

Gamma Ray-Induced Copolymerization of Copper (II) Methacrylate: A Way of Access to Copper-Based Synthetic Micro- and Macroporous Resins

A. BACCANTE,¹ R. QUARESIMA,¹ S. LORA,² G. PALMA,³ R. VOLPE,¹ B. CORAIN¹

¹ Dipartimento di Chimica, Ingegneria Chimica e Materiali, via Vetoio, 67100 L'Aquila, Italy

² Istituto F.R.A.E., C.N.R., 35020 Legnaro, Italy

³ Dipartimento di Chimica Fisica, via Loredan 2, 35131 Padova, Italy

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ABSTRACT: Copper methacrylate undergoes high-yield copolymerization with hydroxiethylmethacrylate in the presence of 1,1,1-tris(hydroximethyl)propane trimethacrylate under γ -rays irradiation at room temperature. The bluish-green materials are characterized by bulk expanded volume measurements and infrared and ultraviolet-visible spectroscopy, and appear to be able to slowly release an appreciable percentage of the metal center embodied in the polymer network. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 11–17, 1998

Key words: copper (II); methacrylate; copolymerization; resin; gamma-rays

INTRODUCTION

We have recently reported on the successful γ -rays-promoted homo- and copolymerization of bis (2-acetoacetoxyethylmethacrylate) copper (II)^{1,2} with dimethylacrylamide, styrene, and hydroxyethyl methacrylate (HEMA) in the presence of methylenebisacrylamide as crosslinking agent, in dimethylformamide. Quite in contrast with literature reports,^{3–5} polymerization yields were higher than 80% and the {Cu^{II}O₄} chromophore did survive the polymerization reaction. Surprisingly enough, the Cu^{II} centers turned out to be extremely resistant to the reduction of Cu^{II} to Cu^I or to Cu⁰ by a variety of reducing agents.^{1,2}

The apparent gamma rays promoted straight polymerization of Cu^{II}-containing vinyl mono-

mers suggested to us the extension of the approach to other Cu^{II}-containing vinyl monomers, such as the commercially available monomer Cu(MA)₂ (methacrylate, MA), suitable to provide Cu^{II}-containing resins potentially able to ensure a slow release of “Cu²⁺” ions upon progressive hydrolytic demolition of the polymer network.⁶ On the basis of this expectation, these materials could be reasonable models for the development of novel Cu^{II}-based biocidal (mainly “antifouling”) preparations against algae and bacteria proliferation.

EXPERIMENTAL

Materials

Reagents and solvents were of reagent grade from various commercial sources. Nominally anhydrous copper methacrylate [Cu(MA)₂] was from Polysciences (Warrington, PA). HEMA and 1,1,1-

Correspondence to: B. Corain.

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Table I Molar Compositions of Monomer Mixtures and Analytical Data of Obtained Resins

Resins	HEMA ^a	CL ^a	Cu(MA) ₂ ^a	NH ₃	C (%)	H (%)	Cu (%)	Yield (%)
1A	95.95	1.35	2.70	—	55.20 ^b 51.78 ^c	7.56 ^b 7.52 ^c	1.27 ^b 1.25 ^c	80
1B	92.96	4.23	2.82	—	55.92 ^b 52.31 ^c	7.56 ^b 7.47 ^c	1.27 ^b 1.06 ^c	70
1C	88.59	8.41	3.00	—	56.40 ^b 52.64 ^c	7.56 ^b 7.32 ^c	1.27 ^b 1.20 ^c	88
2	69.00	0.96	3.82	26.22 ^d	52.18 ^b 50.40 ^c	7.80 ^b 7.10 ^c	2.30 ^b 3.16 ^c	70

^a Molar compositions.

^b Theoretical for a 100% polymerization yield.

^c Experimental.

^d Molar fraction of NH₃ needed to promote perfect homogeneity (see text).

tris(hydroxymethyl)propane trimethacrylate (CL) were from Aldrich (Milano, Italy).

Apparatus

Equipment included: a Biorad FTS7-PC Fourier transform infrared (FTIR) spectrometer, a Cary-5E UV-VIS-NIR spectrometer equipped with a diffusivity reflectance accessory, a Perkin-Elmer 2380 atomic absorption spectrophotometer, and a 505 Philips scanning electron microscope. Elemental analyses (C, H, N) were performed with a Perkin-Elmer 2400 apparatus connected to a Perkin-Elmer AD-4 autobalance. Copper analyses were carried out by atomic absorption spectrometry, after resins mineralization with 98% H₂SO₄ and H₂O₂ (110 vol/s) (20 mg resin in 10 mL H₂SO₄ and 8 mL H₂O₂).

Synthesis

The required amounts of monomers were mixed in suitable plastic vials to give homogeneous greenish-blue mixtures in the case of **1B** and **1C**, which, after purging with nitrogen, were stopped and γ -irradiated for given times (resins **1A**, **1B**, **1C**). In the case of the synthesis of **1A**, the monomer mixture turned out to be slightly turbid, which suggested the addition of moderate amounts of aqueous ammonia and water (see Table I). This led to a limpid, dark-blue mixture which was treated as those relevant to **1A-1C**, resin **2**.

Synthetic details are as follows. The monomer mixtures were γ -irradiated at about 20°C at a “dose rate” equal to 0.47 Gy s⁻¹, for 6 h.

1A: HEMA (1.93 g), CL (0.07 g), Cu(MA)₂ (0.10 g). Blue, hard solid. 1.7 g of product (yield = 80%).

1B: HEMA (1.80 g), CL (0.20 g), Cu(MA)₂ (0.10 g). Greenish-blue, hard solid. 1.5 g of product (yield = 70%).

1C: HEMA (1.60 g), CL (0.407 g), Cu(MA)₂ (0.10 g). Bluish-green, hard solid. 1.85 g of product (yield = 88%).

2: HEMA (3.00 g), CL (0.11 g), Cu(MA)₂ (0.30 g), aqueous ammonia 25% (0.61 g), H₂O (2.41 g). Dark-blue, rubbery solid. 2.4 g of product (yield = 70%).

The values of the polymerization yields refer to samples of crude **1A-1C** and **2** materials after the following treatment. **1A**, **1B**, and **1C** were ground with an impact grinder and then with an agata mortar. The final fine powders were sieved to less than 212 μ m, thoroughly washed 3 times under vigorous stirring with 50 mL of deionized water,

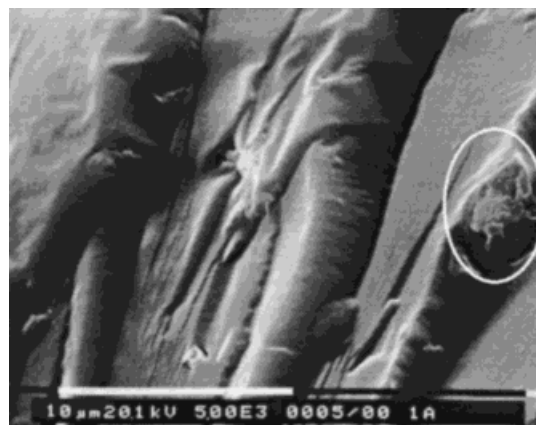


Figure 1 SEM picture: Resin **1A**.

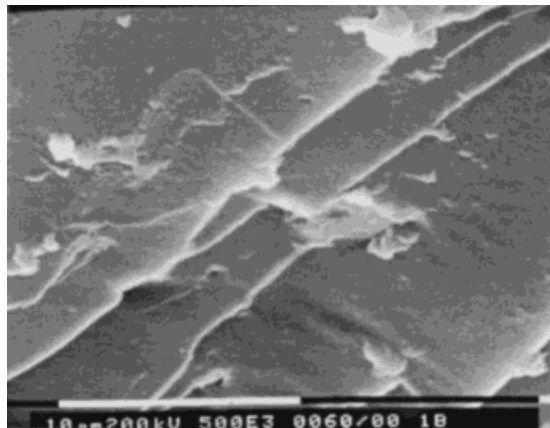


Figure 2 SEM picture: Resin 1B. Circled area shows minor inclusions of $\text{Cu}(\text{MA})_2$.

separated upon filtration, filtrated, and dried *in vacuo*. The surnatant of the first washing steps was bluish; three washings were estimated to be sufficient, as the third surnatant appeared to be colorless.

Copolymer **2**, after γ -irradiation, exhibited a continuous loss of weight and a marked smell of ammonia. The crude blue cylinder was left for 48 h *in vacuo*, after which time both color and physical aspect did not change significantly. The cylinder was cut in slices and washed 3 times with 50 mL of water for 1 h. After filtration and drying *in vacuo*, **2** appeared as brittle slices which, after gentle grinding inside an agata mortar, gave a green powder which was eventually sieved to less than 212 μm .

Bulk Expanded Volume (BEV) Measurements

Weighed amounts of all four resins (typically 0.15 g) were put inside a graduated tube equipped with

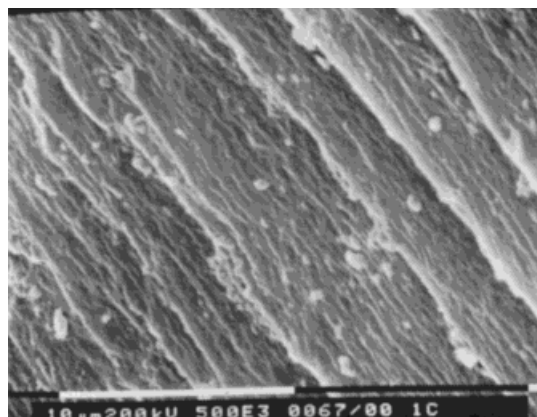


Figure 3 SEM picture: Resin 1C.

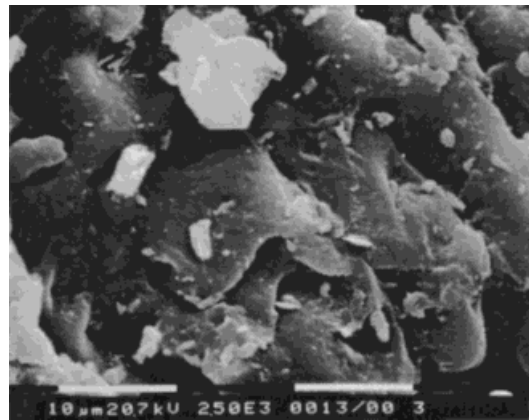


Figure 4 SEM picture: Resin 2.

a fritted glass at the lower end. Excess water was added to the resin and the final volume was read after 1 h, at room temperature.

Hydrolytic Stability Tests

Weighed amounts of all four resins (typically 0.5 g) were suspended in 1 L of water kept inside 2-L Erlenmayer flasks under vigorous stirring. At given times, stirring was stopped and the resin was allowed to sediment overnight. Surnatant solution, 5 mL, was removed and analyzed for Cu^{II} after filtration with a 0.45- μm -millipore membrane. Each aliquot of 5 mL of tested solution was replaced by 5 mL of pure water.

RESULTS AND DISCUSSION

The synthetic strategy was aimed at obtaining three different metalloorganic polymer networks

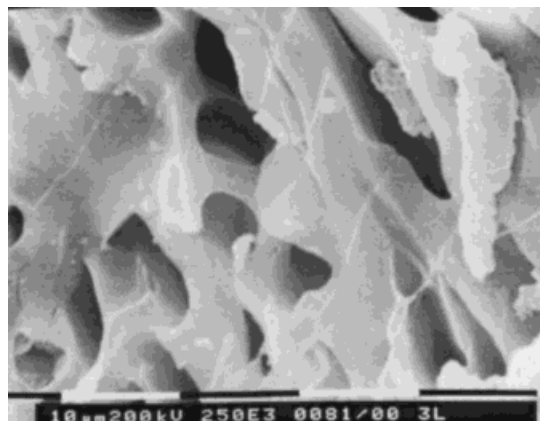


Figure 5 SEM picture: Resin 2.

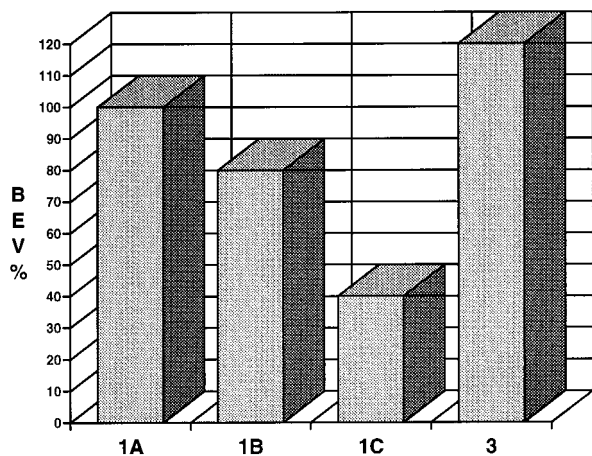


Figure 6 Bulk expanded volumes measured in water.

characterized by similar Cu^{II} contents and different crosslinking degrees (Table I).

While the reaction mixtures in the case of **1B** and **1C** were homogeneous, in the case of **1A** $\text{Cu}(\text{MA})_2$ did not completely dissolve. To obtain a clear mixture, a modest amount of aqueous ammonia was added, which led to a dark-blue solution. The results of a typical experiment of this kind are reported in Table I (resin **2**).

Polymerization yields were fairly high and

the Cu^{II} incorporation turned out to be close to the theoretical one for resins **1A–1C**, thus suggesting rather similar reactivities of HEMA and $\text{Cu}(\text{MA})_2$. In the case of resin **2**, the $\text{Cu}(\text{MA})_2$ incorporation was greater than expected on the basis of similar reactivities of HEMA and $\text{Cu}(\text{MA})_2$.

Scanning electron microscope (SEM) analyses of all four resins offer interesting features (Figs. 1–5). The SEM picture of resin **1A** reveals the expected compact microporous structure (even at the highest magnifications). Interestingly, minor inclusions of $\text{Cu}(\text{MA})_2$ are detectable by combined XRMA analysis (circled feature in Fig. 1). A similar dry-state morphology is exhibited by resin **1B** (Fig. 2). The SEM picture of resin **1C** (Fig. 3) reveals a definitely less vitreous morphology, apparently wrinkled in nature. This observation is not surprising in view of the higher crosslinking degree designed for resin **1C**.⁷ SEM morphology of resin **2** deserves comment (Figs. 4 and 5). In the untreated dry state the material exhibits a structure made by compact “tiles” (Fig. 4) but, after swelling with water followed by liophilization, the dry-state structure appears to be quite different (Fig. 5) and clearly macroporous in nature. Remarkably, only the SEM pictures of **2** display a liophilization effect, resins **1A–1C** being

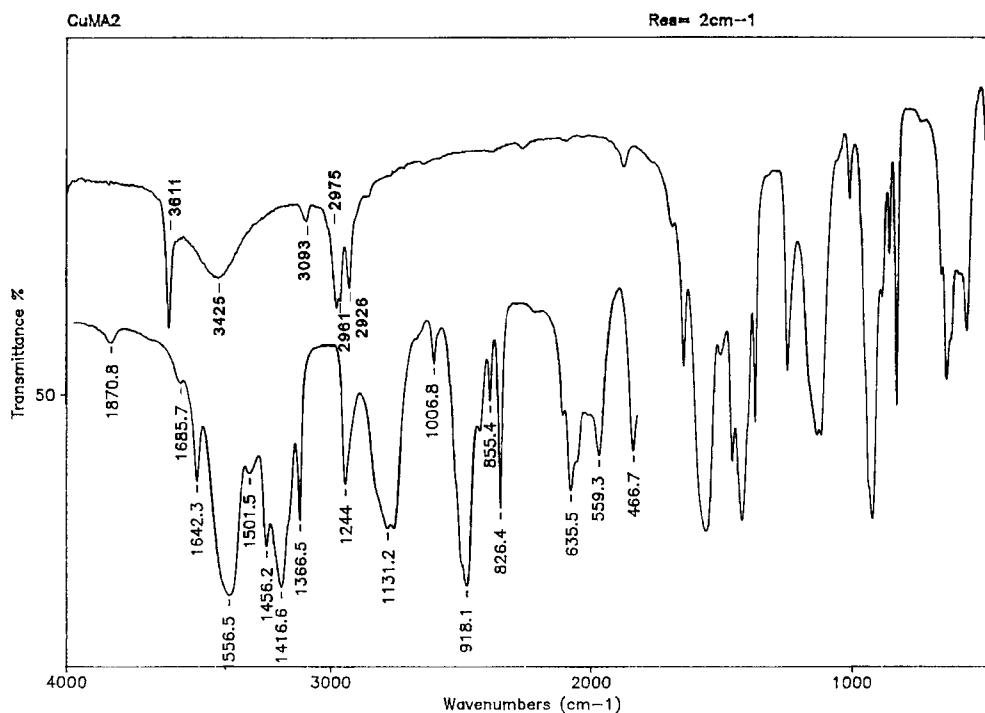


Figure 7 IR spectrum of monomer $\text{Cu}(\text{MA})_2$ (KBr disc).

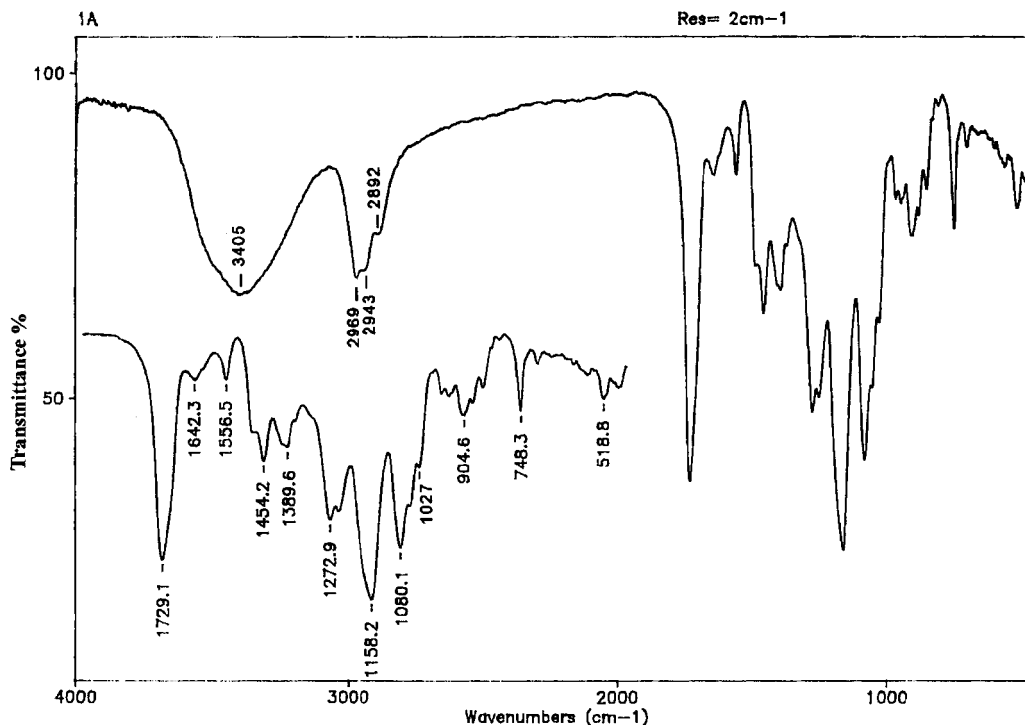


Figure 8 IR spectrum of polymer 1A (KBr disc).

totally unaffected by a sample preparation aimed at picturing a resin in its swelling-state condition.

BEV measurements⁸ are also interesting (Fig. 6). BEV values appear to increase with decreasing crosslinking degree, including the case of resin **2**, which does in fact possess a crosslinking degree lower than **1A**. BEV figures are, of course, significant in view of a chemical utilization of metalloorganic resins as biocidal materials. Thus, in order to optimize a delayed but quantitative release of metal ions from the material, full accessibility of the polymer network has to be made possible.

The macromolecular structure of the metalloorganic copolymers was investigated by means of IR and ultraviolet-visible (UV-Vis) spectrophotometries.

The IR spectra of Cu(MA)₂ and of resin **1A** are depicted in Figures 7 and 8, respectively.

The major features of the Cu(MA)₂ spectrum are the sharp 3611 cm⁻¹ and the broad 3425 ν_{O-H} bands attributable to free and to copper(II)-coordinated water, respectively.⁹ The presence of a significant amount of water in the nominally anhydrous copper methacrylate is suggested by the experimental lower copper percentage figure, i.e., 21.7% versus 27.18% for Cu(MA)₂, and 25.24% for Cu(MA)₂·H₂O. Moreover, it is also known that

copper(II) carboxylates normally exist as [Cu(carboxylate)₂·H₂O] species organized to give dimeric structures in which (1) two "Cu²⁺" ions are connected by four bridging carboxylate ligands, (2) one water molecule per "Cu²⁺" center is bound along the Cu—Cu axis, and (3) a significant metal-metal interaction leads to a pseudooctahedral geometry around each of the two metal centers.¹⁰ This structure is supported by the IR spectrum in which two Cu^{II}-carboxylate stretching bands at 1556 and 1416 cm⁻¹ are observed. In fact, similar values have been observed for Sn^{IV} alkylcarboxylates, in which one RCO₂⁻ ligand bridges two SnR₃ units.¹¹

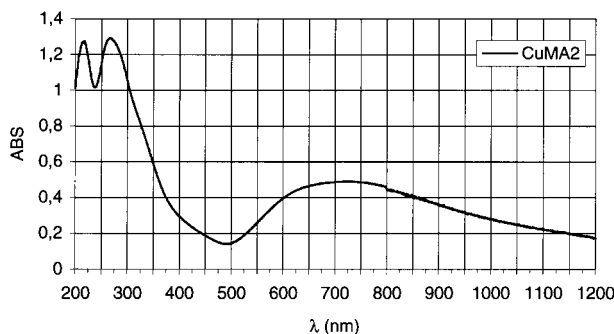


Figure 9 UV-vis spectrum of solid Cu(MA)₂.

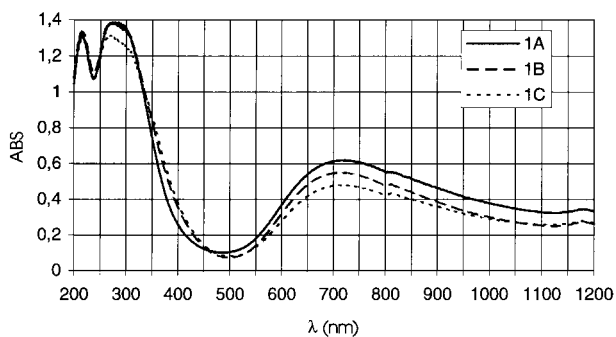


Figure 10 UV-vis spectra of **1A** (—), **1B** (---), and **1C** (-----).

The IR spectrum of polymer **1A** reveals a strong $\nu_{\text{O-H}}$ band at 3405 cm^{-1} due to the OH groups of the HEMA repeating units, as well as a strong $\nu_{\text{C=O}}$ absorption at 1729 cm^{-1} (1717 for HEMA). The 1556 cm^{-1} band due to the metallo-organic ring, albeit weak, is still apparent; and a very weak band at 1642 cm^{-1} ($\nu_{\text{C=C}}$) reveals that a small fraction of unpolymerized $\text{Cu}(\text{MA})_2$ is adsorbed onto the polymer network.

The UV-vis spectra of $\text{Cu}(\text{MA})_2$ and of resins **1A–1C** are collected in Figures 9 and 10.

The very broad band in the $500\text{--}1,000\text{-nm}$ range seen for $\text{Cu}(\text{MA})_2$ is typical of a $\{\text{Cu}^{\text{II}}\text{L}_6\}$ chromophore¹⁰ and is present in the spectra of **1A**, **1B**, and **1C**. The λ_{max} values appear practically unchanged, thus confirming^{1,2} the ability of γ -ray irradiation to preserve the Cu^{II} oxidation state and coordination sphere of the copper-organic monomers. The presence of the dimeric unit $\{\text{Cu}_2(\text{carboxylate})_4(\text{H}_2\text{O})_2\}$ is proposed on the basis of the circumstance that it is expected to be present in $\text{Cu}(\text{MA})_2$,¹⁰ and the substantial similarity of the Vis spectra of $\text{Cu}(\text{MA})_2$ and **1A–1C** leaves little doubt that it has to survive as such in the metalloorganic copolymers.

The whole of the analytical IR and UV-vis data points to the overall structure depicted in Figure 11.

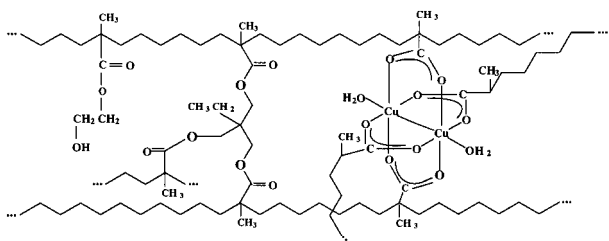


Figure 11 Sketch of the proposed macromolecular structure of resins **1A–1C** and **2**.

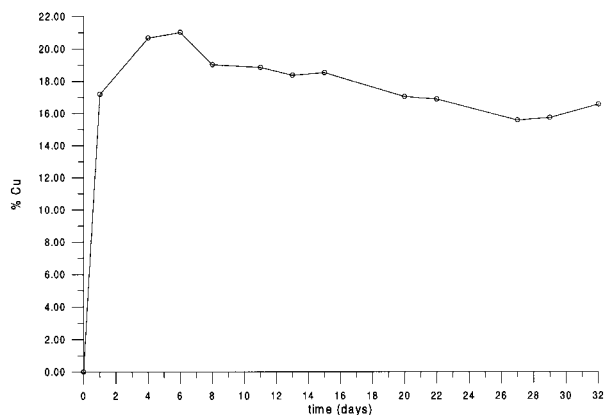


Figure 12 Release of $\text{Cu}^{2+}(\text{aq})$ from **1C** (“% Cu” refers to total Cu).

The expected release of $\text{Cu}^{2+}(\text{aq})$ from copolymers **1A–1C** and **2** was monitored for about 30 days in water at room temperature (Figs. 12 and 13). The release profiles for resins **1A–1C** are rather similar, while that of **2** does not feature the inexplicable maximum observed for resin **1C**. In both cases a rapid release of $\text{Cu}^{2+}(\text{aq})$ is observed, but a gradual further metal release is exhibited only by resin **2**. The substantial moderate but consistent decrease of $\text{Cu}^{2+}(\text{aq})$ concentration with the time apparent for resins **1A–1C** has not been explained, so far.

CONCLUSIONS

The γ -ray-promoted copolymerization of copper methacrylate with HEMA in the presence of 1,1,1-

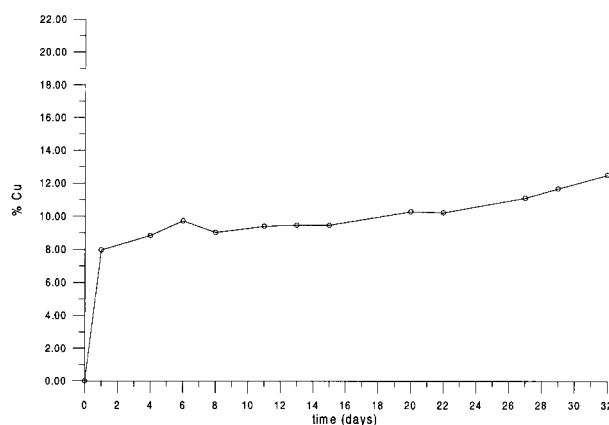


Figure 13 Release of $\text{Cu}^{2+}(\text{aq})$ from **2** (“% Cu” refers to total Cu).

tris(hydroxymethyl)propanetrimethacrylate occurs with remarkable yields at room temperature.

The spectroscopic characterization of copolymers **1A–1C** and **2** reveals the survival of the {Cu^{II}O₁₀} chromophore in the polymer networks.

Very preliminary hydrolytic stability tests reveal that 10 to 20% of analytical copper is released after 2 to 3 days.

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