

Polymers Based on Phenyl Methacrylate: Synthesis via Atom Transfer Radical Polymerization, Characterization, Monomer Reactivity Ratios, and Thermal Stabilities

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ABSTRACT: The atom transfer radical copolymerization of phenyl methacrylate (PMA) with methyl methacrylate (MMA) was performed in bulk at 110°C in the presence of ethyl 2-bromoacetate, cuprous bromide (CuBr), and 2,2'-bipyridine. Also, free-radical copolymerization of PMA with MMA was carried out in the presence of 2,2'-azobisisobutyronitrile in 1,4-dioxane solvent at 60°C. The copolymers were characterized by IR, ¹H NMR, and ¹³C NMR techniques. The compositions of the copolymers were determined from the ¹H NMR spectra. The in situ addition of ethylmethacrylate to a macroinitiator—poly(phenyl methacrylate)[$M_n = 10,560$, $M_w/M_n = 1.68$ —afforded an AB-type block copolymer. The molecular weight and molecular weight distribution were obtained using gel permeation chromatography (GPC). The polydispersities for the living copolymer (48 mol % PPMA units) and the free-radical copolymer (42 mol % PPMA) were 1.43 and 2.40, respec-

tively. For the two copolymerization systems, the monomer reactivity ratios were obtained by using both Kelen–Tüdös and Fineman–Ross equations. The initial decomposition temperatures of the resultant copolymers decreased with increasing mole fraction of PMA, which indicate that heat resistance of copolymer improved by decreasing the PMA units. Blends of poly(PMA) and poly(MMA) obtained via ATRP method were prepared by casting films from dichloromethane solution. The blends were characterized by differential thermal analysis or differential scanning calorimetry and thermogravimetry. The results were comparable with each other. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3344–3354, 2006

Key words: ATRP; blend; thermal analysis; monomer reactivity ratios

INTRODUCTION

One of the most effective methods for precision polymer synthesis is living-radical polymerization. It is free from side reactions such as termination and chain transfer and can thus generate polymers with well-defined architectures and molecular weights, i.e. one polymer chain per molecule of initiator.¹ Living-radical polymerization of methacrylates has been achieved by the use of various complexes as well as metals such as copper, nickel, palladium, and rhodium. Among them, the most precisely controlled polymerizations were reported with the R–Br/Cu,² R–Cl/Ru,³ R–Br/Ni⁴ systems, where R–X means an initiator with a particular halogen (X = Br, Cl). The carbon–halogen bonds derived from methacrylate are highly reactive because of the two substituents, methyl and ester groups, which stabilize the relevant radical species. The Cu(I)-based initiating system for styrene polymerization was first reported by Wang and Matyjaszewski and has subsequently been applied to a wide range of

monomers. The use of CuBr and a bromide initiator narrows the molecular weight distributions (MWDs) of polystyrene and poly(MA) ($M_w/M_n \approx 1.1$), whereas broader MWDs ($M_w/M_n \approx 1.4$) were obtained for poly(MMA).⁵ Atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) has been reported for copper (I) halides^{2,6} and the other catalytic systems.⁷ The homo or copolymers of other methacrylic esters have also been successfully polymerized. These include *n*-butyl methacrylate,⁸ 2-(dimethylamino)ethyl methacrylate,⁹ block copolymer with styrene and *n*-butyl methacrylate,¹⁰ and grafting of poly(styrene-*co-p*-chloromethyl styrene) with ethyl methacrylate via ATRP catalyzed by CuCl/1,2-dipiperidinoethane.¹¹ One of the major advantages of living-radical procedures compared with living anionic or cationic polymerizations, which have numerous problems, is to prepare well-defined random copolymers. For example, monomer reactivity ratios can be extremely large in anionic systems, and so true random copolymerizations do not occur.¹² Therefore, finding the reactivity ratios for monomers under normal free-radical conditions is also fundamentally important, although random copolymers prepared by living free-radical processes are different on a molec-

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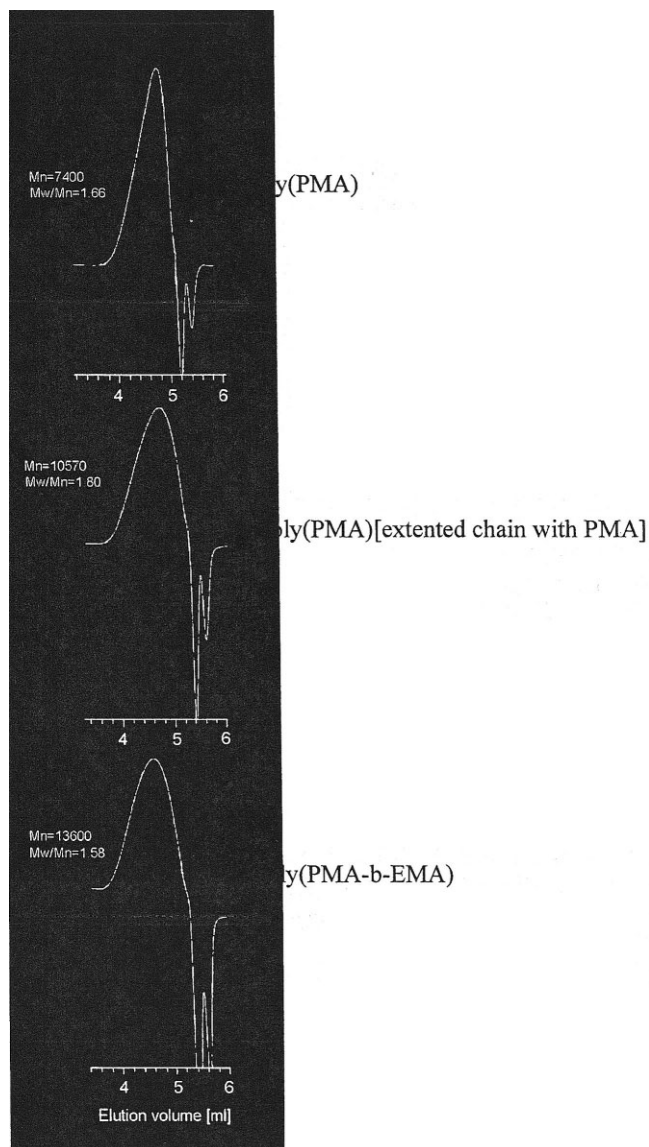


Figure 1 GPC curves of poly(PMA), ([PPMA]:[CuBr]:[bpy]; [25:1:1:3]), poly(PMA) (macroinitiator), and poly(PMA-*b*-EMA).

ular level to those prepared by normal free-radical method.

In this work, our investigation concentrates on both the living-radical copolymerization and free-radical copolymerization of phenyl methacrylate (PMA) and MMA; the characterization of the resulting copolymers and their the monomer reactivity ratios were determined by using both the Kelen-Tüdös (K-T) and Finemann-Ross (F-R) procedures. On the other hand, thermal analysis results are given in comparison with each other. Blends of poly(PMA) and poly(MMA) obtained via ATRP method are characterized by differential thermal analysis or differential scanning calorimetry and thermogravimetry.

EXPERIMENTAL

Materials

MMA and ethyl methacrylate were vacuum-distilled after washing with 5% NaOH aqueous solution just before copolymerization. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform-methanol mixture. Cuprous (I) bromide, 2,2'-bipyridyne, and ethyl bromoacetate (analytical reagent) were used as-received.

Characterization techniques

Infrared spectra were obtained on a Mattson 1000 FTIR spectrometer. NMR spectra were recorded on a Jeol FX 90Q NMR spectrometer at room temperature in CDCl_3 . Thermogravimetric analysis (TGA) measurements were carried out under a nitrogen flow with a TGA-50 thermobalance at a heating rate of $10^\circ\text{C}/\text{min}$. Gel permeation chromatography (GPC) analyses were carried out using Agilent 1100 system equipped with a high-pressure liquid chromatography pump, a vacuum degasser, and a refractive index detector. The eluting solvent was tetrahydrofuran (THF) and the flow rate was 1 mL/min. Calibration was achieved with polystyrene.

Synthesis of pma

PMA was synthesized by the reaction of phenol and methacryloylchloride at $0-5^\circ\text{C}$ with potassium carbonate. It was distilled under vacuum (bp: 114°C at 20 mmHg).

IR (cm^{-1} , the most characteristic bands): 1738 ($\text{C}=\text{O}$ stretching), 1638 ($\text{C}=\text{C}$ in the vinyl group), 1600 ($\text{C}=\text{C}$ stretch in aromatic ring). ^{13}C NMR (CDCl_3 , δ):

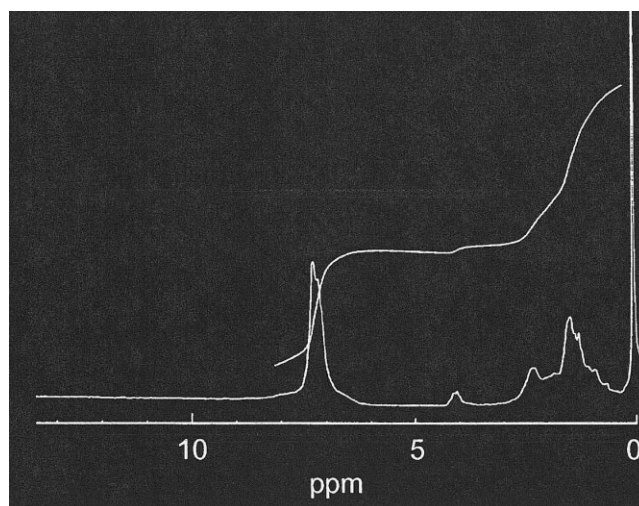


Figure 2 ^1H NMR spectrum of AB-type block copolymer (PPMA-*b*-PEMA) prepared by ATRP.

TABLE I
ATRP of Both PMA and EMA Using CuBr/bpy, Catalyst System, Initiator
(ethyl 2-bromo acetate or PPMA Macroinitiator)

Entry	[Monomer]/ [Initiator]	Time (h)	Temp (°C)	M_n (GPC)	M_w/M_n
1. [Poly(PMA)]	25 : 1	19	110	7,400	1.66
2. [Poly(PMA)]	100 : 1	19	110	10,570	1.66
3. [Poly(PMA- <i>b</i> -EMA)]	100 : 1	19	90	13,560	1.57
4. [Poly(48 mol % PMA- <i>co</i> -MMA)] (prepared by ATRP)	100 : 1	24	110	8,650	1.43
5. Poly(42 mol % PMA- <i>co</i> -MMA)] (prepared by free-radical pol.)		24	60	26,600	2.40

18.9 (CH₃), 120.4 (CH on aromatic ring), 136.8 (=C), 151.9 (ipso carbon on aromatic ring), 166 (C=O). ¹H NMR (CDCl₃, δ): 2.04 (s, 3H), 5.70 (s, 1H), 6.33 (s, 1H), 6.9–7.3 (aromatic ring protons).

Atrp procedures

All ATRP reactions were carried out following the same experimental procedure. CuBr was introduced into a glass tube. The glass tube was sealed with a rubber septum and was cycled twice between vacuum and argon. The mixture containing monomer or monomers, initiator (ethyl 2-bromoacetate or macroinitiator), ligand (bpy), and solvent (if used) was degassed by argon purging for 10 min before adding to the glass tube. The sealed tube was immersed in a preheated oil bath at a desired temperature. The tube was then removed from oil bath and reaction mixture was dissolved in chloroform, filtered, and then dried. Conversion was determined gravimetrically. The polymers were used in determination of molecular structure with ¹H NMR, FTIR, and GPC techniques.

Preparation of polymer blends

Poly(PMA) and poly(MMA) blend samples were prepared by solution casting from dichloromethane at room temperature, and the blends were dried at room temperature under vacuum.

RESULTS AND DISCUSSION

ATRP of PMA

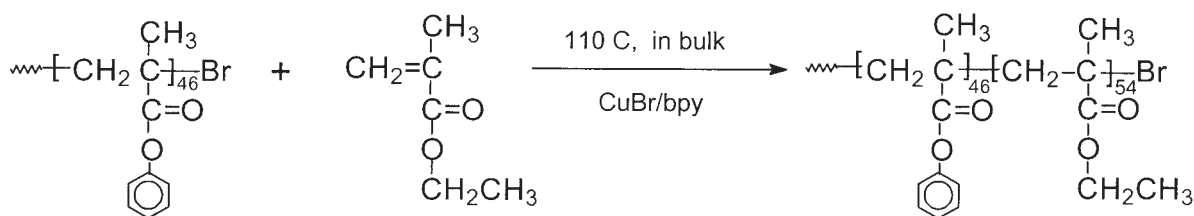
ATRP in bulk

To a two necked round bottom flask, 1.25 g (7.7 mmol) of PMA, required amount of initiator (ethyl 2-bro-

moacetate), and ligand (2,2'-bipyridine) were added. After addition of the calculated amount of CuBr as catalyst, the mixture was degassed and sealed in vacuo. The flask was shaken until the mixture dissolved. Polymerizations were carried out [monomer: initiator; 25 : 1, 100 : 1] at 110°C for 19 h. Upon cooling and addition of dichloromethane, the green color polymer solution was precipitated into ethanol containing 1% aqueous hydrochloric acid. The ester functionalized polymer was isolated by precipitating it several times from dichloromethane solution into ethanol containing 1% aqueous hydrochloric acid, filtered off, and dried.

ATRP copolymerization of PMA with MMA

The general procedure for the copolymerization of PMA with MMA with six compositions was as follows: In all cases, predetermined amounts of monomers, initiator (ethyl 2-bromoacetate), ligand (2,2'-bipyridine), and calculated amount of CuBr as catalyst were added into a flask. The mixture was degassed three times by freeze-pump-thaw cycles and sealed in vacuo. The flask was shaken until the mixture dissolved, immersed in an oil bath, and heated to the required temperature (110°C). After particular time duration, the flasks were opened and dichloromethane was added to the sample to dissolve the copolymer. The heterogeneous solution was filtered. The copolymers were isolated by precipitation in *n*-hexane and dried at 40°C for 24 h. The conversion of the copolymerization was determined gravimetrically and was found to be under 15%.



poly(PMA-*b*-EMA)

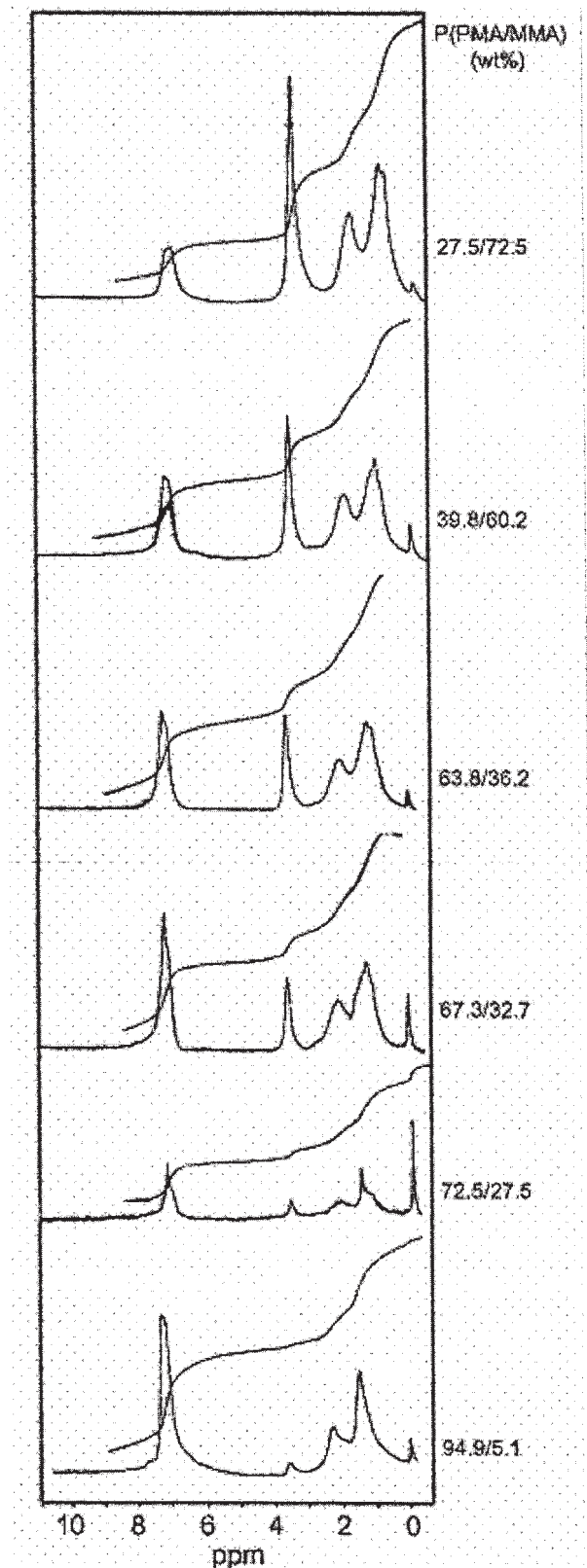


Figure 3 ^1H NMR spectra of random copolymers prepared by ATRP with compositions of PMA and MMA.

Free-radical copolymerization of PMA with MMA

Seven copolymers of PMA with MMA were prepared in 1,4-dioxane at 60°C in the presence of AIBN. Predetermined amounts of the monomers, AIBN, and the solvent were mixed in a polymerization tube. The mixture was degassed for about 10 min with argon and kept in a thermostated oil bath at 60°C. After desired time the mixture was cooled to ambient temperature. The copolymers were precipitated into excess ethanol and purified by reprecipitation, and then the copolymers were dried at ambient temperature for 24 h.

Block copolymerization of EMA using PPMA macroinitiator

Block copolymerization of PMA-*b*-EMA was performed using a two-step ATRP method. The first step was the preparation of macroinitiator [poly(PMA)]. The polymerization of PMA with ethyl 2-bromoacetate as the initiator in conjunction with CuBr/bpy as the catalyst system has been verified to be controlled or living free-radical polymerization. In the synthesis of a block copolymer, we used poly(PMA) macroinitiator with a low conversion (27 mol %). Figure 1 shows the GPC curves of poly(PMA) ([PPMA] : [CuBr] : [bpy]; [25 : 1 : 1 : 3]), poly(PMA) (macroinitiator), and poly(PMA-*b*-EMA), using the following feed ratio [EMA] : [PPMA] : [CuBr] : [bpy]; 100 : 1 : 1 : 3 in bulk at 110°C and 90°C (reaction time 19 h), respectively. From this figure, it is clear that the GPC curve of PPMA as macroinitiator is almost absent and completely shifted to a new higher molecular weight position. The number-average molecular weights of macroinitiator and block copolymer are 10,570 and 13,560, respectively. This indicates that the molecular weight can be controlled, and almost all PPMA macromolecules participated in the initiation, leading to the formation of diblock copolymer, PPMA-*b*-PEMA.

The ^1H NMR spectrum of block copolymer was recorded and shown in Figure 2. The signal at $\delta = 4.03$ is attributed to the methylene protons adjacent to ester oxygen in the PEMA unit; on the other hand, the signal $\delta = 7.28$ is due to phenyl protons in the PPMA unit. ^1H NMR spectrum of poly(PMA-*b*-EMA) showed that EMA and PMA units in copolymer were 29 and 71 mol %, respectively. On the other hand, the amount of EMA repeat units in block copolymer, according to GPC data, is 27 mol %, which is in close agreement with those obtained by ^1H NMR.

Table I summarizes the synthesis conditions and the characteristics of poly(PMA) and poly(PMA-*b*-EMA) obtained by ATRP. Table I showed that at a high monomer-to-initiator ratio for the same reaction temperature the number-average molecular weights, M_n ,

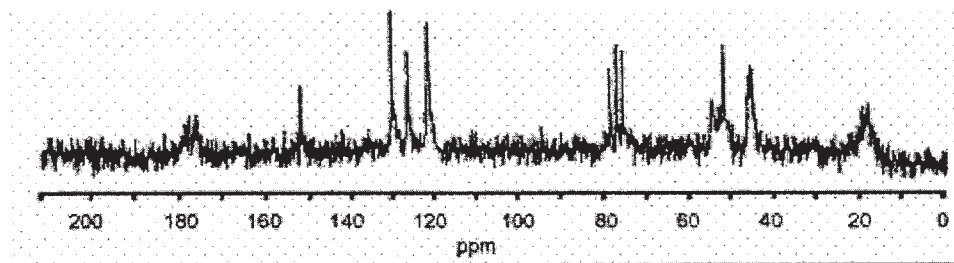
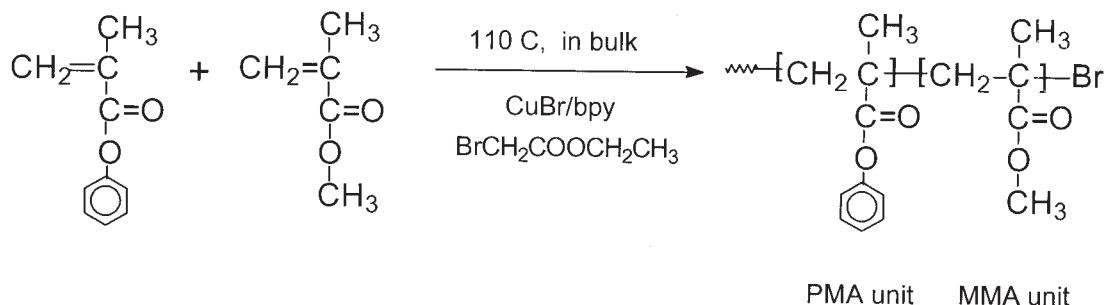


Figure 4 ^{13}C NMR spectrum of poly(PMA:MMA) (48:52 mol %) prepared by ATRP.



Scheme 2

were high. Although the number-average molecular weights, M_n (Entry 1 and 2), were different from each other, the polydispersity (M_w/M_n) was almost same. We aimed to verify the preparation of a block copolymer of ethyl methacrylate using poly(PMA) macroinitiator to be controlled/living free-radical polymerization (Scheme 1). We used a high number-average molecular weight poly(PMA) macroinitiator ($M_n = 10,570$) to verify the effect of loss of bromine during ATRP. The polymerization was initiated by poly(PMA) macroinitiator catalyzed by CuBr/bpy and run at 90°C . Although the M_n increased (Entry 3), the polydispersity significantly decreased, which suggests a good control of polymerization.

Characterization of copolymers

The ^1H NMR spectra of copolymers prepared via living-radical polymerization (ATRP) are shown in Figure 3. The peaks at 6.9–7.3 ppm reveal the monosubstituted phenyl ring protons, and the signal at 3.63 ppm is assigned to methyl adjacent to oxygen in MMA units. As the PMA units in copolymer increases from 19 to 92 mol %, the intensity of phenyl ring protons in PMA units gradually increases. The other signals are due to the methyl and methylene protons of comonomeric units.

The copolymer (with 48 mol % PMA units) has the most characteristic peaks of the monomeric units at 176 ppm (C=O in MMA units), 177 ppm (C=O in PMA units), 51.6 ppm ($-\text{OCH}_3$), 54 and 53 ppm (quaternary carbons of PMA and MMA in both units,

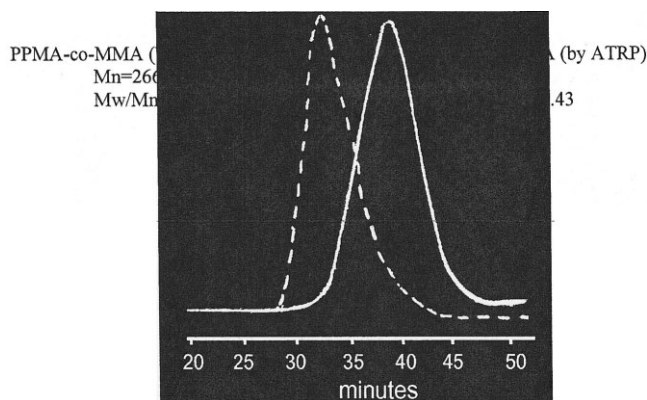


Figure 5 GPC traces of poly(PMA-co-MMA) obtained via ATRP (48:52 mol %) [continuous line] and normal free-radical polymerization (42:58 mol %) [line at half height].

TABLE II
Comonomer Composition in Feed and in Copolymers

Polymers	Feed (M_1)	Copolymer	
		ATRP (m_1)	Free-radical Polymerization (m_1)
1	0.13	0.19	0.18
2	0.27	0.29	0.26
3	0.39	0.48	0.42
4	0.51	0.56	0.53
5	0.64	0.62	0.67
6	0.90	0.92	0.91

M_1 : mole fraction of PMA in feed; m_1 : mole fraction of PMA in copolymer.

TABLE III
Results of the Living-Radical Copolymerization of PMA and MMA

Sample No.	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
1	0.149	0.234	-0.487	0.095	-0.535	0.104
2	0.369	0.408	-0.533	0.333	-0.435	0.289
3	0.639	0.923	-0.053	0.442	-0.042	0.351
4	1.040	1.272	0.282	0.850	0.169	0.509
5	1.777	1.631	0.687	1.936	0.249	0.703
6	9.000	11.5	8.217	7.043	1.045	0.896

M_1 : mole fraction of PMA in feed; M_2 : mole fraction of MMA in feed; m_1 : mole fraction of PMA in copolymer; m_2 : mole fraction of MMA in copolymer. $(H_{\min}, H_{\max})^{1/2} = 0.817$; H_{\min} : lowest value of H ; H_{\max} : highest value of H .

TABLE IV
Results of the Free-Radical Copolymerization of PMA and MMA

Sample No.	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
1	0.149	0.219	-0.531	0.101	-0.530	0.100
2	0.369	0.351	-0.682	0.387	-0.529	0.300
3	0.639	0.724	-0.243	0.563	-0.166	0.384
4	1.040	1.127	0.117	0.959	0.063	0.515
5	1.777	2.030	0.901	1.555	0.367	0.633
6	9.000	10.1	8.108	8.02	0.908	0.899

M_1 : mole fraction of PMA in feed; M_2 : mole fraction of MMA in feed; m_1 : mole fraction of PMA in copolymer; m_2 : mole fraction of MMA in copolymer. $(H_{\min}, H_{\max})^{1/2} = 0.9$; H_{\min} : lowest value of H ; H_{\max} : highest value of H .

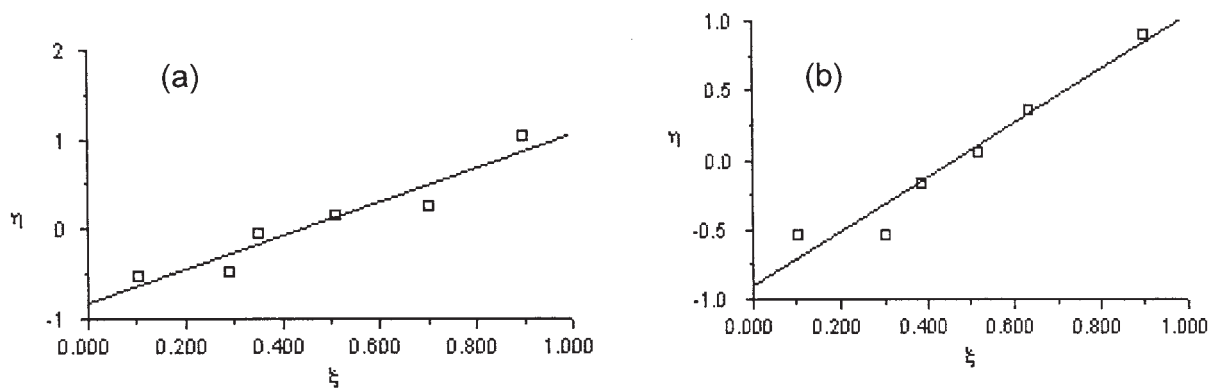


Figure 6 Kelen-Tüdös plots for (a) the ATRP and (b) the free-radical polymerization of PMA and MMA.

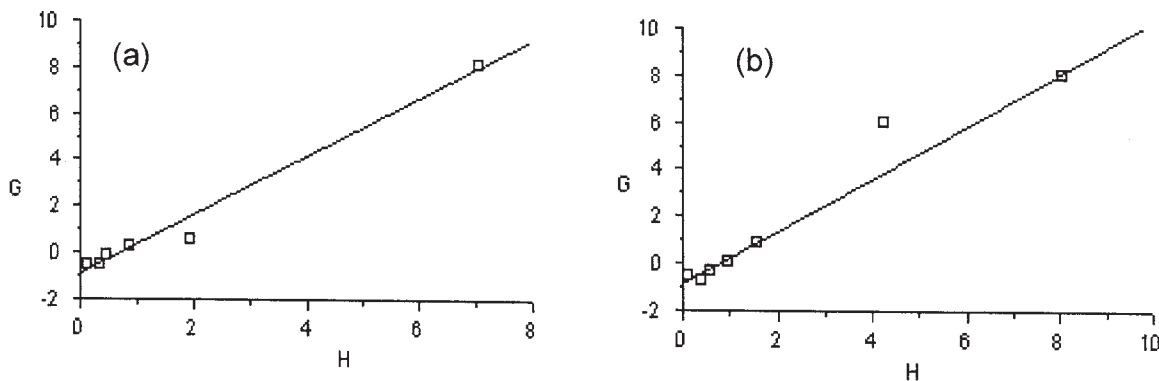


Figure 7 Fineman-Ross plots for (a) the ATRP and (b) the free-radical polymerization of PMA and MMA.

TABLE V
Comparison of Monomer Reactivity Ratios
by Two Methods

System	Methods	R_1	R_2	$r_1 \cdot r_2$
Atom transfer radical copolymerization	K-T	1.06	0.68	0.72
Free-radical copolymerization	F-R	1.26	0.96	1.20
Free-radical copolymerization	K-T	1.04	0.81	0.84
Free-radical copolymerization	F-R	1.20	0.88	1.05

^a r_1 : Monomer reactivity ratio of PMA

respectively), 150 ppm (ipso carbon of the monosubstituted phenyl ring).

Figure 4 shows the IR spectra of the resulting copolymers with various feed ratios of PMA and MMA, prepared by free-radical copolymerization. The absorbance at 748 and 690 cm^{-1} is attributed to a vibration characteristic of a monosubstituted benzene ring in PMA moieties. The band at 1592 cm^{-1} is assigned to aromatic C=C stretch, whose relative intensities gradually increase as the percentage of PMA in the copolymers increases from 18 to 91 mol %. The peak at 1731 cm^{-1} is assigned to the vibration of ester carbonyl in PMA and MMA units. The copolymerization with ATRP is illustrated in Scheme 2. The initiator residue at one end of the copolymer molecules, and bromine atom at the other end, may be attached to both kinds of monomeric units.

The average molecular weight and molecular weight distribution were obtained by GPC (Agilent 1100 RI detector). The number-average molecular weight (M_n) for copolymer having 48 mol % PMA units prepared via ATRP method was 8650, and the polydispersity (M_w/M_n) was 1.43. On the other hand, those of the copolymer (42 mol % PMA) prepared by free-radical polymerization were 26,600 and 2.40. The resulting copolymers possess relatively narrow polydispersities. This suggests that the contribution of chain breaking and transfer as well as termination reactions during copolymerization can be neglected until polymerization conversion is higher. The GPC profiles of copolymers showed a unimodal elution curve (Fig. 5).

Monomer reactivity ratios

The ATR random copolymerization of MMA and PMA initiated by ethyl 2-bromoacetate for various ratios of PMA to MMA has been carried out. Table I shows the influence of the initial molar compositions of the comonomers on those of the comonomers in the copolymers, in both ATR copolymerization and free-radical copolymerization.

The copolymer compositions were analyzed with ^1H NMR spectra. Figure 3 shows ^1H NMR spectra of the copolymer prepared by ATRP. The peaks at 6.6–

7.1 ppm correspond to the aromatic protons in PMA units, the signal centered at 3.8 ppm is assigned to methyl protons adjacent to oxygen in MMA units. The other signals at 1–2.2 ppm are assigned to methylene and methyl in the polymer main chain. Thus, the mole fractions of PMA and MMA in the copolymer were determined from the ratio of the integral intensities of aromatic protons of PMA in 6.8–7.1 ppm and the aliphatic protons between 1 and 3.9 ppm. Copolymer compositions have been calculated from the following equation:

$$\frac{\text{Integral intensities of aromatic protons } (I_{Ar})}{\text{Integral intensities of aliphatic protons } (I_{Alp})} = \frac{5m_1}{5m_1 + 8m_2}$$

On simplification: $m_1 = \frac{8C}{5 + 3C}$

where m_1 is mole fraction of PMA and m_2 is that of MMA in copolymer. Similar calculations have also been made for free-radical copolymerization.

The K–T and F–R parameters were calculated, using data in Table II, for both the living-radical copolymerization and free-radical copolymerization of PMA and MMA, and the results were summarized in Tables III and IV, respectively.

It is well known that monomer reactivity ratios can be indicative of relative reactivity of comonomers.^{13–15} To estimate the relative reactivity of PMA and MMA in both the ATR copolymerization and free-radical copolymerization, the Kelen–Tüdös¹⁶ and Fineman–Ross¹⁷ equation were used, which are $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$ and $G = r_1H - r_2$, respec-

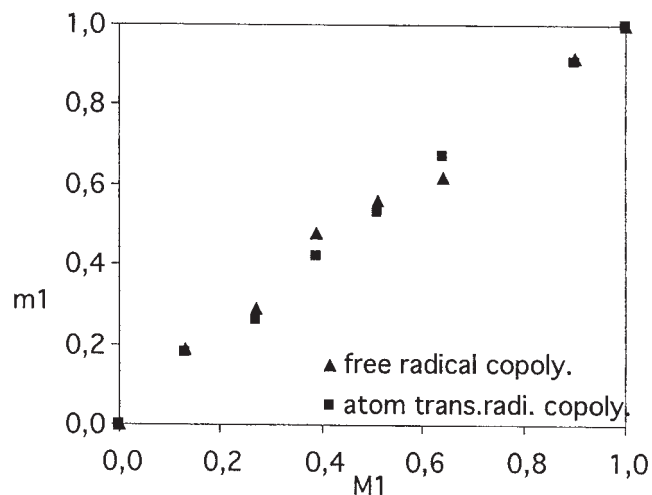


Figure 8 Composition diagrams of ATRP copolymerization and free-radical copolymerization.

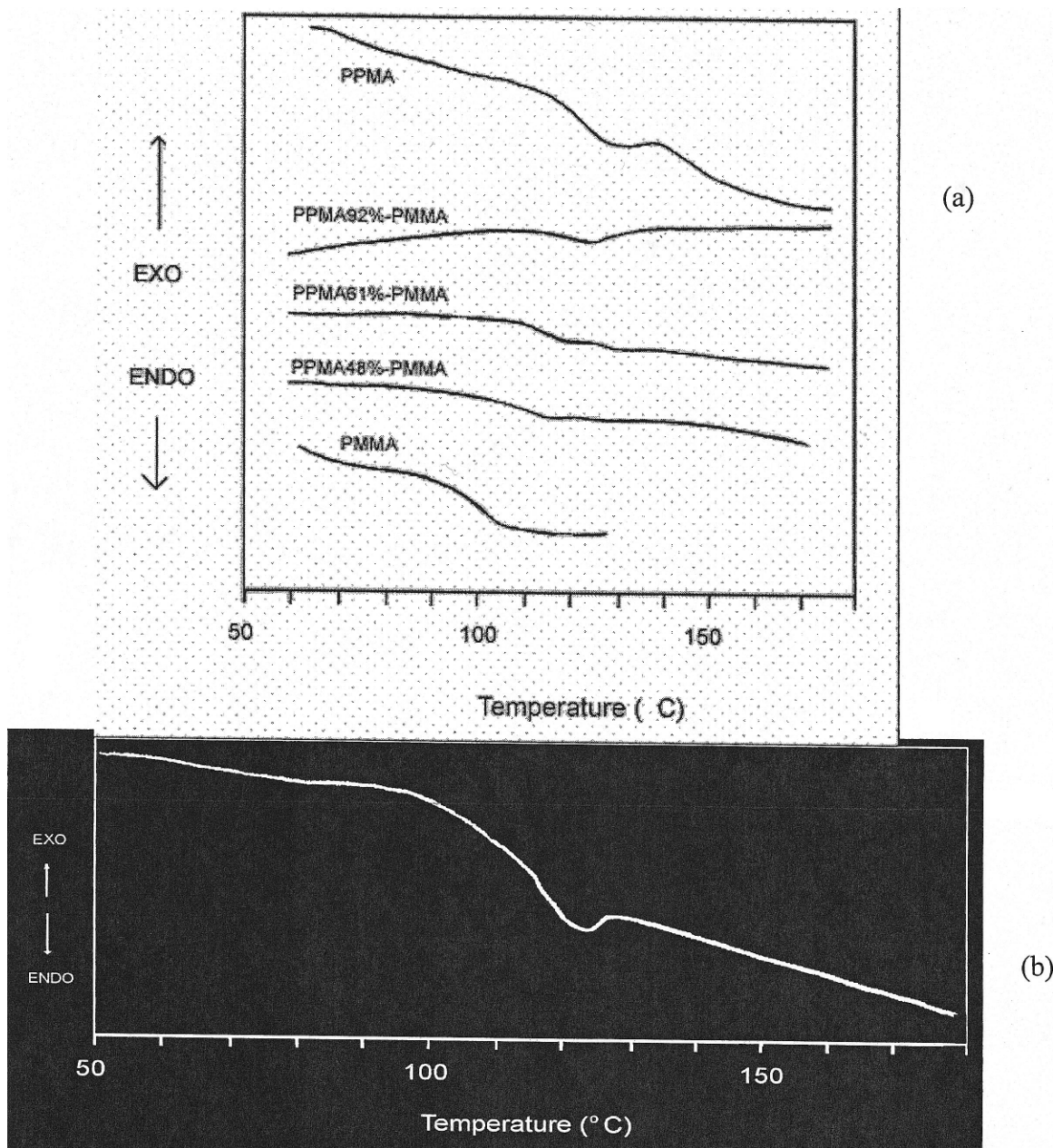


Figure 9 (a) DSC traces of blend polymer and poly(PMA) and poly(MMA) and (b) DTA curve of one copolymer heated at 20°C/min to 200°C.

tively. (Notations in the equations are described in Tables III and IV.) The plots of G versus H and η versus ξ for both systems are shown in Figures 6 and 7, respectively. From the slope and intercept, the monomer reactivity ratios of PMA and MMA were determined and given in Table V. Monomer reactivity ratio of PMA is slightly higher than 1, and that of MMA is slightly lesser than 1, for both the copolymerizations and both the methods.

Apparently, the values of monomer reactivity ratios indicate that the growing radicals with PMA ends were added to PMA or MMA monomers at a

nearly same rate, but the radicals with MMA ends have a lesser tendency to be added to PMA, in both kinds of radical copolymerizations. Distributions of the monomeric units along the copolymer chains are random, and they are slightly richer in PMA units. For both the copolymerizations, the behaviors of the systems were evaluated through plots of the copolymer compositions (m_1) measured from ^1H NMR as the molar fraction of PMA versus the feed compositions is measured as the molar fraction of PMA (M_1) (Fig. 8). It is seen that compositions of copolymer obtained from both the copolymerization tech-

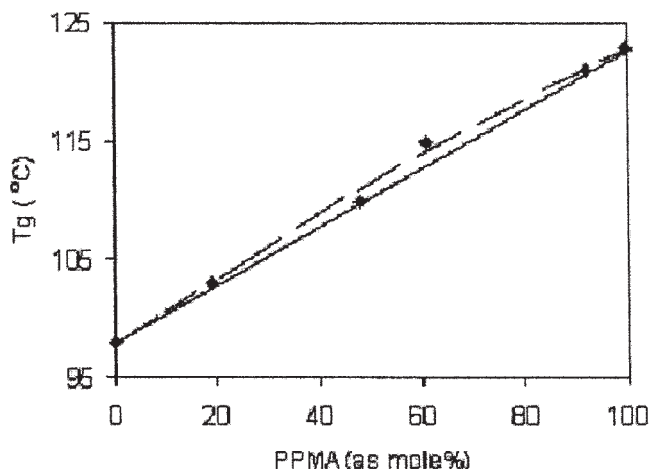


Figure 10 Plots of the T_g of a series blend polymers as a function of PPMA in the blends.

niques are quite close to each other. But it can be suggested that random copolymers prepared by living free-radical processes are different on a molecular level to those prepared by normal free-radical methods. For living-radical systems all chains are initiated at the same time and grow at approximately the same rate, whereas in the case of normal free-radical polymerization, continuous initiation leads to chain initiation and termination at different stages of the polymerization¹⁸.

DSC or DTA measurements

The glass transition temperatures of the homopolymers, the blends, and the copolymer (92 mol % PMA

units) prepared by ATRP were determined by DSC or DTA. The T_g values of poly(PMA) and poly(MMA) were found to be 123°C and 98°C, respectively. The T_g values obtained for the blends were between 108°C and 121°C (Fig. 9(a)), in accordance with the increasing percentage of PPMA. The T_g value of the 92 mol % PMA copolymer was 115°C (Fig. 9(b)). Plots of the T_g values versus mole fractions of PPMA in the blends are shown in Figure 10. The observed T_g 's of the blend polymers indicate a slightly positive deviation with respect to linearity, which can be associated with a slightly lower free volume than that of a mixture of PMA and MMA.

It is known that an immiscible blend shows glass transition temperature of each individual polymer, but a miscible blend shows only one glass transition temperature. Each polymer blend prepared in this study shows single transition, which can be attributed to poly(PMA) and poly(MMA) that give the compatible blends. An inner shift of single T_g 's for poly(PMA):poly(MMA) blends indicate good compatibility of both polymers. Both the polymers contain polar ester and nonpolar alkyl groups, and they indicate similar kinds of interactions, and also, their average molecular weights are relatively low. Most of polymers having these kinds of properties are generally compatible.¹⁹ The T_g values of the blends show clearly positive deviation. Since syndiotactic distribution in the homopolymer units is dominant, interchain interactions along the polymer chains in the blend are low because of steric hindrance. This results in increasing of free volume in the blend, and

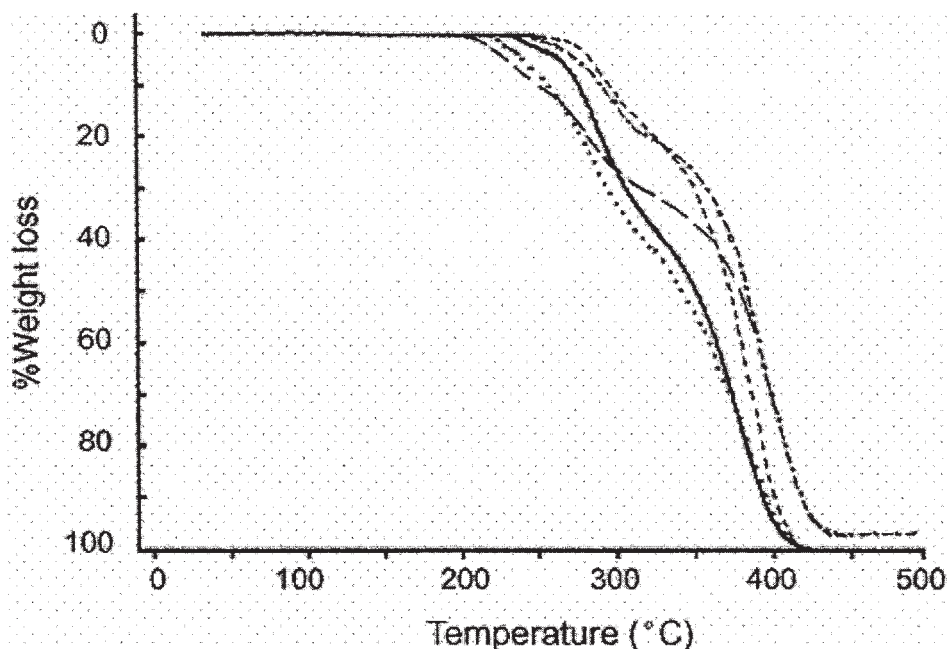


Figure 11 TGA curves of polymers heated under nitrogen at 10°C/min heating rate from room temperature to 500°C. (---): 19% PMA, by ATRP; (—): 48% PMA, by ATRP; (— — —): 62%PMA, by ATRP; (—): 18%PMA, by free radical; (—): 42% PMA, by free radical.

TABLE 6
TGA Data for the Polymers

Polymers	T_i	T_f	$T_{50\%}$	% Weight loss at 300°C	% Weight loss at 350°C	% Weight loss at 400°C	Residue at 400°C (%)
Poly(PMA) by ATRP	220	422	323	46	58	83	6
Poly(PMA-co-MMA) by ATRP (19 mol % PMA)	256	422	377	10	28	88	0
Poly(PMA-co-MMA) by ATRP (48 mol % PMA)	248	435	388	12	27	72	1
Poly(PMA-co-MMA) by ATRP (62 mol % PMA)	206	430	382	25	36	72	1
Poly(PMA) by free-radical polymerization	264	426	342	21	57	93	2
Poly(PMA-co-MMA) by free-radical polymerization (18 mol % PMA)	235	422	350	25	50	95	0
Poly(PMA-co-MMA) by free-radical polymerization (42 mol % PMA)	218	422	348	32	54	95	0
Poly(PMA 92 mol %-PMMA) [blend]	218	428	375	18	31	80	7
Poly(PMA 19 mol %-PMMA) [blend]	216	412	370	10	30	84	7
Poly(PMMA) (by ATRP)	260	410	362	5	35	94	2

T_i : initial decomposition temperature; T_f : final decomposition temperature; $T_{50\%}$: Decomposition temperature at 50% weight loss.

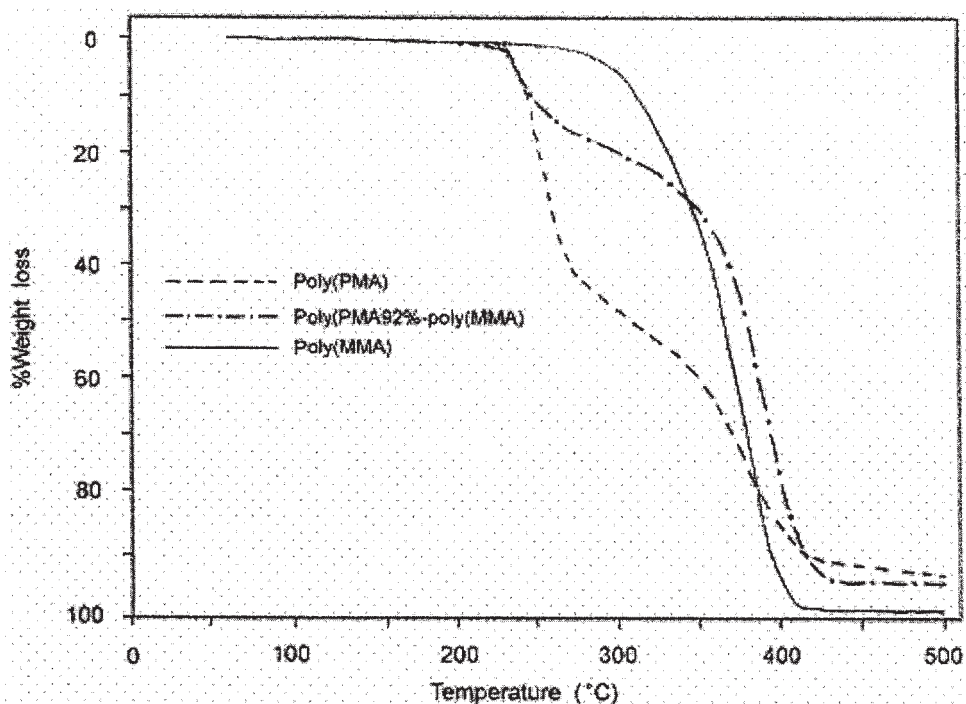


Figure 12 TGA curves of poly(PMA), poly(MMA), and poly(PMA92%-MMA) heated under nitrogen at 10°C/min heating rate from room temperature to 500°C.

decreasing of their T_g values with respect to linearity. The stereoeffects strongly depends on the monomer structures.²⁰ Therefore, enhancing the stereoeffect may be effective in view of syndiotactic for methacrylates with the relatively bulky side group such as phenyl group.

Thermogravimetric study

The thermogravimetric curves for poly(PMA) and the three copolymers prepared by ATRP, obtained between room temperature to 500°C at a heating rate of 10°C/min under nitrogen flow, are given in Figure 11 in comparison with the two copolymers prepared by free-radical polymerization. Decomposition temperature of poly(PMA) prepared by ATRP occurs in two steps at about 220°C and 330°C, respectively. On the other hand, poly(PMA) prepared by free-radical polymerization shows a decomposition with a two stage at about 264°C and 330°C. The thermal stabilities of both polymers are considerably different, the residues of poly(PMA) prepared by ATRP and poly(PMA) by free-radical are about 2% and 6%, respectively, and their initial decomposition temperatures are 220°C and 264°C, respectively. TGA results of copolymers are summarized in Table VI compared with those of poly(PMA) prepared two different methods. The copolymers showed that thermal stability decreased with increasing in PMA for two copolymer systems.

The TGA curves of pol(PMA) used as macroinitiator, poly(MMA) and poly(PMA 92 mol %–MMA) were shown in Figure 12. From these curves, it was observed that thermal stability decreased with increasing in MMA units.

CONCLUSIONS

Six PMA–MMA copolymers were prepared both atom transfer radical polymerization and free-radical polymerization. ¹H, ¹³C NMR, and FTIR techniques revealed the presence of both monomeric units in the copolymer chain. The situ addition of ethylmethacrylate to a macroinitiator of poly(PMA) afforded an AB-type block copolymer. The monomer reactivity ratios were calculated from the feed composition and copolymer composition determined by ¹H-NMR spectroscopy. For two copolymer systems, their monomer reactivity ratios were determined by the K–T and F–R methods. The results obtained via ATRP method are close to those obtained at the conventional radical copolymerization with the usual free-radical initiator. In the both

systems, two monomers have a strong tendency to form ideal copolymer because the value of $r_1 r_2$ is at around 1. In case of poly(PMA-*co*-MMA), initial decomposition temperature of copolymers decreased with an increasing in the molar fraction of PMA. In that of poly(PMA-*b*-EMA), it was decreased with an increasing EMA units. Thermogravimetric measurements for blends of poly(PMA) and poly(MMA) obtained via ATRP method showed that thermal decomposition temperature decreased when poly(PMA) percentage was increased. On the other hand, the each polymer blend prepared in this study showed single transition, which can be attributed to poly(PMA) and poly(MMA) to give the compatible blends. An inner shift of single T_g 's for poly(PMA) : poly(MMA) blends indicated good compatibility of both polymers.

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