

# Hydrophilic Functional Copolymers from *N*-Maleoyl Glycine and Hydroxymethylacrylamide: Synthesis, Characterization, and Thermal Properties

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**ABSTRACT:** The free-radical copolymerization of *N*-maleoylglycine with hydroxymethylacrylamide was studied, with the starting monomer compositions ranging from 25 to 75 mol %. The copolymer compositions were obtained by elemental analysis from the N/C weight percentage ratio. The monomer reactivity ratios were estimated by the classical Fineman–Ross and Kelen–Tüdös linear procedure methods. The experimental data indicated random comonomer

incorporation. The thermal behavior of the copolymers was investigated with differential scanning calorimetry and thermogravimetry techniques under a nitrogen atmosphere. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1903–1908, 2005

**Key words:** radical polymerization; hydrophilic polymers; reactivity ratios; differential scanning calorimetry (DSC); thermogravimetric analyses (TGA)

## INTRODUCTION

Polymers of *N*-substituted maleimide are of considerable interest for achieving excellent thermal stability.<sup>1,2</sup> Among these polymers, aromatic polyimides are one of the most attractive classes of polymers because of their unusual chemical, thermal, and oxidative stability and especially their ease of processing for varnishes, films, adhesives, moldings, and so forth.<sup>3</sup> In general, polymers containing aromatic and heterocyclic ring structures, such as polybenzothiazoles, polyoxadiazoles, and polyimides, are known to have excellent thermal stability because of their minimal number of oxidizable hydrogen atoms and the high extent of double-bond conjugation.<sup>4,5</sup> *N*-Alkoxy-carbonylmaleimide and *N*-maleoylglycine (MG) were prepared and copolymerized with acrylic acid, acrylamide, and *N*-vinylpyrrolidone.<sup>6–8</sup> The resulting copolymers were water-soluble, except with *N*-vinylpyrrolidone,<sup>7</sup> and they were applied as polychelators for the extraction of inorganic ions from aqueous solutions. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been widely used in polymer characterization.<sup>9,10</sup> We also previously

reported the thermal behaviors of different polymers containing the maleimide moiety.<sup>11,12</sup>

The topics of this article are the synthesis, characterization, and thermal behavior of copolymers of MG and hydroxymethylacrylamide (HMAM) with 25–75 mol % in the feed.

## EXPERIMENTAL

### Materials

HMAM was obtained from commercial sources. MG was prepared according to published procedures.<sup>13</sup>

### Preparation of poly(MG-co-HMAM)

A volume of dioxane was transferred to septum-capped, nitrogen-purged flasks after the addition of HMAM (10.0 mmol), 15.6 mg of an initiator [azobisisobutyronitrile (AIBN)], and 10.0 mmol of MG previously synthesized.<sup>6</sup> The ampule was sealed *in vacuo* (10<sup>-3</sup> mmHg), and the copolymerization was carried out at 70°C for 12 h. The polymer material was filtered and washed with diethyl ether. It was collected and dried *in vacuo* up to a constant weight.

### Copolymer composition

The copolymer composition was calculated from the N/C weight percentage ratio determined by elemental analysis [calculated (found)]:

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TABLE I  
Radical Copolymerization of MG and HMAM [poly(MG-co-HMAM)] at 70° C and with 12 h  
of Reaction in 3 mL of Dioxane

Copolymer	$M_1^a$	MG (mmol)	HMAM (mmol)	AIBN (mg)	Yield (%)	N/C <sub>found</sub>	$m_1:m_2$ (mol %) <sup>b</sup>
1	74	14.8	5.2	15.6	45.4	0.2157	70.4 : 29.6
2	63	12.6	7.4	15.6	40.0	0.2228	61.7 : 38.3
3	50	10.0	10.00	15.6	48.0	0.2394	43.5 : 56.5
4	37	7.4	12.6	15.6	45.0	0.2480	35.1 : 64.9
5	26	5.2	14.8	15.6	48.0	0.2599	24.4 : 75.6

<sup>a</sup> Copolymer composition feed in mol %.

<sup>b</sup> Copolymer composition determined from elemental analyses.

Copolymer 1. C 46.69 (44.98); N 10.07 (9.7); H 4.05 (4.58).

Copolymer 2. C 46.77 (44.52); N 10.42 (9.92); H 4.32 (4.88).

Copolymer 3. C 46.95 (44.14); N 11.24 (10.57); H 4.96 (6.04).

Copolymer 4. C 47.04 (43.78); N 11.67 (10.86); H 5.29 (6.41).

Copolymer 5. C 47.17 (43.48); N 12.26 (11.30); H 5.75 (6.52).

The copolymer composition ( $X$ ) was calculated in the monomer molar ratio with the data according to the following equations:

$$X = \frac{N/C_{\text{exp}} \times PF_{\text{CB}} - PF_{\text{NB}}}{PF_{\text{NA}} - N/C_{\text{exp}} \times PF_{\text{CA}}} \quad (3)$$

$$Y = 1$$

where  $N/C$  is the experimental basis for both monomer units,  $PF_{\text{CB}}$  is the formula weight of carbons in monomer B,  $PF_{\text{NB}}$  is the atomic weight of nitrogen in monomer B,  $PF_{\text{NA}}$  is the atomic weight of nitrogen in monomer A, and  $PF_{\text{CA}}$  is the formula weight of carbon in monomer A. For the copolymer, MG is monomer A, and HMAM is monomer B.

### Measurements

The elemental analyses were carried out with a Carlo Erba 1108 Fison elemental analyzer (Italy). The elemental analyses were determined with a reference pattern (of sulfanilamide) incorporated into each of the three samples; the informed values are averages of the determinations (0.3–3% was the error in the measurements).

Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer model 1818 spectrometer (Perkin Elmer, Shelton, CT). The thermal stability of these polymer samples was determined in a nitrogen atmosphere at a heating rate of 10°C/min from 25 to 450°C with a Mettler-Toledo thermal analyzer (822-

DSC module, Spain). A sample size between 3 and 5 ± 0.1 mg and a nitrogen flow rate of 50 mL/min were used. The sample was placed in a hermetically sealed aluminum stander (40 μL), and a second run was performed with the aluminum pan lid pierced. Thermogravimetry (TG) data were obtained with a PerkinElmer TGS-1 thermal analyzer.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The five copolymers of MG and HMAM were synthesized by the variation of the feed ratios of both monomers from 25 to 75 mol %:

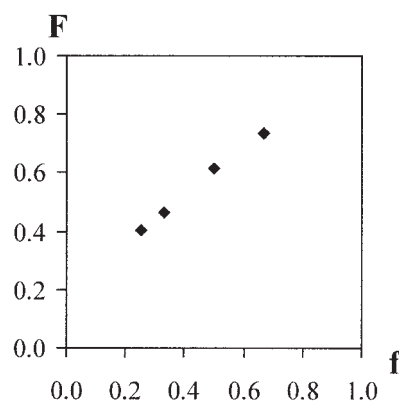
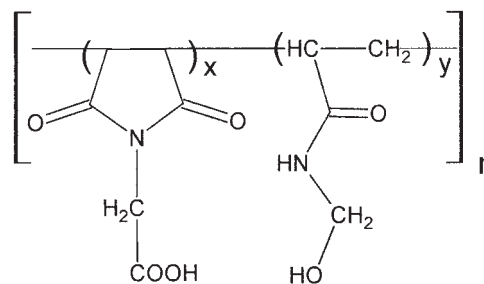
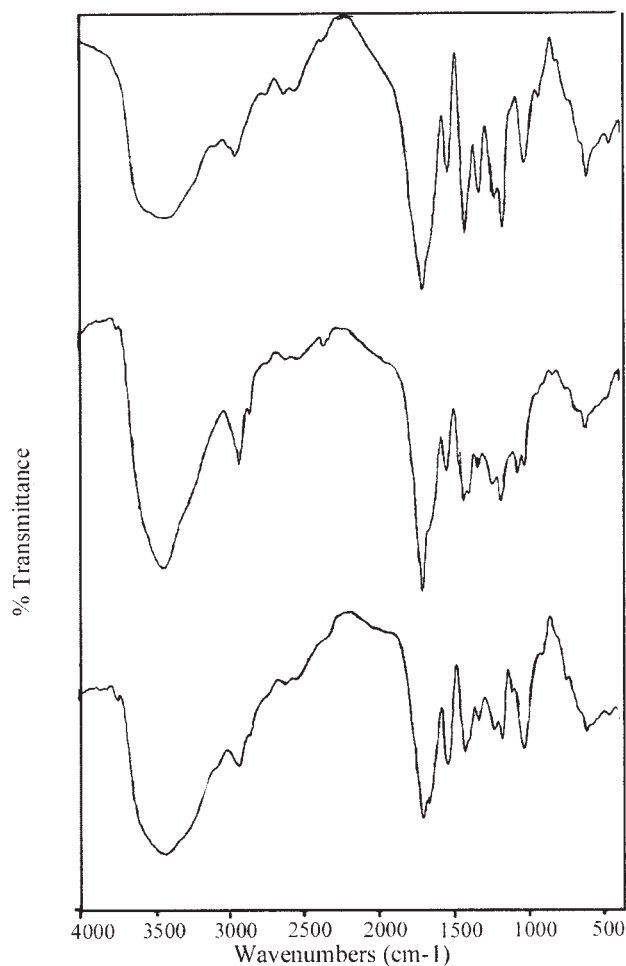


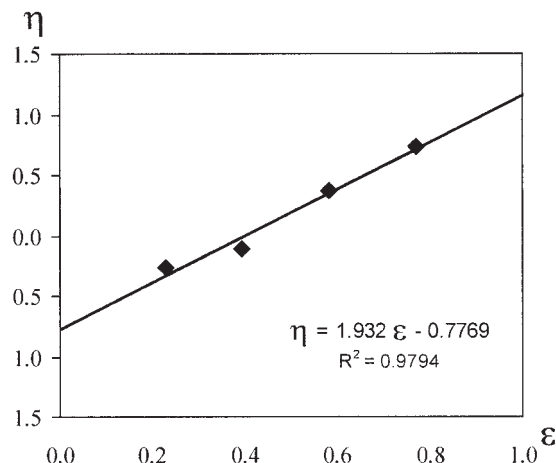
Figure 1 Copolymer composition diagram:  $F$  (copolymer composition) versus  $f$  (monomer feed ratio) for poly(MG-co-HMAM).



**Figure 2** FTIR spectra of poly(MG-co-HMAM): copolymers 1, 3, and 5 respectively (spectra down).

The copolymerization results are summarized in Table I. The weight ratios of MG to HMAM in the copolymers were calculated from the N/C weight percentage ratio. The relationship between the molar percentage of MG incorporated into the copolymers and the monomer feed ratio is shown in Figure 1.

The copolymers were insoluble in water, methanol, acetone, dimethyl sulfoxide, and chloroform.



**Figure 3**  $\eta$ - $\xi$  representation of the copolymerization parameters of poly(MG-co-HMAM) by the K-T method.

The IR spectra (KBr,  $\text{cm}^{-1}$ ) of poly(MG-co-HMAM) are shown in Figure 2. The most characteristic absorption bands are 3400 (OH,  $-\text{COOH}$ ), 2900 (CH,  $\text{CH}_2$ ), 1700 and 1710 ( $\text{C}=\text{O}$  imide and  $\text{C}=\text{O}$ ,  $-\text{COOH}$ ), and  $1620 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$  amide). The IR spectra of copolymers 2-4 show that all the signals are basically the same; only the intensities of the bands are different.

### Monomer reactivity ratios

The reactivity ratios for the comonomers were calculated with the Fineman-Ross (F-R)<sup>14</sup> and Kelen-Tüdös (K-T) methods for high conversion.<sup>15</sup> Figure 3 shows the corresponding  $\eta$ - $\xi$  plots (where  $\eta$  and  $\xi$  are mathematical functions of the molar ratios of the monomers in the feed and in the copolymer, respectively) according to the K-T method, from which the monomer reactivity ratios  $r_1$  and  $r_2$  were determined. In the K-T method, the intercept of the line at  $\xi = 1$  is equal to  $r_1$  (MG), and that at  $\xi = 0$  is equal to  $-r_2/\alpha$ , where  $\alpha$  is an arbitrary parameter.

The  $r_1$  and  $r_2$  values were also determined by the K-T method according to eq. (1):

**TABLE II**  
Reactivity Ratios of MG and HMAM in Poly(MG-co-HMAM) by the K-T Method for High Conversion

$M_2^a$	$M_2^b$	Weight <sup>c</sup>	$X_0$	$Y$	$\delta_1$	$\delta_2$	$z$	$F$	$G$	$\xi$	$\eta$
26.0	29.6	45.4	2.85	2.38	0.438	0.525	0.774	3.961	1.776	0.756	0.339
37.0	38.3	40.0	1.70	1.61	0.394	0.416	0.932	1.859	0.658	0.5923	0.210
50.0	56.5	48.0	1.00	0.77	0.429	0.557	0.688	1.626	-0.334	OR	OR
63.0	64.9	45.0	0.59	0.54	0.431	0.467	0.894	0.677	-0.513	0.347	-0.263
74.0	75.6	48.0	0.35	0.32	0.453	0.494	0.885	0.413	-0.766	0.244	-0.454

$M = 0.65168$ ;  $\alpha = 1.2764$ . OR, values outside range;  $z$ ,  $\log(1 - \delta_1)/\log(1 - \delta_2)$ ;  $\delta_1$ ,  $\delta_2 Y/X_0$ ;  $\delta_2$ , wt%  $(\mu + X_0)/(\mu + Y)/100$ ;  $\mu$ ,  $\mu_2/\mu_1$ ;  $Y$ ,  $M_1/M_2$ ;  $X_0$ ,  $M_1/M_2$ ; wt%, conversion;  $\mu_1$  and  $\mu_2$  are the molecular weights of monomer 1 and 2.

<sup>a</sup> Monomer composition in feed mol %.

<sup>b</sup> Copolymer composition of  $M_2$  in mol %.

<sup>c</sup> Conversion.

TABLE III  
Reactivity Ratios of MG and HMAM in Poly(MG-co-HMAM) by the F-R Method

$X_0$	$Y$	$X_0/Y$	$(Y - 1)$	$X_0^2$	$X_0(Y - 1)/Y$	$X_0^2/Y$
2.846	2.375	1.198	1.375	8.101	1.648	3.411
1.703	1.613	1.056	0.613	2.899	0.647	1.797
1.000	0.770	1.298	-0.230	1.000	OR	OR
0.587	0.541	1.085	-0.459	0.345	-0.498	0.637
0.351	0.322	1.091	-0.678	0.123	-0.740	0.383

OR = values outside range.

$$\eta = (r_1 + r_2/\alpha)\xi \quad (1)$$

where  $\alpha = (F_{\min} \times F_{\max})^{1/2}$  is an arbitrary denominator with any positive value that produces a more homogeneous distribution of data along  $\eta$ - $\xi$  axes.  $F_{\min}$  and  $F_{\max}$  correspond to the smallest and largest fractions in the copolymer, respectively.

The monomer reactivity according to the F-R method was determined by a least-squares method by the plotting of  $G$  versus  $F$ :

$$G = r_1F - r_2 \quad (2)$$

where  $G$  is equal to  $X_0(Y - 1)/Y$ ,  $F$  is equal to  $X_0^2/Y$ ,  $Y$  is the molar fraction of the monomers in the copolymer, and  $X_0$  is the molar fraction of the monomers in the feed.

The copolymer compositions were calculated with elemental analysis data from the N/C weight percentage ratio. The copolymerization of the monomers occurred at low-conversion conditions for poly(MG-co-HMAM) (see Table II). It is known that many comonomer pairs that have  $r_1 < 1$  and  $r_2 > 1$  with  $r_1 \times r_2 \neq 1$  usually have  $r_1 \times r_2 < 1$ . Such copolymerizations give monomer-copolymer relationships that are similar to those for ideal copolymerization but are skewed toward copolymer compositions richer in the repeat units derived from the more reactive monomer.<sup>16</sup>

The results from the K-T method are included in Table II; they yielded reactivity ratios for MG and HMAM of  $r_1 = 0.783$  and  $r_2 = 1.05$  ( $r_1 \times r_2 = 0.82$ ), and they are in agreement with those of the F-R method (Table III),  $r_1 = 0.793$  and  $r_2 = 0.971$  ( $r_1 \times r_2 = 0.770$ ; see Fig. 4). The experimental data indicate that the copolymerization of MG with HMAM can be considered random incorporation with some tendency to block the formation of HMAM.

The values of  $r_1$  and  $r_2$  show that both methods present a slight discrepancy; this may be attributed to the fact that the F-R method may involve large uncertainties in the slopes because experimental data at high conversions are unavailable.

### Thermal behavior

The thermal characteristics of any polymer should be appreciably affected by the introduction of a stable

comonomer (MG) into the polymer chain. It was therefore important to investigate the thermal behavior of the prepared copolymers.

The thermal stability of poly(MG-co-HMAM) was analyzed by programmed TGA from 20 to 500°C under a nitrogen atmosphere (see Table IV). The kinetic parameters—the pre-exponential factor ( $A$ ), the activation energy ( $E_a$ ), and the reaction order ( $n$ )—were evaluated according to the following equation:

$$-d\alpha/dt = K_n(1 - \alpha)^n$$

where  $\alpha$  is the fraction of the sample weight reacted at time  $t$  and  $K_n$  is the specific rate, which was obtained from the Arrhenius relationship  $K_n = A_{\text{exp}}(-E_a/RT)$ . The reaction rate  $d\alpha/dt$  was calculated with a differential technique that includes the heating rate and uses the temperatures versus the sample weight fraction.<sup>17,18</sup> The kinetic parameters were calculated according to the following equation

$$\beta = \ln \frac{-d\alpha/dt}{\nu(1 - \alpha)^n} = \ln A - E_a/RT \quad (5)$$

and with a linear multiple regression program by the plotting of  $\beta$  versus  $1/T$ .  $\nu$  is the heating rate.  $E_a$  and  $A$  were determined from the slope and intercept, respectively. The data are summarized in Table IV. Copolymers 1-3 have a higher composition in MG. The incorporation of the MG comonomer unit into the

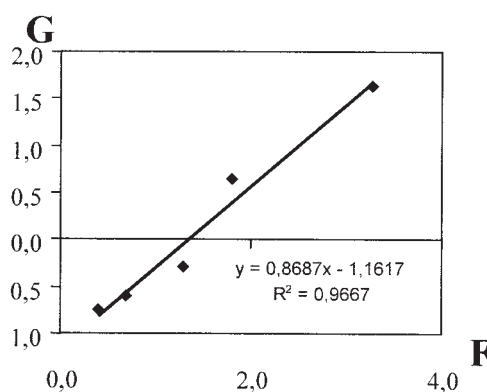


Figure 4  $G$ - $F$  representation of the copolymerization parameters of poly(MG-co-HMAM) by the F-R method.

TABLE IV  
Ranges of Decomposition and Apparent  $E_a$  Values for the Thermal Degradation of the Poly(MG-co-HMAM) copolymers for  $n \approx 1$

Copolymer	$m_1$	Approximate range of decomposition under $N_2$				TDT (K)	$E_a$ (kJ/mol)
		TGA weight loss (%) at different temperatures (K)					
		473.0	573.0	673.0	773.0		
1	73	0.0	5.0	10.0	35.0	583.0	90.3
2	66	0.0	5.0	10.0	40.0	583.0	98.1
3	47	0.0	3.0	10.0	27.0	553.0	85.2
4	32	0.0	5.0	10.0	40.0	553.0	74.9
5	24	0.0	5.0	18.0	38.0	553.0	70.3
Poly(MG) <sup>a</sup>	100	0.0	5.0	20.0	40.0	613.0	84.0

<sup>a</sup> Previously published.<sup>16</sup>

copolymer increased  $E_a$ ; the trend is the same for the thermal decomposition temperature (TDT).

The thermograms obtained by TG show that the polymers degrade in a single-stage process that is characteristic of the thermal decomposition of a great number of macromolecular compounds, and they provide evidence that no other preferred or competitive and simultaneous process occurs.<sup>19</sup> Figure 5(A–C) shows the TG curves for poly(MG-co-HMAM) with different copolymer compositions (copolymers 1, 3, and 5, respectively).

The  $E_a$  values of the copolymers show that copolymer 1 presents a lower content of the HMAM comonomer unit in the copolymer with a higher value of  $E_a$ . The copolymers show a lower TDT than the homopolymer of MG (340°C). The residual mass is approximately 30–40% at 500°C, and this can probably be attributed to a structural difference in the comonomer repetitive unit (see Table IV).

Figure 5 shows the DSC curve of copolymer 5 and the thermal effects shaped as characteristic endothermic and exothermic peaks. The initial deflection is proportional to the sample's heat capacity. The apparent glass transition was found to be approximately at 100°C; it was evident for the copolymer rich in HMAM. Another significant peak for melting was not found in the temperature range from 25 to 460°C.

A broad exothermic transition was observed in the temperature range of 230–280°C. This could be due to a complexation reaction by interchain and intrachain interactions in the case of the copolymers containing both proton-donor (MG) and proton-acceptor (HMAM) comonomers;<sup>20,21</sup> immediately a broad endothermic transition was observed and could be attributed to the decomposition reaction in the temperature range of 280–400°C.

The thermal stability decreases with an increasing amount of HMAM in the copolymer, and this could be

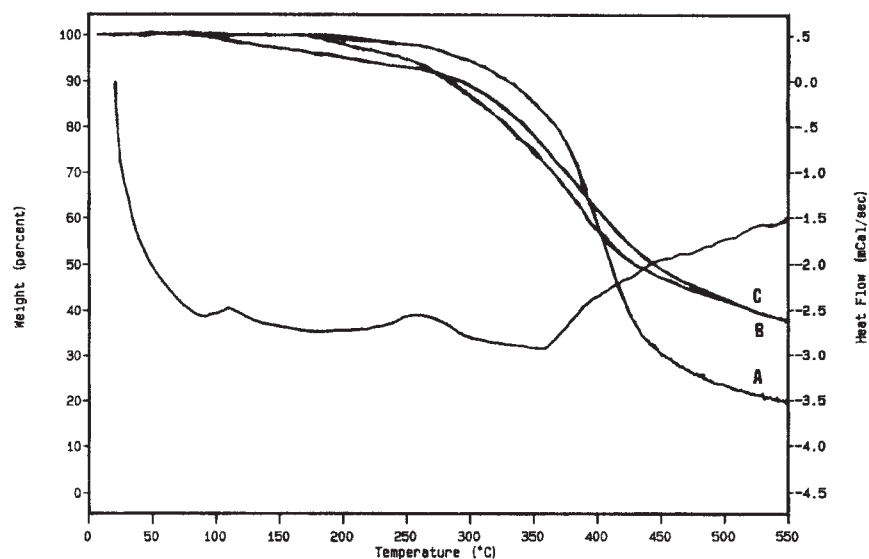


Figure 5 TG curves for poly(MG-co-HMAM) copolymers (A) 1, (B) 3, and (C) 5 and DSC curve for copolymer 5 in a nitrogen atmosphere at a heating rate of 10°C/min.

due to the fact that HMAM is very susceptible to oxidation.

### CONCLUSIONS

The copolymers were insoluble in water, methanol, acetone, dimethyl sulfoxide, and chloroform.

The results from the K-T method yielded reactivity ratios for MG and HMAM of  $r_1 = 0.783$  and  $r_2 = 1.05$  ( $r_1 \times r_2 = 0.82$ ). The experimental data indicate that poly(MG-co-HMAM) can be considered random incorporation with some tendency to block the formation of HMAM.

The TDTs of the poly(MG-co-HMAM) copolymers are greatly influenced by the different unit monomer compositions in the copolymer structure. The incorporation of MG increases the TDT values. The kinetic parameters also show the same trend and obey one-order kinetics.

The residues for the copolymers are approximately 25, 40, 40, 38, and 30% at 500°C; they show a thermal behavior with TDTs similar to that of the homopolymer of MG.

The kinetic parameters associated with the decomposition process show that there is an increase in the thermal stability of the copolymers with respect to the incorporation of MG into the polymer chain.

$E_a$  of copolymers 1-3 is higher than that of copolymers 4 and 5, and this could mean that the influence of both comonomer units is great on the copolymers. The thermal stability is increased by a higher incorporation of MG into the backbone, in the sense that the  $E_a$  and TDT values also increase.

The broadness of the endothermic peak could be due to a slower reaction of decomposition due to a

high percentage of HMAM units in the linear poly(MG-co-HMAM). Increasing the MG content leads to slight increases in the decomposition temperatures.

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