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Characterization and Synthesis of Three-Armed Copolymers of Phenoxycarbonylmethyl Methacrylate and Ethyl Methacrylate Via Atom Transfer Radical Polymerization

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1,3,5-(2′-Bromo-2′-methylpropionato)benzene was used as a three-functional initiator in the synthesis of three-armed star polymer of phenoxycarbonylmethyl methacrylate (PCMMA) and its copolymers with ethylmethacrylate (EMA) via the atom transfer radical polymerization (ATRP) with a Cu(I)Br/2,2′-bipyridine catalitic system at 90°C. The homo- and copolymers were characterized by FT-IR, ^{1}H and ^{13}C NMR techniques. The compositions of the copolymers were calculated from ^{1}H-NMR spectra. The diblock copolymer of poly(PCMMA-b-EMA) synthesized using poly(PCMMA) macroinitiator and Cu(I)Br/bpy catalitic system showed an inefficient polymerization of ethylmethacrylate with low molecular weight and higher polydispersity. The molecular weight and molecular weight distribution were obtained by Gel Permeation Chromatography (GPC). For this copolymerization system, their monomer reactivity ratios were obtained by using both Kelen-Tüdös and Fineman-Ross equations. The thermal behavior of three-armed poly(PCMMA) and its copolymers were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Three-armed poly(PCMMA) heated to 270°C was characterized by GPC.

Keywords ATRP, star polymer, synthesis, monomer reactivity ratio, copolymerization of PCMMA and EMA by ATRP

Introduction

A relatively new method to synthesize well-defined polymers and copolymer is controlled radical polymerization (CRP) (1, 2). ATRP, which is one of the CRP methods, is a radical process (3) that fullfils these requirements by using a transition metal, in combination with a suitable ligand (4, 5). The catalyst complex establishes a reversible equilibrium between growing radicals and dormant species. Since ATRP is a controlled/"living" radical polymerization, well-defined polymers with molecular weights determined by the ratio of consumed monomer to introduced initiator are obtained, $\Delta P_n = \Delta[M]/[I_o]$, the

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polydispersities are generally low. Because of its mechanism, ATRP allows for the preparation of a more precisely controlled polymer (6).

In this new process, the initiator is one of the important components and the choice of a suitable initiator is essential for attaining a well-controlled radical polymerization system. Thus so far, many kinds of organic compounds have been found to use as effective initiators in a variety of polymerizations catalyzed by transition metals, such as haloalkanes (7, 8), haloalkylbenzene (9), α-halocarboxylic acid (10), haloketones (11, 12). An important advantage of ATRP is that one can easily synthesize well-defined star (co)polymers (13) by a core-first technique using multifunctional organic halides as an efficient initiator (14).

This work reports the ATRP of phenoxycarbonylmethyl methacrylate (PCMMA) and its copolymers with ethylmethacrylate (EMA) with 1,3,5-(2′-bromo-2′-methylpropionato)benzene as a three-functional initiator in bulk. The living character was established by the synthesis of a AB-type block copolymer. The FT-IR, GPC, NMR techniques were used for characterization of the resulting polymers. Also, the monomer reactivity ratios were determined by both the Kelen-Tüdös and Finemann-Ross procedures. Thermal analysis results are given as in comparison with each other for all polymers.

Experimental

Materials

Ethylmethacrylate (EMA)(Aldrich) was distilled under vacuum after washing with 5% NaOH aqueous solution just before copolymerization. Cuprous(I) bromide (Aldrich) was used as received. 1,3,5-(2′-bromo-2′-methylpropionato)benzene used as initiator and phenoxycarbonylmethyl methacrylate were synthesized in the our laboratory.

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 $CDCI_3$. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements were carried out under a nitrogen flow with heating rate of $10^\circ C\,min^{-1}$, $20^\circ C\,min^{-1}$, respectively. Gel permeation chromatography (GPC) analyses were carried out using a high pressure liquid chromatography pump with Agilent 1100 system equipped with a vacuum degasser, a refractive index detector. The eluting solvent was tetrahydrofuran (THF), the flow rate was $1\,ml\,min^{-1}$. Calibration was achieved with polystyrene.

Synthesis of 1,3,5-(2′-bromo-2′-methylpropionato)benzene

Synthesis of 1,3,5-(2′-bromo-2′-methylpropionato)benzene was carried out according to a procedure given in the literature (15).

^1H NMR ($CDCI_3$, δ): 2.04 (s, 18H), 6.98 (3H, aromatic ring protons).

FT-IR (cm^{-1}): 1761 (C=O stretch), 1615 (C=C on aromatic ring), 1261 (asymetric C-O stretch), 1146 (symetric C-O stretch).

Synthesis of Phenoxycarbonylmethyl Methacrylate (PCMMA)

Phenoxycarbonylmethyl methacrylate was synthesized by the reaction of phenyl bromoacetate with sodium methacrylate by using triethylbenzylammonium chloride

(TEBAC)(Aldrich) as a phase transfer catalyst and distilled under vacuum (bp: 162°C at 5 mm-Hg).

IR (cm^{-1}, the most characteristic bands): 1784 (C=O stretching adjacent to phenoxy group), 1730 (C=O stretching), 1638 (C=C in the vinyl group), 1592 (C=C stretching on aromatic ring).

^{1}H-NMR ($CDCI_3$, δ): 2.03 (s, 3H), 5.72 (s, 1H), 6.29 (s, 1H), 6.9–7.4 (aromatic ring protons).

ATRP Procedures in Bulk

All ATRP reactions were carried out following the experimental procedure. CuBr was introduced to a glass tube. The glass tube was sealed with a rubber septum and cycled twice between vacuum and argon. The monomer or the mixture of monomers, initiator [1,3,5-(2′-bromo-2′-methylpropionato)benzene or macroinitiator], ligand (bpy) and solvent (if used) were 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 an oil bath and the reaction mixture was dissolved in chloroform, filtered, and the polymer was precipitated in ethylalcohol, and then dried. The polymers were used in determination of a moleculer structure with ^{1}H-NMR, FT-IR and GPC techniques. Conversion % was determined by ^{1}H-NMR.

Atom Transfer Radical Copolymerization of PCMMA with EMA

The general procedure for the copolymerization of PCMMA with EMA of six compositions was as follows: In all cases, predetermined amounts of monomers, initiator [1,3,5-(2′-bromo-2′-methylpropionato)benzene], the calculated amount of CuBr and ligand (2,2′-bipyridine) as a catalyst were added to a flask. Argon gase was passed through the mixture for 15 min. The flask was shaken until the mixture was dissolved, immersed in an oil bath, and heated to the required temperature (at 90°C). After a given time, the flasks were opened and dichloromethane was added to the sample to dissolve the copolymer, and the heterogeneous solution was filtered. The copolymers were isolated by precipitation in ethylalcohol and dried *in vacuo* at 70°C for 24 h. The conversion of the copolymerization was below 15%.

Synthesis of Block Copolymer

The diblock copolymer of PCMMA and EMA was synthesized using poly(PCMMA) as macroinitiator and Cu(I)Br complexed with 2,2′-bipyridine as catalyst in bulk polymerization of EMA. After the reaction was completed, the polymer was dissolved in methylenechloride and precipitated in ethanol. The diblock copolymer was then dried under vacuum at 60°C.

Results and Discussion

The Three-Armed Polymerization of PCMMA

The three-armed polymerization of PCMMA was carried out in bulk at 90°C. Figure 1(a) illustrates a kinetic plot of conversion vs. time, showing that monomer conversion increases with time, and that the reaction rate is relatively high (94% conversion in 48 h). Figure 1(b) shows the plot of ln[Mo/M] vs. time (h). The polymerization

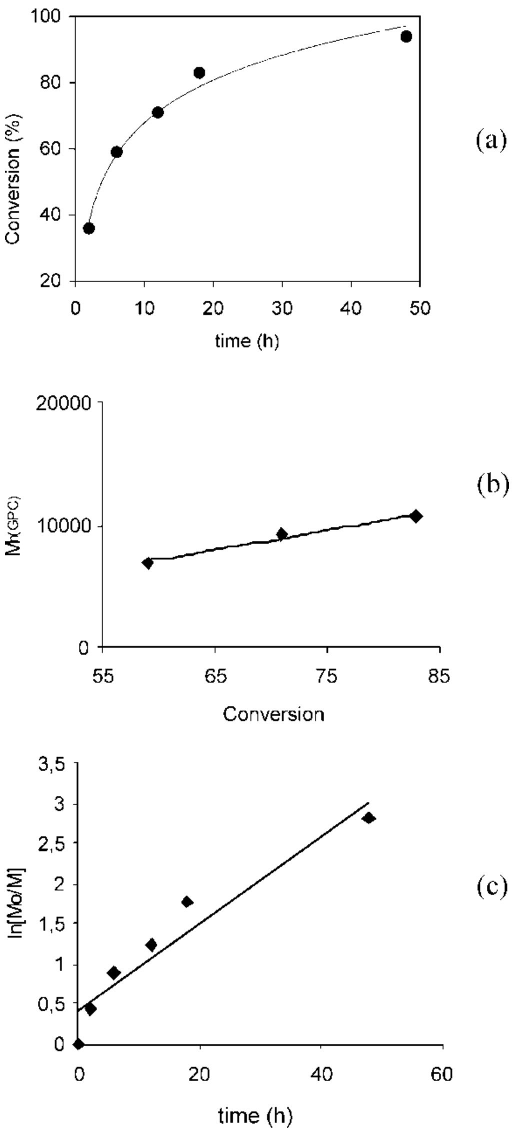


Figure 1. (a) Plots of conversion (%) vs. the reaction time for the polymerization, (b) Semilogarithmic kinetic plot versus time for ATPR of PCMMA, (c) Evolution of Mn with conversion in the bulk polymerization, Conditions: [PCMMA]/[R-X]/[CuBr]/[bpy] = 100 : 1 : 1 : 2, temperature = 90°C.

of PCMMA under ATRP conditions is first order with respect to the monomer, and the concentration of the propagating radicals remained constant during the polymerization. The Mn values of the three-armed poly(PCMMA) are 7000 and 9300 for 6 h and 12 h, respectively. As the Mn of poly(PCMMA) increases, polydispersities decreases from 1.4 to 1.18. This means that polymerization conditions provide good control of molecular weights and polydispersities. The number average of polymerization is a linear function of monomer conversion. This result comes from a constant number of chains throughout the polymerization. Figure 1(c) illustrates a linear

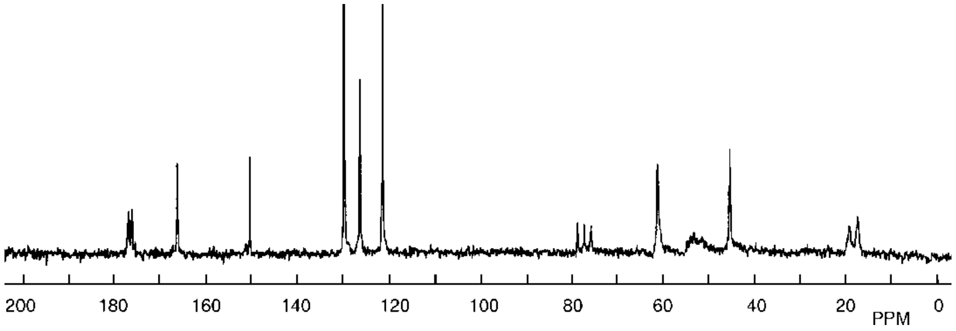


Figure 2. ^{13}C-NMR spectrum of three armed poly(PCMMA).

increase of molecular weights with conversion. Simultaneously, in ATRP, polydispersities (Mw/Mn) decrease with the conversion, depending on the relative rate of deactivation (16).

^{13}C-NMR spectrum of the three-armed poly(PCMMA) was illustrated in Figure 2. It has the most characteristic peaks of the monomeric units at 176 ppm (ester C=O signal), 166 ppm (C=O signal adjacent to phenoxy group), 150.6 ppm (ipso carbon of mono substituted phenyl ring), and 60.8 ppm (CH_2 signal adjacent to ester).

Characterization of Three-Armed Copolymers of PCMMA and EMA

Figure 3 shows the FT-IR spectra of the resulting copolymers and three-armed poly(PCMMA) and poly(EMA) prepared in various feed ratios of PCMMA to EMA by atom transfer radical polymerization method. The bands at 770 cm^{-1} and 692 cm^{-1} not observed at FT-IR spectrum of poly(EMA) are attributed to a vibration characteristic of a mono substituted benzene ring in PCMMA moities. The peak at 1728 cm^{-1} is assigned to the vibration of ester carbonyl in PCMMA and EMA units. The relative intensities of the band at 1782 cm^{-1} (carbonyl adjacent to phenoxy in side chain of PCMMA unit) and the band at 1595 cm^{-1} (aromatic C=C stretching) gradually increase as the percentage of PCMMA in the copolymers from 12 to 86% (by mole) increased. There is the initiator residue at one end of the copolymer molecule, and bromine atom at the other end, and there may be one of two monomeric units at ends of the copolymer. The structure of the star copolymer is shown schematically in Scheme 1. Unfortunately, no poly(PCMMA-co-EMA) arm could be isolated for the characterization and determination of the functionality of the final star.

In addition, the ester carbonyl band in PCMMA or EMA units bromine terminated was not observed due to an overlap with overton bands of aromatic ring of the PCMMA unit. However, an ester carbonyl band at 1783 cm^{-1}, as seen in Figure 4, which characterizes monomeric unit bromine terminated in the three-armed poly(ethyl methacrylate), was observed. The ^{1}H-NMR spectra showed the peaks at 6.9–7.3 ppm revealing the mono substituted phenyl ring protons, the signal at 4.01 ppm assigned to methylene adjacent to oxygene in the EMA units, and the signal at 4.67 ppm assigned to methylene adjacent to oxygene in PCMMA units. As the PCMMA units in the copolymer increases from 12% to 86%, the intensitiy of phenyl ring protons in PCMMA units gradually increases. The other signals are due to the methyl and methylene protons of comonomeric units.

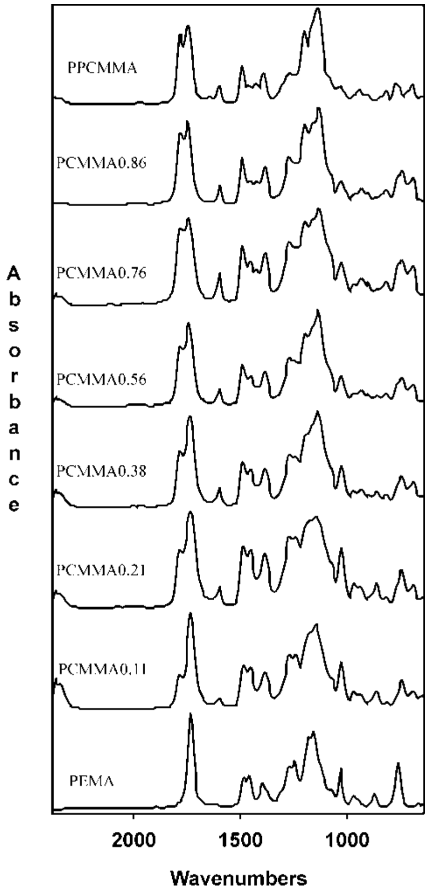
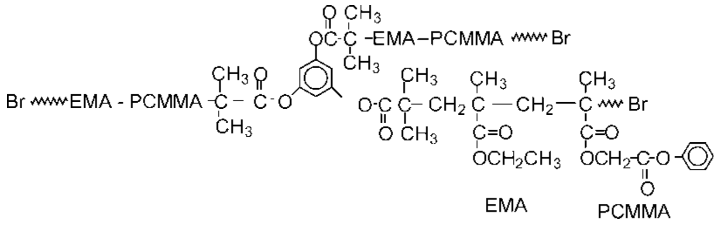


Figure 3. FT-IR spectra of three-armed poly(PCMMA-co-EMA).

ATR random copolymerization and homopolymerization of PCMMA and EMA by a three-functional initiator are summarized in Table 1. In the case of three-armed poly(EMA) and poly(PCMMA0.12-co-EMA), polydispersities are 1.48 and 2.27, respectively, and relatively high. It can be seen that bulk polymerization of EMA and a mixture of PCMMA and EMA (rich in EMA) give a fast polymerization rate and the obtained polymers have broad polydispersities. This means that the bulk copolymerization of



Scheme 1. The structure of the EMA-PCMMA star copolymer.

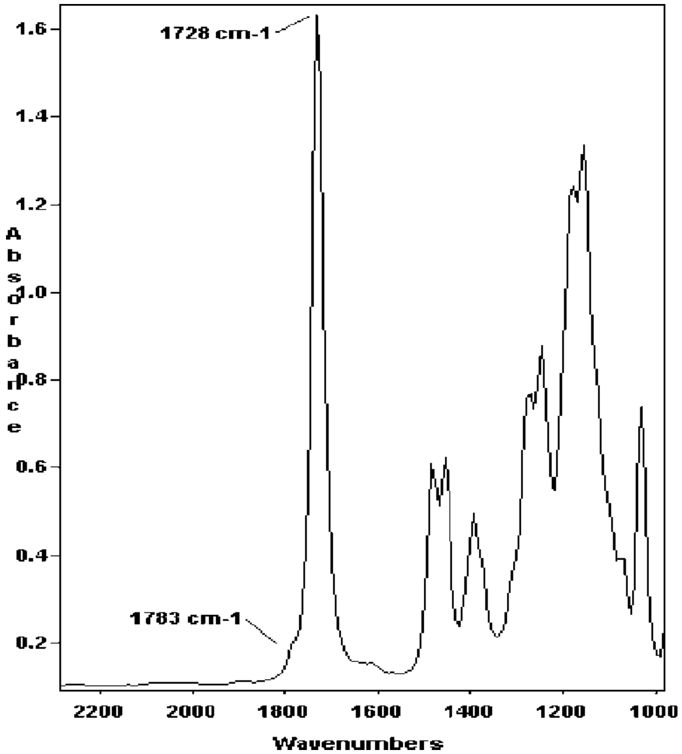


Figure 4. FT-IR spectrum of three-armed poly(ethyl methacrylate) prepared at 90°C via ATRP.

PCMMA and EMA is not well controlled under the conditions that were used. This might be due to the some reasons: there are some irreversible termination reactions and some propagating species have died (17) in the PCMMA/EMA copolymerization; the fast initiation that could not be balanced by a relatively slow bromine transfer reaction and the excess viscosity of the reaction mixture.

Table 1

Summary of ATR random copolymerization and homopolymerization of PCMMA and EMA by three-functional initiator catalyzed by Cu(I)Br/bpy in bulk polymerization at 90°C

Entry	Reaction time (h)	Mn (GPC)	Mw/Mn
Poly(PCMMA)	6	7000	1.40
Poly(PCMMA)	12	9300	1.18
Poly(EMA)	15	11700	1.48
Poly(PCMMA 0.12-co-EMA)	12	25600	2.27
Poly(PCMMA 0.38-co-EMA)	12	5800	1.29
Poly(PCMMA 0.76-co-EMA)	12	4200	1.24

Atom Transfer Radical Copolymerization Behavior of EMA by Using Poly(PCMMA) Macroinitiator

The polymers such as difunctional and three-armed star polymers have recently gained attention because they are easy to prepare via controlled radical polymerization methods (18, 19) and new block copolymers can be prepared. Here, we targeted low molecular weight polymers, focusing on polymers with DPs per arm of 13. The three-armed star poly(PCMMA) was generated from 1,3,5-(2′-bromo-2′-methylpropionato)benzene. The block copolymer of PCMMA-b-EMA was synthesized using poly(PCMMA) as a macroinitiator and Cu(I)Br complexed with 2,2′-bipyridine as a catalyst in bulk polymerization. To further establish the controlled nature of the bulk polymerization achieved here, the poly(PCMMA) macroinitiator [Mn = 8600, PD = 1.28; prepared using Cu(I)Br/bpy/1,3,5-(2′-bromo-2′-methylpropionato)benzene] was chain-extended under bulk polymerization conditions [Cu(I)Br/bpy] at 90°C as established above with a fresh feed of ethyl methacrylate monomer. So, in order to synthesize well-defined copolymers, a macroinitiator with low conversion is preferable to avoid thermal loss of the halogens (20). The gel permeation chromatography (GPC) traces of the resulting three-armed P(PCMMA-b-EMA), diblock copolymer showed a bimodal distribution and the shoulder on the high molecular weight tail did not exhibit the same molecular weight as the macroinitiator. The molecular weight of the resulting A-B type block copolymer was quite a bit higher than that of the macroinitiator, and molecular weight distribution was somewhat broad (PD = 2.1). This is likely due to the slow initiation from the three-armed poly(PCMMA) macroinitiator and also possibly to some side reactions on the terminal Br end groups. Nonetheless, there was a small elevated molecular weight shoulder in the GPC trace for poly(PCMMA-b-EMA) that was attributed to some star-star coupling. This indicates that the molecular weight can be controlled, and almost all poly(PCMMA) macromolecules participated in the initiation, leading to the formation of a diblock copolymer, poly(PCMMA-b-EMA). The GPC curves obtained from this study are shown in Figure 5. From this figure, it is clear that the GPC curve of poly(PCMMA) 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 8600 and 35600, respectively. This indicates that

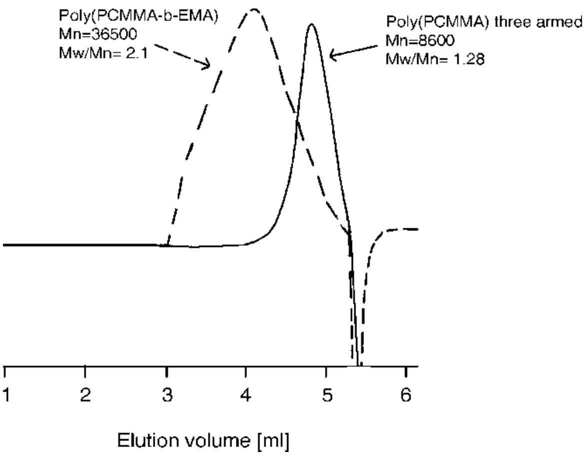


Figure 5. GPC curves of three-armed poly(PCMMA) and poly(PCMMA-b-EMA).

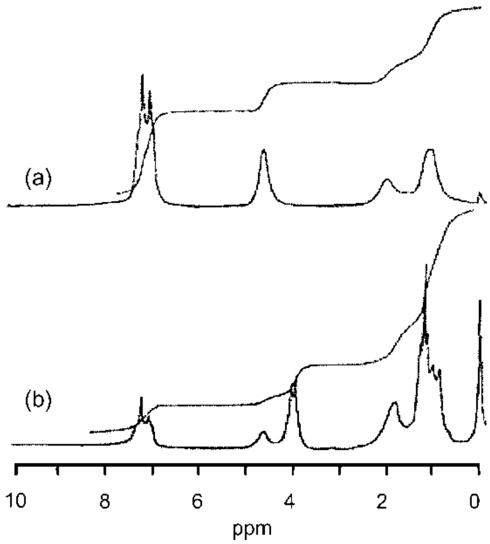


Figure 6. ^{1}H-NMR spectra of three-armed a) poly(PCMMA) and b) poly(PCMMA-b-EMA).

the molecular weight can be controlled, and almost all poly(PCMMA) molecules participated in the initiation, leading to the formation of diblock copolymer, poly(PCMMA-b-EMA).

The typical ^{1}H-NMR spectra of three-armed PCMMA homopolymer, PCMMA-b-PEMA block copolymer are given in Figure 6. Figure 6a indicates characteristic signals of PCMMA unit at 7.0–7.3 ppm (aromatic protons), 4.7 ppm (-OCH_2CO- protons), 2.0 ppm (-CH_2- protons in polymer backbone) and 1.0 ppm (-CH_3 protons on the polymer backbone). The ^{1}H-NMR spectrum of poly(PCMMA-b-EMA) indicates two diferents esteric methylene groups, one of them is at 4.0 ppm and corresponds to the EMA unit. The other signal at 4.7 ppm belongs to PCMMA unit as mentioned above. Multiple signals between 1.3–0.8 ppm can be attributed to -CH_3 protons in all the block copolymer structures. ^{1}H-NMR spectrum of poly(PCMMA-b-EMA) showed that PCMMA and EMA units in copolymer were 16% and 84%, respectively. On the other hand, PCMMA units repeating, which is 14% in block copolymer according to GPC data is in close agreement with those obtained by ^{1}H-NMR.

Figure 7 shows the DSC traces obtained from the homo poly(PCMMA) (Mn = 4000) and one copolymer poly(PCMMA12%-co-EMA)(Mn = 8000). The DSC thermograms of the three-armed poly(PCMMA) showed Tg at 74°C. The Tg of poly(EMA) is at 86°C. The Tg of three-armed copolymers occurs at 80°C. It therefore, appears that the Tg of the EMA units is lowered somewhat by the presence of the flexible PCMMA units in the copolymer.

Monomer Reactivity Ratios of PCMMA and EMA

The atom transfer radical random copolymerization of PCMMA and EMA initiated by 1,3,5-(2′-bromo-2′-methylpropionato)benzene for various ratios of PCMMA to EMA has been carried out. The copolymer compositions were analyzed with ^{1}H-NMR spectra. Table 2 shows the influence of the initial molar compositions of the comonomers in feed on the molar fraction of PCMMA in the copolymer.

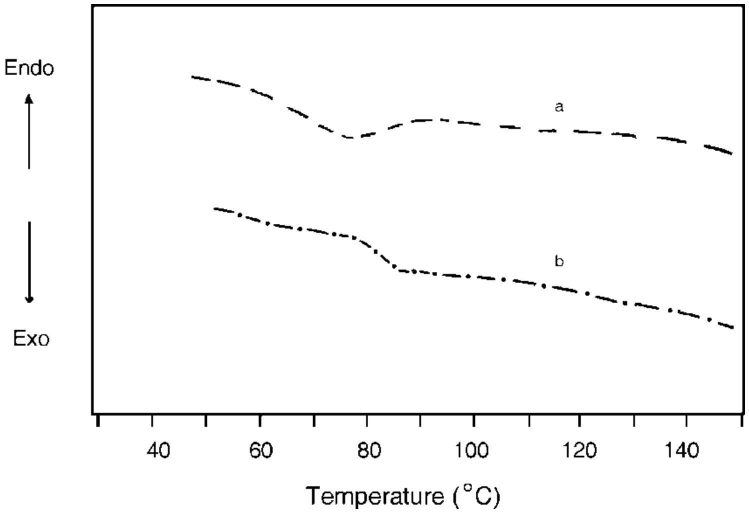


Figure 7. DSC curves of (a) poly(PCMMA) and (b) poly(PCMMA0.12-co-EMA) heated to 200°C at 20°C/min.

It is well known that monomer reactivity ratios can offer the meaning of relative reactivity of comonomers (21–23). The monomer reactivity ratios were evaluated according to the Kelen-Tüdös and Fineman-Ross methods. The obtained η, ξ, G, and H data as a basis of calculation are presented in Table 3. To estimate the relative reactivity of PCMMA and EMA in the atom transfer radical copolymerization, the Kelen-Tüdös (24) and Fineman-Ross equations (25) were used, which are $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$ and $G = r_1F - r_2$, respectively. We obtain a straight line, which extrapolated to $\xi = 0$ and, $\xi = 1$ gives $-r_{EMA}/\alpha = 0{,}606$, and $r_{PCMMA} = 1{,}08$; $r_{EMA} = 0{,}40$ $(r_1 . r_2 = 0{,}43)$ according to the K-T method. On the other hand, these values are $r_{PCMMA} = 1{,}03$; $r_{EMA} = 0{,}56$ $(r_1 . r_2 = 0{,}57)$ according to the F-R method. These results also come close to the values in both methods. In both methods, $r_{PCMMA} \cdot r_{EMA}$ is $0 < r_{PCMMA} \cdot r_{EMA} < 1$, which means that the atom transfer radical copolymerization of PCMMA and EMA has a

Table 2
Comonomer composition in feed and copolymers

Entry	M_1^a	m_1^b
1	0.10	0.12
2	0.15	0.21
3	0.30	0.38
4	0.50	0.56
5	0.70	0.76
6	0.85	0.86

M_1^a: mole fraction of PCMMA in feed.
m_1^b: mole fraction of PCMMA in copolymer prepared via ATRP.

Table 3
Results of the living radical copolymerization of PCMMA and EMA

Sample no	$F = {}^{a}M_1/M_2$	$f = m_1/m_2$	$G = F(f-1)/f$	$H = F^2/f$	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
1	0,111	0,150	−0,629	0,082	−0,560	0,073
2	0,176	0,265	−0,488	0,116	−0,422	0,100
3	0,428	0,613	−0,270	0,298	−0,201	0,222
4	1,000	1,270	0,212	0,787	0,116	0,430
5	2,333	3,160	1,594	1,722	0,577	0,623
6	5,666	6,140	4,743	5,228	0,806	0,888

[a] M_1 = Mole fraction of PCMMA in feed; M_2 = mole fraction of EMA in feed, m_1 = mole fraction of PCMMA in copolymer, m_2 = mole fraction of EMA in copolymer.

$\alpha = (H_{min}\ H_{max})^{1/2} = 0{,}654$; H_{min}: lowest value of H, H_{max}: highest value of H.

tendency to be ideal. For living radical systems, all chains are initiated at the same time and grow at approximately the same rate, in the case of traditional free radical polymerization, continous initiation leads to chains initiating and terminating at different stages of the polymerization (26).

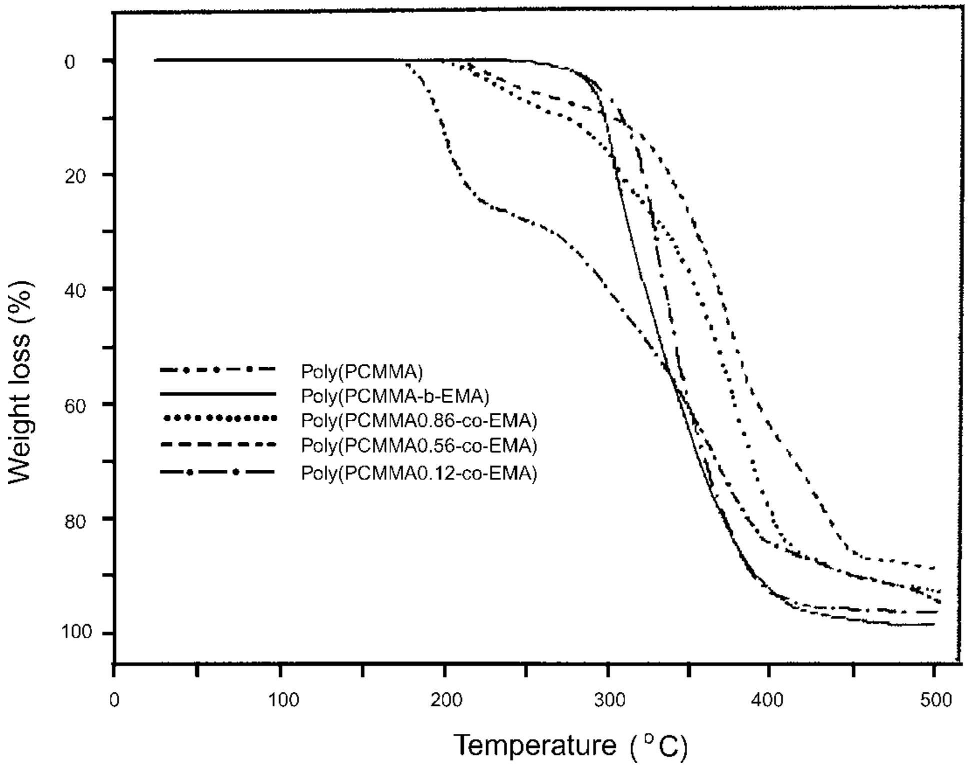
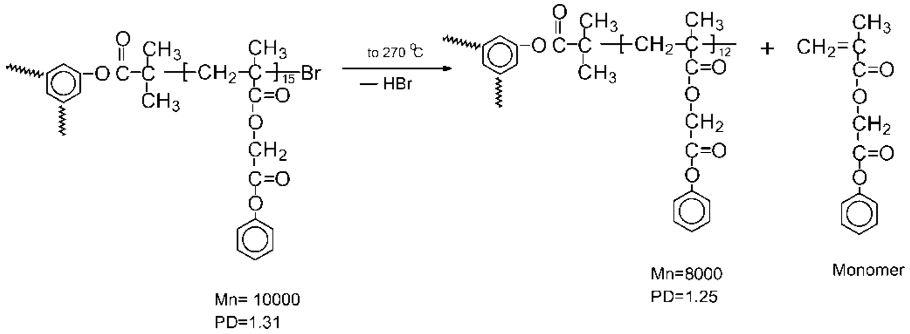


Figure 8. TGA curves of the polymers [heating rate under N_2 flow: 10°C/min].



Scheme 2. Mechanism of the first stage three-armed poly(PCMMA) thermal degradation.

Thermogravimetric Study

The thermogravimetric curves for three-armed poly(PCMMA), three-armed poly(PCMMA-b-EMA), and three different random copolymers prepared by ATRP, which are obtained from room temperature to 500°C at a heating rate of 10°C/min under nitrogen flow, are given in Figure 8 as compared with each other. The decomposition of three-armed poly(PCMMA) is produced in two steps, the first one, which is 170°C, consists of depolymerization as shown in Scheme 2, and probably hydrogen bromide elimination. The second stage, at about 270°C, a more rapid weigth loss is attributed to the degradation reaction by either the side chain decomposition or the random chain scission in the backbone. TGA results of the polymers are summarized in Table 4. When three-armed poly(PCMMA) was heated to 300°C, FT-IR spectrum (Figure 9) of the residue polymer did not show any change as compared to the original poly(PCMMA). But, when it was heated to 330°C bands were shown at 1804, 1019 cm^{-1}. These bands are characteristic in giving a six-membered cyclic anhdride structure. This behavior is similar to those of many poly(acrylic or methacrylic ester)s (27, 28). The thermal behavior of a polymer depends on its structure and type of substituents in the main chain. Therefore, a detailed analysis of the first step (to 270°C) was also carried out by Gel Permeation Chromatography (GPC). The GPC curve of residue polymer heated to 270°C and original three-armed poly(PCMMA) are illustrated in

Table 4

TGA data for the polymers

Polymers	[a]T_i	%Wt loss at 300°C	%Wt loss at 400°C	Residue (%) at 450°C	Temperature of a wt loss of 50% (°C)
Poly(PCMMA)	170	43	86	10	319
Poly(PCMMA0.12-co-EMA)r	230	7	95	4	337
Poly(PCMMA0.38-co-EMA)r	205	8	78	6	365
Poly(PCMMA0.56-co-EMA)r	190	12	66	13	372
Poly(PCMMA0.86-co-EMA)r	183	18	82	10	363
Poly(PCMMA0.84-b-EMA)	235	16	95	3	331

[a] Initial decomposition temperature.

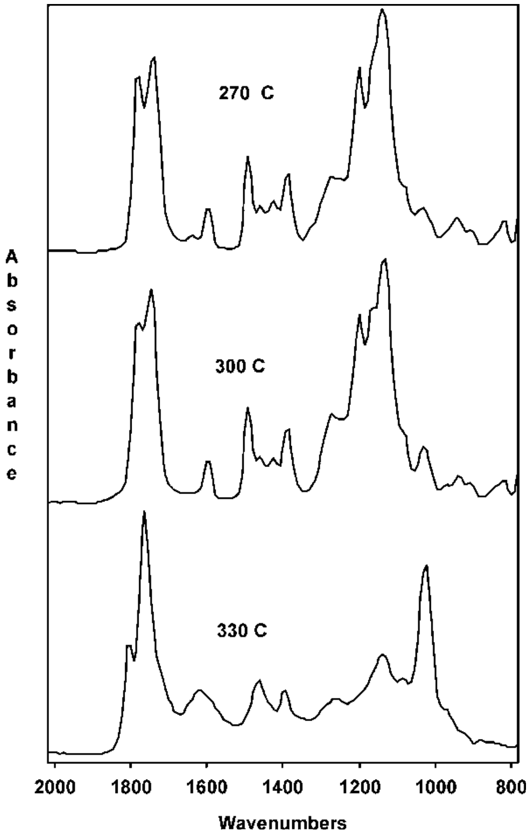


Figure 9. FT-IR spectra of poly(PCMMA) partially degraded on NaCl windows under argon atmosphere.

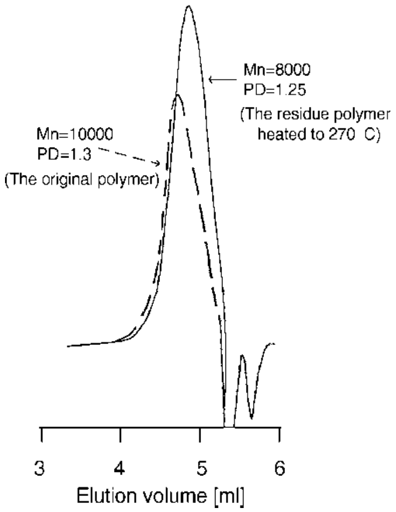


Figure 10. GPC curves of original three-armed poly(PCMMA) and residue of poly(PCMMA) heated to 270°C.

Figure 10. GPC showed that the Mn and PD of the residue polymer is 8000 and 1.25. This means that three or four units per arm decrease. When three-armed poly(PCMMA) heated to 270°C, the residue polymer was completely dissolved in most of the solvents such as methylenechloride, chloroform, acetonitrile, 1,4-dioxane and dimethylsulphoxide. This means that three-armed poly(PCMMA) heated to 270°C at least was not crosslinked. Thus, during degradation of three-armed poly(PCMMA), a rupture of an allylic carbon-carbon bond forms two radicals, one tertiary and the other a resonance stabilized allylic radical. Then decomposition of poly(PCMMA) continues by elimination of monomer, the driving force being formation of tertiary radical. On the other hand, this state is propably correct ın the case of poly(PCMMA-co-EMA) prepared by the ATRP method.

Conclusions

The three-armed star homopolymer, random, and block copolymers of PCMMA with EMA have been synthesized by the ATR polymerization of PCMMA with 1,3,5-(2′-bromo-2′-methylpropionato)benzene as a three-functional initiator. ^{1}H, ^{13}C-NMR, and FTIR techniques revealed the presence of both monomeric units in the copolymer chain. The *situ* addition of ethyl methacrylate to a macroinitiator of poly(PCMMA) afforded an AB-type block copolymer. The monomer reactivity ratios were calculated from the feed composition and copolymer composition was determined by ^{1}H-NMR spectroscopy. For the copolymerization systems in six different feed ratios, their monomer reactivity ratios were determined by the K-T and F-R methods. In this copolymerization system, two monomers have a tendency to form the ideal copolymer because the value of $r_1 . r_2$ is at around 0.5. In the case of poly(PCMMA-co-EMA), the initial decomposition temperature of copolymers increased with an increasing in EMA content. In that of poly(PCMMA-b-EMA), it was also increased with increasing EMA units.

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