

# Synthesis and Characterization of Porous Poly(methacrylic acid-co-triethylene glycol dimethacrylate) by Seed Emulsion Polymerization

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Received 4 January 1999; accepted 8 March 2000

**ABSTRACT:** Porous poly(methacrylic acid-co-triethylene glycol dimethacrylate) (poly MAA-co-3G) particles in the size range of 10–40  $\mu\text{m}$  were prepared via seed emulsion polymerization. Mixtures of linear polymer, solvent, and/or nonsolvent were used as inert diluents. The prepared porous polymer was converted using hydroxylamine hydrochloride and sodium methoxide into the corresponding poly(hydroxamic acid). The surface area of the porous copolymer particles was determined colorimetrically. The effect of the diluent type and concentration on the surface area of the prepared porous polymer was examined. The metal ion absorption capacity of the resin toward the different metal ions was examined using an atomic absorption spectrophotometer. The thermal stability of the polymers was examined by thermal gravimetric analysis. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1209–1215, 2000

**Key words:** seed polymerization; porous polymer; triethylene glycol dimethacrylate; methacrylic acid; poly(hydroxamic acid)

## INTRODUCTION

Porous polymeric materials are used as sorbents, the stationary phase for gas chromatography, ion-exchange resins, membrane materials, and carriers for catalysts as well as biologically active substances.<sup>1–2</sup> In recent years, mono- or narrow dispersed porous resins were developed for use in high-performance chromatography among other uses. Best known perhaps are the monodisperse polymer particles developed by Ugelstad's group using an activated two-step swelling process.<sup>3–5</sup> In their process, monodisperse seed particles are prepared by aqueous emulsion polymerization and are then swollen with low molecular weight hydrocarbons (activation) followed by a mixture of a monomer, crosslinker, initiator, and optional

porogen. The resulting suspensions are polymerized to form monodispersed porous particles.<sup>6–9</sup> Several studies have reported details about the preparation of these resins using porogenic solvents.<sup>10,11</sup> As a consequence of our previously published work,<sup>12,13</sup> we prepared and characterized porous polyhydroxamic acid and a polyhydroxamic-metal catalyst, with a high surface area, by the seed emulsion polymerization technique.

## EXPERIMENTAL

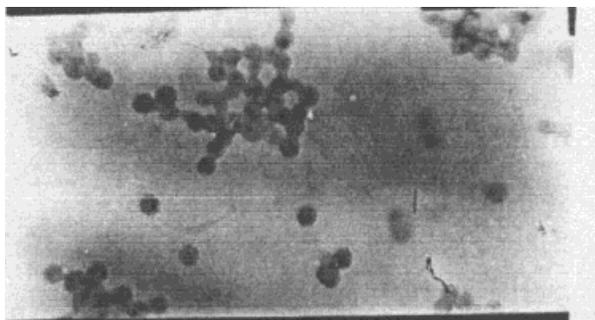
### Materials

Methacrylic acid (MAA) (Redel de Häen, Germany) and triethylene glycol dimethacrylate (3G) (Sigma, St. Louis, MO) were purified by treatment with active alumina. Benzoyl peroxide reprecipitated from a chloroform solution by methanol was supplied by Sigma. *n*-Hexane and all the

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*Journal of Applied Polymer Science*, Vol. 78, 1209–1215 (2000)  
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**Figure 1** Transmission electron microscopy ( $\times 10,000$ ) of the PS seed particles.

metal salts supplied by the El Nasr Pharmaceutical Co. (Cairo, Egypt) were of analytical grade. Ammonium persulfate, sodium dodecyl benzene sulfonate, and active alumina were supplied by the Fluka Chemical Co. (Neu-Ulm, Switzerland).

#### Preparation of Polystyrene (PS) Seed Particles

Monodisperse PS seed particles of an average particle size of  $9 \mu\text{m}$  were prepared by emulsifier free-emulsion polymerization (see Fig. 1). Styrene monomer (30 mL) was purified by treatment with active alumina. The purified monomer was added to distilled water (100 mL) containing ammonium persulfate (0.5 g) in a stepwise manner. The polymerization mixture was stirred at 300 rpm and  $65^\circ\text{C}$  for 3 h.

#### Preparation of Polyvinylpyrrolidone (PVP)

The vinylpyrrolidone monomer (10 mL) was purified by treatment with active alumina. Benzoyl peroxide (0.1 g) was added to the monomer; then, it was introduced into a nitrogen-flushed test tube. The test tube was sealed and heated at  $65^\circ\text{C}$  for 3 h without stirring in a water bath, giving a viscous solution.

#### Determination of the Molecular Weights of the Prepared Polymers

The intrinsic<sup>14</sup> viscosity  $[\eta]$  for the prepared PS and PVP was determined in chloroform at  $20^\circ\text{C}$  by the usual method of extrapolation. The viscosity-average molecular weights  $[M_v]$  for the PS and PVP were calculated according to the following equation:  $[\eta] = K[M_v]^\alpha$ , where  $K$  and  $\alpha$  [ $K = 11.8 \times 10^5$  and  $19.4 \times 10^5$  (g/dL) and  $\alpha = 0.72$  and  $0.64$  for PS and PVP, respectively] are constants depending on the type of solvent, the temperature, and the polymer. From the above equation, the

viscosity-average molecular weights were found to be  $2.1 \times 10^5$  and  $1.4 \times 10^3$  for PS and PVP, respectively.

#### Seed Activation Step

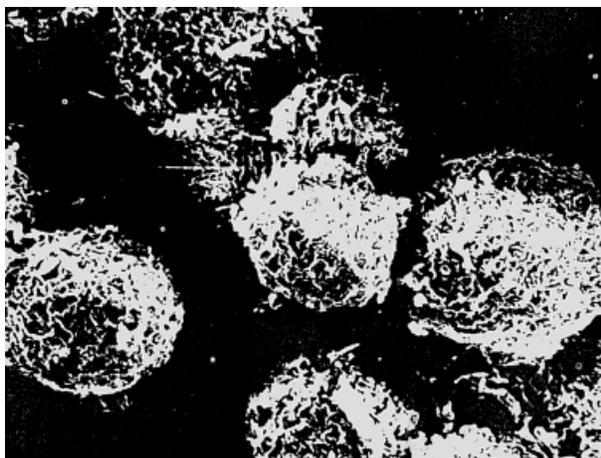
To a dispersion<sup>15,16</sup> of PS particles (7.5 g), an emulsion of a swelling agent (*n*-hexane 5 mL) is added containing a free-radical initiator, benzoyl peroxide (0.2 g), in an aqueous solution (20 mL) of sodium dodecyl benzene sulfonate (SDS 1%). The mixed dispersion was stirred with a magnetic stirrer at room temperature for 24 h until the drops of the swelling agent had disappeared. A mixture of MAA (10 mL) and 3G (5 mL) and the porogenic agent *n*-hexane (5 mL) was emulsified by an (20 mL, 0.5%) aqueous solution of SDS added to the dispersion. The mixture was stirred at room temperature at 200 rpm for 24 h to allow complete swelling of the monomer phase into the activated PS particles. The final dispersion is supplemented by a 20 mL, 1% aqueous solution of PVP (solid content 52%) to reach the required concentration for dispersion stabilization during the polymerization. PVP increases the viscosity of the medium and the interfacial tension at the boundary of the two phases and thus facilitates the process of phase separation.

#### Polymerization

The reactor (250-mL Q.F. conical flask) content was flushed with nitrogen to remove the dissolved oxygen; the reactor was sealed and heated at a stirring rate 100 rpm to  $65^\circ\text{C}$  for 24 h. The resulting copolymer was separated by repeated decantation in water and methanol. The resulting copolymer particles were dried and subjected to Soxhlet extraction for 36 h using chloroform as a solvent.

## RESULTS AND DISCUSSION

The process of pore-structure formation using a mixture of a linear polymer and a nonsolvent as an inert diluent is complex because the copolymerization reaction takes place in the presence of precipitating diluents; both diluents (*n*-hexane and PS) are nonsolvents for the poly(MAA-co-3G) chains. In the early stage, the PS polymer chains will be in the swollen state; as the reaction proceeds, the monomers are transformed into the crosslinked polymer chains and phase separation



**Figure 2** SEM of the prepared poly(MAA-co-3G) particles.

occurs between the poly(MAA-co-3G) copolymer and the linear PS and the nonsolvent (*n*-hexane). The consumption of the monomers MAA and 3G leads to copolymers whose macromolecular chains become less swollen and also entangled by continuing copolymerization; therefore, the pores of the porous polymer particles are attributed to the interspaces formed between the growing copolymer chains.

## Characterization

### Scanning Electron Microscopy (SEM)

The polymer solid particles [poly(MAA-co-3G)] were subjected to gold plating and then to a scanning electron microscope. Figure 2 shows the porous structure of the surface and Figure 3(a,b) shows the bulk of the particles.

The particle size of the prepared porous copolymer is shown to be in the range 10–40  $\mu\text{m}$ . This could be attributed to the nonideal transfer of the whole monomeric phase into the domain of the primary particles. The residual part of the monomeric phase remains in the system and is polymerized by normal suspension polymerization, which gives a polydisperse product.

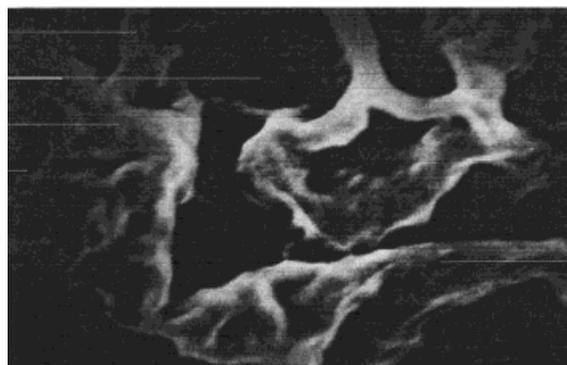
### Surface Area Measurements

The polymer particles' surface area is determined colorimetrically.<sup>17</sup> A polymer sample (1.0 g) is left for 24 h in a methylene blue solution (100 mg/L). The decrease in light absorbance at 670 nm is a measure of the polymer surface area (1 mg of methylene blue  $\sim 2.4 \text{ m}^2$ ).

*Effect of Diluent (*n*-Hexane) Amount on the Surface Area of the Prepared Polymer Particles.* A series of experiments was devoted to the description of the effect of the activating diluent (*n*-hexane) on the surface area of the polymer particles. The choice of suitable solvents is predominantly limited by the requirements of solubility in the dispersing medium, ability to swell the PS seed particles, miscibility with the components of the mixture of the monomers, and, finally, inertness. Figure 4 shows that the surface area of the polymer particles increases as the amount of the diluent increases until a certain point, after which the surface area decreases in the domain of high fraction of porogen in the mixture. This is due to the difficulty for the monomers at a given composition to form a macroporous structure with the necessary pore volume able to accommodate the whole amount of porogen. Second, at a high fraction of the diluent, the seed particles are not able

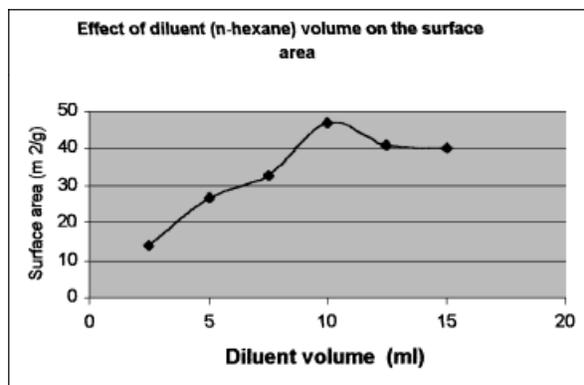


(a)



(b)

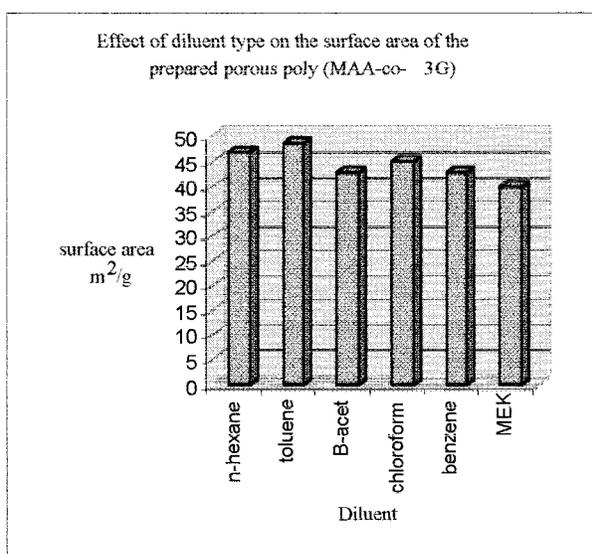
**Figure 3** SEM of the prepared poly(MAA-co-3G): (a)  $\times 12,000$ ; (b)  $\times 14,000$ .



**Figure 4** Effect of diluent (*n*-hexane) volume on the surface area of the prepared porous poly(MAA-co-3G).

to receive a high feed composition. Thus, when the feed composition concentration exceeds the capacity of the seed particles, the feed composition is directed to the dispersing phase, which, in turn, decreases the monomer concentration within the seed particles.

*Effect of Diluent Type (10 mL) on the Surface Area of the Prepared Porous Poly(MAA-co-3G).* A series of experiments was devoted to the description of the effect of the activating diluent type on the surface area of the porous copolymer particles. The data are shown in Figure 5. From Figure 5, the effect of the chemical nature of the solvent on the surface area of the prepared copolymer is not



**Figure 5** Effect of diluent type (5 mL) on the surface area of the prepared copolymer (MAA-co-3G).

**Table I** Elemental Analysis of the Prepared Porous (a) Poly (MAA-co-3G), (b) Polyhydroxamic Acid (Hydrolysis Time 2 h), and (c) Poly(hydroxamic acid) (Hydrolysis Time 3 h)

Polymer	C %	H %	N %
a	62.5	4.6	0
b	47.3	5.2	13
c	32.9	6.9	21

very significant; the specific surface area was found to be about  $44.5 \text{ m}^2/\text{g} \pm 10\%$ .

#### *Hydroximation of the Crosslinked Copolymer (MAA-co-3G)*

The crosslinked<sup>18</sup> copolymer (MAA-co-3G) was subjected to base hydrolysis using triethylamine (20 mL), hydroxylamine (5 g), and freshly prepared sodium methoxide as a base in methanol (100 mL). The reaction mixture was refluxed for 3 h. The resulting polymer was washed several times with methanol and finally dried at 40°C for 24 h. The hydroximation process changes the carboxylic and ester groups into hydroxamic groups, —CONHOH, which have a high affinity for metal ions. The porous polymer particles were subjected to elemental analysis to determine the extent of the conversion to poly(hydroxamic acid). The data are given in Table I.

#### *Absorption of Metal Ions by Poly(hydroxamic acid) Resin*

The metal ion absorption capacity of the polymer before and after base hydrolysis was determined by the batch method.<sup>19–21</sup> Accurately weighed resin samples (0.1 g) were equilibrated with 100 mL of a 4000 ppm metal ion solution in 100-mL volumetric measuring flasks for 24 h. After reaching equilibrium, the amount of metal ions remaining in solution was determined using atomic absorption spectrophotometry. The data are given in Table II.

All the absorption experiments were carried out in a pH range of 5.5–6.5. Table I shows that the modification of the polymer particles to poly(hydroxamic acid) increased the absorption capacity of the resin several times, which indicates that the metal chelation is predominantly on the lone pair of electrons of the nitrogen atom of the polyhydroxamic group —CONHOH.

**Table II Metal Ion Extracted Percent from 4000 ppm (B) Before and (A) After Modification**

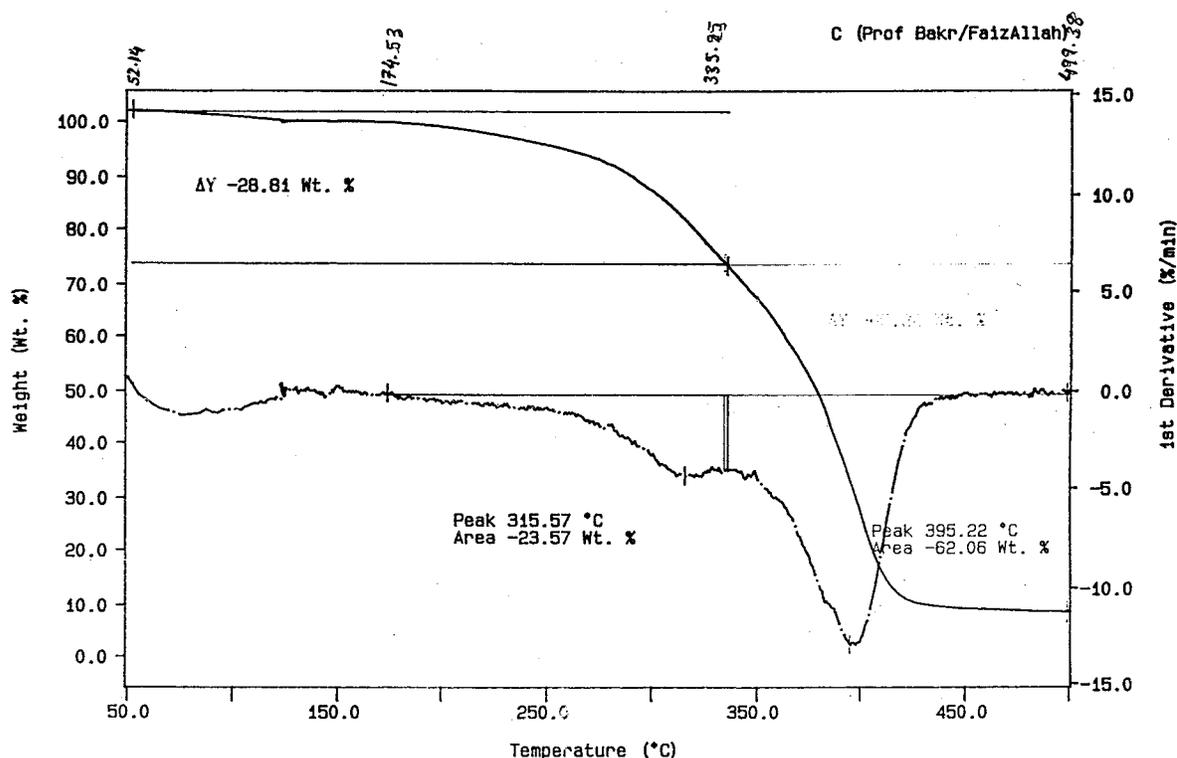
$M^{n+}$	$Cd^{2+}$	$Cr^{3+}$	$Fe^{2+}$	$Co^{2+}$	$Ni^{2+}$	$Cu^{2+}$	$Pd^{2+}$	$Na^+$	$Pb^{2+}$
A	67	79	90	92	89	87	82	79	88
B	17	25	41	37	38	29	30	31	33

### Thermal Gravimetric Analysis (TGA)

Figures 6–8 show three thermal gravimetric analyses: of poly(MAA-co-3G), its base hydrolyzed form [poly(hydroxamic acid)], and its copper complex. The differential curves show that the poly(hydroxamic acid) is less thermally stable (weight loss 40.62% at 301.95°C); however, the original poly(MAA-co-3G) loses 23.57% of its original weight at 315.57°C, which is attributed to the decomposition effect of the strongly basic hydrolyzing medium. The copper-polymer complex is the most thermally stable, that is, it loses 17.64% of its original weight at 330°C. This thermal stability enables the use of such metal-polymer complexes as a supporting material for catalyst and chromatographic separation processes.

### Poly(hydroxamic acid) as a Catalyst-supporting Material

The following procedures<sup>6</sup> were used to support the prepared polymer with metal and metal oxide catalysts: The porous poly(hydroxamic acid), 1.0 g, was immersed in different salt solutions (5000 ppm) of Cr, Fe, Co, Ni, Pd, Cd, and Cu and stirred at room temperature for 1 h. After the polymer turned to the characteristic color of the salt solution, it was filtered and dried at 60°C. The polymer was resuspended in ethanol; after that, 1.0 g of  $NaBH_4$  was added to the suspension to reduce the metal ions  $M^{2+}$  and  $M^{3+}$  to the metallic state  $M^0$ . After 30 min, the polymeric material changed to a metallic luster. The material was then left in benzene for 3 days, after which it was redried and kept in a vial as a

**Figure 6** TGA spectrum of poly (MAA-co-3G).

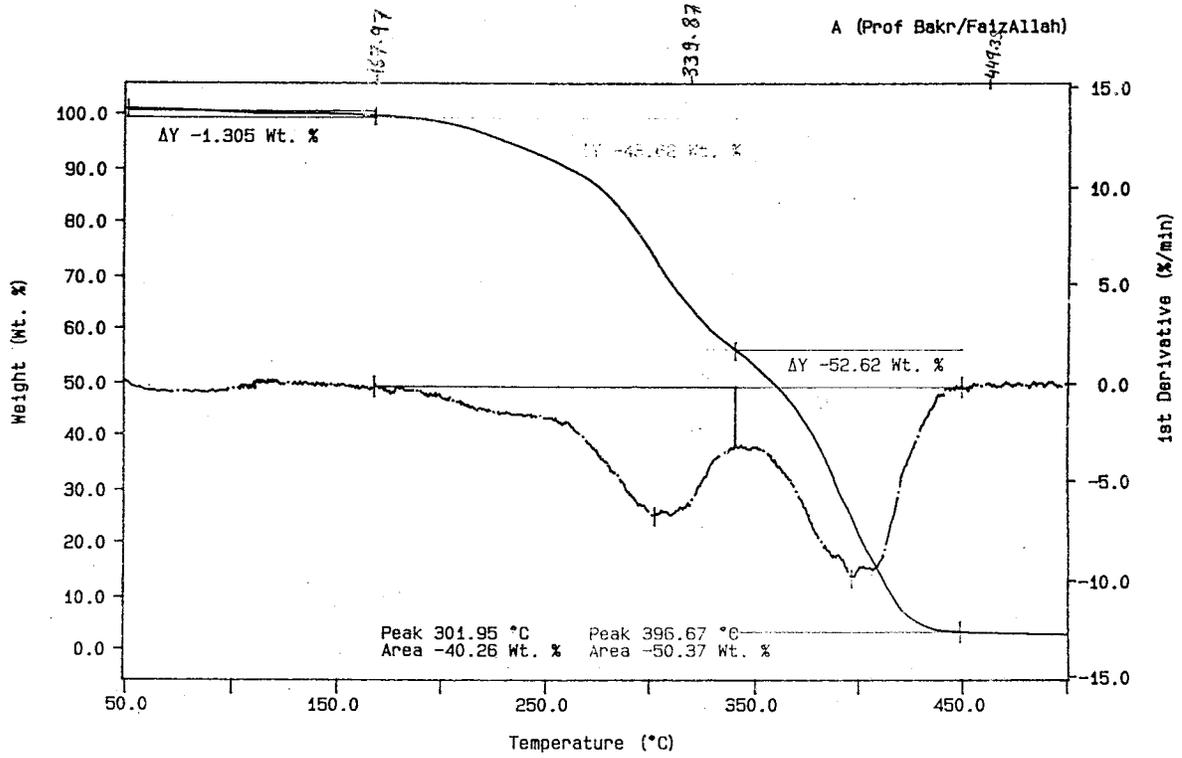


Figure 7 TGA spectrum of poly(hydroxamic acid).

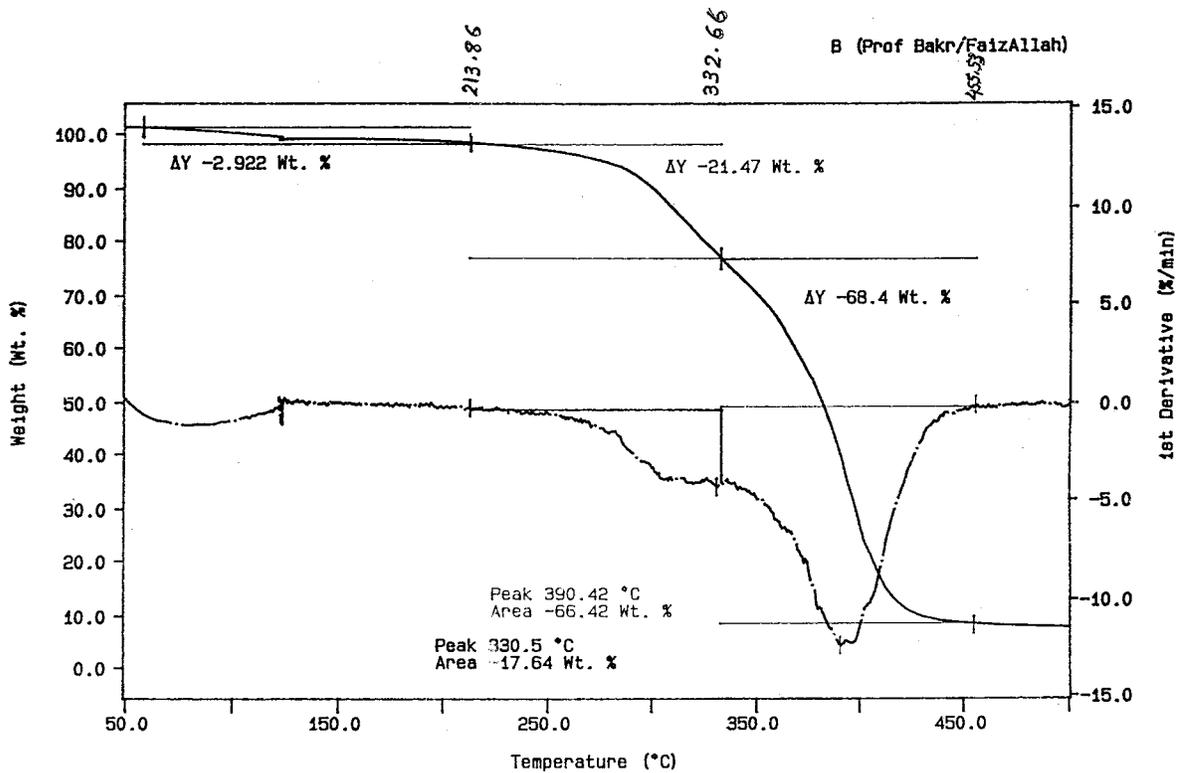


Figure 8 TGA spectrum of copper complex of poly(hydroxamic acid).

metal-porous copolymer supporting material. To prepare the metal oxide-polymer catalyst, the above procedures were repeated except the reduction process was carried out in water instead of ethanol, where the material changed after a few minutes.

## CONCLUSIONS

Porous poly(MAA-co-3G) was prepared by the seed emulsion polymerization technique and converted to a porous poly(hydroxamic)acid resin by base hydrolysis. The prepared poly(hydroxamic acid) showed a very high metal absorption capacity and a moderate specific surface area. The prepared polymers were shown to be thermally stable up to 180°C as evidenced by TGA. Metal-poly(hydroxamic acid) catalysts were prepared by metal ion reduction using sodium tetrahydroborate, NaBH<sub>4</sub>.

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