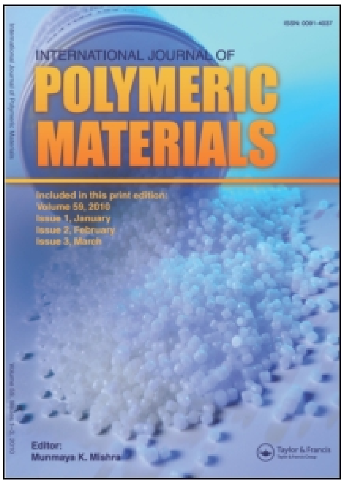

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Copolymers of Phenoxyethyl Methacrylate with Glycidyl Methacrylate: Synthesis, Characterization and Reactivity Ratios

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Copolymers of Phenoxyethyl Methacrylate with Glycidyl Methacrylate: Synthesis, Characterization and Reactivity Ratios

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The free radical copolymerization of phenoxyethyl methacrylate (POEMA) and glycidyl methacrylate (GMA) was carried out using α,α'-azobisisobutyronitrile (AIBN) in 2-butanone solution at 333 ± 1K. The copolymers were characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods. Thermal properties of the copolymers were also studied by thermogravimetric analysis (TGA). The compositions of the copolymers were established by ^{1}H-NMR analysis. The monomer reactivity ratios were computed using the Fineman–Ross (F-R) and Kelen–Tüdos (K-T)

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methods. These parameters were also estimated using a nonlinear computational fitting procedure, known as reactivity ratios error in variable model (RREVM). The mean sequence lengths determination indicates that the copolymers obtained are random in nature. Differences in the reactivity ratios obtained by the classical methods and RREVM were observed. GMA is more reactive than POEMA and although the copolymers are random, some tendency to GMA small block formation is reported.

Keywords: copolymers, FT-IR, glycidyl methacrylate, nonlinear fitting, phenoxyethyl methacrylate, reactivity ratios, thermogravimetry

INTRODUCTION

The reactivity and the structure-property relationships in the radical polymerization of vinyl copolymers has been extensively studied due to their intrinsic importance [1]. The introduction of hetero atoms into small or moderately sized alkyl groups of alkyl methacrylate is expected to increase polar effects, thereby modifying their reactivities in radical copolymerization with desired physico-mechanical properties. Poly(glycidyl methacrylate) (PGMA) and some of its copolymers have a wide range of applications, comprising biological applications for the binding of drugs, biomolecules [1–3], host material for laser dyes [4], electronic application as a resistant of negative electron beam [5], tested as adhesives for leather-to-leather bonding [6], or to improve autoadhesive and adhesive propertiesof poly(ethylene) plates by photografting with PGMA [7]. On the other hand, diethylenetriamine-grafted poly(glycidyl methacrylate) is used as adsorbent for effective copper ion adsorption [8]. Vapor deposition of poly(glicidyl methacrylate gives rise to thin films [9], and the preparation of magnetic poly(glycidyl methacrylate) microspheres in the study of nanoparticles is among the many applications of PGMA [10,11]. This ability of glycidyl methacrylate (GMA) to enter into a vast number of chemical reactions is due to the reactive epoxide group it possesses [12]. Another interesting polymer with a wide range of chemical and biochemical properties is poly(phenoxyethyl methacrylate) (POEMA) [13]. In fact, this polymer is used in several applications like photoabsorption in extreme ultraviolet regions, in the preparation of nanocomposites, or as part of block copolymers for drug release [14–16]. For these reasons the combination of both structures through the synthesis of a copolymer should be a good way to obtain products with the mixed properties of both homopolymers. However, the copolymerization gives rise to structures with different compositions, depending on the reactivity of the corresponding monomers. Therefore, in order to obtain a copolymer with the desired composition and the appropriate property, it is necessary to know the reactivities of the comonomers.

Monomer reactivity ratios (MRR) are frequently determined by linear procedures, and these methods are still widespread although their gross inaccuracies have been well-documented [17–19]. However, in a few cases it has been demonstrated that well-chosen experiments could provide acceptable results by linear methods [20]. The linearization of nonlinear models involving these reactivity ratios may result in faulty parameter estimates, an improper error structure and inaccurate estimates of the error. With the availability of microcomputers, nonlinear parameter estimation is now equally simple. Nonlinear procedures are nowadays most usually based on the statistically valid error-in-variables model (RREVM) [21,22]. The starting point for the experimental determination of MRR is usually the instantaneous copolymer composition equations. For this reason the results obtained from the classical linearization methods such as those of Fineman–Ross (F-R) [23] and Kelen-Tüdos (K-T) [24] are the starting point for nonlinear estimation of MRR.

The present article deals mainly with the synthesis and characterization of POEMA-co-GMA copolymers of different compositions by free-radical polymerization and the reactivity ratios determined by the F-R [23], K-T [24] and RREVM method [21,22].

EXPERIMENTAL

Materials

Phenoxyethylmethacrylate (POEMA, ALDRICH) and glycidylmethacrylate (GMA) were purified by vacuum distillation. α,α'-azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. 2-butanone, methanol and chloroform were purified by standard procedures.

Copolymerization

Copolymerization reactions were carried out in 2–butanone solutions (50 ml) in glass vessels with an inlet and outlet. The reaction tube containing the required amount of monomers (total concentration of the comonomer was 1.5 mol L^{-1}) and initiator (1% total mass of monomer) dissolved in 2–butanone was deaerated by flushing with pure, dry nitrogen gas for 30 min prior to immersion in a waterbath kept at a temp of 333 K. The comonomer mixtures in ratios ranging from POEMA/GMA $= 20/80$ to $80/20$ were prepared. The reaction was carried out for 3–5 h to give a conversion of $<10\%$ in order to satisfy the differential copolymerization equation. The copolymers were precipitated in an excess of cold methanol. The pure white powdery mass which separated out was dissolved in chloroform and then reprecipitated in methanol to ensure the complete removal of residual monomers. It was then dried in a vacuum oven at 313 K for 24 h.

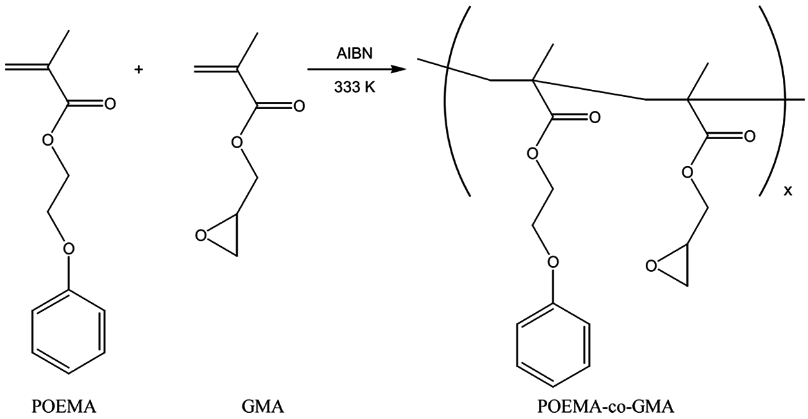
Measurements

The FT-IR spectra of the copolymers in the range 500–4000 cm^{-1} were recorded on a Perkin-Elmer paragon 1000 Fourier Transform Infrared (FT-IR) spectrometer using the potassium bromide pellet technique. ^{1}H-NMR spectra of the copolymers were run on a Jeol GSX-400 MHz spectrometer at room temperature in $CDCl_3$ and TMS was used as the internal standard. ^{13}C-NMR spectra of the copolymers were also recorded using a Jeol GSX-400 MHz spectrometer. The protons were decoupled by broad-band irradiation. Thermogravimetric analysis was performed using a Mettler TA 3000 thermal analyzer at a heating rate of 20° min^{-1} under dry nitrogen.

RESULTS AND DISCUSSION

Several POEMA-co-GMA copolymers were prepared at predetermined ratios of monomer feed using AIBN as initiator in 2-butanone solution at 333 K.

The monomeric constituents units of the copolymers are represented in Scheme 1.



SCHEME 1 Chemical structure of the monomers and copolymer: phenoxyethyl methacrylate, glycidyl methacrylate and phenoxyethylmethacrylate-co-glycidylmethacrylate (POEMA-co-GMA).

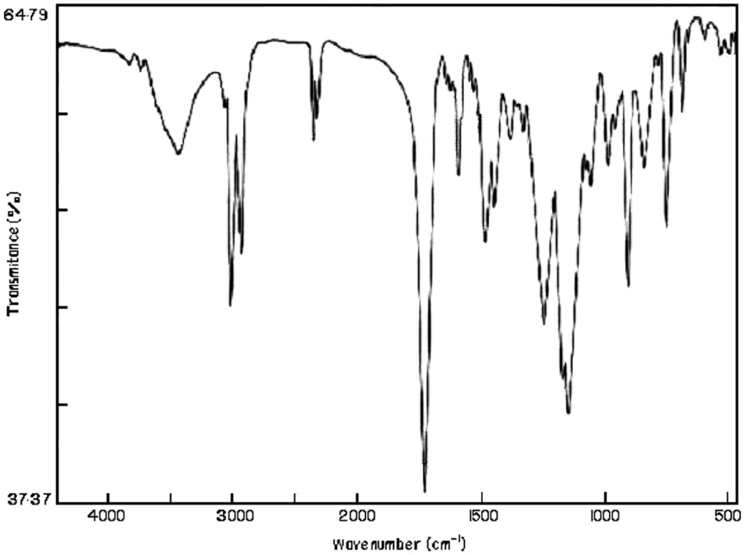


FIGURE 1 FT-IR spectrum of poly(POEMA-co-GMA) system.

The FT-IR spectra of the products represented in Figure 1 show that the bands at 3000–2950 cm^{-1} are due to the aromatic and aliphatic stretching vibrations. The carbonyl stretching of both methacrylates appeared at 1731 cm^{-1}. The appearance of a band at 907 cm^{-1} explains the incorporation of GMA units in the copolymer and also confirms the participation of the double bond in the copolymerization. These results indicate that the expected copolymers were obtained.

The ^{13}C-NMR spectrum of the copolymer is shown in Figure 2. The spectrum shows the characteristic peaks of the two monomeric units. The ester carbonyl of the POEMA unit is observed at 174.5 ppm. Carbons in positions 1, 2, 3 and 4 of the phenyl ring gave more intense peaks at 158.2, 129.4, 121.1 and 114.6 ppm respectively. The well-resolved peak at 76.6 ppm is due to the $-O-CH_2$ group. The epoxy ring carbons of GMA gave a peak at 48.7 ppm. The tertiary carbon and α –methyl carbon of GMA appeared at 45.1 and 18.3 ppm respectively. These results are in good agreement with the chemical structure of the expected copolymer.

The ^{1}H-NMR spectra of the copolymer is shown in Figure 3. The doublet signals at 7.0–6.8 and 7.4–7.2 ppm are due to the aromatic protons present in the POEMA unit. The signals at 4.45–4.1, 3.9–3.6, 3.25–2.15 ppm are due to the $O-CH_2$ protons, methylene and methyne

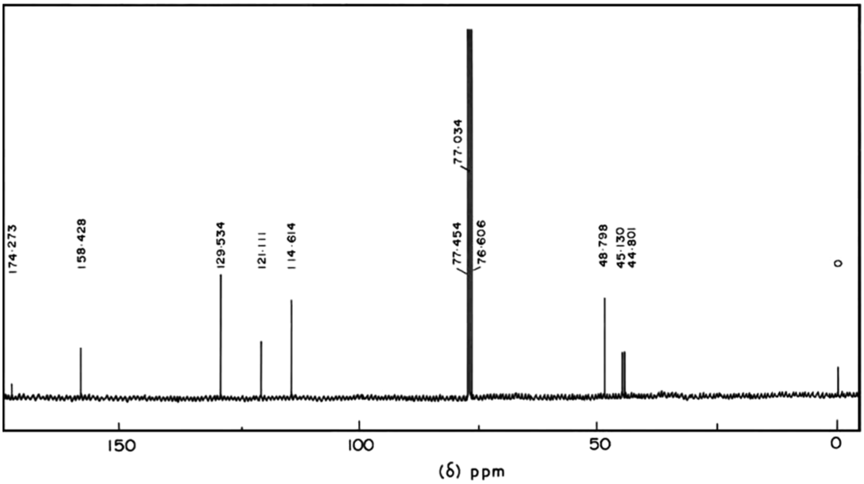


FIGURE 2 ^{13}C-NMR spectrum of poly (POEMA-co-GMA) system.

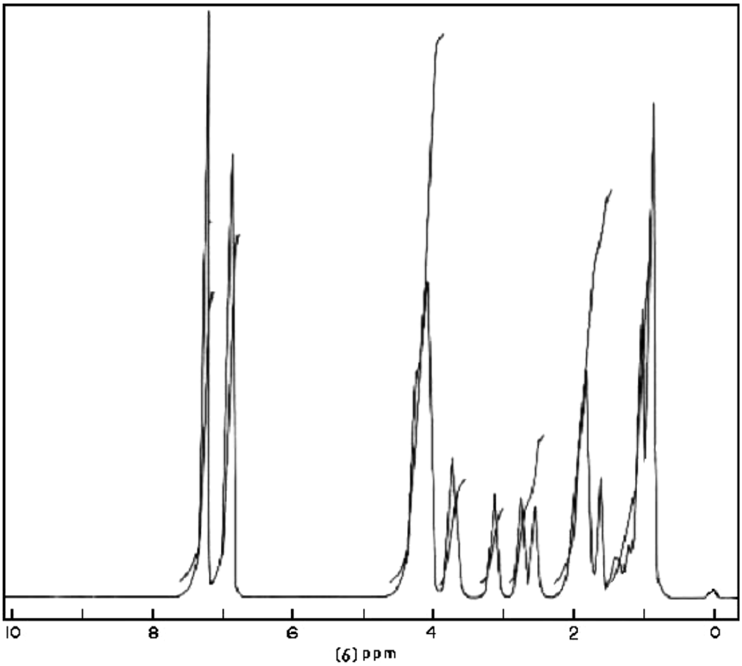


FIGURE 3 HNMR spectrum of poly (POEMA-co-GMA) system.

TABLE 1 Copolymer Composition for the Different Copolymers. Decomposition Temperature of the Copolymers at Different Compositions

	Copolymer composition			Temperature (K) of weight loss (%) of copolymers			
Polymer	m_1	M_2	IDT	20%	40%	60%	80%
(POEMA-co-GMA)	0.20	0.80	492	529	565	611	648
	0.50	0.50	501	542	575	615	654
	0.80	0.20	512	555	589	637	671

protons of the epoxy group respectively. The other peaks are due to the backbone protons. Therefore, according to the spectroscopic results from FT-IR, ^{13}C-NMR and ^{1}H-NMR the copolymer chemical structure is confirmed.

The thermal stability of the copolymers was studied by a programmed thermogravimetric analysis under nitrogen atmosphere. The TGA data for POEMA-co-GMA copolymers of different compositions are shown in Table 1. The TGA curves for POEMA-co-GMA copolymers which undergoes single stage decomposition are shown in Figure 4. The thermal stability decreases with the increase in GMA concentration in the copolymer, irrespective of the weight loss zone of the degradation profile considered. Therefore, increased GMA content in the copolymers enhances their thermal stability.

Determination of Monomer Reactivity Ratios

With the help of ^{1}H-NMR spectroscopy from the integral values of the signals, the content of each monomeric unit incorporated into the copolymer chain can be calculated. The mole fraction of POEMA in the copolymer chain was determined from the ratio of integrated intensities of aromatic protons of POEMA to those of the total aliphatic protons and GMA units.

$$C = \frac{\text{Intensities of aromatic protons } (I_A)}{\text{Intensities of alphatic protons } (I_a)} \tag{1}$$

$$C = \frac{5m_1}{9m_1 + 10(1 - m_1)} \tag{2}$$

On simplification,

$$m_1 = \frac{10C}{5 + C} \tag{3}$$

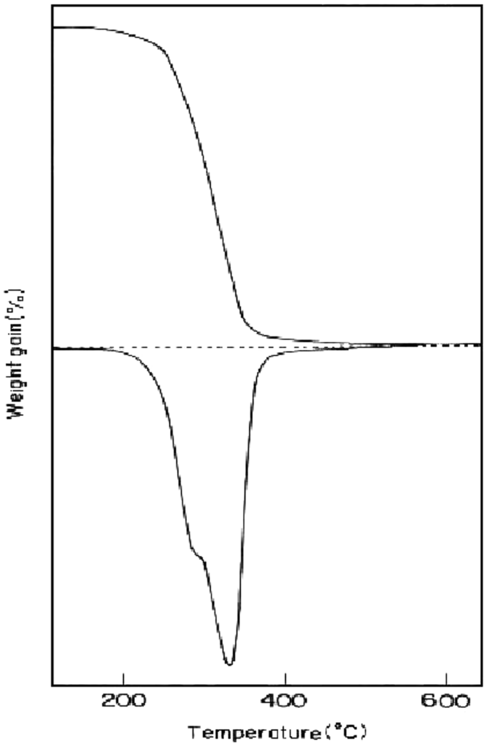


FIGURE 4 TGA profiles of POEMA-CO-GMA system.

Based on the above equation the mole fractions of POEMA in the copolymer system was calculated and their values are presented in Tables 2 and 3 respectively. It can be observed that the incorporation of GMA in the copolymer is higher than that of POEMA. This result indicates that GMA is more reactive than POEMA.

A plot of the mole fraction of POEMA in the feed against the mol fraction in the copolymer is shown in Figure 5. There is no azeotropic copolymer composition and from this plot it is also possible to observe that GMA is more reactive than POEMA.

Reactivity Ratios

The reactivity ratios were determined by the application of the linear K-T [23] and F-R [24] methods using the experimental data compiled in Table 3, and by the nonlinear RREVM [21,22] where the 95% posterior probability contour is represented in Figure 6. A comparison of

TABLE 2 Feed Composition in Copolymers (M_1, M_2), Conversion (%), Intensity of Aromatic and Aliphatic Protons (I_A, I_a protons), Ratio of Intensities of Aromatic and Aliphatic Protons (C) and Copolymer Composition (m_1, m_2)

S. no.	Feed composition in copolymer		Conversion %	Intensity of aromatic protons I_A	Intensity of aliphatic protons I_a	$C = I_A/I_a$	Copolymer composition in mole fraction	
	M_1	M_2					m_1	m_2
1.	0.20	0.80	6.1	1.3512	20.1230	0.067	0.1322	0.8678
2.	0.35	0.65	3.7	2.6348	21.3125	0.1236	0.2412	0.7588
3.	0.50	0.50	8.4	0.882	5.89	0.1497	0.2096	0.7094
4.	0.65	0.35	5.3	1.737	7.743	0.2243	0.4293	0.5707
5.	0.80	0.20	7.8	3.9754	11.977	0.3319	0.6224	0.3776

the reactivity ratios obtained from these methods is presented in Table 4. Considering that the RREVM method is the most accurate, it is possible to observe the important differences in the values of the reactivity ratios with the classical ones. By this way the reactivity ratios are obtained with the highest accuracy.

Mean Sequence Length

From the analysis of these reactivity ratios the estimation of the mean sequence length can be performed. Table 5 compiles these data as a function of the copolymer composition. It shows that the number of GMA units decrease in the polymer chain as the concentration of GMA decreases in the monomer feed. The copolymer sequence is of a random nature with more GMA units. Depending on the composition

TABLE 3 Classical Fineman-Rose and Kelen-Tudös Parameters for the Copolymerization Process

S. no.	$F = \frac{M_1}{M_2}$	$f = \frac{m_1}{m_2}$	$^{a}\frac{G=F(f-1)}{f}$	$H = \frac{F^2}{f}$	$^{b}\eta = \frac{G}{\alpha+H}$	$\xi = \frac{H}{\alpha+H}$
1	0.2500	0.1523	– 1.3914	0.4103	– 0.5784	0.1705
2	0.5385	0.3178	– 1.1559	0.9124	– 0.3975	0.3138
3	1.0000	0.4096	– 1.4414	2.4414	– 0.3249	0.5503
4	1.8571	0.7522	– 0.6117	4.5849	– 0.0929	0.6968
5	4.0000	1.6483	1.5732	9.7069	0.1344	0.8295

$^{a}G = F\,r_1 - r_2$, $^{b}\eta = \left(r_1 + \left(\frac{r_2}{\alpha}\right)\right)\xi - \frac{r_2}{\alpha}$, $\alpha = \left(\frac{F_1}{F_h}\right)$ where F_1 F_h are the lowest and highest values of F respectively.

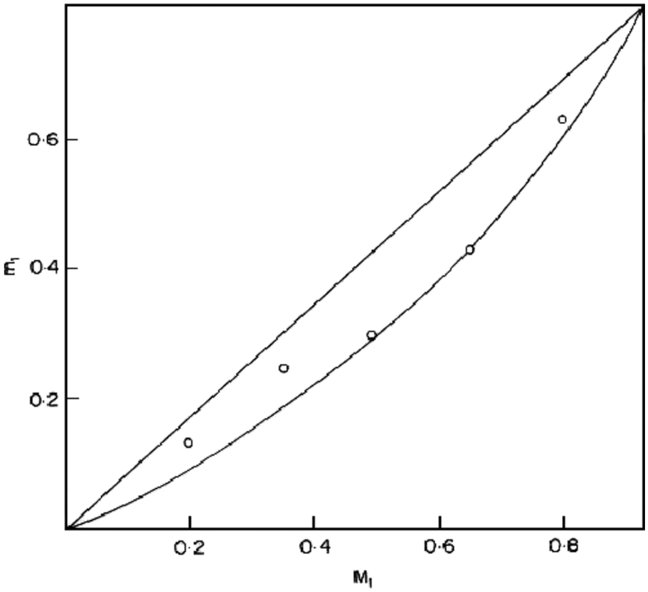


FIGURE 5 Composition curves of POEMA-GMA copolymer system.

of the copolymer, some tendency to give small blocks is observed. Based on the higher feed composition of GMA, with the help of the reactivity ratios, it can be concluded that a tendency of small blocks formation takes place. This may be attributed to a higher reactivity

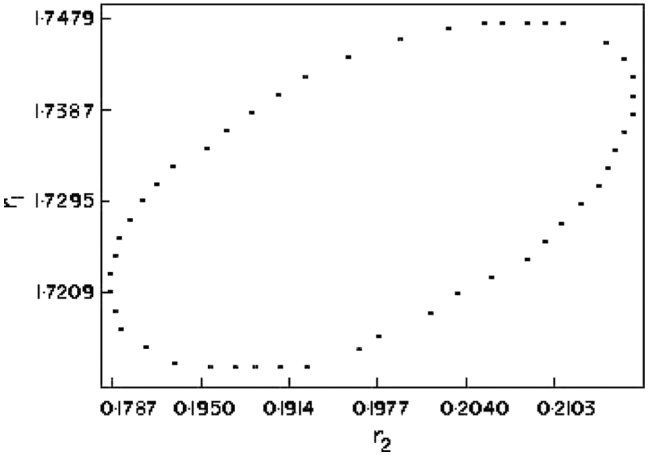


FIGURE 6 95% posterior probability contour (PPC) for estimated r_1 and r_2.

TABLE 4 Monomer Reactivity Ratios Obtained by the Three Different Methods and the $r_1 \cdot r_2$ Product

Methods	r_1	r_2	$1/r_1$	$1/r_2$	$r_1 \cdot r_2$
F-R	0.33	1.32	3.0	0.76	0.435
K-T	0.36	1.27	2.8	0.78	0.457
RREVM	0.20	1.73	5	0.58	0.350

TABLE 5 Mean Sequence Lengths in POEMA and GMA Copolymerization

Mole fraction of GMA in feed, M_2	$\bar{l}_1$	$\bar{l}_2$	$\bar{l}_1 : \bar{l}_2$	Distribution
80	1.09	7.4	1:7	PGGGGGGGP
65	1.19	3.97	1:4	PGGGGp
50	1.36	2.6	1:2	PGGP
35	1.66	1.86	1:1	PGP
20	2.44	1.4	2:1	PPGPP

of GMA toward the growing chain regardless of whether the radical was derived from GMA or POEMA.

CONCLUSIONS

Five copolymers of POEMA-co-GMA were prepared using AIBN as an initiator in 2-butanone solution at 333 K. FT-IR, ^{1}H and ^{13}C NMR spectroscopies reveal the presence of both monomeric constituents in the copolymer structure in agreement with the expected chemical structure. The copolymer composition was determined by ^{1}H-NMR spectroscopy. The reactivity ratios obtained by the F-R, K-T show differences from that obtained by RREVM method. The reactivity ratio value indicates that GMA is more reactive than POEMA and the copolymer structure will be of random nature. Thermal stability of the copolymer increases as the incorporation of GMA units in the copolymer increases.

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