Homo- and Copolymerization of Phenacyl Methacrylate via the Atom Transfer Radical Polymerization Method

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The homo- and copolymers via atom transfer radical (co)polymerization (ATRP) of phenacyl methacrylate (PAMA) with methyl methacrylate (MMA) and t-butyl methacrylate (t-BMA) was performed in bulk at 90°C in the presence of ethyl 2-bromoacetate, cuprous(I)bromide (CuBr), and 2,2′-bipyridine. The polymerization of PAMA was carried out at 70, 80, and 100°C. Also, free-radical polymerization of PAMA was carried out at 60°C. Characterization using FT-IR and ^{13}C-NMR techniques confirmed the formation of a five-membered lactone ring through ATRP. The in situ addition of methylmethacrylate to a macroinitiator of poly(phenacyl methacrylate) [Mn = 2800, Mw/Mn = 1.16] afforded an AB-type block copolymer [Mn = 13600, Mw/Mn = 1.46]. When PAMA units increased in the living copolymer system, the Mn values and the polydispersities were decreased (1.1 < Mw/Mn < 1.79). The monomer reactivity ratios were computed using Kelen-Tüdös (K-T), Fineman-Ross (F-R) and Tidwell-Mortimer (T-M) methods and were found to be $r_1 = 1.17$; $r_2 = 0.76$; $r_1 = 1.16$; $r_2 = 0.75$ and $r_1 = 1.18$; $r_2 = 0.76$, respectively ($r_1 = $ is monomer reactivity ratio of PAMA). The initial decomposition temperatures of the resulting copolymers were measured by TGA. Blends of poly(PAMA) and poly(MMA) obtained via the ATRP method have been characterized by differential thermal and thermogravimetric analyses.

Keywords: ATRP; blend; thermal analysis; monomer reactivity ratio; lactone end

1 Introduction

One of the most effective methods for precision polymer synthesis is living radical polymerization. It is essentially free from side reactions such as termination and chain transfer and can thus generate polymers of 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 including 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/Ni (4) systems, where R-X means an initiator with a particular halogen (X = Br, CI). The carbon-halogen bonds derived from methacrylate are higly reactive due to the two substituents, methyl and ester groups, which stabilize the relevant radical species. The Cu(I)-based initiating system was first reported for styrene polymerization 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 MWDs of polystyrene and poly(MA)(Mw/Mn≈1.1), while broder MWDs (Mw/Mn≈1.4) were obtained for poly(MMA) (5). ATRP of methyl methacrylate (MMA) has been reported for copper(I) halides (6, 7) and the other catalytic systems (8). The homo or copolymers of other methacrylic esters have also been succesfully polymerized. These include n-butyl methacrylate (9), 2-(dimethylamino)ethyl methacrylate (10), block copolymer with styrene and n-butyl methacrylate (11), grafting of poly (styrene-*co-p*-chloromethyl styrene) with ethyl methacrylate via atom transfer radical polymerization catalyzed by CuCl/1,2-dipiperidinoethane (12). One of the major advantages of living radical procedures compared to living anionic or cationic polymerizations, which there are 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. The finding that the monomer reactivity ratios for monomers under living free-radical conditions are essentially the same as under normal free radical conditions is also fundamentally important. Random copolymers prepared by living free radical processes are different on a molecular level to those prepared by normal free radical methods. In the case of traditional free radical polymerization, continuous initiation leads to chains initiating and

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terminating at different stages of the polymerization. For a living radical system, all chains are initiated at the same time and grow at approximately the same rate, as a consequence of the growing chains experience the same exchange in monomer concentrations (13).

Lactones are present in a large variety of natural products and exhibit interesting biological properties (14). Natural insect feeding deterrents are one group of natural products considered to be useful tools to manipulate insect pest populations. They are usually not neurotoxic to insects and other animals, are specific in action and easily biodegradable. These features render antifeedants potential environmentally safe agents for the production of plant and stored products against insect pestes (15). Formation of a lactone five membered for polymethylmethacrylate have already reported with a loss of MeBr followed by cyclisation of the final two monomer repeat units to give a lactone end group by appropriate techniques (16, 17). In our previous study, lactone formation via ATRP of benzyl methacrylate has been characterized and in the lactone formation was effected the stability of a benzylic radical or carbocation (18).

In this paper, we describe a chain end dissociation reaction in PAMA oligomers produced by ATRP that has not been reported previously. Sample of low molecular weight poly(PAMA) characterized by FT-IR and ^{13}C-NMR gave spectra consistent with a loss of phenacylbromide followed by a cyclization reaction to give a lactone end group. The effect of a phenacyl group in place of methyl or t-butyl in side group is discussed. In addition, we report homo- and copolymerization via the living radical polymerization of phenacylmethacrylate (PAMA), methylmethacrylate (MMA), t-butylmethacrylate (t-BMA). We discussed lactone formation produced at chain ends via atom transfer radical polymerization of phenacyl methacrylate between $70°C-100°C$. The FT-IR, GPC, NMR techniques were used for characterization of the resulting copolymers. Also, the monomer reactivity ratios were determined by both the Kelen-Tüdös, Finemann-Ross and Tidwell-Mortimer procedures. Blends of poly(PAMA) and poly(MMA) obtained via ATRP method are characterized by differential thermal and thermogravimetric analyses. Thermal analysis results are given in comparison with each other for all polymers.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA, Aldrich), and t-butyl methacrylate (t-BMA, Aldrich) were vacuum-distilled after washing with a 5% NaOH aqueous solution just before polymerization. 2,2′-Azobisizobutyronitrile (AIBN) was recrystallized from a chloroform-methanol mixture. Cuprous(I)bromide (Aldrich), 2,2′-bipyridine (Aldrich) and ethyl 2-bromoacetate (analytical reagent, Aldrich) was used as received. Prior to

polymerization, all solvents, monomers and other reagents were degassed by argon purging.

2.2 Characterization Techniques

Infrared spectra were obtained on a Mattson 1000 FTIR spectrometer. NMR spectra were recorded on Bruker Spektrospin Avance DPX-400 Ultra Shield 400 MHz High Performance Digital FT-NMR and a Jeol FX 90Q 22.50 MHz ^{13}C-NMR at room temperature in CDCl$_3$. The DTA curves were obtained using a Shimadzu DTA-50 instrument programmed for heating at $20°C/min$. Thermogravimetric analysis (TGA) measurements were carried out under a nitrogen flow with a TGA-50 thermobalance at a heating rate of $10°C\,min^{-1}$. Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump with a Agilent 1100 system equipped with a vacuum degasser, a refractive index detector. Tetrahydrofurane (THF) was used as carrier solvent at a flow rate of 1 mL/min and at room temperature. The instrument was calibrated with polystyrene (PSty) standards.

2.3 Synthesis of Phenacyl Methacrylate (PAMA)

Phenacylmethacrylate (PAMA) was synthesized by the reaction of phenacylbromide and sodium methacrylate in the presence of hydroquinone at $85-90°C$. It was distilled under vacuum (b.p.: $174°C$ at 15 mmHg).

IR (cm^{-1}, the most characteristic bands): 1736 (C=O stretching in ester), 1638 (C=C in the vinyl group), 1605 (C=C stretching in aromatic ring).

^{13}C-NMR (CDCl$_3$, δ): 17.8 (CH$_3$), 66.3 (CH$_2$ adjacent to keto carbonyl), 133.3 (CH$_2$=), 166.9 (C=O in ester), 192.3 (C=O in keto group).

^{1}H-NMR (CDCl$_3$, δ): 1.98 (s, H), 5.62 (s, 1H), 6.22 (s, 1H), $6.9-7.3$ (aromatic ring protons).

2.4 ATRP Procedures

A typical ATRP procedure is given below. First, CuBr was put into a glass tube. The glass tube was sealed with a rubber septum and was cycled between vacuum and argon twice. 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. Then, the tube was removed from an oil bath and reaction mixture was dissolved in chloroform and was precipitated in ethylalcohol. This process was repeated two times to purify the polymer. After the filtration, all polymers were dried for 24 h in vacuum at $70°C$.

2.5 Free Radical Polymerization of PAMA

In the first step, PAMA was treated with a 5% NaOH solution, then it was dried and distilled under reduced pressure before polymerization. Polymerization of PAMA occurred at 60°C in 1,4-dioxane in the presence of AIBN as initiator. Afterwards, purification by reprecipitation in ethylalcohol was done. This process was repeated twice. Lastly, the polymer was dried for 24 h in vacuum at 70°C.

2.6 Preparation of Polymer Blends

Poly(PAMA) and Poly(MMA) blend samples were prepared by casting from a dichloromethane solution at room temperature, then the blends were dried for 24 h under vacuum at 70°C.

3 Results and Discussion

3.1 Characterization of Polymers

The ^{1}H-NMR spectrum of poly(PAMA) showed signals at 5.30 (OCH$_2$CO, 2H) and 7.35 ppm (aromatic metha, 2H), 7.50 ppm (aromatic para, 1H), 8.27 (aromatic orto, 2H).
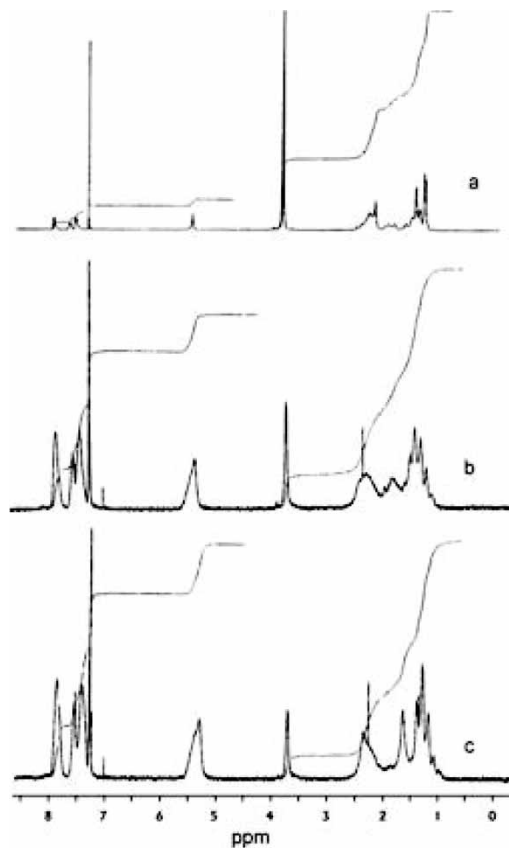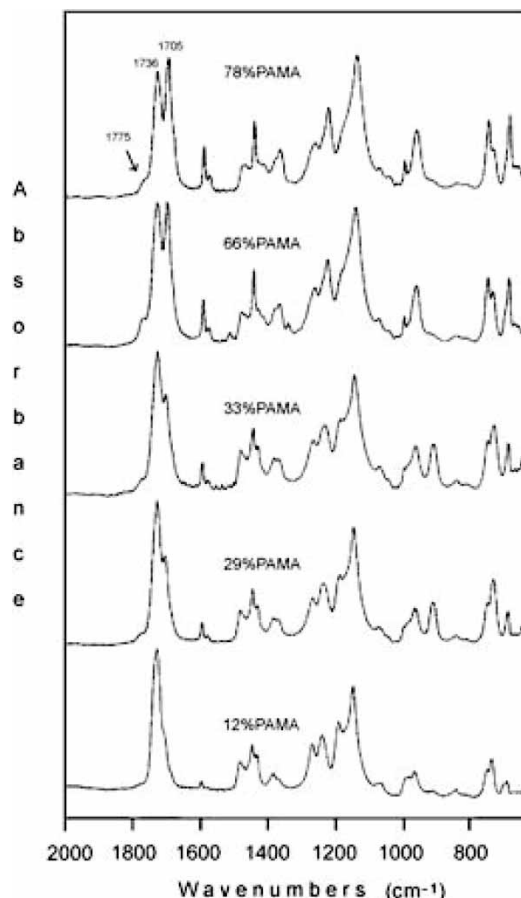

Fig. 1. ^{1}H-NMR spectra of random copolymers prepared via ATRP with compositions of PAMA and MMA, [a) poly(PAMA12%-co-MMA), b) poly(PAMA66%-co-MMA), c) poly(PAMA78%-co-MMA)].
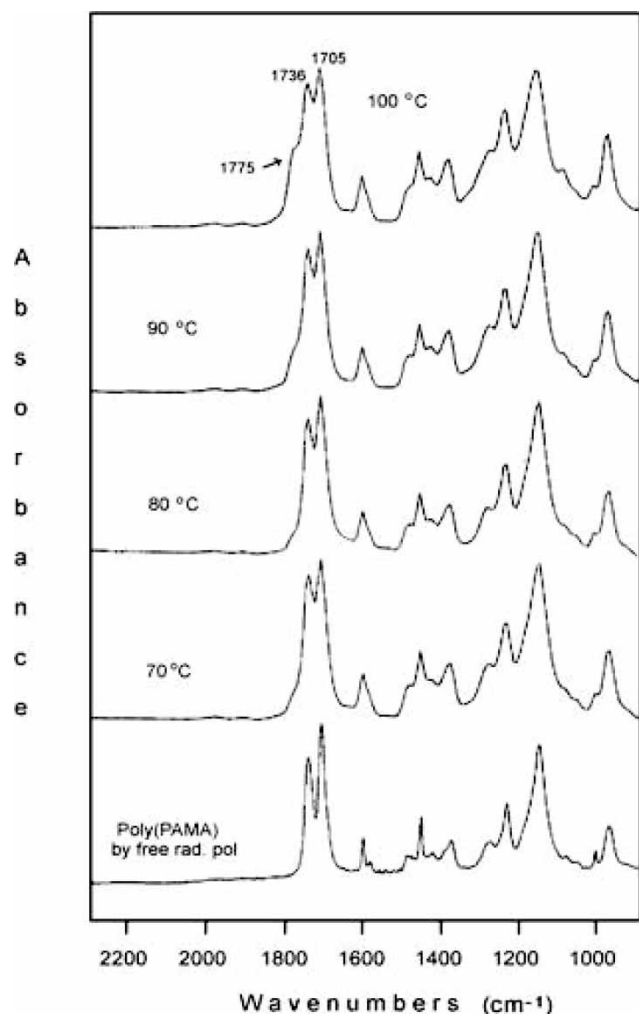
The ^{1}H-NMR spectra of the copolymers prepared by ATRP at 90°C in various feed ratios of PAMA and MMA are illustrated in Figure 1. The peaks at 7.3−7.9 ppm reveal the phenyl ring protons, and the signal at 5.2 ppm was assigned to methylene protons adjacent to keto carbonyl in the PAMA. The signal at 3.52 ppm is assigned to methyl, adjacent to oxygen in the MMA unit. While the PAMA units in the copolymer increase from 12% to 78% in copolymer composition, the intensity of the methylene protons adjacent to keto carbonyl increases gradually. Figure 2 shows the IR spectra of the copolymers resulting in various compositions of PAMA to MMA. The FT-IR spectra for copolymers showed ester and keto carbonyl bands at 1736 and 1705 cm^{-1}, respectively. As the PAMA units in the copolymer increased, the strong keto carbonyl band in the 1705 cm^{-1} gradually increases.

3.2 End-Group Characterization

The end group of well-defined poly(PAMA) prepared via ATRP at various temperatures were characterized by FT-IR (Figure 3). The FT-IR spectra of poly(PAMA) prepared via ATRP method at different temperatures is compared with that prepared via free radical polymerization. In both

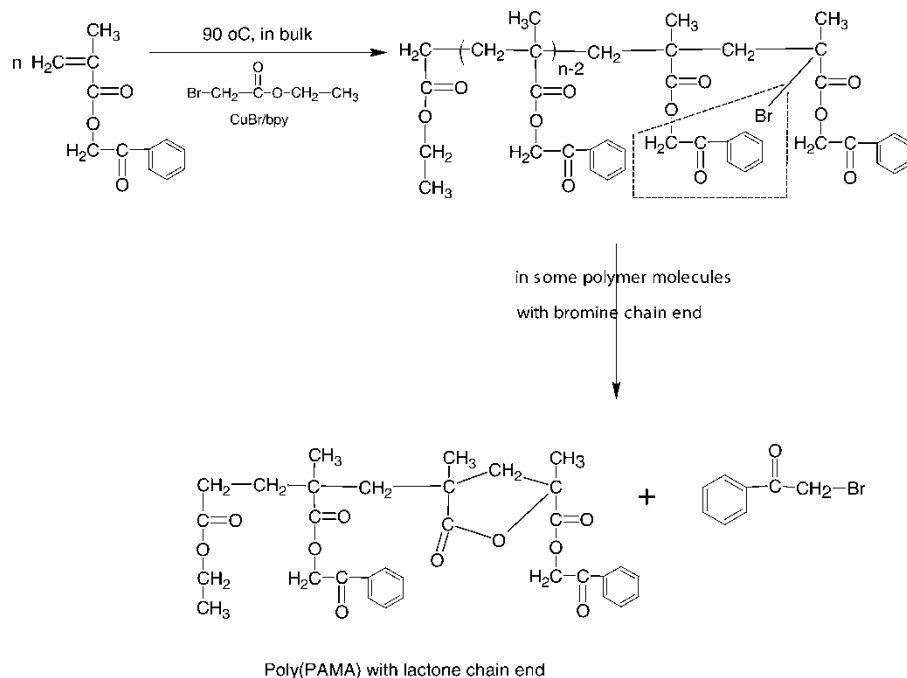**Fig. 2.** FT-IR spectra of poly(PAMA-co-MMA) prepared via ATRP method.

Fig. 3. FT-IR spectra of poly(PAMA) prepared by ATRP and free radical polymerization methods.

^{13}C-NMR spectrum of poly(PAMA) prepared by ATRP method is illustrated in Figure 4. New sets of signals appeared in the region δ: 178 (c and d: C=O in adjacent to its and the lactone ring; 176.4 ppm is arising from carbonyl moiety in the repeat unit and the CH_3CH_2OCO group in the initial unit of the chain), 81(e: quaternar carbon), 50.6 (f: quaternar carbon), 26.6 (a,a′:CH_3) ppm which are assigned to carbonyl and the other carbons of the lactone ring in the end group, as the scheme in Figure 4. It seems most likely, from the evidence presented here, that the reaction proceeds via loss of phenacylbromide and cyclization of the chain end, giving rise to the observed lactone ring. The FT-IR spectra of the copolymers prepared through ATRP in various feed ratios PAMA to MMA also showed carbonyl bands corresponding to a lactone ring at 1775 cm^{-1}. As seen in Figure 2, the intensity of the band at 1775 cm^{-1} increased relatively when the PAMA units increased in the copolymer. Studies carried out thus far have indicated that the form of lactone ring through ATRP at high temperatures have been also observed in the polymerization of benzyl methacrylate and methyl methacrylate. In the previous study, we have reported that polymer molecules with a lactone end-group have produced in increasing ratio from 80°C to 110°C in ATRP of benzyl methacrylate by the same initiator and catalyst system (18). The formation of lactone at the chain ends is not reported during ATRP of methylmethacrylate using CuX/N,N,N′,N′,N″-pentamethyldiethylenetriamine as the catalyst and initiator, respectively, at ambient temperature (19). Also, although mechanism of lactone form is not given, it is reported by MALDI-TOFF analysis that polymer molecules with a lactone end-group through ATRP of methylmethacrylate is formed (16). Also, formation of lactone on poly(methylmethacrylate) was characterized by MALDI-TOFF, MALDI-CID and ^{13}C-NMR gave spectra consistent with loss of methylbromide followed by a cyclization reaction to give a lactone end group (17).

GPC data showed that the Mn value of poly(PAMA) obtained at 90°C for 30 h was 2800 (Mw/Mn = 1.16). It is known that well-defined polymers with molecular weights ranging from 1000 to 150.000 have been successfully synthesized (20). This result is in good agreement with the literature. The effect of temperature and time on the polymerization of PAMA was investigated. For this purpose, the polymerization temperature was changed from 70°C to 100°C for 120 h. While the molecular weight of polymers decrease with increasing temperature to 100°C, their polydispersities were quite low (1.057 < Mw/Mn < 1.075), as well. The results are summarized in Table 1. This means that the formation of a chain with lacton-end accelerates as the temperature increases.

In order to prepare block copolymer, the ATRP of MMA was carried out in the presence of CuBr/2,2′-bpy catalyst and poly(PAMA) (Mn = 2800; Mw/Mn = 1.16) as macroinitiator in 1,4-dioxane at 90°C for 30 h. Although the macroinitiator has a monomodal GPC trace, the polymer

spectra, there are two common bands at 1736 cm^{-1} (C=O in ester) and 1705 cm^{-1} (C=O in ketone). In addition, poly(PAMA) prepared via ATRP showed a new band at 1775 cm^{-1}. The small band at 1775 cm^{-1}, which is not observed in that of poly(PAMA) prepared via free radical polymerization in Figure 3, is characteristic for the carbonyl group in a lactone ring five membered observed for poly(PAMA) prepared via ATRP. The formation of a lactone ring might be because of removing phenacylbromide at the chain end. As illustrated schematically in Scheme 1 for poly(PAMA), this results in a dead polymer chain, containing an lactone chain end. These termination reactions decrease the living character of the polymerization. This also explains why its molecular weight did not increase considerably when ATRP time was changed from 30 h to 120 h. In Figure 3, FT-IR spectra shows that the relative intensity of this small band at 1775 cm^{-1} increases when ATRP conditions were changes from 70 to 100°C. This means that the polymerization of PAMA with increasing temperature is not well controlled under the conditions that were studied.
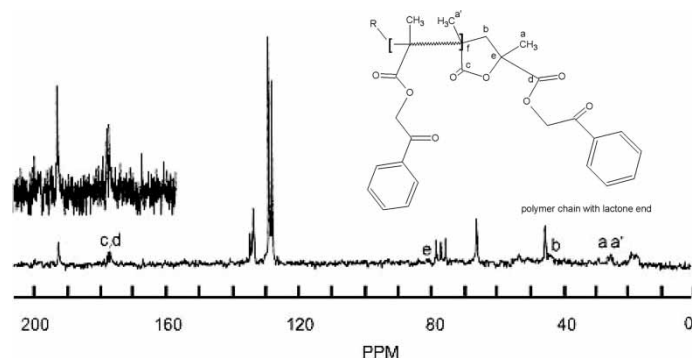
Sch. 1. The formation of a lactone ring because of removing phenacylbromide at the chain end.

Fig. 4. ^{13}C-NMR spectrum of poly(PAMA) prepared by the ATRP method.

**Table 1.** ATRP of PAMA at various temperatures for 120 h

Temp (°C)	^{a}Conversion %	Mn	Mw/Mn
70	24	4000	1.057
80	21	3800	1.054
90	20	3400	1.046
100	18	2750	1.075

^{a}The conversions were measured as gravimetric.

obtained from this procedure indicates clearly a GPC trace (Figure 5) with a shoulder. The right part of GPC curve corresponds to a Mn value of 2800 (Mw/Mn = 1.05), but the left part of the curve corresponds to 13600 (Mw/Mn = 1.46). This means that only a small amount of the polymer was consumed as macroinitiator in the block copolymerization and other parts of the polymer unchanged or remained

without any significant change. It is observed that not all of the end groups of the macroinitiator chains participated in chain extention reaction as some of them bears chains with lactone end.
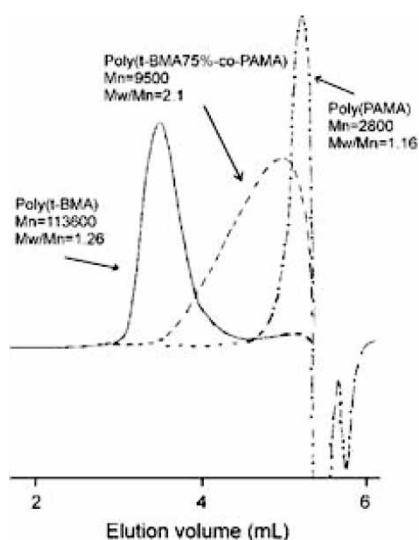
The aim of this study is to synthesis copolymers at two different feed ratios, and to investigate the effect of t-BMA over polymerization of PAMA. Table 2 summarizes the synthesis conditions and the characteristics of poly(PAMA), poly(t-BMA) and poly(PAMA-co-t-BMA) obtained by
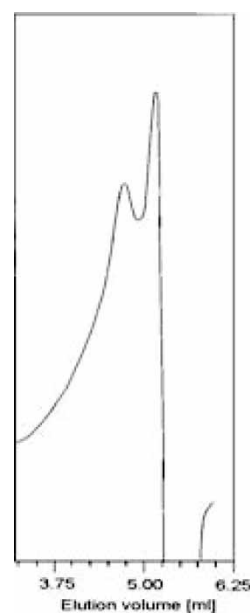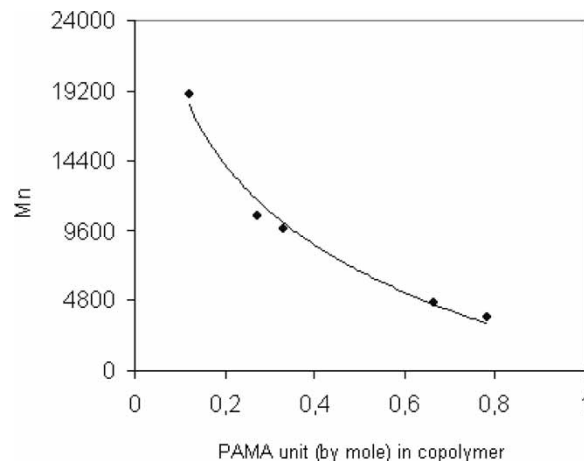

Fig. 5. GPC trace of poly(PAMA-co-MMA) prepared via ATRP at 90°C.

Table 2. ATRP of both PAMA and t-BMA at 90°C using CuBr/ bpy, as catalyst system, initiated ethyl 2-bromoacetate

Entry	Monomer/ [Initiator]	Time (h)	Mn (GPC)	Mw/Mn
1 [Poly(t-BMA)]	100:1	1	8200	1.03
2 [Poly(t-BMA)]	100:1	11	64000	1.11
3 [Poly(t-BMA)]	100:1	30	113000	1.26
4 [Poly(t-BMA75%- co-PAMA]	100:1	30	9500	2.11
5 [Poly(t-BMA25%- co-PAMA]	100:1	30	3400	1.31
6 Poly[PAMA]	100:1	30	2800	1.16

Fig. 7. The plot of Mn vs. PAMA% in copolymer.

As a result, the controlled polymerization of t-BMA using CuBr/2,2′bpy complex at 90°C has gone on at a very high rate. But, as PAMA increased in feed random copolymerization Mn of the copolymer considerably decreased. Thus, the final properties of the products from these reactions are summarized in Table 2 (Entry 4, 5). The single GPC profiles of poly(t-BMA), poly(PAMA) and are illustrated in Figure 6.

Table 3 lists the results of the molecular characterization of copolymers. The Mn of the copolymers were linearly decreased with the increase of the PAMA units in copolymer, as shown in Figure 7. The decrease in Mn values with an increasing molar fraction of PAMA in the both copolymer systems mentioned above is probably because of an increase in lactone ring formation. Although it is not known whether the mechanism of lacton formation proceed by way of radical or ionic, phenacyl radical or phenacyl carbocation is more stable than that of methyl. Thus, it may be suggested that lactone formation results from PAMA units in copolymer. On the other hand, as MMA units in copolymer increased, Mn values of the resulting copolymers increase. This means that the well-defined controlled polymeization can be manipulated by conversion of MMA units. The polydispeersities of copolymers is relatively

Fig. 6. GPC traces of poly(t-BMA), poly(PAMA) and a copolymer.

ATRP. Table 2 shows that the number-average molecular weights with increasing in time for the same reaction temperature via ATRP of t-BMA was increased. Although the Mn values (Table 2, Entry 1−3) were different from each other, the polydispersity (Mw/Mn) was almost the same.

Table 3. Copolymerization of PAMA and MMA at various monomer feeds[a] and copolymer characteristics

Sample[d] no.	M_1[b]	Intensitiy of aromatic protons in PAMA unit	Intensitiy of -OCH$_3$ protons in MMA unit	m_1[c]	Mn (Mw/Mn) (GPC)
1	0.10	9	38	0.12	19000 (1.61)
2	0.20	19	30	0.27	10700 (1.79)
3	0.30	17	21	0.33	9800 (1.63)
4	0.40	30	24	0.45	—
5	0.60	51	16	0.66	4750 (1.23)
6	0.75	64	11	0.78	3800 (1.10)

[a]Conditions of polymerization; [PAMA]:[MMA]:[CuBr]:[bpy] = 10:90:1:1:2, at 90°C.
[b]Mole fraction of PAMA in Feed.
[c]Mole fraction of PAMA in copolymer.
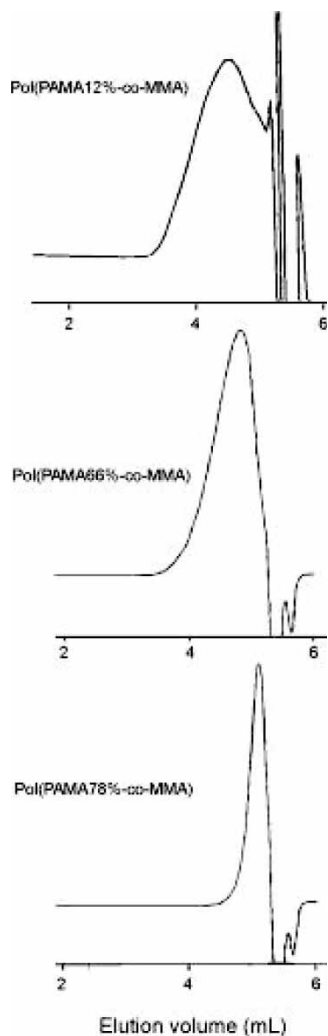[d]The conversions changed from 5% to 14%.

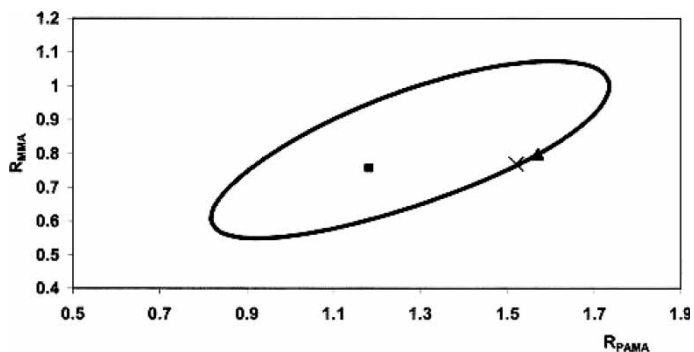**Fig. 8.** GPC traces of poly(PAMA-co-MMA) prepared via ATRP.

Fig. 9. T-M plots for copolymer systems prepared via the ATRP method.

3.3 Monomer Reactivity Ratios

The atom transfer radical copolymerization of PAMA and MMA initiated by ethyl 2-bromoacetate has been carried out in various feed ratios of PAMA to MMA. Table 3 shows the influence of the initial molar compositions of the comonomers on the copolymer composition in ATRP.

The copolymer compositions were estimated from ^{1}H-NMR spectra. Figure 1 shows ^{1}H-NMR spectra of the copolymer prepared by ATRP. The peaks at 7.3–7.9 ppm correspond to the aromatic protons in PAMA units, the signal centered at 3.52 ppm is assigned to methyl protons adjacent to oxygene in MMA units. The signal at 5.2 ppm is methylene protons adjacent to keto carbonyl in PAMA units. The other signals at 0.7–2.1 ppm are assigned to methylene and methyl in polymer main chain. Thus, the mole fractions of PAMA and MMA in the copolymer were determined from the integral intensities of aromatic protons of PAMA units in 7.3–7.9 ppm and the OCH_3 protons in MMA units observed at 3.52 ppm. Copolymer compositions

narrow (1.10Mw < Mn < 1.79) (21). This indicates that might be a consequence of the undesirable side reaction such as lactone formation, transfer and termination reactions. Thus, it is known that termination and other side reactions are also present in ATRP, and they become more prominent as higher molecular weight polymers are targeted (22). The single GPC curves of three resulting copolymers are illustrated in Figure 8.

Table 4. Comparison of monomer reactivity ratios by three different methods

System	Methods	$r_1{}^a$	r_2	$r_1 \cdot r_2$
Atom transfer radical copolymerization	K-T	1.17	0.76	0.88
	F-R	1.16	0.75	0.87
	T-M	1.18	0.76	0.89

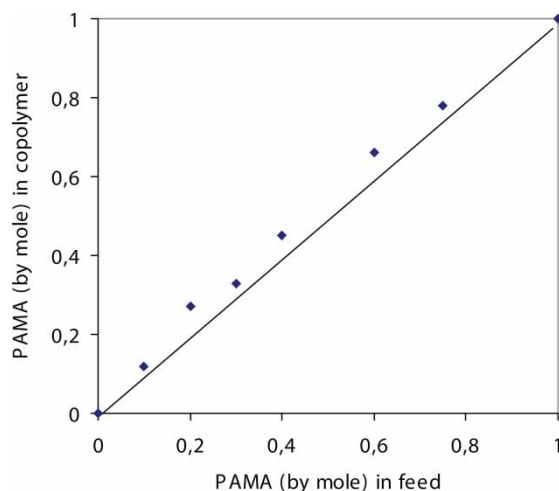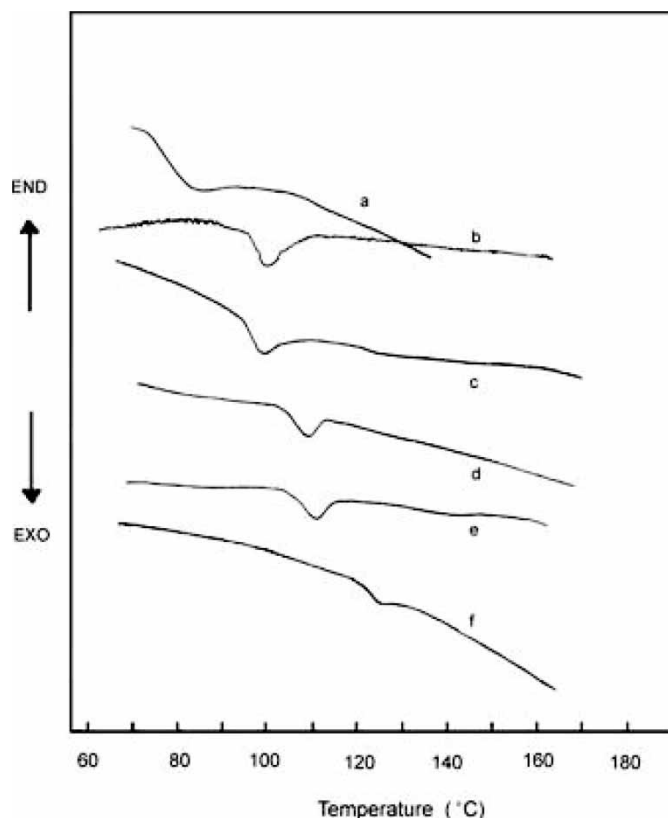^{a}r_1:Monomer reactivity ratio of PAMA.

Fig. 10. Plot of mole fraction of PAMA in feed (M_1) vs. that of PAMA in copolymer.

Fig. 11. DTA traces of polymers heated at $20°C/min$ to $200°C$. [a] Poly(PAMA) prepared via ATRP, b)Poly(PAMA78%-co-MMA), c) Poly(PAMA33%-co-MMA), d) Poly(PAMA29%-co-MMA), e) Poly(PAMA12%-co-MMA), f) Poly(MMA)].

have been calculated from the following equation:

$$C = \frac{\text{Integral intensities of aromatic protons}}{\text{Integral intensities of OCH}_3 \text{ protons}} = \frac{5\,m_1}{3\,m_2}$$

Where m_1 is mole fraction of PAMA and m_2 is that of MMA in copolymer.

The K-T and F-R parameters were calculated for the living radical copolymerization of PAMA and MMA, and the results were summarized in Table 4.

It is well known that monomer reactivity ratios can offer the message of relative reactivity of comonomers (22, 23). To estimate the relative reactivity of PAMA and MMA in the atom transfer radical copolymerization, the Kelen-Tüdös (23) and Fineman-Ross (24) equations, which are $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$ and $G = r_1 H - r_2$, respectively (notations in the equations have been described in Table 4) were used. The r_1 and r_2 were determined by the plots of G vs. H and η vs. ξ for ATRP system. Also, the reactivity ratios of the monomers were determined according to the general copolymerization equation by application of the non-linear least squars treatment proposed by Tidwell and Mortimer (T-M) (25). T-M plots for copolymer systems prepared via the ATRP method is illustrated in Figure 9.
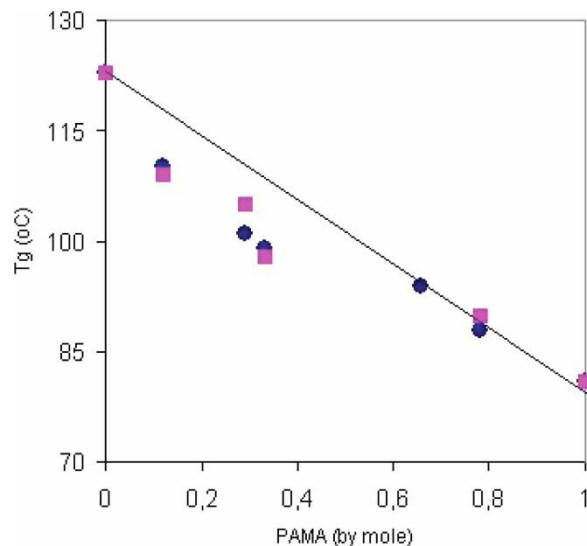
Fig. 12. Plots of the Tg of a series blend polymer and copolymer as a function of PAMA [Blends (•) and copolymer (◆)].

For the copolymer system, this diagram confirms the good approximation of the r_1 and r_2 values as indicated by the reduced dimensions of the ellipse. According to three different methods, from the slopes and intercepts of the straight lines, the monomer reactivity ratios of PAMA and MMA were determined and given in Table 4. The results of three methods for the monomer reactivity ratios are in quite good agreement with each other and the monomer reactivity ratio of PAMA is somewhat larger than that of MMA. Apparently, the values of monomer reactivity ratios indicate that the growing radicals with PAMA end were added to the PAMA monomer with a some higher tendency, but the radicals with MMA end have a slightly higher tendency to be added
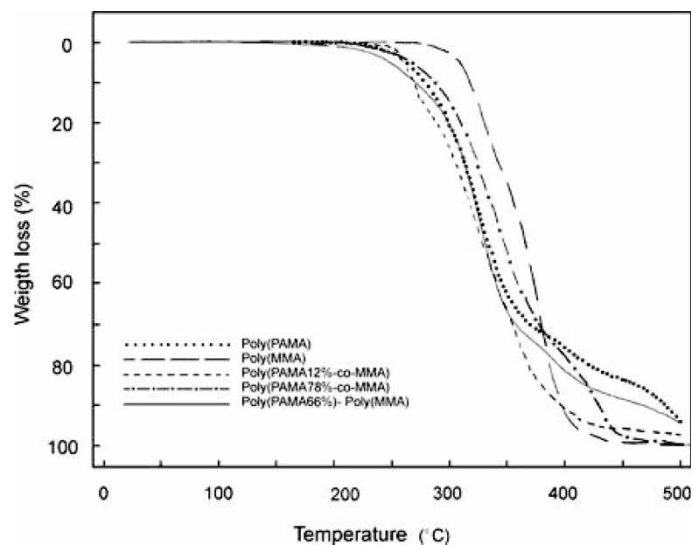
Fig. 13. TGA curves of poly(PAMA), poly(MMA), two copolymers, one blend polymer, heated under nitrogen at $10°C\ min^{-1}$ heating rate from room temperature to $500°C$.

Table 5. TGA data for the polymers

Polymers	^{a}T$_{i}$ (°C)	^{b}T$_{\%50}$ (°C)	%Wt loss at 300°C	%Wt loss at 350°C	Residue at 400°C (%)
Poly[PAMA]	215	325	19	63	29
Poly[MMA]	272	365	3	35	8
Poly(PAMA78%-co-MMA)	211	350	15	50	2
Poly(PAMA12%-co-MMA)	240	340	28	36	5
Poly(PAMA33%-co-MMA)	245	360	18	54	19
^{c}Poly(PAMA)66%-Poly(MMA)	212	330	22	67	18
^{c}Poly(PAMA)33%-Poly(MMA)	215	329	22	73	12

^{a}Initial decomposition temperature.
^{b}Decomposition temperature at 50% weight loss.
^{c}Polymer blend.

to PAMA in atom transfer radical copolymerization. Distributions of the monomeric units along the copolymer chains are random, but they are slightly richer in PAMA units. The behaviors of the copolymer system were evaluated through plots of the copolymer compositions (m$_1$) measured from ^{1}H-NMR as the molar fraction of PAMA vs. the feed compositions measured as the molar fraction of PAMA (M$_1$) (Figure 10).

3.4   Differential Termal Analysis (DTA) Measurements

The glass transition temperatures of the homopolymers, their blends and the copolymers prepared by ATRP were measured by DTA. Representative DTA curves of the polymers were shown in Figure 11. The Tg's of the copolymers and blends increase obviously with increasing the content of MMA in copolymer and blend systems. The Tg values of poly(PAMA) and syndiotactic poly(MMA) were determined to be 81°C, and 123°C, a value lying in the range of those reported in the literature (26), respectively. Tg values of the copolymer and the blends in similar compositions for the blends were observed between 110 and 90°C by depending on increasing MMA units. Plots of the Tg values vs. mole fractions of PAMA unit in the blends and copolymers are shown in Figure 12. The observed Tg for both of the blends and copolymers indicated a slightly negative deviation with respect to linearity, which can be associated with a slightly higher free volume than that of a mixture of PAMA and MMA. In addition, it is known that an immiscible blend shows glass transition temperature of each individual polymer, but a miscible blend does show only one glass transition temperature. The each polymer blend prepared in this study shows a single transition, which can be attributed to poly(PAMA) and poly(MMA) to give compatible blends. Most of the polymers having relatively low molecular weight are generally compatible (27).

3.5   Thermogravimetric Study

The thermogravimetric curve for poly(PAMA) prepared by ATRP, which are obtained from room temperature to 500°C

with a heating rate of 10°C/min under nitrogen flow, are given in Figure 12. For poly(PAMA), three degradation stages were observed, and considered that have been initiated by the scission of weak links and random chain scission. At the first stage, while the initial decomposition of poly(PAMA) synthesized via ATRP are slow at about the 210−300°C range, the second stage, decrease of weight of poly(PAMA) is faster. But the third stage, which is between 360 and 500°C, is slower than those of the first and second stages. TG curve of poly(MMA) prepared via ATRP at 90°C showed a decomposition with two stages. The first stage is observed between 273−340°C, and the second stage is at 340−440°C range.

The thermogravimetric curves of poly(PAMA) and poly(MMA) via ATRP, two copolymers and one blend polymer are showed in Figure 13. All the polymers showed a thermal degradation with two stages. The first random chain scission starts between 210°C and 370°C by depending on the composition of the copolymers and the blends. The second stage changes between 350 and 450°C by depending on the composition of the copolymers and the blends. In summary, for both the copolymers and blend polymers showed that thermal stability decreased with increasing in PAMA. TGA results of polymers are summarized in Table 5.

4   Conclusions

The poly(PAMA) was synthesized by the ATRP at 70, 80, 90, and 100°C. As temperature increased from 70 to 100°C, Mn values of ploy(PAMA) decreased from 4000 to 2750. In ATRP of PAMA, the formation of lactone at chain ends increased with increasing temperature. In the copolymerization of PAMA with MMA at 90°C, when the PAMA unit increases, the Mn values of the copolymers decreased. The monomer reactivity ratios were determined as r$_1$ = 1.17, r$_2$ = 0.76; r$_1$ = 1.16, r$_2$ = 0.75 and r$_1$ = 1.18, r$_2$ = 0.76 by the K-T, F-R, and T-M methods, respectively. If initial decomposition temperature was taken as a measurement of thermal stability, as the percentage of PAMA

in the copolymer increased, the thermal stability of the copolymer decreased. Also, in the thermal stability of the blends of poly(PAMA) and poly(MMA), similar tendency was observed. When Tg values of poly(PAMA) and poly(MMA) were measured by DTA as 81 and 123°C, respectively, those of the copolymers and the blends in similar composition were obtained between 90−110°C with decreasing in PAMA units. The Tg values for both of the copolymers and blends indicate negative deviation with respect to the linearity.

5 Acknowledgements

6 References

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