

Graft Copolymerization of Poly(methyl methacrylate) with Some Alkyl Methacrylates by Atom Transfer Radical Polymerization Method and Thermal Properties

Adnan Kurt,¹ Kadir Demirelli²

¹Department of Chemistry, Faculty of Arts and Science, University of Adiyaman, Adiyaman 02040, Turkey

²Department of Chemistry, Faculty of Science and Arts, University of Firat, Elazig 23169, Turkey

Received 11 September 2009; accepted 3 October 2011

DOI 10.1002/app.36282

Published online 17 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The preparation of graft copolymers of poly(methyl methacrylate) with some alkyl methacrylates were carried out via atom transfer radical polymerization method catalyzed by CuCl/2,2'-bipyridine and using a macroinitiator, poly[(methyl methacrylate)-*co*-(3,5-bis(chloroacetoxy)phenyl methacrylate)], including an amount of 1 mol % having α -halogeno carbonyl group in the side groups. Although the number-average molecular weights of a graft copolymer series of *n*-butyl methacrylate (*n*-ButMA) ended at different times increased from 55,700 to 99,500, the polydispersities decreased from 1.85 to 1.39 with time. The thermal degradation kinetics of macroinitiator and a two-armed graft copolymer of *n*-ButMA with this macroinitiator, PMMA-*g*-PnButMA: 4% (by mol), were carried out at different heating rates by thermogravimetric

analysis and the results were compared. Using both the Flynn–Wall–Ozawa and Kissinger methods, the decomposition activation energies for macroinitiator were determined as 168 and 162 kJ/mol, respectively; they were also calculated as 233 and 239 kJ/mol for PMMA-*g*-PnButMA: 4%. The solid state thermodegradation mechanisms of both macroinitiator and PMMA-*g*-PnButMA: 4% are R₁-type mechanism, a phase boundary-controlled reaction, and F₁-type mechanism, a random nucleation with one nucleus on the individual particle, respectively. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1855–1866, 2012

Key words: two-armed graft copolymer; atom transfer radical polymerization; activation energy; thermodegradation mechanism; thermal properties

INTRODUCTION

Living radical polymerization is one of the most targeted goals for synthetic polymer chemistry. In the past few years, well-defined linear polymers have usually been prepared via living radical polymerization techniques. Successful examples of these techniques include nitroxide-mediated radical polymerization,¹ atom transfer radical polymerization (ATRP),^{2,3} and reversible addition fragmentation chain transfer polymerization.⁴ These techniques can also be applied to the synthesis of polymers of various architectures (block, comb, graft, hyperbranched, star, etc). Depending on the structure of the used initiators and monomers, homopolymers, block or graft copolymers can arise.

The importance of graft copolymers is that they combine the properties of two immiscible polymers and act as compatibilizers for polymer blends, and can also be used as amphiphilic copolymers.

Although the free radical grafting technique is usually applied to synthesize graft copolymers,^{5,6} it is not suitable for preparing well-defined graft copolymers because the side reactions, such as chain scission and crosslinking, result in loss of mechanical properties. To control the graft copolymer structure well, ionic polymerization techniques are employed.⁷ However, strict conditions are required, such as complete absence of moisture and other acidic impurities. From this point of view, a better approach may be the controlled/living free radical techniques, which enable the control of both molecular weights and polydispersities under mild conditions, and can be applied to a larger number of monomers.

ATRP has proved to be a very robust and versatile controlled/living free radical process.^{8–11} It has recently been used to prepare graft copolymers from polymeric macroinitiators; polymer chains with regularly spaced, pendant chemical groups containing radically transferable halogen atoms.^{12,13} The halogen atoms serve as initiation sites for the polymerization of side chains by ATRP.

The study of the thermal degradation of a polymer is of major interest since it can, in many cases, determine the upper temperature limit of use for a material. Considerable attention has been directed

Correspondence to: A. Kurt (akurt@adiyaman.edu.tr).

Contract grant sponsor: Firat University Research Fund; contract grant number: FUBAP-1197.

toward the exploitation of thermogravimetric data for the determination of kinetic parameters. For this purpose, thermogravimetric analysis (TGA) is a technique widely used because of its simplicity and the information afforded by a simple thermogram. Many of the methods of kinetic analysis are based on the hypothesis that, from a simple thermogravimetric trace, meaningful values may be obtained for parameters such as activation energy, pre-exponential factor, and reaction order.^{14–17}

In this study, we present the preparation of graft copolymers of poly(methyl methacrylate) with ethyl methacrylate (EMA), styrene (St), and *n*-butyl methacrylate (*n*-ButMA) via ATRP method by using a macroinitiator, poly[(methyl methacrylate)-*co*-(3,5-bis(chloroacetoxy)phenyl methacrylate)], including an amount of 1 mol % having α -halogeno carbonyl group in the side groups. The incorporated chloroacetoxy groups [1 mol % compared to methyl methacrylate (MMA)] were utilized as initiators for ATRP. A comparison of the ¹H-NMR, GPC, and TGA data of the two-armed graft copolymers along with that of its macroinitiator is shown as figures. The thermal degradation kinetics and reaction mechanisms of macroinitiator and a two-armed graft copolymer, PMMA-*g*-PnButMA: 4% (by mol), were also reported.

EXPERIMENTAL

Materials

MMA, EMA, styrene (St), and *n*-ButMA were distilled under vacuum after washing with 5% NaOH aqueous solution just before copolymerization. Cuprous(I)bromide, 2,2'-bipyridine (bpy), trihydroxybenzene, chloroacetylchloride, 2,2'-azobis(isobutyronitrile) (AIBN), methacryloyl chloride, NaHCO₃, MgSO₄, triethylamine, tetrahydrofuran (THF), 1,4-dioxane, ethyl alcohol, dichloromethane (CH₂Cl₂), chloroform (CHCl₃), and diphenylether were used as received. All solvents were purified and dried by standard methods. 3,5-bis(chloroacetoxy)phenol and 3,5-bis(chloroacetoxy)phenyl methacrylate (DCPMA) were synthesized in the our laboratory.

Characterization techniques

Infrared spectra were obtained on a Mattson 1000 FT-IR spectrometer. NMR spectra were recorded on a Bruker AC-300 MHz Fourier transform NMR spectrometer at room temperature in CDCl₃. TGA measurements were carried out under a nitrogen flow with a TGA-50 thermobalance at a heating rate of 15°C/min. The average molecular weights were measured on an Agilent 1100 series, gel permeation chromatography (GPC). Polystyrene standards were

used to generate the universal calibration curve. All the determinations were carried out at 23°C from silica gel column, with THF as an eluent at a flow rate of 1 mL/min, by using a refractive-index detector.

Preparation of 3,5-bis(chloroacetoxy)phenol

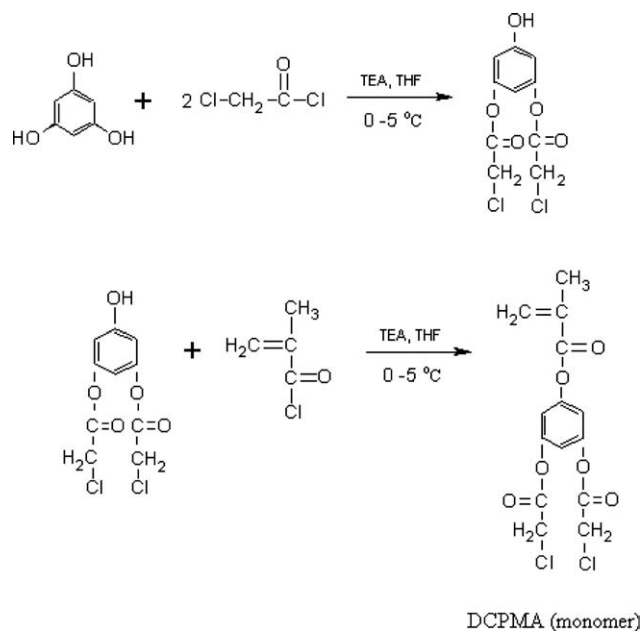
The synthesis of 3,5-bis(chloroacetoxy)phenol was accomplished by the reaction of trihydroxybenzene with chloroacetylchloride in the molar ratio of 1 : 2, respectively. For this purpose, trihydroxybenzene (0.1 mol), triethylamine, (0.21 mol), and THF (100 mL) were placed in a 250-mL flask. The chloroacetylchloride (0.20 mol) was added slowly by stirring and then stirred at room temperature for 6 h. On completion of the reaction, triethylammonium chloride was removed by filtration and the solvent was removed in vacuum. The side products such as 1,3,5-tris(chloroacetoxy)benzene, monochloroacetoxy dihydroxybenzene, and trihydroxy benzene were isolated by column chromatography in the presence of solvents such as CH₂Cl₂ : CHCl₃ (1 : 4 ratio). The structure of 3,5-bis(chloroacetoxy)phenol were characterized by ¹H-NMR and mass spectrometry (MS).

Preparation of 3,5-bis(chloroacetoxy)phenyl methacrylate (DCPMA)

For synthesis of DCPMA monomer, 3,5-bis(chloroacetoxy)phenol (0.01 mol), triethylamine (0.011 mol), and anhydrous THF (200 mL) were placed into a three-necked round-bottomed-flask equipped with a magnetic stirrer and a CaCl₂ tube. Methacryloyl chloride (0.01 mol) was slowly dropped between 0 and -5°C, and then stirred for 2 h at ambient temperature. The reaction mixture was subsequently filtered and the solvent was removed in vacuum. The resulting mixture was taken up in dichloromethane and washed with a saturated solution of NaHCO₃; the organic layer was dried over anhydrous MgSO₄ and concentrated in vacuum. Finally, the crude product was separated by column chromatography at 1 : 4 ratios (CH₂Cl₂/CHCl₃). The structure of synthesized products is illustrated in Scheme 1.

Synthesis of copolymer of 3,5-bis(chloroacetoxy)phenyl methacrylate and methyl methacrylate (macroinitiator)

A typical procedure of free radical polymerization (FRP) of DCPMA with MMA is as follows: MMA (5.0 g), DCPMA (0.20 g), and AIBN (0.039 g) are added to a reaction vessel and dissolved in 20 mL of 1,4-dioxane. The mixture is passed through the argon gas for about 15 min, and then the reaction vessel is closed and immersed in a preheated oil bath at



Scheme 1 The synthesis of 3,5-bis(chloroacetoxy)phenyl methacrylate.

60°C for 24 h. At the end of this time, the polymeric product is obtained by precipitation of the reaction mixture in ethyl alcohol. The precipitation is repeated twice by using the solvent/nonsolvent system, dichloromethane/ethyl alcohol. Finally, the polymer is dried at 40°C in vacuum for 24 h. $M_{n,GPC}$ of macroinitiator is 55,700 and PDI is 1.85. The structure of the macroinitiator is shown in Scheme 2.

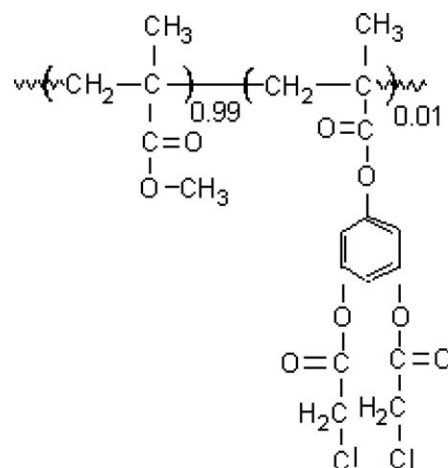
ATRP procedures in bulk

All ATRP reactions were carried out according to the following experimental procedure. Take ATRP of *n*-ButMA: 11.8 mg CuBr, 26.2 mg 2,2'-bipyridine (bpy), and tri-drops of diphenyl ether were added to a dried glass tube to produce ATRP complex. Macroinitiator (0.4 g) and *n*-ButMA (1.2 g) were added to this mixture and then degassed by argon gas purging for 10 min. The glass tube was then closed with a rubber septum and immersed in a preheated oil bath at 100°C for 20 h. After that, the tube was removed from the oil bath and polymerization mixture was dissolved in chloroform, filtered, and precipitated in *n*-hexan. The graft copolymer of *n*-ButMA was isolated and dried in a vacuum oven at 40°C for 24 h. ATRP of EMA was accomplished similar to that of *n*-ButMA. However, the graft block copolymer of EMA with styrene was carried out by ATRP using 0.24 g PMMA-*g*-PEMA as a block graft macroinitiator, 6.7 mg CuBr and 14.8 mg 2,2'-bipyridine as catalyst system, 0.49 g styrene, tri-drops of diphenyl ether to solve the macroinitiator and to prepare complex. The polymerization temperature

was adjusted to 130°C. The purification steps are also similar to that of *n*-ButMA.

RESULTS AND DISCUSSION

Synthesis of DCPMA monomer having α -halogeno carbonyl group was performed by condensation of 3,5-bis(chloroacetoxy)phenol with methacryloylchloride according to the method in literature,¹⁸ and characterized by FT-IR, ¹H-NMR, and MS techniques. Although the most characteristic signals of FT-IR spectrum for 3,5-bis(chloroacetoxy)phenol were observed for C=O stretching at 1772 cm⁻¹ and C=C stretching on aromatic ring at 1607 cm⁻¹, its ¹H-NMR spectrum [Fig. 1(a)] showed the signals at 6.56 and 4.27 ppm for aromatic ring protons and two CH₂ protons adjacent to chlorine, respectively. The integrals of these two proton groups were also obtained as 2.5 and 3.5, respectively. The integral intensities are compatible with proton numbers of aromatic (3H) and methylene (4H) protons. On the other hand, according to mass spectrum [Fig. 2(a)] of 3,5-bis(chloroacetoxy)phenol, the signal in *m/e*: 279 corresponds to its molecular weight. The most characteristic signals in ¹H-NMR spectrum of DCPMA [Fig. 1(b)] are at 6.97 ppm (protons round aromatic ring, integral = 0.9), 5.8 and 6.35 ppm (protons in vinyl group, integral per proton = 0.3), 4.25 ppm (methylene protons attached to chlorine, integral = 1.2). Also, FT-IR spectrum showed the bands at 1782 cm⁻¹ (ester C=O in chloroacetate group), 1737 cm⁻¹ (ester C=O in methacrylate group), 1634 cm⁻¹ (C=C in vinyl group), 1607 cm⁻¹ (C=C on aromatic ring). Mass spectrum of DCPMA (monomer), which is in a good agreement with its structure, is illustrated in Figure 2(b). The molecular weight of DCPMA is *m/e*: 347. The *m/e* values of some important fragments are 69 for CH₂=C(CH₃)CO(+), 77 for ClCH₂CO(+), and 126 for trihydroxybenzene.



Scheme 2 The structure of macroinitiator.

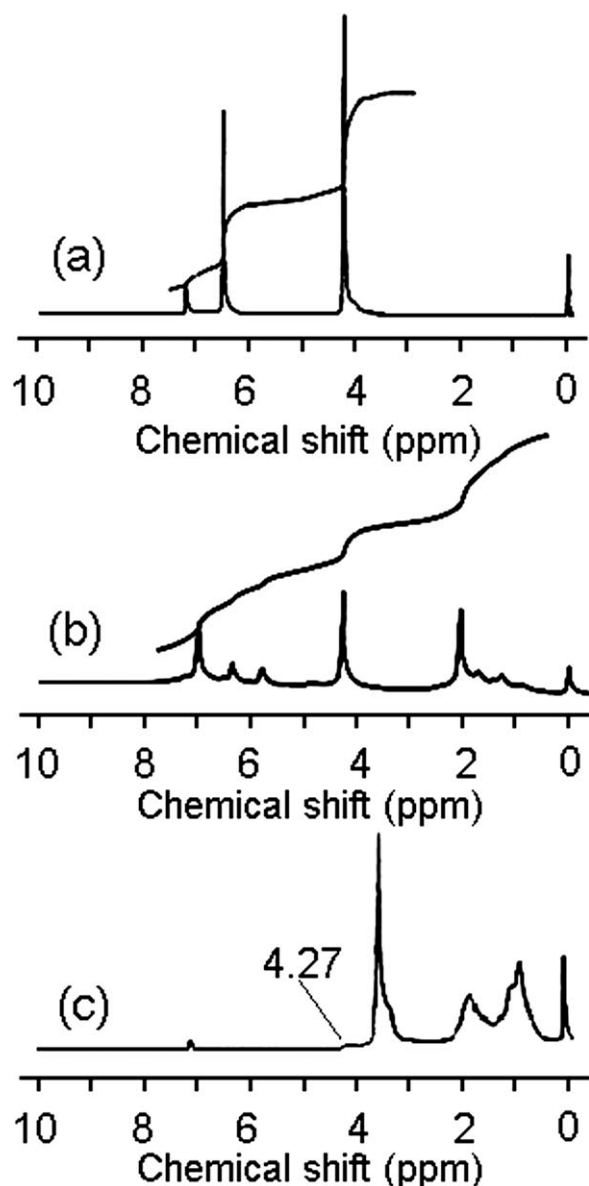


Figure 1 $^1\text{H-NMR}$ spectra of (a) 3,5-bis(chloroacetoxy)phenol, (b) 3,5-bis(chloroacetoxy)phenyl methacrylate (DCPMA), (c) macroinitiator.

In the present study, we used two polymerization systems: FRP used to prepare macroinitiator, and ATRP used to prepare graft copolymers. We did not use the ATRP system in the preparation of macroinitiator, because DCPMA monomer might initiate the ATRP copolymerization of DCPMA with MMA as a side reaction since it has two active Cl atoms. Therefore, two types of initiating system would have existed in ATRP. So, macroinitiator was synthesized by the FRP method as a result of copolymerization of DCPMA with MMA. The structure of macroinitiator was confirmed by $^1\text{H-NMR}$ and FT-IR techniques. Figure 3(a) shows FT-IR spectrum of macroinitiator. The absorbance at 1789 cm^{-1} (very small) and 1732 cm^{-1} are attributed to a vibration characteristic

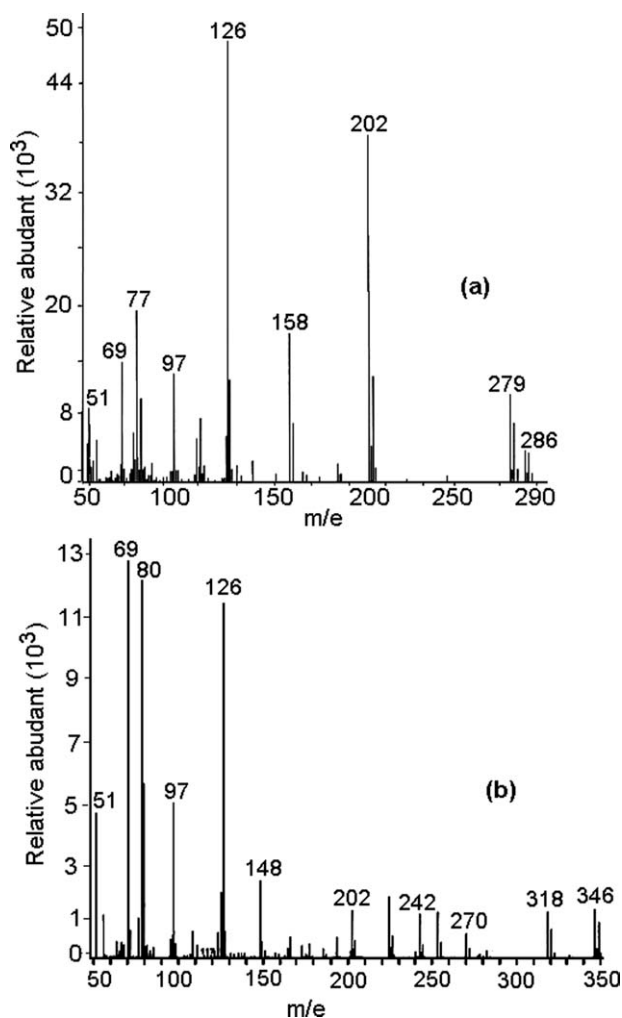


Figure 2 MS spectra of (a) 3,5-bis(chloroacetoxy)phenol, (b) 3,5-bis(chloroacetoxy)phenyl methacrylate.

of an ester $\text{C}=\text{O}$ in DCPMA and repeating MMA units, respectively.

The compositions (by mol %) of all copolymers were determined by the $^1\text{H-NMR}$ technique. The

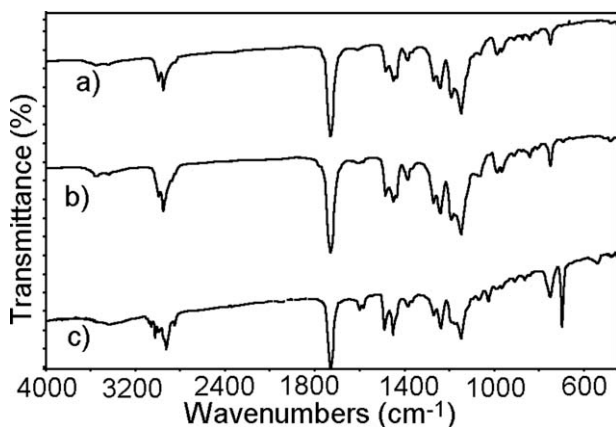


Figure 3 FT-IR spectra of (a) macroinitiator, (b) PMMA-g-PnButMA: 4%, (c) PMMA-g-(PEMA-b-PS).

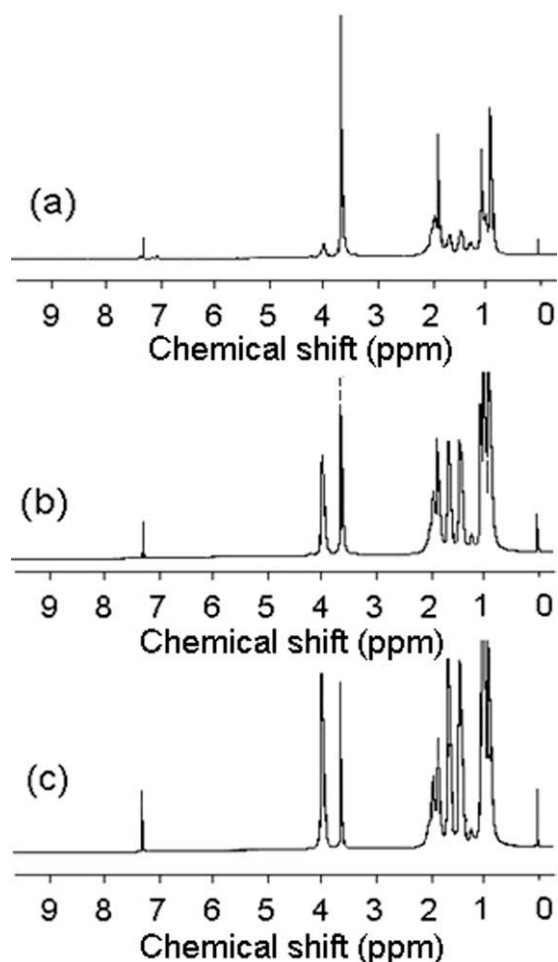


Figure 4 $^1\text{H-NMR}$ spectra of (a) PMMA-*g*-PnButMA: 4%, (b) PMMA-*g*-PnButMA: 28%, (c) PMMA-*g*-PnButMA: 61%.

copolymer composition determination by NMR spectra is widely accepted and used both in industrial and academic areas.^{19,20} The assignment of the proton integrals in the $^1\text{H-NMR}$ spectrum leads to accurate evaluation of each monomer content in the copolymer chains. Thus, the mole fraction of monomers in the copolymer can be determined by measuring the integral peak heights of proton groups. In the $^1\text{H-NMR}$ spectrum of the macroinitiator [Fig. 1(c)], the resonance at 4.27 ppm (proton integrals = 0.10) shows $-\text{OOCCH}_2\text{Cl}$ protons in DCPMA units and the signal at 3.65 ppm (proton integrals = 5.90) is attributed to $-\text{OCH}_3$ protons in MMA units. These signals can be used as the internal standard to determine the copolymer composition. Thus, the compositions (by mol %) of DCPMA and MMA units in the copolymer were determined as 1 and 99% from the ratio of integral peak areas of $-\text{OOCCH}_2\text{Cl}$ protons at 4.27 ppm to that of $-\text{OCH}_3$ protons at 3.65 ppm.

A series of two-armed graft copolymers of *n*-ButMA and AB-type graft-block copolymer of EMA with styrene was prepared by ATRP. Figure 4 shows

$^1\text{H-NMR}$ spectra of graft copolymer series at different compositions of *n*-ButMA. The intensity of signal at 4.01 ppm for $-\text{OCH}_2-$ protons in the *n*-ButMA units increased with the increase of the *n*-ButMA ratio in the copolymer composition. The compositions of these copolymer series were also determined from the ratio of integral intensities of the peak at 4.01 ppm for $-\text{OCH}_2-$ protons in the *n*-ButMA units to that of $-\text{OCH}_3$ protons in the MMA units at 3.65 ppm. For three graft copolymers of *n*-ButMA, the intensities at 4.01 and 3.65 ppm were found to be 0.34/12.50, 3.19/12.50, and 5.46/5.19, respectively. Thus, the percentages of *n*-ButMA units in the graft copolymer series, ended at different times, were calculated as 4, 28, and 61% with time, respectively.

The FT-IR spectrum of block graft copolymer of EMA with St is shown in Figure 3(c), where the most characteristic bands are for aromatic CH stretching in St units at $3021\text{--}3085\text{ cm}^{-1}$, aliphatic CH stretching at $2848\text{--}2984\text{ cm}^{-1}$, C=O stretching in EMA units at 1731 cm^{-1} , and for aromatic C=C stretching in St units at 1601 cm^{-1} . The $^1\text{H-NMR}$ spectra of graft copolymer of EMA (PMMA-*g*-PEMA) and block graft copolymer of EMA with St [PMMA-*g*-(PEMA-*b*-PS)] are shown in Figure 5(a,b), respectively. From Figure 5(a), the signal at 4.08 ppm (proton integrals = 1.51) is characteristic of $-\text{OCH}_2-$ protons in EMA units. From the ratio of this integral to that of 3.65 ppm (proton integrals = 12.50), the EMA composition was found to be 16%. By the block copolymerization [Fig. 5(b)], new signals were shown at 7.08–6.45 ppm (proton integrals = 10.72) attributed to aromatic ring protons in the styrene units. The observed signals of both aromatic

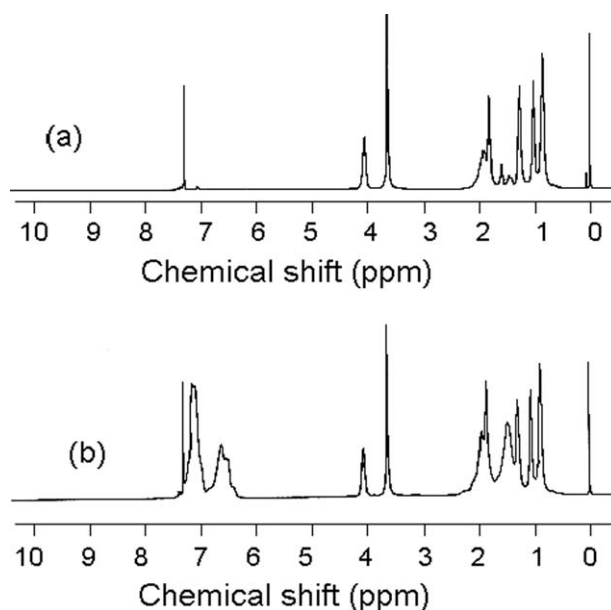


Figure 5 $^1\text{H-NMR}$ spectra of (a) PMMA-*g*-PEMA, (b) PMMA-*g*-(PEMA-*b*-PS).

and $-\text{OCH}_2-$ protons (proton integrals = 1.51) in EMA units explain that the graft block copolymerization was accomplished.

In the $^1\text{H-NMR}$ spectrum of the macroinitiator [Fig. 1(c)] as mentioned above, the resonance at 4.27 ppm shows $-\text{OOCCH}_2\text{Cl}$ protons in the chloroacetoxy group. Consumption of these chlorine groups by initiation in ATRP was confirmed in the different compositions of graft copolymers of *n*-ButMA (Fig. 4) and also graft block copolymer of EMA with St (Fig. 5). For example, all graft copolymers of *n*-ButMA showed a new signal at about 4.01 ppm, which is characteristic for $-\text{OCH}_2-$ protons. This shows the consumption in the macroinitiator of $-\text{OOCCH}_2\text{Cl}$ protons. On the other hand, the formation of the graft copolymers was also supported by FT-IR analysis. The FT-IR spectrum of the macroinitiator [Fig. 3(a)] showed a band at 1789 cm^{-1} , which corresponds to $\text{C}=\text{O}$ stretching in the chloroacetoxy group. After copolymerization with *n*-ButMA, a new carbonyl peak was observed at 1728 cm^{-1} corresponding to the carbonyl stretching from *n*-ButMA [Fig. 3(b)]. This new band was also observed at 1731 cm^{-1} for $\text{C}=\text{O}$ stretching in EMA units in the graft-block copolymer of EMA with St [Fig. 3(c)]. Clear disappearance of the band corresponding to the 1789 cm^{-1} from chloroacetoxy group supports that it was consumed by initiation and confirmed in all graft copolymers.

The molecular parameters of the macroinitiator and two-armed graft copolymers were confirmed by GPC technique. Figure 6(a) shows the GPC trace of macroinitiator. The average molecular weights and molecular weight distribution of macroinitiator were determined as 55,700 and 1.85, respectively. These values are given in Table I. As seen from that, the polydispersity of macroinitiator was relatively high due to the variable number of chloroacetoxy groups in DCPMA units. This height can also result from a free radical polymerization process. Two-armed grafting kinetics of *n*-ButMA were investigated in detail. Figure 6 also shows the GPC traces of graft copolymer series of *n*-ButMA. These traces suggest the formation of graft copolymers. Although the number-average molecular weights of a graft copolymer series of *n*-ButMA ended at different times (≈ 20 h) were increasing from 55,700 to 99,500, the polydispersities decreased from 1.85 to 1.39 with time and these alteration are shown in Figure 7. The GPC data of graft copolymers of *n*-ButMA are given in Table I. These results show that two-armed grafting kinetics of *n*-ButMA follow controlled polymerization kinetics.²¹ The number-average molecular weight and polydispersity of graft copolymer of EMA (PMMA-*g*-PEMA) were found to be 69,900 and 1.81. This result indicates that the graft copolymerization of EMA has been performed. When this

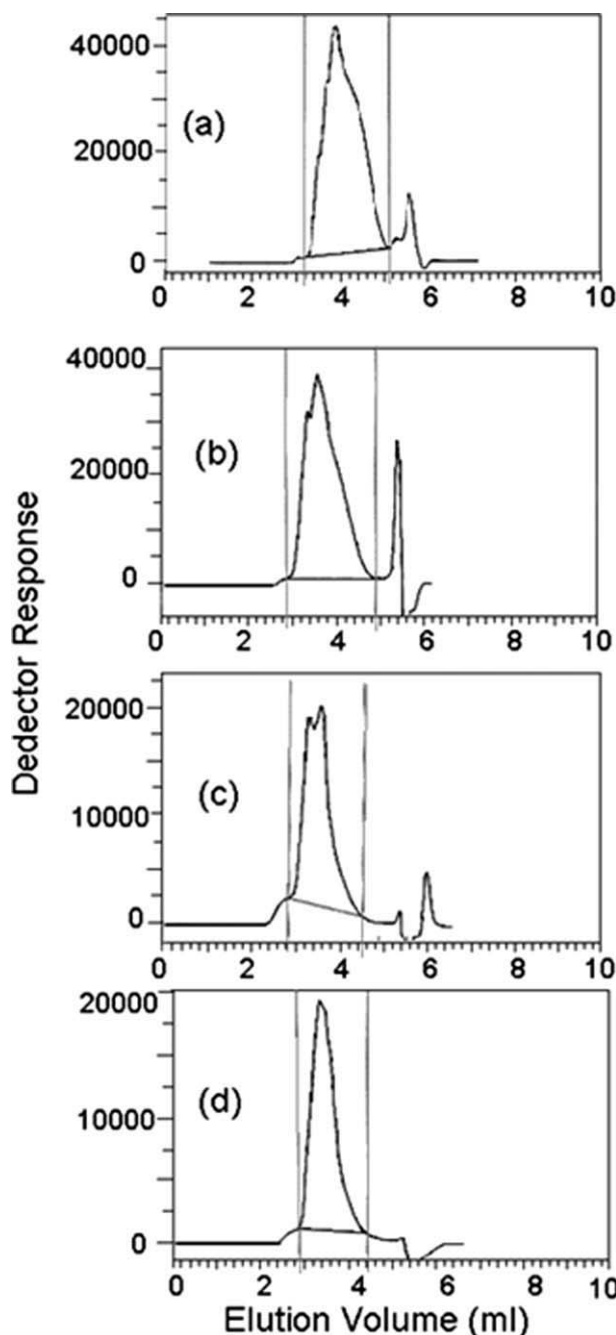


Figure 6 GPC curves of (a) macroinitiator, (b) PMMA-*g*-PnButMA: 4%, (c) PMMA-*g*-PnButMA: 28%, (d) PMMA-*g*-PnButMA: 61%.

PMMA-*g*-PEMA graft copolymer was used as a new graft macroinitiator, the graft block copolymerization of EMA with styrene [PMMA-*g*-(PEMA-*b*-PS)] was also performed in the conditions of ATRP. Thus, the number-average molecular weight of graft copolymer increased from 69,900 to 89,100 by graft blocking, while the polydispersity decreased from 1.81 to 1.49. These results show that the graft block copolymerization conforms to a living and controlled radical polymerization.^{2,3,11} However, the polydispersities of graft copolymers are still partly high, even

TABLE I
GPC and T_g Data of Two-Armed Graft Copolymers

Polymer	M_n	M_w	M_z	PDI	T_g (°C)
Macroinitiator	55,700	103,300	185,800	1.85	127
PMMA- <i>g</i> -PnButMA: 4%	70,860	126,060	212,300	1.78	111
PMMA- <i>g</i> -PnButMA: 28%	94,300	134,250	186,800	1.42	107
PMMA- <i>g</i> -PnButMA: 61%	99,500	138,600	191,500	1.39	98
PMMA- <i>g</i> -PEMA	69,900	126,850	201,500	1.81	110
PMMA- <i>g</i> -(PEMA- <i>b</i> -PS)	89,100	132,800	193,600	1.49	88 and 133

The molar ratio of monomer/macroinitiator/CuBr/bpy was set to 200/1/2/4 for all the ATRP systems. The ATRP temperatures were 100°C (for *n*-ButMA and EMA) and 130°C (for St). Solvent/nonsolvent system : chloroform/*n*-hexan for all the ATRP runs. Experimental conditions of macroinitiator (FRP): monomer/solvent = 1/4(wt/vol), initiator (5.5 wt % of monomer), temperature = 60°C, precipitator = ethyl alcohol.

though the ATRP system is used in their syntheses, because of the high polydispersity of macroinitiator influence the polydispersities of graft copolymers.

The DSC curve of macroinitiator was illustrated in Figure 8(a). The macroinitiator has one transition temperature (T_g) at 127°C. It has been reported that the main chain and the side chain show a higher glass transition temperature than those of corresponding homopolymers when phase separation occurs in the graft or block copolymerization. According to one study reported by Coşkun and Temüz,²² polystyrene-graft-poly(ethyl methacrylate) showed two T_g s at 79–85°C and 103–105°C depending upon grafting degree, the first value of which belongs to poly(ethyl methacrylate) and the second belongs to polystyrene. However, poly(ethyl methacrylate) and polystyrene homopolymers show a glass transition at about 65–70°C and 103°C, respectively. The graft copolymer of EMA (PMMA-*g*-PEMA) showed one transition at 110°C shown in Figure 8(b). This means that macroinitiator and EMA form a homogeneous phase. Figure 8(c) shows DSC thermogram of graft block copolymer of EMA with St, [PMMA-*g*-(PEMA-*b*-PS)]. This thermogram showed two transitions at 88 and 133°C in which the higher T_g corresponds to polystyrene and the lower value is

for poly(ethyl methacrylate). From this result, it can be said that a phase separation appears between EMA and St units in the graft block copolymer. DSC curves of *n*-ButMA graft copolymer were illustrated in Figure 9. As the ratio of *n*-ButMA in the graft copolymers is increased, the T_g values decrease. In these graft copolymer series, it was observed that the side chains of *n*-ButMA units increased the chain mobility and free volume. This means that the glass transition temperature decreases.

Thermogravimetric measurements of graft copolymers

The thermogravimetric curves obtained from room temperature to 500°C at a heating rate of 15°C/min under nitrogen flow for macroinitiator and two-armed graft copolymers, PMMA-*g*-PnButMA: 4%, PMMA-*g*-PEMA, and PMMA-*g*-(PEMA-*b*-PS) are shown in Figure 10. If the initial decomposition temperature, T_i , has been assumed simply as a measurement of thermal stability, these temperatures are 254, 276, 287, and 300°C for macroinitiator, PMMA-

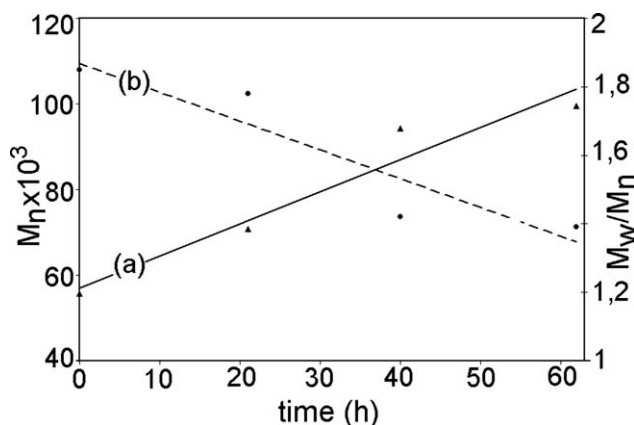


Figure 7 The plots of M_n (a) and M_w/M_n (b) vs. time.

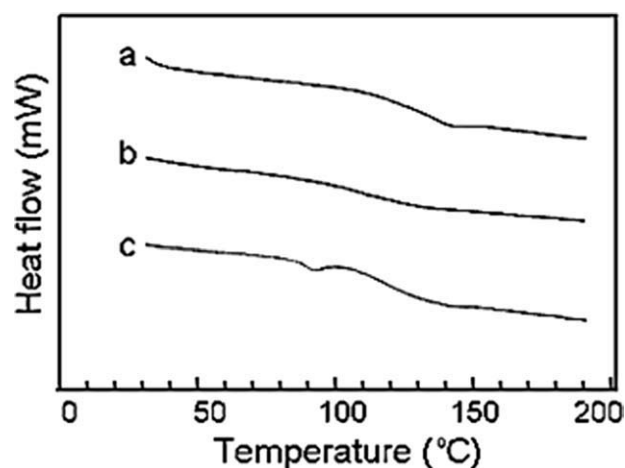


Figure 8 DSC curves of (a) macroinitiator, (b) PMMA-*g*-PEMA, (c) PMMA-*g*-(PEMA-*b*-PS).

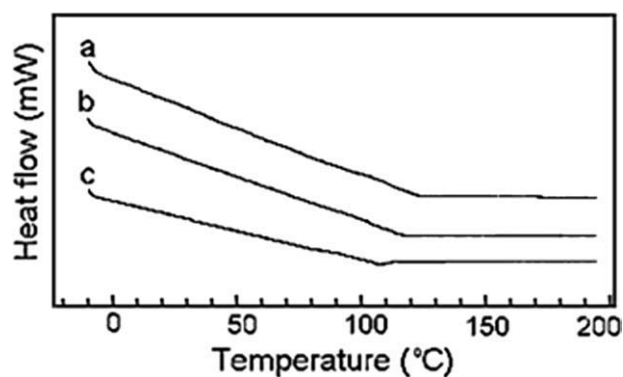


Figure 9 DSC curves of (a) PMMA-g-PnButMA: 4%, (b) PMMA-g-PnButMA: 28%, (c) PMMA-g-PnButMA: 61%.

g-PnBMA:4%, PMMA-g-PEMA, and PMMA-g-(PEMA-*b*-PS), respectively. The decomposition of macroinitiator took place in two steps, the first was 254°C and the second step was 340°C. All of the graft copolymers are more stable than macroinitiator up to 330°C. On the other hand, PMMA-g-(PEMA-*b*-PS) is the most stable according to other graft copolymers. Residue at 500°C of all polymers is between 1.4 and 4%. The TGA data of the two-armed graft copolymers are summarized in Table II.

Kinetic analysis

The following equation is used to define the kinetics of polymer degradation^{11,23}:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α represents the extent of reaction, which can be determined from TGA runs as a fractional mass loss, t is time, $k(T)$ a temperature-dependent rate constant, and $f(\alpha)$ denotes the particular reaction model, which describes the dependence of the reaction rate on the extent of reaction. If an Arrhenius-type expression is used to describe the temperature dependence of $k(T)$, then eq. (1) yields:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (2)$$

with A and E being the pre-exponential factor and the activation energy, respectively. Integrating this equation gives the integral function of conversion, $g(\alpha)$, as follows:

$$g(\alpha) = \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_p} e^{-\frac{E}{RT}} dT \quad (3)$$

The degradation process follows either a sigmoidal function or a deceleration function in the case of poly-

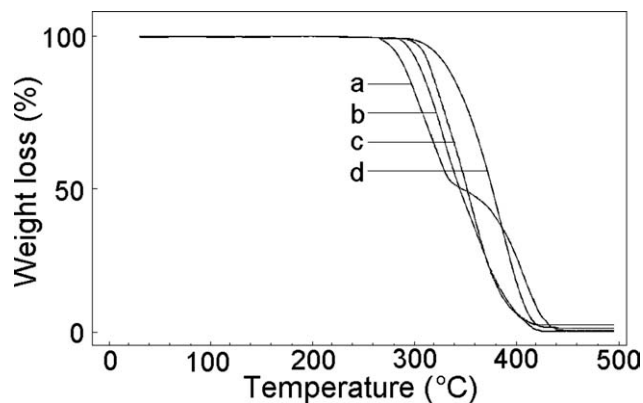


Figure 10 TGA curves of copolymers (a) macroinitiator, (b) PMMA-g-PnButMA: 4%, (c) PMMA-g-PEMA, (d) PMMA-g-(PEMA-*b*-PS).

mers. Different expressions of $g(\alpha)$ for the different solid state mechanisms are well known in literature.²⁴⁻²⁶ These functions were satisfactorily employed in the only known method for the estimation of reaction mechanisms from dynamic TG curves.²⁷

The information about thermal kinetics of polymers can also be evaluated from dynamic experiments by means of different methods, such as the Flynn-Wall-Ozawa,^{28,29} Kissinger,³⁰ and Coats-Redfern³¹ methods.

Flynn-Wall-Ozawa method

The kinetics equation as obtained by Flynn-Wall-Ozawa^{28,29} on the basis of an Arrhenius equation is as follows:

$$\log \beta = \log \left[\frac{AE}{g(\alpha)R} \right] - 2.315 - \frac{0.457E}{RT} \quad (4)$$

where β , A , E , and T have known values. This is one of the integral methods that can determine the activation energy without knowledge of reaction order. It is used to determine the activation energy for given values of conversion. The E value can be calculated from the slope of a plot of $\log \beta$ versus $(1/T)$ for a constant weight loss, which is equal to $(-E/R)$. The correlation between $\log \beta$ and $(1/T)$ is linear.

TABLE II
TGA Data for Two-Armed Graft Copolymers at Heating Rate of 15°C/min

Reaction rate (°C/min)	T_i^a	T_{50}^b	%Weight loss at 350°C	Residue (%) at 500°C
Macroinitiator	254	342	53	1.4
PMMA-g-PnButMA: 4%	277	343	57	1.39
PMMA-g-PEMA	287	350	51	3.76
PMMA-g-(PEMA- <i>b</i> -PS)	300	376	22	3.90

^a Initial decomposition temperature(°C).

^b Decomposition temperature(°C) at 50%.

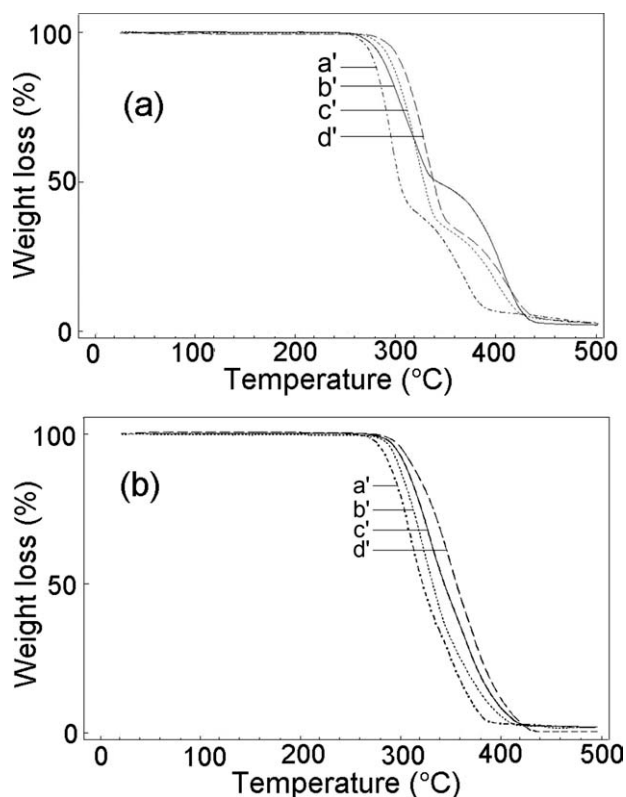


Figure 11 TGA curves of macroinitiator (a) and PMMA-g-PnButMA: 4% graft copolymer (b) at different heating rates: (a') 5°C/min, (b') 15°C/min, (c') 25°C/min, (d') 35°C/min.

Kissinger's method

The activation energy E of thermal degradation is often determined under linear heating conditions with an equation derived by Kissinger.³⁰

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{ \ln\frac{AR}{E} + \ln\left[n(1 - \alpha_{\max})^{n-1}\right] \right\} - \frac{E}{RT_{\max}} \quad (5)$$

where β is the heating rate, T_{\max} is the temperature corresponding to the maximum reaction rate, A is the pre-exponential factor, α_{\max} is the maximum conversion, and n is the reaction order. The activation energy E can be calculated from the slope of a plot of $\ln(\beta/T_{\max}^2)$ versus $1000/T_{\max}$ and can fit to a straight line.

Coats-Redfern method

By the resolution of eq. (3), the following equation can be obtained:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (6)$$

According to the Coats-Redfern method,³¹ the activation energy for every degradation process can

be determined from a plot of $\ln g(\alpha)/T^2$ versus $1000/T$.

Determination of activation energies and decomposition mechanisms of macroinitiator and PMMA-g-PnButMA: 4% graft copolymer

The dynamic experiments of TGA of both macroinitiator and PMMA-g-PnButMA: 4% graft copolymer were carried out at different heating rates: 5, 15, 25, and 35°C/min. These TGA curves are shown in Figure 11(a,b) for macroinitiator and PMMA-g-PnButMA: 4% graft copolymer, respectively. It was observed that an increase in the heating rate shifts the TGA curves and peak temperatures to higher values, as was expected, and is common in different types of polymers.³²⁻³⁵ The temperatures related to the maximum decomposition rates for macroinitiator were found to be 296.5, 309.4, 318.1, 329.2, and for PMMA-g-PnButMA: 4% they were found to be 318.5, 331.65, 334.3, and 343.03°C from the corresponding differential TGA plots at heating rates: 5, 15, 25, and 35°C/min, respectively.

Using the Flynn-Wall-Ozawa method, eq. (4) provides the calculation of the corresponding activation energy by plotting $\log \beta$ versus $1000/T$. Such plots for macroinitiator and PMMA-g-PnButMA: 4% graft copolymer appear in Figure 12(a,b), respectively.

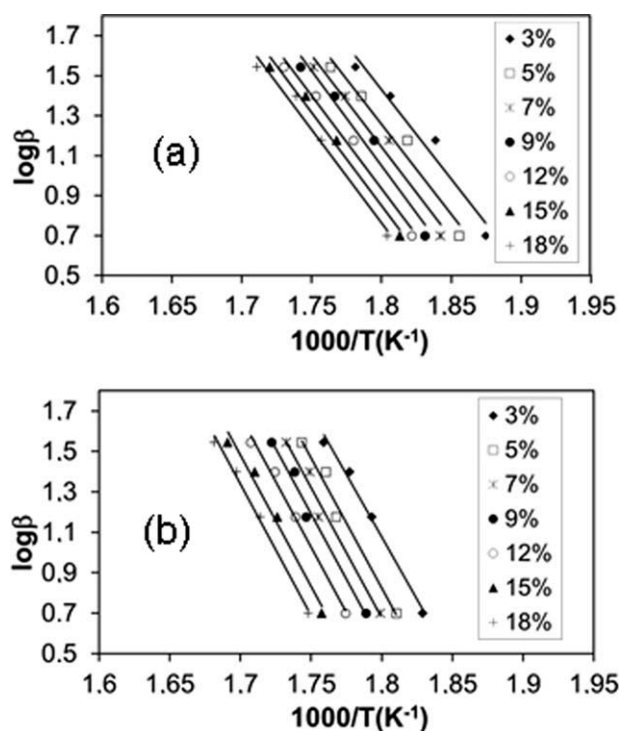


Figure 12 Flynn-Wall-Ozawa method applied to (a) macroinitiator and (b) PMMA-g-PnButMA: 4% graft copolymer at different conversion values.

TABLE III
Activation Energies Obtained Using the Flynn–Wall–Ozawa Method for Macroinitiator and PMMA-g-PnButMA: 4% Graft Copolymer

α (%)	Macroinitiator		PMMA-g-PnButMA: 4%	
	E_a (kJ/mol)	R	E_a (kJ/mol)	R
3	163	0.9607	225	0.9910
5	165	0.9690	234	0.9791
7	167	0.9691	234	0.9755
9	173	0.9695	234	0.9836
12	169	0.9840	235	0.9928
15	169	0.9848	237	0.9817
18	170	0.9808	236	0.9935
Mean	168		233	

From the slope of these lines, the activation energies estimated at different conversions are given in Table III. Conversion values at intervals of 3–18% were used due to the fact that eq. (4) was derived using the Doyle approximation.³⁶ From Table III, a mean value $\bar{E} = 168$ kJ/mol was calculated for macroinitiator. On the other hand, it was found that the mean value $\bar{E} = 233$ kJ/mol for the PMMA-g-PnButMA: 4% graft copolymer. By the Kissinger's method, the activation energy E can be calculated from the slope of a plot of $\ln(\beta/T_{\max}^2)$ versus $1000/T_{\max}$ using eq. (5). Figure 13(a,b) show the activation energies obtained using this method, which are 162 and 239 kJ/mol for macroinitiator and PMMA-g-PnButMA: 4%. These values are very close to the mean values, $E = 168$ kJ/mol for macroinitiator and $E = 233$ kJ/mol for PMMA-g-PnButMA: 4%, calculated using the Flynn–Wall–Ozawa method. From the results of both the Flynn–Wall–Ozawa and Kissinger's methods, it can be seen that the activation

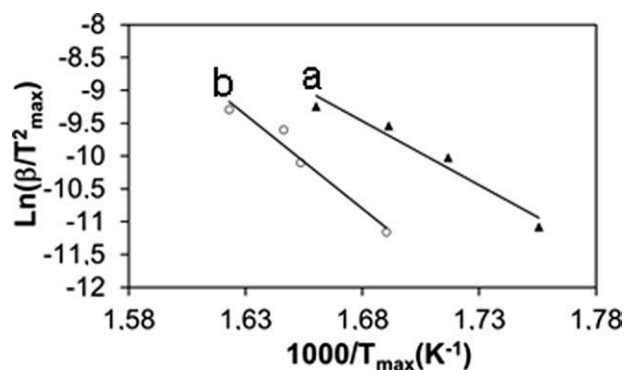


Figure 13 Kissinger method applied to (a) macroinitiator and (b) PMMA-g-PnButMA: 4% graft copolymer at different heating rates.

energy of PMMA-g-PnButMA: 4% graft copolymer is higher than the activation energy of macroinitiator, and it can also be seen that the activation energies are increased by graft copolymerization.

The activation energies for different expressions of $g(\alpha)$ functions for different solid state mechanisms can be calculated from the plots of $\ln(g(\alpha)/T^2)$ versus $1000/T$, which have been represented by the Coats–Redfern method using eq. (6). The activation energies and correlations for thermal degradation of macroinitiator and PMMA-g-PnButMA: 4% copolymer calculated in the range of 3–18% considering the heating rates of 5, 15, 25, and 35°C/min are summarized in Tables IV and V, respectively. From these tables, it can be seen that the optimum heating rate value is 15°C/min for both macroinitiator and PMMA-g-PnButMA: 4% graft copolymer; because analysis of Table IV showed that the activation energy corresponding to R_1 -type mechanism for thermal degradation of macroinitiator at a heating rate of 15°C/min was 173 kJ/mol, very close to the

TABLE IV
Activation Energies Obtained Using the Coats–Redfern Method for Several Solid State Processes at Different Heating Rates for Macroinitiator

Mechanism	Heating rate of 5°C/min		Heating rate of 15°C/min		Heating rate of 25°C/min		Heating rate of 35°C/min	
	E_a (kJ/mol)	R	E_a (kJ/mol)	R	E_a (kJ/mol)	R	E_a (kJ/mol)	R
A ₂	103	0.9990	86	0.9933	107	0.9976	101	0.9967
A ₃	65	0.9989	54	0.9924	68	0.9974	64	0.9963
A ₄	47	0.9988	38	0.9914	49	0.9972	46	0.9959
R ₁	204	0.9989	173	0.9919	213	0.9981	202	0.9955
R ₂	209	0.9990	177	0.9930	218	0.9980	207	0.9963
R ₃	211	0.9991	179	0.9933	219	0.9980	209	0.9965
D ₁	417	0.9990	355	0.9923	435	0.9982	415	0.9957
D ₂	424	0.9991	361	0.9930	441	0.9981	421	0.9962
D ₃	430	0.9991	366	0.9937	448	0.9980	427	0.9967
D ₄	426	0.9991	363	0.9932	444	0.9981	423	0.9964
F ₁	214	0.9991	181	0.9940	223	0.9978	212	0.9970
F ₂	11	0.8013	8	0.8557	11	0.7760	10	0.8579
F ₃	30	0.8899	25	0.9357	32	0.8744	30	0.9269

TABLE V
Activation Energies Obtained Using the Coats–Redfern Method for Several Solid State Processes at Different Heating Rates for PMMA-*g*-PnButMA: 4%

Mechanism	Heating rate of 5°C/min		Heating rate of 15°C/min		Heating rate of 25°C/min		Heating rate of 35°C/min	
	E_a (kJ/mol)	E_a (kJ/mol)	E_a (kJ/mol)	E_a (kJ/mol)	E_a (kJ/mol)	R	E_a (kJ/mol)	R
A ₂	94	0.9930	109	0.9958	107	0.9902	104	0.9824
A ₃	60	0.9929	69	0.9954	68	0.9892	66	0.9806
A ₄	42	0.9913	50	0.9950	49	0.9881	47	0.9785
R ₁	189	0.9916	216	0.9956	214	0.9892	208	0.9809
R ₂	193	0.9927	221	0.9959	219	0.9902	213	0.9825
R ₃	195	0.9931	223	0.9960	220	0.9905	215	0.9830
D ₁	386	0.9920	442	0.9958	437	0.9897	425	0.9818
D ₂	392	0.9927	449	0.9960	444	0.9903	432	0.9828
D ₃	398	0.9934	456	0.9962	450	0.9909	439	0.9837
D ₄	394	0.9930	451	0.9961	446	0.9905	434	0.9831
F ₁	198	0.9937	227	0.9962	224	0.9910	218	0.9839
F ₂	9	0.8728	12	0.8185	12	0.8668	11	0.9104
F ₃	28	0.9378	33	0.8991	33	0.9282	32	0.9538

168 kJ/mol obtained by the Flynn–Wall–Ozawa method. Also, Table V showed that the activation energy corresponding to a F₁-type mechanism for thermal degradation of PMMA-*g*-PnButMA: 4% at heating rate of 15°C/min was 227 kJ/mol. This value is also in better agreement with 233 kJ/mol by the Flynn–Wall–Ozawa method. These facts strongly suggest that the solid state thermodegradation mechanisms of both macroinitiator and two-armed graft copolymer of *n*-ButMA with this macroinitiator (PMMA-*g*-PnButMA: 4%) are deceleration types that are R₁-type mechanism, which is a phase boundary-controlled reaction, and F₁-type mechanism, which is a random nucleation with one nucleus on the individual particle, respectively.

CONCLUSIONS

The graft copolymers of poly(methyl methacrylate) with some alkyl methacrylates were prepared by the ATRP method. The thermal degradation kinetics of macroinitiator and a two-armed graft copolymer of *n*-ButMA with this macroinitiator, PMMA-*g*-PnButMA: 4%, were carried out at different heating rates by TGA and the results were compared. Some conclusions for this work are as follows:

- Although the number-average molecular weights of a graft copolymer series of *n*-ButMA ended at different times increased from 55,700 to 99,500, the polydispersities decreased from 1.85 to 1.39 with time.
- The GPC results showed that the AB-type graft-block copolymerization of EMA and styrene was accomplished due to the increase of M_n from 69,900 to 89,100, while the polydispersities decreased from 1.81 to 1.49.

- The graft copolymers prepared with *n*-ButMA and EMA showed a lower glass transition temperature than that of the macroinitiator.
- Using both the Flynn–Wall–Ozawa and Kissinger's methods, the activation energies for macroinitiator were determined as 168 and 162 kJ/mol, respectively. The energies were also calculated as 233 and 239 kJ/mol for the PMMA-*g*-PnButMA: 4% graft copolymer.
- The optimum heating rate value was found to be 15°C/min by the Coats–Redfern method for both the macroinitiator and PMMA-*g*-PnButMA: 4%.
- The solid state thermodegradation mechanisms of both the macroinitiator and PMMA-*g*-PnButMA: 4% graft copolymer are deceleration types: R₁-type mechanism, a phase boundary-controlled reaction, and F₁-type mechanism, a random nucleation with one nucleus on the individual particle, respectively.

References

- Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem Rev* 2001, 101, 3661.
- Matyjaszewski, K.; Xia, J. H. *Chem Rev* 2001, 101, 2921.
- Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
- Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.
- Chmela, S.; Teissedre, G.; Lacoste, J. *Macromolecules* 1996, 29, 3055.
- Wirsen, A.; Linberg, K. T.; Albertsson, A. C. *Polymer* 1996, 37, 761.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
- Shen, D.; Huang, Y. *Polymer* 2004, 45, 7091.
- Demirelli, K.; Kurt, A.; Coskun, M. F.; Coskun, M. *J Macromol Sci* 2006, 43, 573.

10. Matyjaszewski, K.; Teodorescu, M.; Miller, P. J.; Peterson, M. L. *J Polym Sci Part A: Polym Chem* 2000, 38, 2440.
11. Demirelli, K.; Kurt, A.; Coskun, M. *Eur Polym J* 2004, 40, 451.
12. Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* 1998, 31, 9413.
13. Gu, L.; Zhu, S.; Hrymak, A. N. *J Polym Sci Part B: Polym Phys* 1998, 36, 705.
14. Peterson, J. D.; Vyazovkin, S.; Wight, C. A. *Macromol Chem Phys* 2001, 202, 775.
15. Paik, P.; Kar, K. K. *Mater Chem Phys* 2009, 113, 953.
16. Al-Mulla, A.; Shaban, H. I. *Int J Polym Mater* 2008, 57, 275.
17. Achilias, D. S.; Karabela, M. M.; Sideridou, I. D. *Thermochim Acta* 2008, 472, 74.
18. Haddleton, D. M.; Waterson, C. *Macromolecules* 1999, 32, 8732.
19. Dhal, P. K.; Babu, G. N.; Nada, R. K. *Macromolecules* 1984, 17, 1131.
20. Rudin, A.; Odriscoll, K. F.; Rumack, M. S. *Polymer* 1981, 22, 740.
21. Demirelli, K.; Kurt, A.; Coskun, M. *Polym Plast Technol* 2004, 43, 1245.
22. Coşkun, M.; Temüz, M. M. *J Polym Sci Part A: Polym Chem* 2003, 41, 668.
23. Nunez, L.; Fraga, F.; Nunez, M. R.; Villanueva, M. *Polymer* 2000, 41, 4635.
24. Hatakeyama, T.; Quinn, F. X. *Thermal Analysis. Fundamentals and Applications to Polymer Science*; Wiley: England, 1994.
25. Criado, J. M.; Ma'lek, J.; Ortega, A. *Thermochim Acta* 1989, 147, 377.
26. Ma, S.; Hill, J. O.; Heng, S. *J Therm Anal* 1991, 37, 1161.
27. Zivkovic, Z. D.; Sestak, J. *J Therm Anal Calorim* 1998, 53, 263.
28. Flynn, J. H.; Wall, L. A. *J Polym Sci Polym Lett* 2003, 5, 191.
29. Ozawa, T. *J Therm Anal* 1986, 31, 547.
30. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
31. Coats, A. W.; Redfern, J. P. *Nature* 1964, 201, 68.
32. Peterson, J. D.; Vyazovkin, S.; Wight, C. A. *J Phys Chem B* 1999, 103, 8087.
33. Chrissafis, K.; Paraskevopoulos, K. M.; Bikiaris, D. N. *Thermochim Acta* 2006, 440, 166.
34. Chrissafis, K.; Paraskevopoulos, K. M.; Bikiaris, D. N. *Polym Degrad Stab* 2006, 91, 60.
35. Kurt, A. *J Appl Polym Sci* 2009, 114, 624.
36. Doyle, C. D. *J Appl Polym Sci* 1961, 5, 285.