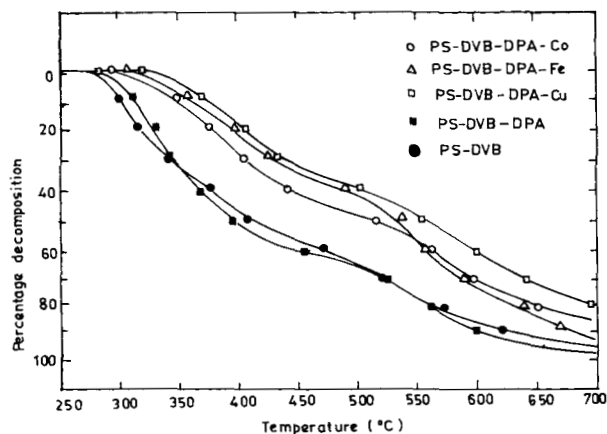


(b)

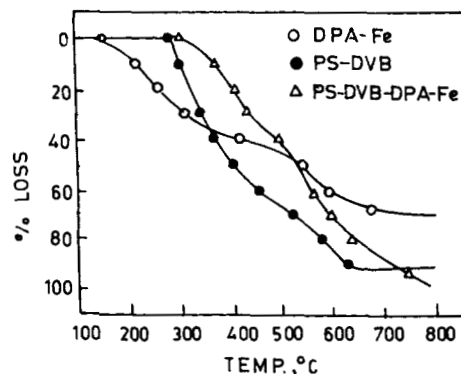
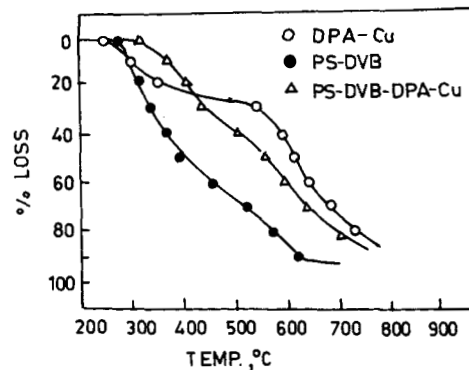
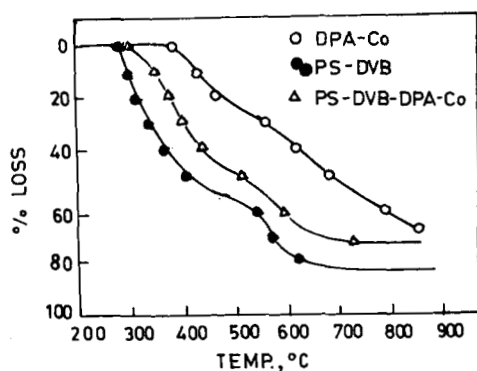
**Figure 4** Scanning electron micrographs of heat-treated polymer samples: (a) PS-DVB-DPA-Cu(II); (b) PS-DVB-DPA-Co(II).

the PS-DVB matrix does not involve any major structural change to cause any perceptible stability enhancement.

The appreciable increase in the thermal stability of the metal-loaded polymers relative to the base



**Figure 5** TG curves of PS-DVB, PS-DVB-DPA, and PS-DVB-DPA-M, [M = Cu(II), Fe(III), Co(II)].



**Figure 6** TG curves of PS-DVB, DPA-M, and PS-DVB-DPA-M [M = Cu(II), Fe(III), Co(II)].

polymers may be due to several reasons: First, the base polymer matrix must have been rendered more cross-linked by the metal complex anchored on it. One possible way by which this can happen is the coordination of the 3d-metal ions with the nitrogens of the dipyridyl units attached to different PS-DVB chains; in addition to the usual coordination involving nitrogens in a single chain, M-DPA not anchored onto any polymer chain is expected to show tetrahedral geometry as pointed out by Hendricker and co-workers<sup>6</sup> and others.<sup>18-20</sup> The exact geometry of M-DPA anchored on PS-DVB is not known with certainty, but assuming a tetrahedral geometry, it

may be supposed that dipyridyl nitrogens attached to various PS-DVB chains might provide the coordinating sites. Of course, coordination of anions of the salts ( $\text{Cl}^-$ ) or solvent moieties need not be ruled out in this regard. This situation would imply interchain cross-linking, which would obviously enhance the stability. The fact that the initial decomposition temperatures of the metal-loaded polymers have increased considerably relative to PS-DVB or PS-DVB-DPA, in particular, is consistent with such a situation.

A second point to consider is the contribution of the inherent thermal stability of the M-DPA complexes to the overall stability. Apparently, the ther-

mal energy required to break the PS-DVB-DPA-M matrix will involve energy to break the polymer matrix as well as the M-DPA moieties anchored on the PS-DVB matrix. To appreciate this point, the thermal stability of the M-DPA complexes was examined and the thermograms are presented in Figure 6. The data suggest two typical features: (i) that the stability trend for the M-DPA complexes is  $\text{DPA-Co} > \text{DPA-Cu} > \text{DPA-Fe(II)}$ , and (ii) that in all three instances the stability of the base polymer seemingly appears to have been enhanced by sharing a contribution from the M-DPA moiety. However, a direct correlation will be difficult as it will require knowledge about the precise extent of loading of M-

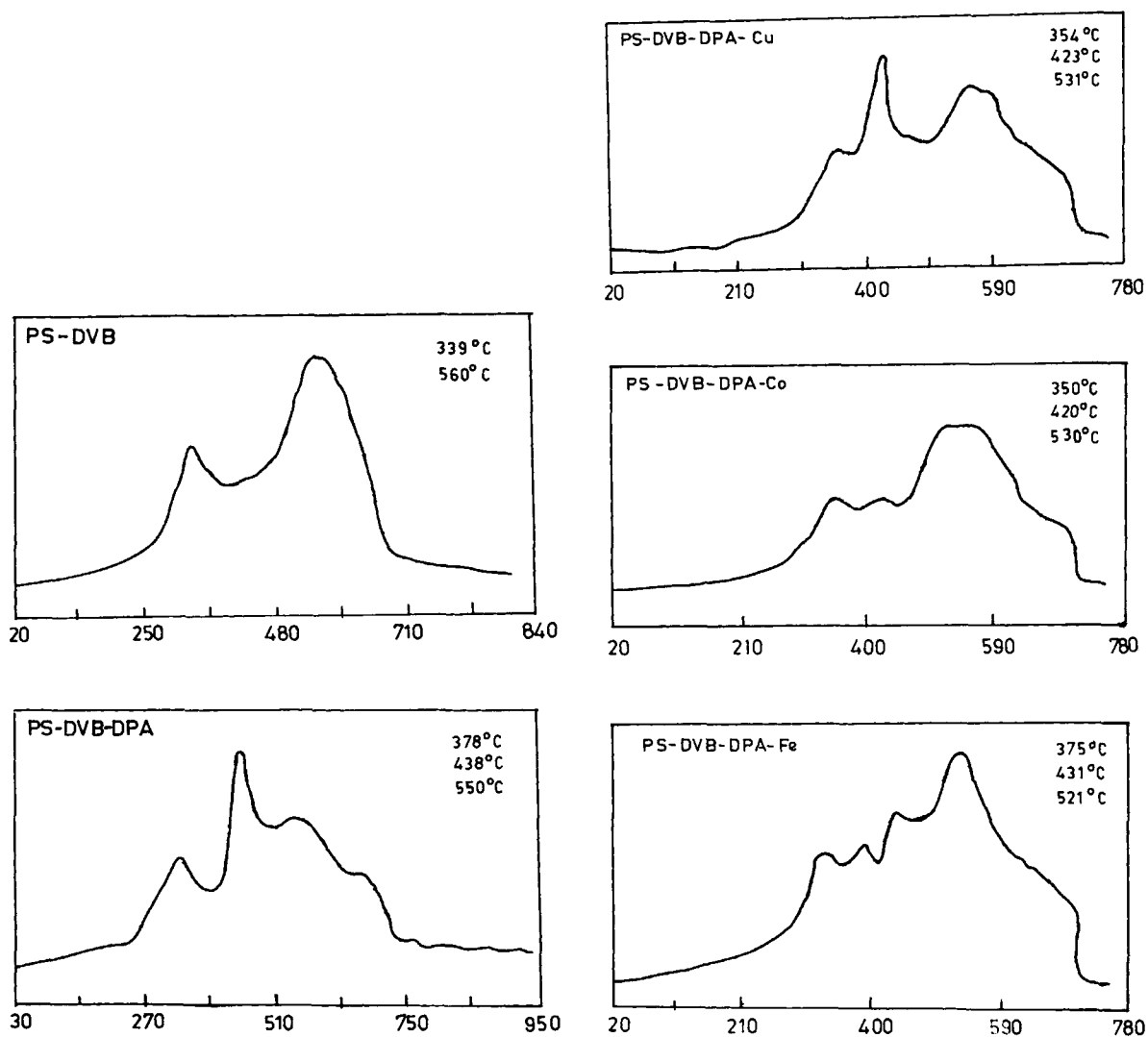


Figure 7 DTA traces of PS-DVB, PS-DVB-DPA, and metal-loaded PS-DVB [M = Co(II), Cu(II) and Fe(III)].

**Table II** DTA Characteristic Peaks of PS-DVB, PS-DVB-DPA, and PS-DVB-DPA-M

Polymer	Temperature	Peak Nature
PS-DVB	339	Exothermic
	560	Exothermic
PS-DVB-DPA	375	Exothermic
	438	Exothermic
	550	Exothermic
PS-DVB-DPA-Co(II)	350	Exothermic
	420	Exothermic
	530	Exothermic
PS-DVB-DPA-Fe(III)	375	Exothermic
	393	Exothermic
	431	Exothermic
	521	Exothermic
PS-DVB-DPA-Cu(II)	354	Exothermic
	423	Exothermic
	551	Exothermic

DPA moiety on the PS-DVB matrix as well as the extent of cross-linking induced in the polymer network through the anchored complex structure.

A further feature of interest in this context is that although Co-DPA exhibits by far the highest stability the corresponding PS-DVB anchored Co-DPA shows inferior stability relative to the Fe(III)- or Cu(II)-loaded polymers (Fig. 3). The exact reason for this behavior is obscure at the moment, although the lowest extent of loading as observed in this case (Table I) and also reported by Hendricker and co-workers<sup>6</sup> may have some influence, in addition to other factors like the geometry of the an-

chored complex<sup>21</sup> vis-à-vis the steric constraints of such structures particularly in a macromolecular network.

### Differential Thermal Analysis

Table II summarizes the characteristic DTA peaks (Fig. 7) of the various polymers. Between 300 and 380°C, the manifestation of the exothermic peaks is well in accord with the reported behavior of PS or the PS-DVB matrix corresponding to selective depolymerization and oxidative degradation.<sup>22</sup> Between 420 and 440°C, a new exothermic peak is identified in all the thermograms except that of the base polymer. This new peak may be ascribed to oxidative cleavage related to DPA. IR analyses carried out with samples heated to these temperatures also endorse the loss of DPA units. As suggested by Hendricker and co-workers and also confirmed in the present study, the selective IR bands at 1620, 1530, 1470, and 1150 cm<sup>-1</sup> are indicative of the attachment of DPA to the PS-DVB matrix. Table III shows how with increase in temperature "DPA" absorptions become progressively weak, virtually disappearing above 420°C.

In the temperature range between 500 and 700°C, the broad exotherms that manifest possibly correspond to oxidative degradation and depolymerization of the base polymer. The reported thermal characteristics of PS agree with this trend and it is fairly well established that  $\beta$ -scission and intramolecular hydrogen abstraction<sup>23</sup> reactions degrade the PS matrix into styrene, monoaromatics, and styrene oligomers in this temperature range.<sup>24</sup> As revealed by all the thermograms, the breakdown of the matrix as a whole occurs in this temperature

**Table III** Variation of DPA IR Absorption Peaks with Temperature

Polymer	Temp (°C)	IR Peaks Due to DPA (cm <sup>-1</sup> )			
PS-DVB	RT	—	—	—	—
PS-DVB-DPA	RT	1620	1530	1470	1150
	416 <sup>a</sup>	—	—	—	—
PS-DVB-DPA-Cu(II)	RT	1620	1530	1470	1150
	415 <sup>a</sup>	1620 (vw) <sup>b</sup>	—	—	—
PS-DVB-DPA-Fe(III)	RT	1620	1530	1470	1150
	415 <sup>a</sup>	1620 (vw) <sup>b</sup>	—	—	—
PS-DVB-DPA-Co(II)	RT	1620	1530	1470	1150
	412 <sup>a</sup>	—	—	—	—

<sup>a</sup> The temperatures chosen are such where the rate of the exothermic reaction is maximum.

<sup>b</sup> vw = very weak.

range. The residues remaining are presumably the metal oxides, with different degrees of inherent stability.

### Glass Transition Temperature ( $T_g$ )

The glass transition temperatures as determined by a thermochemical analyzer for the base polymer (PS-DVB) as well as the metal-anchored polymers are in the range 121–125°C. These data do not suggest any particular variation in the  $T_g$  values for the various polymers. This feature seems to be in contradiction to the expected enhancement in  $T_g$  after structural modification.<sup>25,26</sup> Perhaps, the extent of metal-ion loading in this instance is insufficient to cause large structural changes to arrest segmental motion in the modified PS-DVB matrix, which would show up in an enhanced  $T_g$ .

### CONCLUSION

Thermal stability of the polystyrene-divinylbenzene copolymer can be significantly modified by anchoring dipyrindylamine complexes of Fe(III), Co(II), and Cu(II). The glass transition temperatures of these polymers do not reveal any difference between the various polymers.

Thanks are due to Professors P. G. Mukund, Metallurgical Engineering Department, and D. Dasgupta, Geology and Geophysics Department of IIT Kharagpur, for help in the TMA and ICP-ES analyses of the polymers, and to the authorities of IIT Kharagpur for use of their facilities.

### REFERENCES

1. M. Biswas and A. Mukherjee, *Adv. Polym. Sci.*, to appear.
2. M. Biswas and S. Moitra, *Polym. Prepr.*, **27**, 76 (1986).
3. M. Biswas and S. Moitra, *J. Appl. Polym. Sci.*, **38**, 1243 (1989).
4. M. Biswas, S. Moitra, and T. Uryu, *Polym. Commun.*, **30**, 225 (1989).
5. M. Biswas, S. Moitra, A. S. Brar, and R. G. Mendiratta, *Polym. Commun.*, **31**, 237, (1990).
6. Mark, R. Kratz, and D. J. Hendricker, *Polymer*, **27**, 1641 (1986).
7. M. Biswas and A. Mukherjee, *J. Appl. Polym. Sci.*, **46**, 1453 (1992).
8. B. S. Furniss, A. J. Handford, P. W. G. Smith, and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., Longman, Harlow, Essex, 1989, pp. 407, and 406.
9. M. E. Fernandopulle, P. A. Gillespie, and W. R. McWhinnie, *Inorg. Chim. Acta*, **29**, 137 (1978).
10. J. C. Bailer and S. Kirschner, *Inorg. Syn.*, **5**, 184 (1957).
11. S. Kirschner, *Inorg. Syn.*, **5**, 14 (1987).
12. B. Merrifield, in *Polymer Science in Next Decade*, O. Vogl and E. H. Immergut, Eds., Wiley, New York, 1987, p. 63.
13. B. Merrifield, *J. Am. Chem. Soc.*, **85**, 2149 (1963).
14. R. S. Drago et al., *J. Am. Chem. Sci.*, **102**, 1033 (1980).
15. M. G. Dibbs, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., J. I. Kroschwitz, Ed., Wiley-Interscience, New York, 1989, Vol. 16, p. 152.
16. W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **27**, 1619 (1965).
17. K. Nakamoto, in *Infrared and Raman Spectra of Inorganic and Co-ordination Compounds*, 3rd ed., Wiley, New York, 1978, p. 214.
18. M. Goodgame, *J. Chem. Soc. A*, 63 (1966).
19. M. E. Fernandopulle, P. A. Gillespie, and W. R. McWhinnie, *Inorg. Chim. Acta*, **29**, 197 (1978).
20. W. R. McWhinnie, *J. Chem. Soc. A*, 5165 (1964).
21. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, 1988, pp. 718, 726, 766.
22. J. J. R. Nerten, *Makromol. Chem. Rapid Commun.*, **3**, 350 (1982).
23. N. L. Macker, in *Encyclopaedia of Polymer Science and Engineering*, 2nd ed., J. I. Kroschwitz, Ed., Wiley-Interscience, New York, 1989, Vol. 16, p. 180.
24. U. K. O. Schroder and K. H. Ebert, *Makromol. Chem.*, **185**, 991 (1984).
25. J. R. Critchley, in *Encyclopedia of Physical Science and Technology*, R. A. Meyers, Ed., Academic Press, New York, 1987, Vol. 11, p. 144.
26. M. E. Brown, in *Introduction to Thermal Analysis*, 1st ed., Chapman and Hall, London, 1988, p. 66.

Received December 3, 1992

Accepted April 22, 1993