

Atom Transfer Radical Copolymerization of Glycidyl Methacrylate and Methyl Methacrylate

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ABSTRACT: Glycidyl methacrylate (GMA) and methyl methacrylate (MMA) copolymers were synthesized by atom transfer radical polymerization (ATRP). The effect of different molar fractions of GMA, ranging from 0.28 to 1.0, on the polymer polydispersity index (weight-average molecular weight/number-average molecular weight) as the indicator of a controlled process was investigated at 70°C, with ethyl 2-bromoisobutyrate as an initiator and 4,4'-dinonyl-2,2'-bipyridyne (dNbpy)/CuBr as a catalyst system in anisole. The monomer reactivity ratios (r values) were obtained by the application of the conventional linearization Fineman–Ross method ($r_{\text{GMA}} = 1.24 \pm 0.02$ and $r_{\text{MMA}} = 0.85 \pm 0.03$) and by the Mayo–Lewis method ($r_{\text{GMA}} =$

1.19 ± 0.04 and $r_{\text{MMA}} = 0.86 \pm 0.03$). The molecular weights and polydispersities of the copolymers exhibited a linear increase with GMA content. The copolymer compositions were determined by ¹H-NMR and showed a domination of syndiotactic structures. The glass-transition temperatures (T_g) of the copolymers analyzed by differential scanning calorimetry (DSC) decreased in the range 105–65°C with increasing GMA units. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2209–2215, 2012

Key words: atom transfer radical polymerization (ATRP); copolymerization; glass transition

INTRODUCTION

Poly(glycidyl methacrylate)s (PGMAs) belong to the reactive polymers because of the presence of pendant epoxide groups, which give them relevant industrial importance. The highly reactive oxirane rings in the polymer can be easily opened and transformed via chemical reactions; this leads to a polymer with other properties. For example, they can be hydrolyzed to yield new hydroxylated derivatives (amphiphilic copolymers) or crosslinked structures (gel polymers) via chemical reactions, mainly with amines.¹ The simultaneous ring opening of the epoxy group of glycidyl methacrylate (GMA) with succinic anhydride results in photocurable polyesters,² whereas the attachment of bulky organosilyl groups forms polymers with potential use as membranes for fluid separation.³ Because of such ability, drugs and other biomolecules can be also covalently bound to GMA polymers; in this case, they are used as carriers in drug-delivery systems.⁴ They have also

numerous applications in the electronics industry as negative electron-beam resists.⁵

In other hand, the properties of PGMAs can be modified by the copolymerization of GMA with other monomers to enhance the solubility, hydrophilicity, biodegradability, and thermomechanical properties. Poly[(glycidyl methacrylate-co-methyl, ethyl, butyl) methacrylate]s synthesized by free-radical polymerization (FRP) indicate that the glass-transition temperature (T_g) decreases with increasing number of carbon atoms in the substituent.⁶ The incorporation of phenyl (meth)acrylate units, such as 4-benzoyloxycarbonylphenyl (meth)acrylate^{7,8} and 3,5-dimethylphenyl (meth)acrylate^{9,10} or 4-benzoylphenyl,¹¹ 4-biphenyl,¹² 4-nitro-3-methylphenyl methacrylates,¹³ increases the thermal stability and tensile strength of GMA-based polymers. They gain much interest because of potential industrial uses, such as in the manufacturing of pharmacologically active polymers, photosensitive polymers, liquid-crystalline polymers, and adhesive polymers, especially for leather. GMA copolymers containing units of phenacyl methacrylate with ketone groups are applied as photodegradable packaging materials and photoresists for microlithography.¹⁴ Their photosensitivity can be also used in many applications, such as microelectronics, printing, and UV-curable lacquers and inks. Copolymers of GMA and *N*-isopropylacrylamide are known as a thermosensitive hydrogels because of the crosslinking reaction between the

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epoxy functional groups and amines, which occur in response to temperature changes.¹⁵

Studies of the degradation behaviors of GMA polymers have shown the influence of the selected polymer synthesis method. PGMA and poly(glycidyl methacrylate-*co*-methyl methacrylate) prepared by group-transfer polymerization (GTP) indicated degradation in a single step by random chain scission, whereas free-radically prepared GMA polymers degraded in four steps; this was attributed to initiation at weak H—H linkages, unsaturation, the presence of $-\text{CCl}_3$ groups at the chain ends, and random chain scission.¹⁶

Some GMA copolymers were also synthesized by one of the controlled radical methods, that is, atom transfer radical polymerization (ATRP).^{17,18} This method allowed researchers to obtain the well-defined copolymers of GMA with styrene¹⁹ and butyl acrylate^{20,21} using catalytic copper halide. In both cases, the GMA reactivity ratio was higher than that of the comonomer, which successfully resulted in structures with a spontaneous gradient. In the literature, there is also a report of an interesting example of statistical copolymers with dual functionality, based on GMA and allyl methacrylate, which were synthesized under ATRP conditions.²² Allyl pendant groups are proficient to a crosslinking reaction by irradiation or thermal treatment, and they can participate in numerous chemical modification reactions with double bonds (addition, oxidation) and the allylic position (bromination, hydroxylation).

In this article, the synthesis of statistical (co)polymers of GMA under ATRP conditions is reported. Methyl methacrylate (MMA) was selected as the comonomer; it gave us the opportunity to obtain copolymers with various densities of oxirane rings along the chain. This resulted in the well-defined (co)polymers [poly(glycidyl methacrylate-*co*-methyl methacrylate)] [P(GMA-*co*-MMA)] and PGMA with polymerization degrees (DP_n 's) up to 150 and polydispersities [weight-average molecular weight (M_w)/number-average molecular weight (M_n)] below 1.5. Two different methods were used for the determination of the reactivity ratios of both comonomers; this allowed us to define the distribution of monomeric units in the copolymer chain. Their structures were confirmed by NMR spectroscopy, whereas the influence of the compositions on the thermal properties was defined by differential scanning calorimetry (DSC) analysis.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and glycidyl methacrylate (GMA) both from Sigma-Aldrich Chemicals Co. (St Louis, MO, USA) were passed through an alumina column to remove the antioxidant inhibitor monomethyl ether hydroquinone (MEHQ) and distilled

before use. Copper(I) bromide (CuBr; Aldrich) was purified by stirring it with glacial acetic acid (Fisher Scientific, Schwerte, Germany) and then filtering and washing the solid three times with ethanol and twice with diethyl ether. The solid was dried *in vacuo* (1×10^{-2} mbar) for 2 days. *N,N,N',N'',N''*-Pentamethyldiethyltriamine (PMDETA; Aldrich), 4,4'-dinyonil-2,2'-bipyridyne (dNbpy; Aldrich), ethyl 2-bromoisobutyrate (EBiB; Aldrich), and all of the other solvents and internal standards were used without purification.

Characterization

Gel permeation chromatography (GPC) measurements were conducted in tetrahydrofuran at 40°C at a flow rate of 1 mL/min with Shodex columns (KF-805L 300 \times 8.0 mm) (Shodex Europe, Munich, Germany). The molecular weights and polydispersity indices of the copolymers were determined on the basis of linear PMMA standards with low polydispersity indices.

¹H-NMR spectroscopy was performed on a Bruker DRX 400-MHz spectrometer (Bruker, Rheinstetten, Germany) in chloroform-*d* at room temperature.

Characterization of the monomers

GMA ¹H-NMR (CDCl_3 , δ , ppm): 6.16 and 5.61 [2H, $\text{CH}_2=\text{C}(\text{CH}_3)-$], 4.48 and 4.01 (2H, $-\text{O}-\text{CH}_2-\text{CH}_\text{OX}$), 2.67 and 2.86 (2H, CH_2OX), 3.25 (1H, CH_OX), 5.52 [1H, $\text{CHH}=\text{C}(\text{CH}_3)-$], 1.96 [3H, $\text{CH}_2=\text{C}(\text{CH}_3)-$].

MMA ¹H-NMR (CDCl_3 , δ , ppm): 6.10 and 5.56 [1H, $\text{CH}_2=\text{C}(\text{CH}_3)-$], 3.75 (3H, $-\text{O}-\text{CH}_3$), 1.95 [3H, $=\text{C}(\text{CH}_3)$].

DSC was performed with a TA-DSC 2010 calorimeter (TA Instruments, New Castle, DE, USA). Heating runs were performed at a rate of 20°C/min in the temperature range from -80 to 200°C. In all cases, T_g 's were determined during the second heating runs.

Synthesis

Synthesis of P(GMA-*co*-MMA) by ATRP (example)

The comonomers GMA (0.1 g, 0.36 mmol) and MMA (1 mL, 9.4 mmol) and anisole (0.2 mL) and dNbpy (10.5 μL , 0.05 mmol) were placed in a Schlenk flask. Next, Cu(I)Br (7.0 mg, 0.05 mmol) was added under an argon flow, and then, the mixture was purged by an inert gas for 1 h to minimize oxygen contamination. Finally, the Schlenk flask with the reaction mixture was placed in a thermostated oil bath at 70°C and after 1 min, EBiB (7.0 μL ; 0.05 mmol) was added to start the reaction. The polymerization, at a significantly larger viscosity of the reaction mixture, was stopped by exposure of the solution to air, and then, it was diluted with chloroform and filtered through a column of activated (neutral)

TABLE I
ATR (Co)polymerization of GMA with MMA

Number	Initial monomer ratio of MMA to GMA		Time (min)	Conversion (%)		DP _n	M _n (g/mol)	M _w /M _n	F _{GMA} (mol %) ^b	T _g (°C)
	wt %	mol %		x _{MMA}	x _{GMA}					
I ^a	0/100		15	—	79.2	158	12,000	1.80	1.0	—
II	0/100		20	—	70.2	140	21,800	1.49	1.0	65.4
III	4/96	5/95	25	59.4	64.4	128	19,200	1.42	0.965	—
IV	31/69	39/61	40	71.2	75.9	146	17,800	1.38	0.66	80.1
V	47/53	56/44	80	71.8	77.0	148	14,400	1.27	0.53	89.7
VI	64/34	72/28	100	65.3	73.3	135	14,200	1.25	0.33	103.1
VII	94/6	95/5	160	68.5	72.9	137	12,700	1.20	0.055	—
VIII ^a	100/0		40	76.0	—	152	14,800	1.17	0	—
IX	100/0		180	64.2	—	128	10,700	1.13	0	121.5

Conditions: [MMA + GMA]₀/[EBiB]₀/[CuBr]₀/[dNbpy]₀ = 200/1/0.5/1, anisole 10 vol % monomer mixture, and temperature = 70°C.

^a [CuBr]₀/[PMDETA]₀ = 1/1.

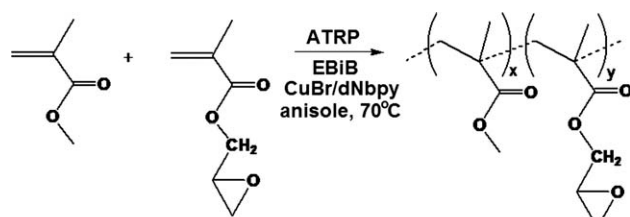
^b Calculated on the basis of ¹H-NMR. F_{GMA}, content of GMA units in the copolymer chain; I_{GMA}, peak area of protons in —O—CH₂— (δ = 3.81 and 4.3 ppm, 2H) characteristic for GMA units; I_{MMA}, peak area of protons in —O—CH₃ (δ = 3,6 ppm, 3H) for MMA units.

alumina to remove the copper catalyst. Finally, the polymer was precipitated in methanol and dried *in vacuo* at room temperature to a constant mass. A similar procedure was also used for the homopolymerizations of GMA and MMA.

P(GMA-*co*-MMA) ¹H-NMR (CDCl₃, δ, ppm): 0.85 [syndiotactic (rr)], 1.09 (mr + mm, heterotactic), 1.25 [mm, isotactic, 3H, —CH₂—C(CH₃)—], 1.8–2.1 [2H, —CH₂—C(CH₃)—], 3.6 (3H, —O—CH₃), 4.3 and 3.81 (2H, —O—CH₂—CH_{OX}), 2.64 and 2.85 (2H, CH₂OX, 3.23 (1H, CH_{OX}).

RESULTS AND DISCUSSION

PGMA (I) yielded in ATRP, which was catalyzed by the system [CuBr]₀/[PMDETA]₀ (1/1) in anisole at 70°C, indicated an uncontrolled polymerization reaching a relatively high polydispersity index (M_w/M_n = 1.8) within 15 min (Table I). This means that the activation rate was higher than that of deactivation; this generated heterogeneous polymer chains. The use of a catalyst system with a lower activity, that is [CuBr]₀/[dNbpy]₀ = 0.5/1, gave a slower reaction with better control, which led to a significantly reduced molecular weight distribution of homopolymer II (M_w/M_n < 1.5). The same effect was observed for PMMA homopolymers VIII versus



Scheme 1

IX, which were obtained in the presence of PMDETA and dNbpy ligand, respectively. However, in those cases, the polymers were characterized by much lower values of polydispersities (both <1.2), but their preparation at similar conversions (~70%) needed longer time. Initially, this allowed us to conclude that there was a higher polymerization rate for GMA in comparison to that of MMA.

The less activated system CuBr/dNbpy was also applied to the controlled atom transfer radical (ATR) copolymerization of MMA with GMA at various initial comonomer ratios, that is, 5/95, 39/61, 56/44, 72/28, and 95/5 mol % (samples III–VII, Scheme 1). The kinetics presented in Figure 1 indicate that the

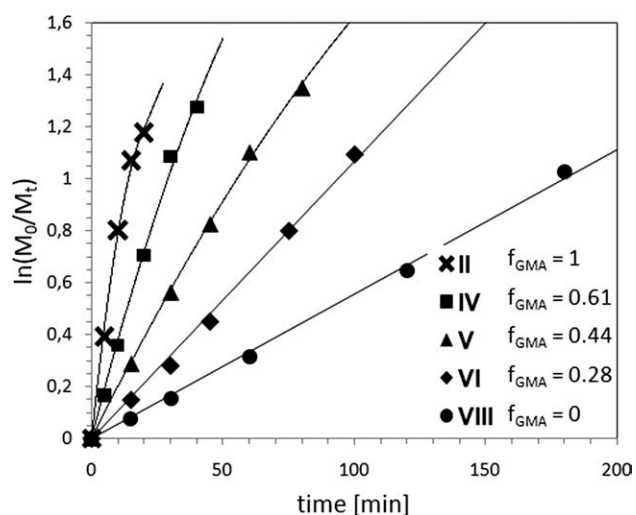


Figure 1 Semilogarithmic plot of the monomer consumption versus time for the polymerization of GMA and MMA at various initial concentrations of comonomers. The conditions are presented in Table I.

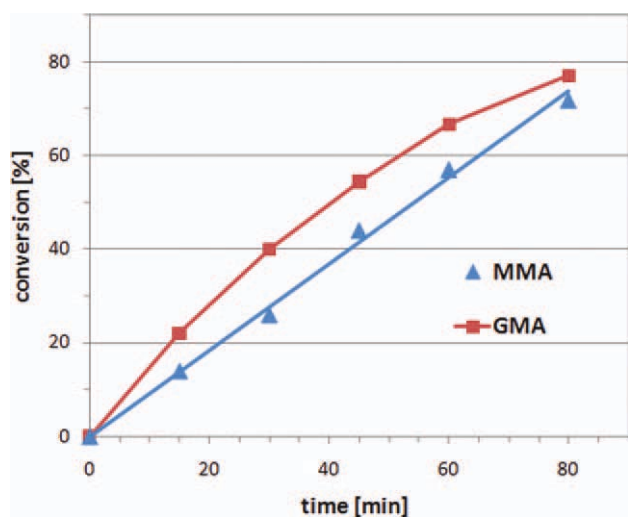


Figure 2 First-order plot of the monomer consumption versus time for the copolymerization of GMA and MMA (V) at the initial ratio 44/56. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization rate increased with the initial proportion of GMA to MMA, and at around 70% conversion, the linearity started to be slightly missing. This allowed us to conclude the small contribution of side reactions, including chain-transfer reactions and termination, which influenced the broadening of the molecular weight distribution of the P(GMA-co-MMA) copolymers. The polydispersity was changed in the range 1.2–1.4, which was correlated with the increase in the reaction rate corresponding to the reduced time of polymerization. As shown in the plot of the monomer consumption versus time, the polymerization of GMA and MMA (V) proceeded at slightly different rates to moderate conversion after 45 min, that is, 54 and 44%, respectively (Fig. 2). The kinetic plot of MMA was linear, whereas some deceleration at higher conversion of GMA may have indicated termination. This also explained the higher polydispersity and faster polymerization at larger initial concentrations of GMA comonomer. The values of M_n determined by conventional GPC were apparent due to a systematic error becoming from the use of homopolymer PMMA standards.

The copolymer microstructure was defined by $^1\text{H-NMR}$ analysis. The spectrum in Figure 3(b), which is presented for the precipitated and dried P(GMA-co-MMA) IV, combines both signals typical for PGMA II [a–c, Fig. 3(a)] and PMMA IX [a, b, d–f, Fig. 3(d)]. This allowed us to determine the content of comonomer units $F_{\text{GMA}}/F_{\text{MMA}}$ by the evaluation of signals at 3.81 and 4.35 ppm (d, 2H in GMA units) and 3.6 ppm (c, 3H in MMA units). In the case of the spectrum shown in Figure 3(c), which is representative for P(GMA-co-MMA) V (sample taken from the reac-

tion mixture), it shows more signals due to the presence of unreacted comonomers together with the formed copolymer and let calculate the comonomer conversions. The amount of incorporated GMA in the copolymer was established by taking advantage of the vinyl protons of unreacted GMA (a'_2 , $\delta = 5.62$ and 6.15 ppm) to the integration of peak e at 3.25 ppm, which corresponded to one of the protons in the oxirane ring in the monomer and copolymer. For MMA conversion, the peak area of signals ascribed to the vinyl protons [$\text{CH}_2=\text{C}(\text{CH}_3)-$] in the methacrylate group of unreacted monomer (a'_1 , $\delta = 5.47$ and 6.03 ppm) was compared with the signal of methoxy protons [$-\text{OCH}_3$] in MMA units in the copolymer (c, $\delta = 3.6$ ppm). This also gave an opportunity to estimate the content of both comonomer units ($F_{\text{GMA}}/F_{\text{MMA}}$) by the use of nonoverlapped signals. Additionally, the stereochemical configuration of monomeric units along the copolymer chain was defined by the resonance signal of protons in the $\alpha\text{-CH}_3$ splitting into three well-resolved peaks at 0.89, 1.06, and 1.24 ppm (b), which were assigned to syndiotactic (rr), heterotactic (mr + rm), and isotactic (mm) triads, respectively. This showed good agreement with the literature, in which the similar assignment of the $\alpha\text{-CH}_3$ signals for PGMA^{23,24} and PMMA^{25,26} obtained by conventional and controlled polymerization is reported. Previously, it was observed that the differences in chemical shifts between the two signals in PGMA ($\delta_{\text{mm}} - \delta_{\text{mr}} = 0.14$ ppm and $\delta_{\text{rm}} - \delta_{\text{rr}} = 0.18$ ppm) were very

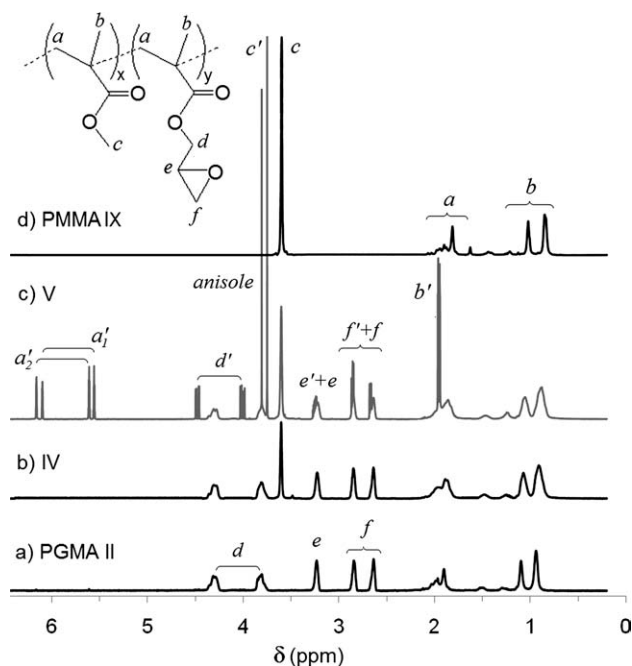


Figure 3 $^1\text{H-NMR}$ spectra of the copolymers (a) PGMA (II), (b,c) P(GMA-co-MMA) (IV and V), and (d) PMMA (IX). The conditions are given in Table I.

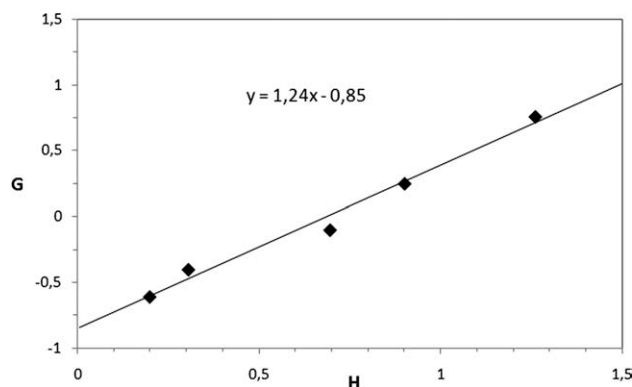


Figure 4 Fineman–Ross plot for the determination of the comonomer reactivity ratios. $H = f_{\text{GMA}}^2 / (1 - f_{\text{GMA}})^2 \times (1 - F_{\text{GMA}}) / F_{\text{GMA}}$; $G = -f_{\text{GMA}} / (1 - f_{\text{GMA}}) \times (1 - 2 F_{\text{GMA}}) / F_{\text{GMA}}$.

close to that of PMMA (0.15 ppm). In all cases, the calculated molar fractions of mm, mr + rm, and rr tactic triads (0.6/0.33/0.07) indicated predominantly syndiotactic copolymers, whereas the differences in the chemical shifts between the two signals reached the following value: $\delta_{\text{mm}} - \delta_{\text{mr}} = \delta_{\text{rm}} - \delta_{\text{rr}} = 0.18$ ppm.

The Fineman–Ross method²⁷ was applied to determine the comonomer reactivity ratios, which yielded following values: $r_{\text{GMA}} = 1.24 \pm 0.02$ and $r_{\text{MMA}} = 0.85 \pm 0.03$ (Fig. 4). The conversion was kept within about 25 wt % because, at high conversions, the changes in the initial and final feed compositions were significant; this yielded a quite high error in monomer reactivity ratios, whereas at very low conversions, the composition may have been influenced by preferential initiation of one monomer by the initiating radical.²⁸ According to the literature, it was expected that both methacrylate monomers should copolymerize with comparable reactivity, such as MMA and *n*-butyl methacrylate ($r_1 = 0.98$, $r_2 = 1.26$),²⁹ or a slightly higher reactivity of GMA, such as in the pair with allyl methacrylate ($r_1 = 1.22$, $r_2 = 0.82$).²² A similar reactivity of GMA to the comonomer was also observed in the FRPs with 4-benzyloxycarbonylphenyl methacrylate ($r_1 = 0.82$, $r_2 = 1.02$, and $r_1 r_2 \sim 1$),⁷ phenacyl methacrylate ($r_1 = 1.51$, $r_2 = 1.40$, and $r_1 r_2 \sim 2$),¹⁴ and 4-biphenyl methacrylate ($r_1 = 0.36$, $r_2 = 0.39$, and $r_1 r_2 \sim 0.2$),¹² although it happened that GMA was significantly less reactive than the second methacrylate, such as 4-benzoylphenyl methacrylate ($r_1 = 0.82$, $r_2 = 1.49$)¹¹ and 4-nitro-3-methylphenyl methacrylate ($r = 0.89$, $r = 1.71$).¹³ In those cases where $r_1 = r_2$, the random compositions of the copolymers were postulated, whereas the gradient structures were for $r_1 > r_2$ and $r_1 < r_2$. However, the studied comonomer pair GMA/MMA presented $r_1 \geq r_2$; this led to postulate the formation of a copolymer structure between a random and spontaneous gradient. The values $r_{\text{GMA}} > 1$ and $r_{\text{MMA}} < 1$ indicated

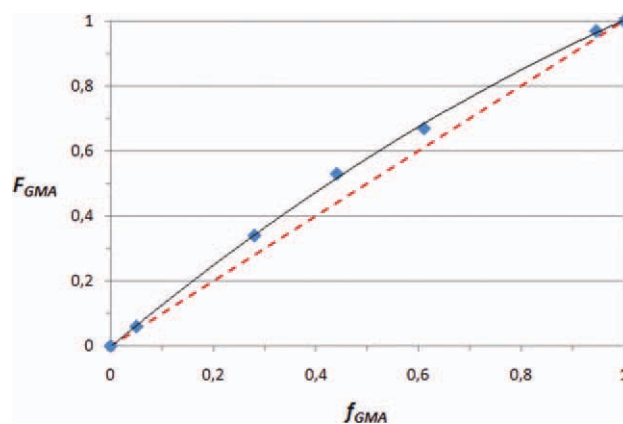


Figure 5 Instantaneous monomer–copolymer composition for the ATRP copolymerization of GMA with MMA (F_{GMA} vs initial amounts of GMA used for polymerization (f_{GMA}) diagram). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that both free-radical types, GMA and MMA, easily reacted with the GMA monomer; this demonstrated that the homopropagation constant was slightly higher than the cross-propagation one and that GMA reacted preferentially with GMA units rather than with MMA molecules, whereas the MMA-type radicals preferred to bind the other monomer, that is,

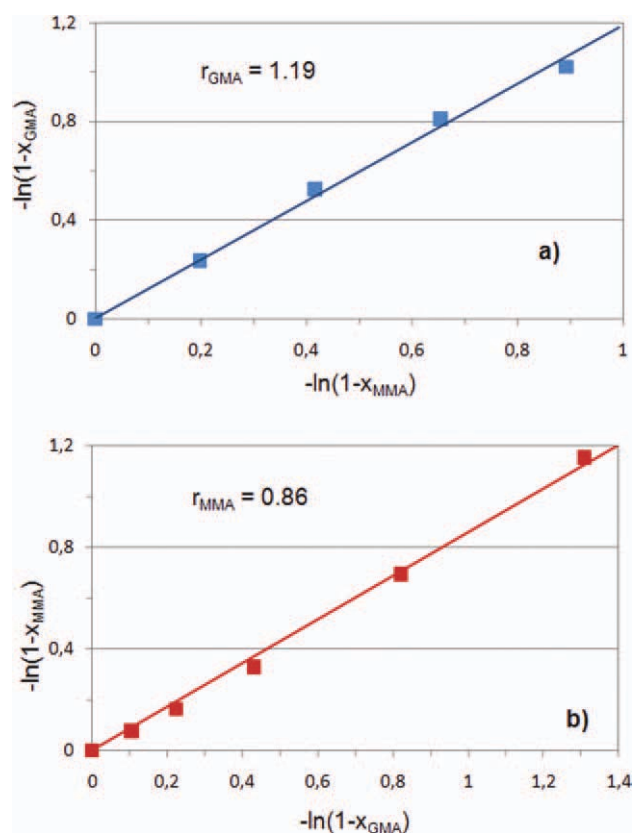


Figure 6 Jaacks plots of the ATRP at comonomer ratios of $[\text{GMA}]_0$ to $[\text{MMA}]_0$ = (a) 19 (III) and (b) 0.05 (VII). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

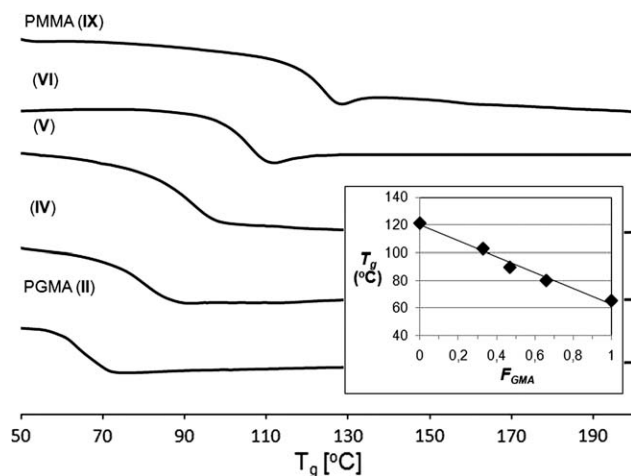


Figure 7 DSC thermograms of the P(GMA-*co*-MMA) copolymers (IV–VI) and PGMA (II) and PMMA (IX) homopolymers obtained in the second heating runs. The inset shows the dependence of the polymer T_g on the content of GMA units. The conditions are given in Table I.

GMA. This means the copolymer formed instantaneously was slightly richer in GMA than the monomer mixture it originated from. It was confirmed in the plot of instantaneous monomer–copolymer composition in Figure 5, which shows some discrepancy from the dependence typical for the formation of a random copolymer (dashed line). Additionally, the product of $r_{GMA}r_{MMA} \sim 1$ suggested that longer sequences of GMA units were statistically distributed with the MMA units in the copolymer chains. The monomer reactivity ratios, for the system presented in this article, were also estimated by the Jaacks method³⁰ at high and low monomer feed ratios ($[GMA]_0:[MMA]_0 = 19$ and 0.05 for III and VII, respectively). Their values were calculated from the Jaacks plots: $[-\ln(1 - x_{GMA}) = r_{GMA}x - \ln(1 - x_{MMA})]$ to yield $r_{GMA} = 1.19 \pm 0.04$ [Fig. 6(a)] and $[-\ln(1 - x_{MMA}) = r_{MMA}x - \ln(1 - x_{GMA})]$ to yield $r_{MMA} = 0.86 \pm 0.03$ [Fig. 6(b)]. These values were close to the reactivity parameters obtained by the Fineman–Ross method.

The DSC thermograms in Figure 7 present an amorphous morphology with one transition for all of the polymer samples. The lack of an exotherm in the curve allowed to eliminate the thermal opening of the oxirane ring during heating in the range: -80 – 200 °C. The T_g 's, which were determined during the second heating runs, decreased linearly with increasing GMA content in the polymers; they varied between 120 °C for the homopolymer PMMA (IX) and 65 °C for the homopolymer PGMA (II; Table I, inset in Fig. 7). Previously reported studies of the synthesis of PGMA by FRP indicated its T_g in the range 74 – 78 °C,^{8,9} whereas PMMA homopolymer exhibited T_g 's at 127 °C (FRP)³¹ and 109 – 104 °C (ATRP).^{32,33}

CONCLUSIONS

The controlled polymerization of statistical copolymers [P(GMA-*co*-MMA)s] with various amounts of pendant reactive functional groups was described. The standard ATRP conditions with a CuBr/dNBpy catalytic system allowed to obtain (co)polymers with $DP_n = 130$ – 160 , but the molecular weight distribution significantly increased with the GMA fraction content reaching $M_w/M_n = 1.38$ at 66 mol % GMA and $M_w/M_n = 1.5$ for the homopolymer PGMA. The relative reactivity ratios of the comonomers were determined by the Fineman–Ross and Mayo–Lewis methods. Their similar values ($r_{GMA} \geq r_{MMA} \sim 1$) and unlinear dependence of the copolymer composition versus initial comonomer concentration led us to conclude a statistical composition with longer sequences of GMA units in the resulting copolymers, which presented mainly syndiotactic microstructures. Thermal analysis by DSC confirmed a totally amorphous morphology and indicated that T_g increased with decreasing units containing oxirane rings. Further, these polymers could be modified by the ring-opening of oxirane, for example, in an amination or phosphonation reaction.

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