

High-Yield γ -Ray-Induced Polymerization of Bis-2-Acetoacetoxyethyl methacrylate Copper. II.

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ABSTRACT: The copper (II) acrylic monomer Cu(aaem)₂ (aaem = 2-acetoacetoxyethyl methacrylate) undergoes high-yield γ -ray copolymerization with dimethylacrylamide, styrene, and hydroxyethyl methacrylate in the presence of methylene bisacrylamide as crosslinking agent in dimethylformamide. The metalloorganic copolymers are fully characterized. Polymer-protected Cu(II) results in being extremely stable toward a number of reducing agents in different media. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2201–2207, 1997

Key words: 2-acetoacetoxyethyl methacrylate copper (II); γ -rays; copolymerization; crosslinked copolymers

INTRODUCTION

A clear interest in copper (II) [Cu(II)]-containing macromolecular materials is apparent in the recent literature.^{1,2} A straightforward route to a variety of such materials would be the polymerization of convenient metalloorganic monomers. However, the co- and, especially, homopolymerization of Cu(II)-containing olefinic monomers has been an elusive goal in macromolecular chemistry so far. The major obstacle to this achievement has been considered the effi-

cient termination of the radical chain propagation by the Cu(II) centers, which are reduced to Cu(I) species.³

We recently reported⁴ on the very successful homopolymerization of Cu(aaem)₂ (aaem = 2-acetoacetoxyethyl methacrylate) under γ -ray irradiation to give a metalloorganic matrix in which the molecular identity of the [CuO₄] chromophore is perfectly maintained through the polymer network. We report in this article the successful copolymerization of Cu(aaem)₂ with dimethylacrylamide (DMAA), styrene (STYR), and hydroxyethyl methacrylate (HEMA) in the presence of methylene bisacrylamide (MBAA) as the crosslinking agent in dimethylformamide (DMF).

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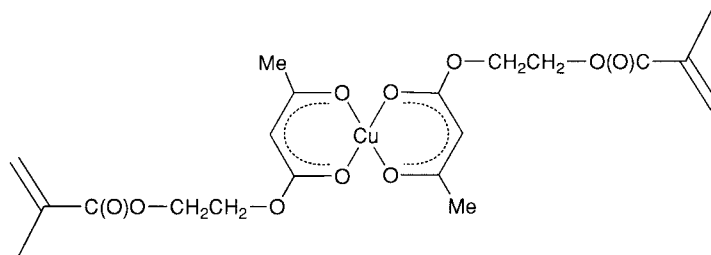


Figure 1 Sketch of the molecular structure of $\text{Cu}(\text{aaem})_2$.

EXPERIMENTAL

Materials

Reagents and solvents were of reagent grade from various commercial sources. 2-Acetoacetoxyethyl methacrylate was from Jannssen (Geel, Belgium) and was used as received. $\text{Cu}(\text{aaem})_2$ (Fig. 1) was prepared according to Ref. 4.

Apparatus

The instrumental analyses were performed using a Biorad FTS7-PC FTIR spectrometer, a Cary-5E spectrophotometer UV-VIS-NIR equipped with a

diffusive reflectance accessory, a Perkin-Elmer TGS-2 thermobalance, a Perkin-Elmer DSC-4 differential calorimeter, a Faraday magnetic balance from Oxford Instruments, equipped with a Cahn 2000 microbalance, and a Carlo Erba 1106 elemental analyzer.

Synthesis

The required amounts of monomers and MBAA (ca. 4% mol/mol) were dissolved in the minimum amount of DMF. After flushing the solutions with dinitrogen to remove dioxygen, the samples were irradiated at 0.50 Gy s^{-1} for 72 h at room tempera-

Table I Analytical and Spectroscopic Data on Monomer $\text{Cu}(\text{aaem})_2$ and Its Copolymers 1–3

	Yield %	Elemental Analysis ^a				FTIR (cm^{-1})					
		C %	H %	N %	Cu %	ν_{CO}	$\nu_{\text{C}=\text{C}}$	$\nu_{\text{Ring}}^{\text{b}}$	$\nu_{\text{COC}}^{\text{c}}$	π_{CH}	Other
$\text{Cu}(\text{aaem})_2$						1722 (s) ^f	1637(w)	1598(s) 1529(s)	1283(s) 1169(s)	774(m) ^d	937(m) ^e 3443(s) ^g
1	83	45.5 (44.9)	5.1 (6.1)	1.3 (1.33)	10.6 (10.5)	1729(s) ^f 1646(w) ^h	—	1604(s) 1520(s)	1286(s) 1172(s)	782(m) ^d	974(m) ^e
2	85	54.6 (54.4)	5.5 (5.7)	0.4 (0.3)	10.6 (10.5)	1730(s) ^f	—	1602(s) 1518(s)	1287(s) 1171(s)	781(m) ^d 702(m), 761(m) ⁱ	973(m) ^e
3	7	48.4 (50.5)	6.0 (5.8)	0.5 (0.5)	9.7 (9.9)	1732(s) ^f	1637(sh)	1603(s) 1521(s)	1286(s) 1171(s)	781(m) ^d	972(m) ^e

^a Expected figures in parentheses (see the text for the calculation of the theoretical values for 1).

^b Breathing of the chelate rings.

^c Ester groups.

^d Out-of-plane deformation of methyne in the chelate rings.

^e Out-of-plane deformation of vinylic methylenes.

^f Ester groups (methacrylate).

^g Broad, ν_{OH} .

^h Amide groups.

ⁱ Out-of-plane deformation of methynes in the aromatic rings.

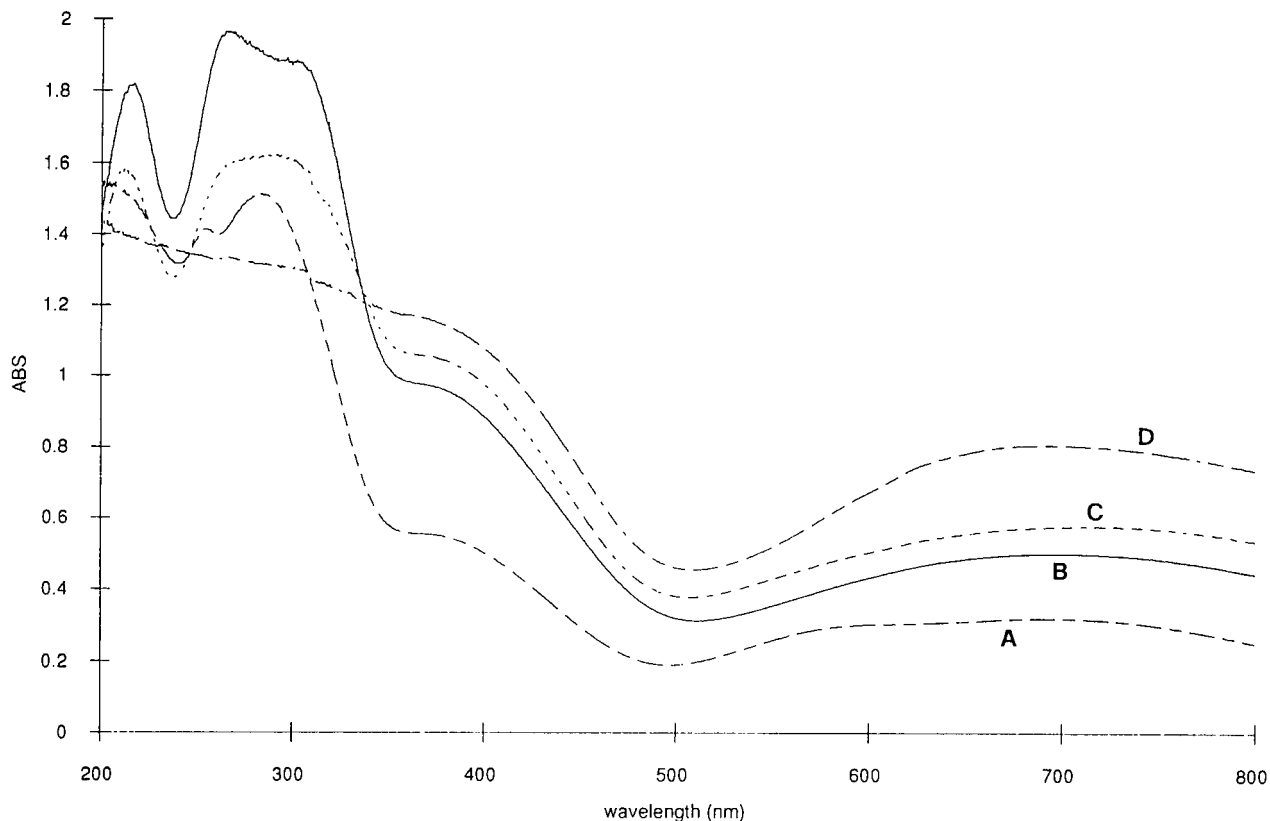


Figure 2 Reflectance UV-vis spectra of $\text{Cu}(\text{aaem})_2$ and **1**: (A) $\text{Cu}(\text{aaem})_2$; (B) **1**, dry; (C) **1**, swollen in DCE; (D) **1**, swollen in MeOH).

ture. The obtained products precipitated as green, very fine powders, which were filtered off, washed with DMF, methanol, and diethyl ether ($3 \times 3 \times 3 \times 30$ mL):

Poly- $\{\text{Cu}(\text{aaem})_2\text{-DMAA-MBAA}\}$ (**1**), $\text{Cu}(\text{aaem})_2$ (1.03 g), DMAA (0.21 g), MBAA (0.028 g), in 10 mL DMF. Bright green powder; 1.05 g of product (yield = 83%).

Poly- $\{\text{Cu}(\text{aaem})_2\text{-STYR-MBAA}\}$ (**2**), $\text{Cu}(\text{aaem})_2$ (1.02 g), STYR (0.21 g), MBAA (0.028 g),

in 10 mL DMF. Dark green powder; 1.08 g of product (yield = 85%).

Poly- $\{\text{Cu}(\text{aaem})_2\text{-HEMA-MBAA}\}$ (**3**), $\text{Cu}(\text{aaem})_2$ (0.67 g), HEMA (0.19 g), MBAA (0.023 g), in 10 mL DMF. Pale green powder; 0.63 g of product (yield = 71%).

Acidolysis Tests

Typically, 100 mg of polymer was suspended in methanol and treated with a large excess of differ-

Table II Relative Expanded Volumes (REV) of Materials 1–3 in Various Solvents

Polymer	H_2O	MeOH	DCE	Toluene	<i>n</i> -Hexane
1	0.9	0.9	1.0	1.2	1.2
2	1.1	1.3	1.1	1.0	1.2
3	1.5	1.6	1.5	1.6	1.6

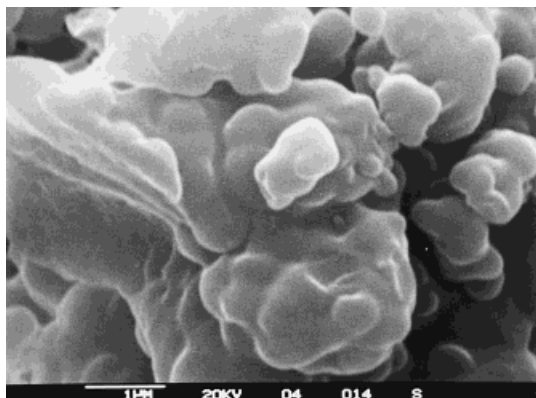


Figure 3 SEM picture of 1.

ent acidic reagents. Reaction with 0.2M aqueous HCl gave rapid discoloration and produced a white material, which was filtered and thoroughly washed with methanol and water.

Attempted Reduction of Cu(II) in Polymers 1, 2, and 3

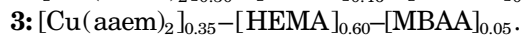
Typically, 100 mg of the polymer was suspended in ethanol or water and treated with a large excess of NaBH_4 , N_2H_4 , or COH_2 (under nitrogen) or with an excess of hydrogen, under vigorous stirring.

RESULTS AND DISCUSSION

Synthetic, Structural, Morphological, and Thermal Features

The copolymers poly-Cu(aaem)₂-DMAA-MBAA (**1**), poly-Cu(aaem)₂-STYR-MBAA (**2**), and poly-Cu(aaem)₂-HEMA-MBAA (**3**) were prepared in high yields as green powders. Yields and analytical data are collected in Table I.

The experimental results of the elemental analyses (C, H, N, Cu) of **2** and **3** are in agreement with those expected for materials in which the monomer proportion is the same as in the starting polymerization mixture. Accordingly, their experimental compositions are as follows:



As for **1**, the low nitrogen weight proportion indicates that the conversion of DMAA is far from

being quantitative (MBAA is a tetrafunctional monomer and is assumed to react quantitatively). Moreover, the FTIR spectrum of **1** presents a very strong, broad ν_{OH} band (3443 cm^{-1}), which suggests the presence of a substantial amount of water in the material. Thus, the theoretical figures for the elemental composition of **1**, reported in Table I, were calculated on the basis of the following assumptions: (i) Cu(aaem)₂ and MBAA conversion equal to 100%; (ii) DMAA conversion equal to 40%; and (iii) water weight proportion equal to 10% of the total weight of the material. The agreement between the found and the calculated values is good and we propose the following molar composition for **1**:



The IR spectra of the finely crushed metalloorganic materials turn out to be particularly well resolved and the evidence of the typical group frequency of the metalloorganic ring in polymers **1–3** demonstrates the survival of the $[\text{CuO}_4]$ chromophore. This circumstance is further confirmed by the UV-vis reflectance spectra (Fig. 2). The electronic spectra were recorded both on dry and swollen materials (in methanol and 1,2-dichloroethane [DCE]).

The spectra appear fairly well resolved from 350 to 800 nm. The charge transfer band at 380 nm turns out to be practically identical for solid Cu(aaem)₂ and polymer **1**, under different conditions. The typical $d-d$ band of Cu(II) square planar chromophores is observed at ca. 700 nm for solid Cu(aaem)₂ and for **1** both in the dry

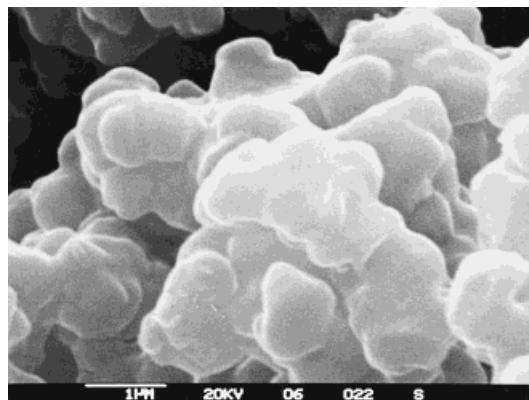


Figure 4 SEM picture of 2.

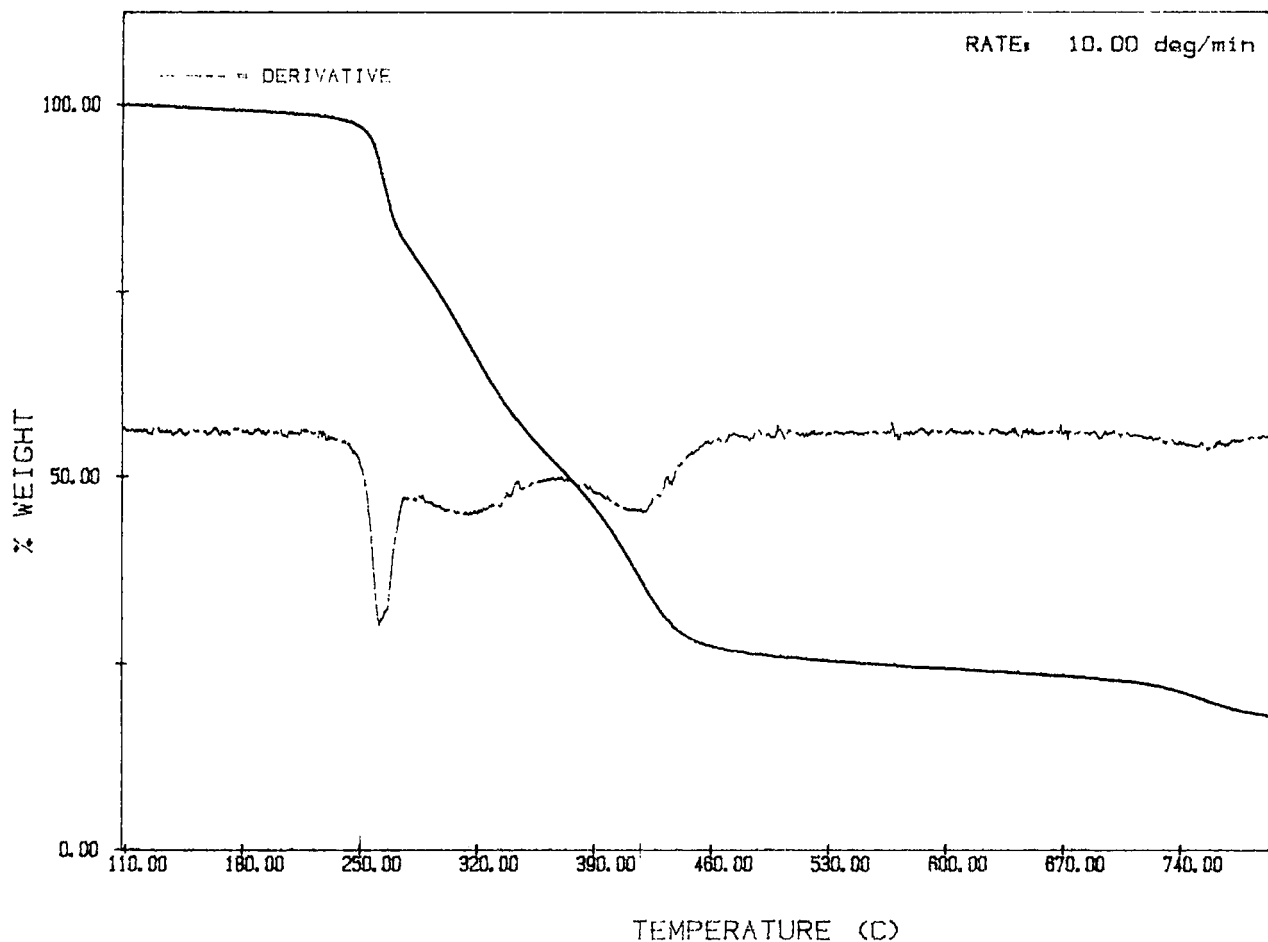


Figure 5 TG profile of copolymer 1.

state and after swelling in methanol. In dichloroethane, λ_{max} is seen at ca. 670 nm. This modest ipsochromic effect is likely to be the consequence of a slight geometric distortion of the $[\text{CuO}_4]$ chromophore in the polymer network, which brings out a little modification of the energy levels of the d orbitals in the metal ions.

The presence of the $[\text{CuO}_4]$ chromophore in the metalloorganic polymers is shown also by magnetic moment measurements which give μ figures (BM) equal to 2.13 (**2**) and 1.99 (**3**) to be compared with 1.87 for pure $\text{Cu}(\text{aaem})_2$.⁴ The magnetic moment for the Cu(II) square planar complexes is known to range from 1.7 to 2.2 BM (Ref. 5) and the observed figures appear to be normal ones.

Electrical conductivity measurements carried out on a sample of polymers **1-3** revealed that they are nonconducting at room temperature (σ

$< 10^{-6} \Omega^{-1} \text{m}^{-1}$). The solvent compatibility of materials **1-3** has been roughly estimated on the basis of relative expanded volume measurements (REV, the ratio between the swollen volume and the dry volume of the polymeric materials; Table II).

REV values are small, particularly in the case of **1** and **2**. Copolymer **3** reveals an appreciable amphiphilic character,⁶ i.e., REV values practically independent of the nature (hydrophilic/hydrophobic) of the liquid medium. The low values of REV are not unexpected in that the metalloorganic monomer is potentially a tetrafunctional monomer and could act as a crosslinking agent. As a consequence, the crosslinking degree can be much higher than that expected on the basis of the experimentally determined molar fraction of MBAA. In spite of the presence of $\nu_{\text{C}=\text{C}}$ bands attributable to dangling methacrylate groups in the IR spectra of **1, 2**, and **3** (see Table I), a crosslinking

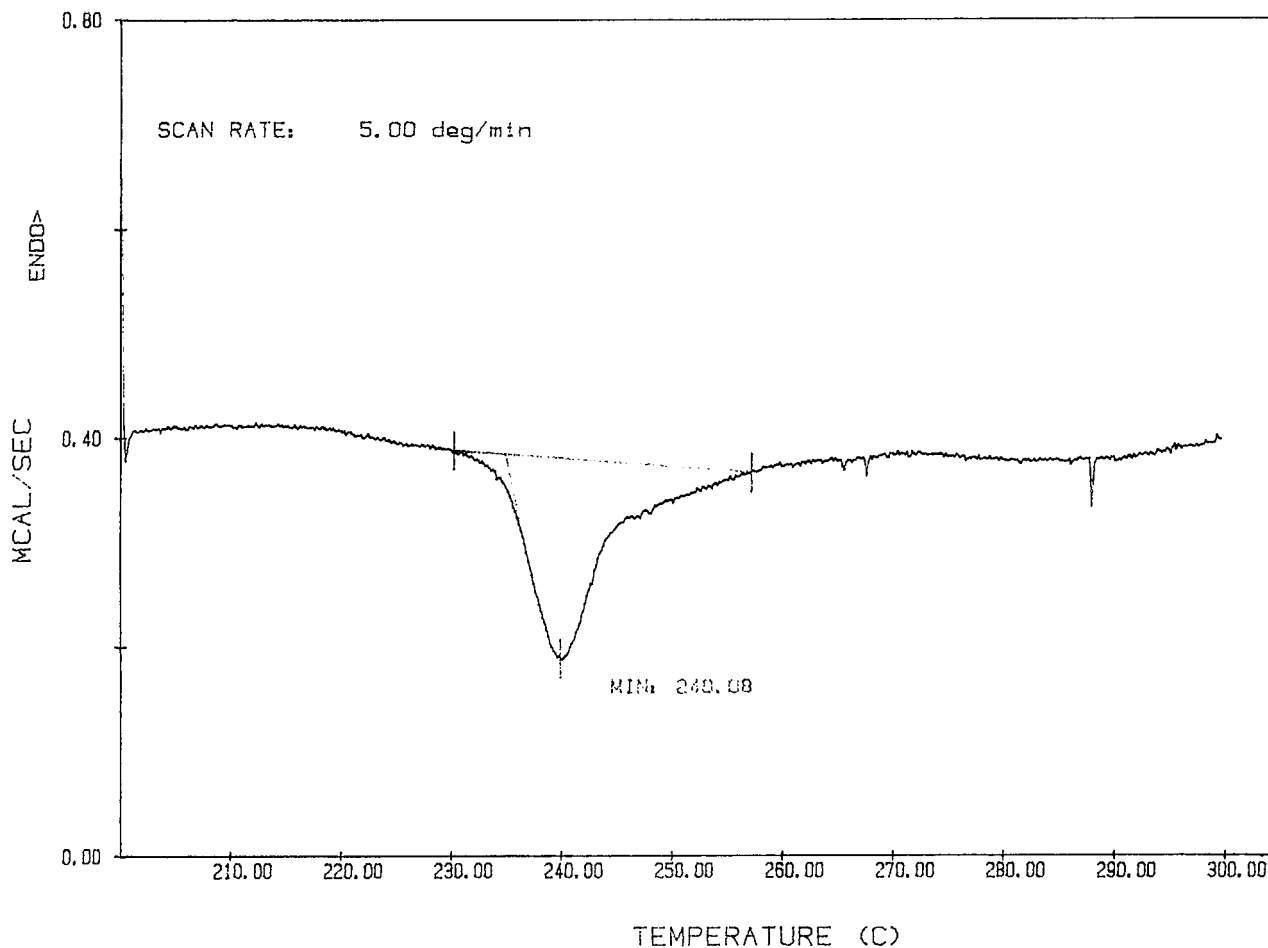


Figure 6 DSC profile of copolymer 1.

degree higher than expected is apparent from the microscopic features of polymers **1–3** (Figs. 3, 4). In fact, SEM pictures reveal that materials **1–3** are obtained as powders built up by microparticles cauliflowerlike as already observed and interpreted for highly crosslinked polystyrene resins.⁷

Polymers **1–3** were examined by TG and DSC analysis. TG profiles are similar and they reveal a clear thermal stability up to 250°C (**1**), ca. 220°C (**2**), and 230°C (**3**) under nitrogen. The TG profile of **1** is depicted in Figure 5.

The profile exhibits a sharp weight loss at 250°C followed by a more gradual one up to 420°C. The final weight at 800°C is essentially attributable to CuO. DSC profiles of polymers **1–3** are also similar (Fig. 6). In all cases, a clear hexothermal peak is observed (onset) at 235°C (-51.6 kJ kg^{-1}) (**1**), 220°C (-49.7 kJ kg^{-1}) (**2**), and 230°C (-34.5 kJ kg^{-1}) (**3**).

We propose that the first sharp weight loss associated with the hexothermal event is due to the disruption of the metalloorganic crosslinks which release small organic fragments and produce CuO. In the subsequent 280–400°C range, the gradual thermal decomposition of the remaining polymer networks occurs. On the basis of this proposal, the hexothermal peak should be due to the balance of the endothermal decomposition of the metalloorganic crosslinks and of the likely hexothermal formation of CuO.

Chemical Behavior

Matrices **1–3** were tested in acidolysis experiments. The action of 0.2M aqueous HCl in MeOH produces instantaneous Cu(II) release for **1** and **3** and a slower one (after 60 min) for **2**. The demetallated resin stemming from **1** appears white in

color and much more swellable in methanol than is **1**. FTIR spectra fit with the quantitative removal of the $[\text{CuO}_4]$ chromophore. TGA–DSC measurements revealed that metal removal produces a marked decrease of the thermal stability of the polymer network (onset of the decomposition at ca. 170 vs. 250°C). Remetallation experiments performed upon contacting the demetallated resin with Cu(II) acetate in ethanol fails after 24 h.

Materials **1** and **3** were treated with various reducing agents in ethanol (NaBH_4) and in water (N_2H_4 , CH_2O) at ambient temperature under nitrogen and with gaseous hydrogen in water. Although reference experiments showed that $\text{Cu}(\text{aaem})_2$ undergoes an instantaneous reduction to metallic copper upon reaction with NaBH_4 in ethanol and with N_2H_4 in water, only modest visual evidence of reactivity [i.e., Cu(II) reduction] is obtained. The green color of resins **1** and **3** turns to yellow–green with very few changes in the reflectance UV-vis spectra. Magnetic susceptibility

measurements carried out on these materials give magnetic moments ranging from 1.77 to 2.20 BM, thus in agreement with lack of any reduction of Cu(II) to Cu(I).

REFERENCES

1. E. Chiessi, M. Branca, A. Palleschi, and B. Pispisa, *Inorg. Chem.*, **34**, 2600–2609 (1995).
2. E. C. Theil and K. N. Raymond, in *Bioinorganic Chemistry*, I. Bertini, H. B. Grey, S. J. Lippard, and J. S. Valentine, Eds., University Science Books, Mill Valley, CA, 1994.
3. A. D. Pomogailo and I. E. Uflyand, *Adv. Polym. Sci.*, **97**, 61 (1990).
4. B. Corain, P. Mastroilli, and M. Zecca, *Makromol. Chem. Rapid Commun.*, **14**, 799 (1993).
5. R. Arshady, *Adv. Mater.*, **3**, 182 (1991).
6. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, 1988.
7. A. Guyot, in *Syntheses and Separations Using Functional Polymers*, D. C. Sherrington and P. Hodge, Eds., Wiley, New York, 1988, p. 1.