

Graft Copolymerization of Methylmethacrylate with N-Substituted Maleimide-Styrene Copolymer by ATRP

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ABSTRACT: Atom transfer radical polymerization (ATRP) was employed to prepare graft copolymers having poly(MBr)-*alt*-poly(St) copolymer as backbone and poly(methyl methacrylate) (PMMA) as branches to obtain heat resistant graft copolymers. The macroinitiator was prepared by copolymerization of bromine functionalized maleimide (MBr) with styrene (St). The polymerization of MMA was initiated by poly(MBr)-*alt*-poly(St) carrying bromine groups as macroinitiator in the presence of copper bromide (CuBr) and bipyridine (bpy) at 110°C. Both macroinitiator and graft

copolymers were characterized by ¹H NMR, GPC, DSC, and TGA. The ATRP graft copolymerization was supported by an increase in the molecular weight (MW) of the graft copolymers as compared to that of the macroinitiator and also by their monomodal MW distribution. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1993–2001, 2006

Key words: N-substituted maleimide; polymaleimide; alternating copolymers; ATRP; graft copolymers

INTRODUCTION

Because well-defined polymer microstructures promise new material properties, the control of the macromolecular architecture has become an important topic of polymer science. Recently, significant progress has been made in the field of living free radical polymerization (FRP), such as nitroxide-mediated stable FRP, atom transfer radical polymerization (ATRP), reverse ATRP, and reversible addition-fragmentation chain transfer.^{1,2} Among them ATRP has been successively applied to the synthesis of well-defined macromolecular architectures such as comb, star, branched, and dendritic macromolecules.^{3–12}

Meanwhile, rapidly increasing attention has been paid to graft copolymers, which exhibit good phase separation, and are used for a variety of applications such as impact resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers.^{13–17} They also have lower melt viscosities because of their branched structure, which is advantageous for processing. Furthermore, if controlled polymerization techniques are employed for the synthesis of graft copolymers, advantages of these techniques can be combined with the excellent properties of graft copolymers to have promising polymer materials.

Maleimide-incorporated vinyl polymers exhibit superior mechanical and thermal stability.^{18,19} It is well-known that high dipole moment of the maleimide unit at right angle to the backbone and its cyclic structure impart great stiffness to the polymer chain, resulting in high T_g due to the presence of imide rings in the backbone. These polymers find application in several fields related to their dielectric and nuclear magnetic relaxation characteristics, asymmetric induction polymerization, or Langmuir-Blodgett film forming properties.²⁰

Copolymerizations of N-substituted maleimides with various vinyl monomers have been investigated by many authors.^{21–27} Specifically, copolymerization with electron-donor monomers such as styrene is well-known to yield alternating copolymers, and the copolymerization mechanism has been discussed by others.^{26–29}

This article describes the preparation of graft copolymers via ATRP, using a bromine functional macroinitiator poly(MBr)-*alt*-poly(St). For this purpose, bromine functional, N-substituted maleimide monomer (MBr) was synthesized by the esterification of N-methylolmaleimide (NMM) with 2-bromopropionyl bromide. MBr was then copolymerized with St to obtain bromine functional macroinitiator. The incorporated bromine groups were used as initiators for ATRP of MMA (Scheme 1).

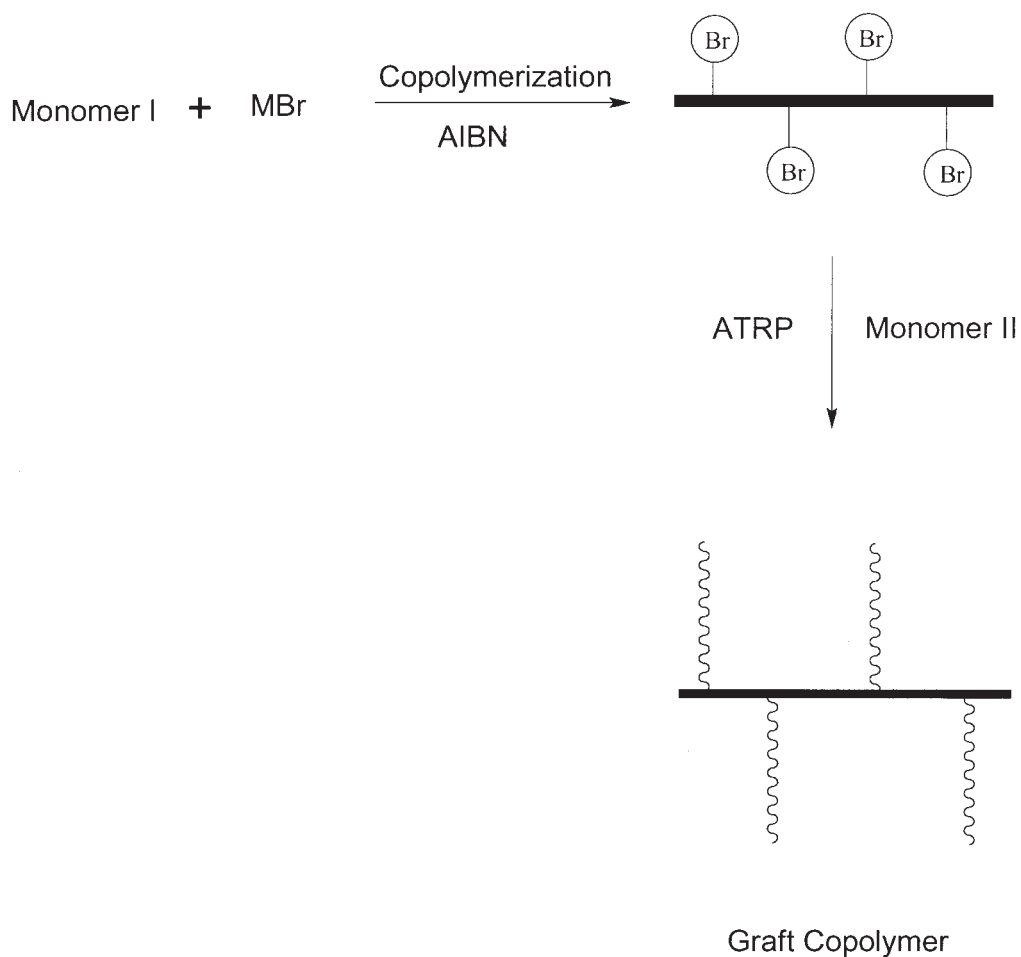
EXPERIMENTAL

Materials

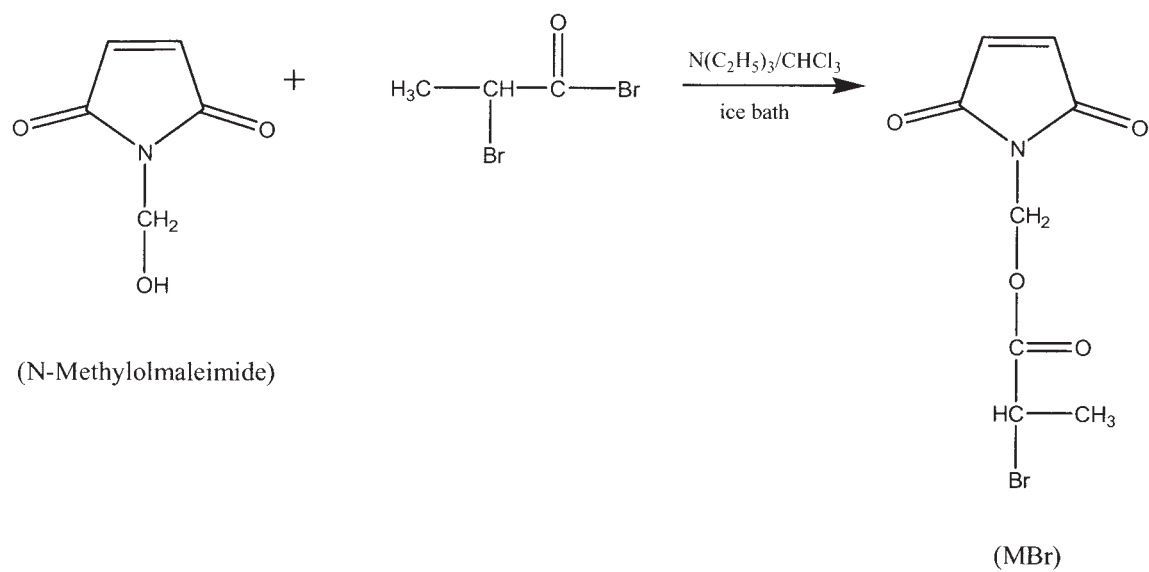
St (Fluka), MMA (Fluka), Tetrahydrofuran (J.T. Baker), Chloroform (J.T. Baker) were purified by

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Scheme 1 Schematic Representation of Graft Copolymerization by ATRP.



Scheme 2 Synthesis of MBr.

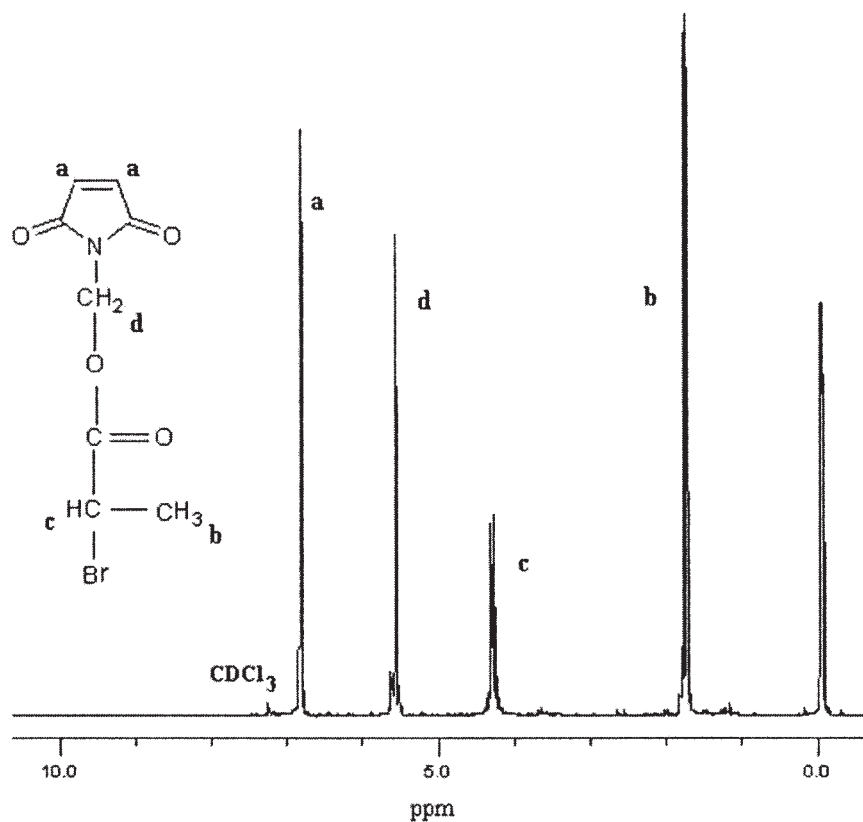
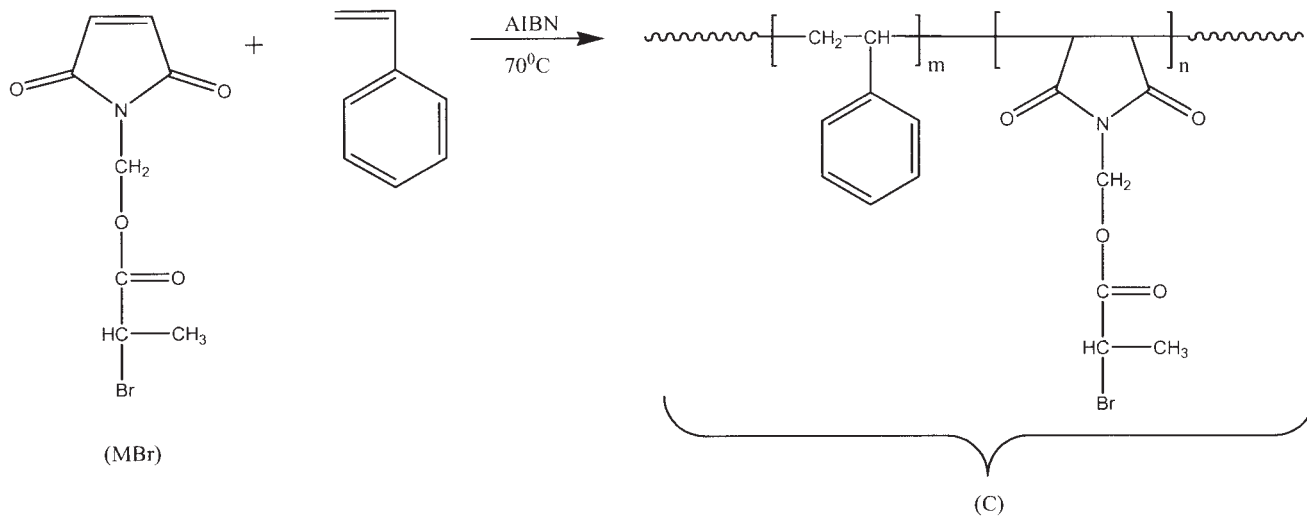


Figure 1 ¹H NMR spectrum of MBr.

conventional drying and distillation procedures. Other chemicals, Maleimide (Aldrich), Copper (I) Bromide (Aldrich), Bipyridine (Aldrich), Formaldehyde (Acros), Anisole (Acros), Triethylamine (Acros), 2-bromopropionyl bromide (Aldrich), were used without further purification. NMM was prepared according to the modified method of Tawney et al.³⁰

Synthesis of (2,5-dioxo-2,5-dihydro-1*h*-pyrrole-1-yl)methyl 2-bromopropanoate (MBr)

Under nitrogen, 6.24 mL (0.059 mol) 2-bromopropionyl bromide was added dropwise to a stirring mixture of NMM (6 g, 0.047 mol) and triethylamine (8.22 mL, 0.058 mol) in 140 mL of CHCl₃ in an ice bath for 1 h. After complete addition of the acid bromide, the reaction was stirred at room temperature for 3 h. The



Scheme 3 Synthesis of poly(St)-alt-poly(MBr) (C).

TABLE I
Copolymerization of St and MBr at 70°C

Run	[MBr] (mol/L)	[St] (mol/L)	[AIBN] (mol/L)	Time (min)	Conv. (%)	M_n^a	M_n^b	M_w/M_n^a	MBr (wt %)
C1	0.572	1.739	0.549	15	54	16900	18300	3.6	50
C2	0.790	2.380	0.034	30	67	37090	20030	6.4	61
C3	0.790	2.380	0.034	120	70	32600	17030	5.2	42

^a Determined from GPC, based on PSt standards.

^b Determined from ¹H NMR Spectrum.

reaction mixture was washed with water (3 × 140 mL) and then dried over MgSO₄. After filtration and evaporation of CHCl₃, a greasy dark red product was obtained. It was dried under vacuum and recrystallized from ethanol (m.p., 68–71°C; Yield, 47%).

¹H NMR (CDCl₃), δ (ppm): 4.2–4.3 (m, 1H), 1.6–1.8 (d, 3H), 5.5–5.6 (m, 2H), 6.8 (s, 2H). FTIR (KBr), ν (cm⁻¹): 1720 (C=O of ester stretching), 1419 (C–N), 694 (C–Br).

Elemental analysis: (262 g mol⁻¹). Calcd: C, 36.64%; H, 3.05%; N, 5.34%. Found: C, 36.22%; H, 2.98%, N, 4.95%.

Synthesis of the poly(MBr)-*alt*-poly(St) macroinitiators by free radical copolymerization

To a schlenk tube equipped with a magnetic stirrer, vacuum and dry nitrogen was applied three or four times, then certain amounts of monomers (St, MBr), initiator (AIBN), and solvent were introduced under nitrogen. The flask was sealed and then immersed in an oil bath held by a thermostat at 70°C. At the end of the given reaction time, copolymers were obtained from the reaction mixture by precipitation into methanol and drying. Polymers were purified by reprecipitation from the THF solution into excess methanol and then dried *in vacuo* for several hours.

Synthesis of the graft copolymers of MMA by ATRP

To a schlenk tube equipped with a magnetic stirrer, vacuum and dry nitrogen were applied three or four times, and then certain amounts of MMA, anisole, ligand, copper(I) bromide, bpy, and macroinitiator poly(MBr)-*alt*-poly(St) were added in the order mentioned under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by a thermostat at 110°C, with rigorous stirring. The polymerization was performed for a determined time. Then, the tube was cooled to room temperature and the contents were dissolved in large amount of THF. The THF solution was passed through a short neutral alumina column to remove copper complex and then excess THF was removed by evaporation. The polymer was precipitated into excess methanol, isolated by

vacuum filtration, and dried at room temperature *in vacuo* for 24 h. The conversion was determined gravimetrically.

Analysis and characterization

FTIR was measured using Jasco model FT-IR-5300 fourier transform infrared spectra. ¹H NMR analysis was recorded on a Bruker 250 MHz Spectrometer with CDCl₃ as a solvent and tetramethylsilane as the internal standard. Elemental analysis results were performed on a CHNS-932 LECO instrument. Gel permeation chromatography (GPC) analyses were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and four Waters Styragel Columns (HR 5E, HR 4E, HR3, and HR2). THF was used as the eluent at a flow rate of 0.3 mL/min at 30°C. The molecular weights (MWs) of the polymers were calculated with the aid of PSt and PMMA standards. The thermal properties of the copolymers were measured by differential scanning calorimetry (TA, DSC Q10) in a flowing nitrogen atmosphere from the room temperature to 300°C, at scan-

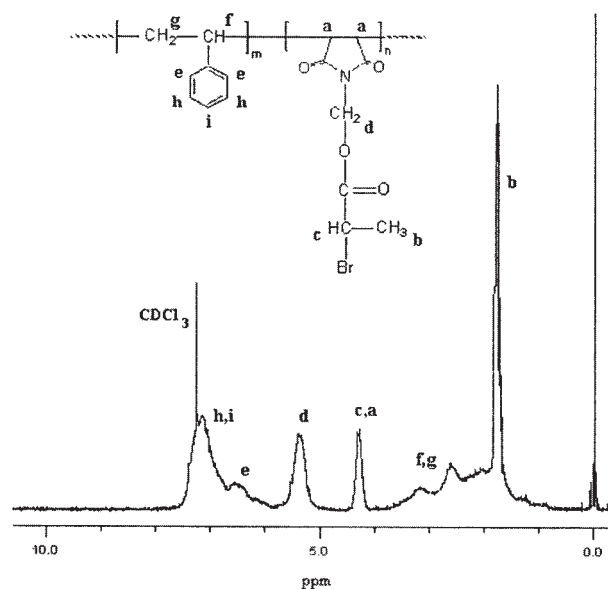
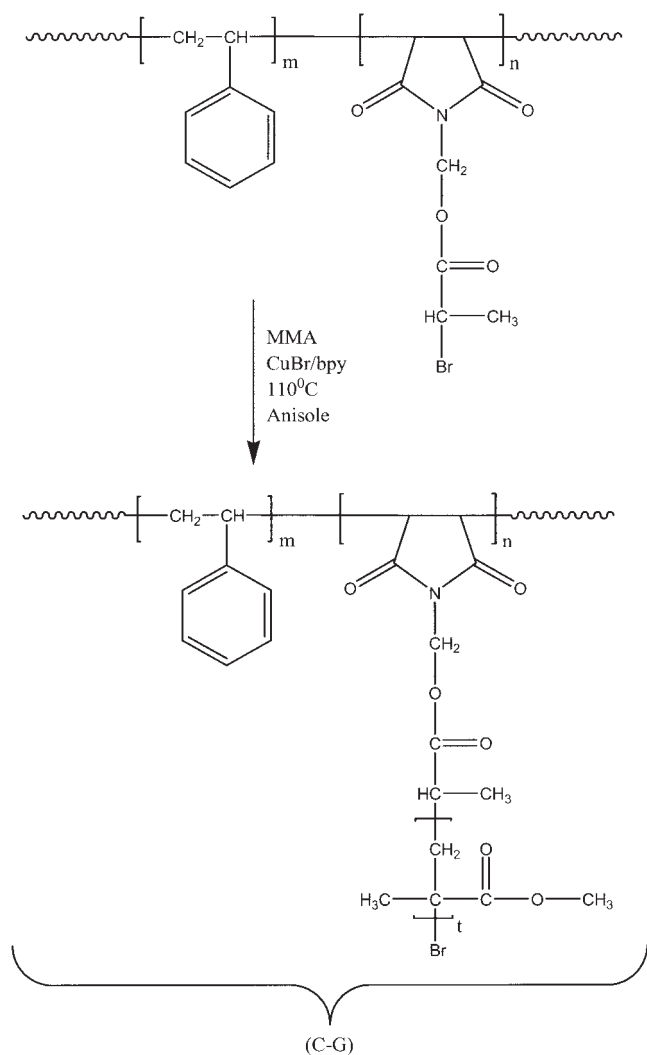


Figure 2 ¹H NMR spectrum of poly(St)-*alt*-poly(MBr).



Scheme 4 Synthesis of [poly(St)-alt-poly(MBr)]-g-poly(MMA).

ning rate of 10°C/min. Thermal stability of copolymers was measured by thermogravimetric analysis (TA, TGA Q50) in a flowing nitrogen atmosphere at heating rate of 20°C/min.

RESULTS AND DISCUSSION

In this study, graft copolymers of MMA with N-substituted maleimide-styrene copolymers were synthesized via a two-step procedure, involving FRP and ATRP. For this purpose, a functional initiator having bromine group was synthesized by esterification of the NMM with 2-bromopropionyl bromide (Scheme 2).

The structure of the product (MBr) was confirmed by spectroscopic investigations. ^1H NMR spectrum recorded in CDCl_3 evidenced resonance signals of $-\text{CH}_3$, $-\text{CH}-$, $-\text{OCH}_2$, and monomeric maleimide, protons of relative intensities corresponding to the

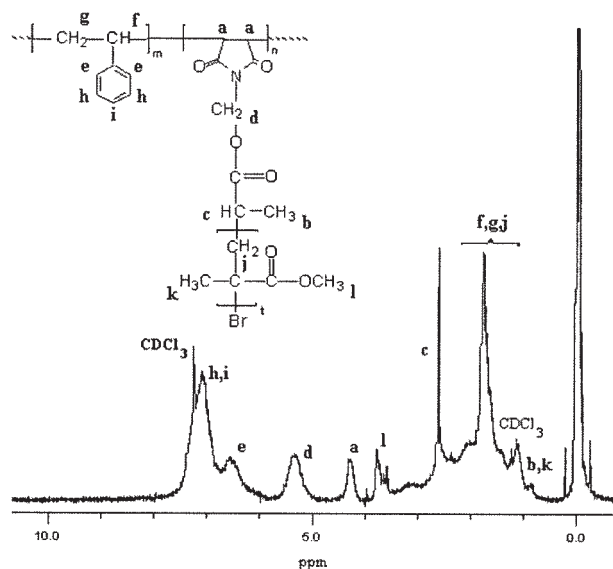


Figure 3 ^1H NMR spectrum of poly(St)-alt-poly(MBr)-g-MMA.

number and type of protons (Fig. 1). The FTIR spectrum of MBr also showed no signal corresponding to $-\text{OH}$ groups of the starting NMM and shows the characteristic CO ester band at 1720 cm^{-1} .

In the first stage, MBr was copolymerized with St in the presence of AIBN at 70°C to obtain alternating copolymers having one reactive bromine group in every repeating unit. In the second stage, the ATRP of MMA was performed with the obtained Br functional polymers as an initiator.

Synthesis of alternating copolymers of St and MBr by the FRP mechanism

St and Maleimide represent a monomer pair with a strong tendency towards radical alternating copoly-

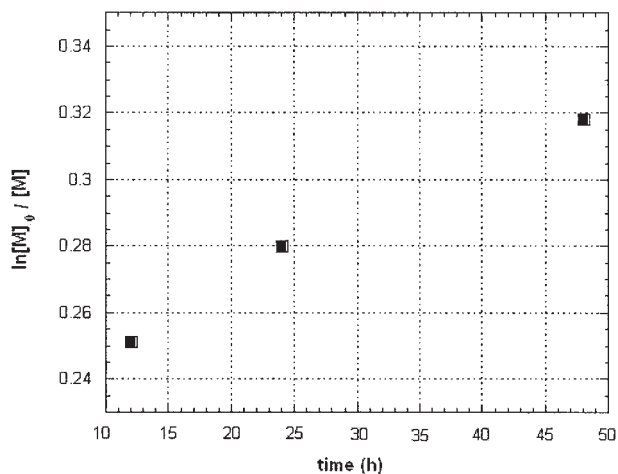


Figure 4 Semilogarithmic kinetic plot for the copolymerization of MMA initiated by C2.

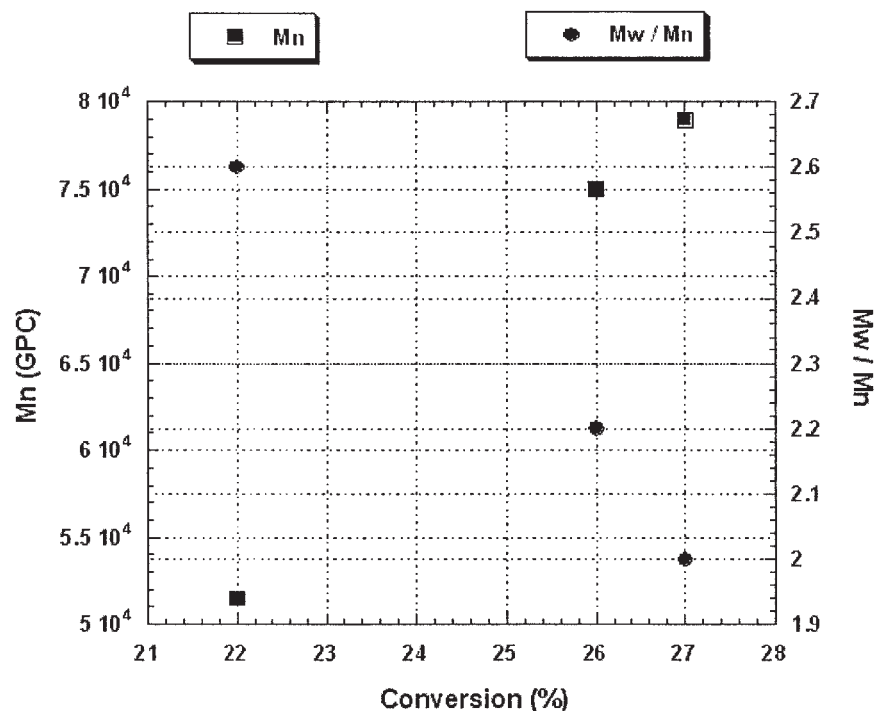


Figure 5 Dependence of molecular weight and polydispersities on conversion of graft copolymerization of MMA with C2.

merization. The copolymerization of these monomers proceeds much faster than their homopolymerization when St and MBr were copolymerized according to FRP in the presence of AIBN as an initiator (Scheme 3). Typical results concerning the copolymerization of St with MBr are presented in Table I.

The ¹H NMR spectrum of a typical alternating copolymer displays signals at 1.7 ppm (CH₃), 2.3–2.6 ppm (CH₂, CH of St), 4.3 ppm (—CH—Br and maleimide ring protons), 5.3 ppm (O—CH₂), and 6.5–7.1 ppm (C₆H₅). Ratio of the monomer units in alternating copolymer was determined by the integral areas in the ¹H NMR spectrum. (Fig. 2)

TABLE II
Graft Copolymerization of C3 by ATRP^a at 110°C

Run	[M] ₀ (mol/L)	Time (h)	Conv. (%)	M _n ^b	M _n ^c	M _w /M _n ^b
C1-G1	1.8	12	7.8	36,000	34,800	2.4
C1-G2	1.8	24	8.2	39,700	34,900	2.1
C1-G3	1.8	48	11	42,600	38,600	1.9
C2-G1	1.8	12	22.0	51,500	61,800	2.6
C2-G2	1.8	24	26.0	75,000	64,000	2.2
C2-G3	1.8	48	29.0	79,000	63,600	1.8
C3-G1	1.8	12	18.0	74,000	46,750	2.0
C3-G2	1.8	24	18.4	75,150	58,300	1.9
C3-G3	1.8	48	21.0	78,600	49,330	1.5

^a [I]₀ : [CuBr]₀ : [Bpy]₀ : [MMA]₀ = 1 : 4 : 12 : 800.

^b Determined from GPC, based on PMMA standards.

^c Calculated by ¹H NMR.

Synthesis of graft copolymers of MMA by ATRP

[poly(MBr)-*alt*-poly(St)]-*g*-poly(MMA) copolymers with different MWs and polydispersities were synthe-

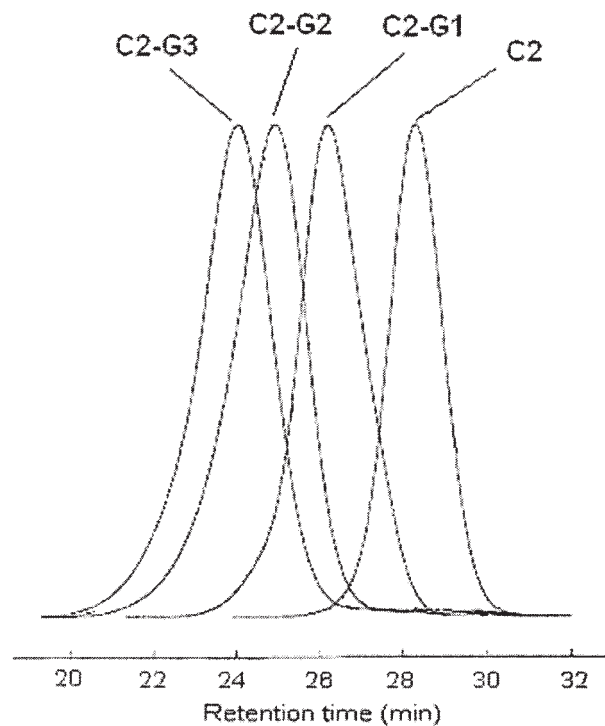


Figure 6 GPC traces of C2 and C2-G1, C2-G2, and C2-G3.

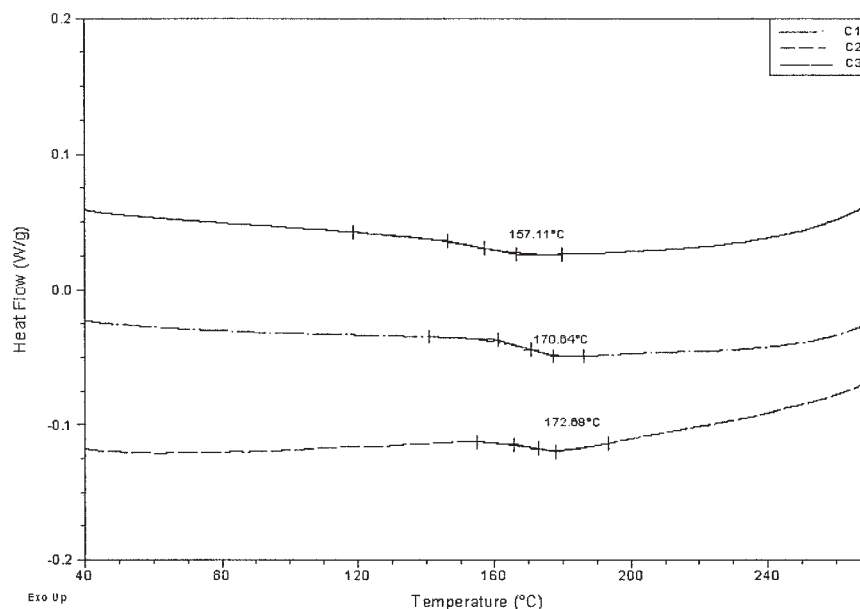


Figure 7 DSC thermograms of precursor copolymers.

sized via ATRP of MMA in anisole at 110°C using CuBr-complexed bpy (Scheme 4).

^1H NMR spectrum indicates the presence of OCH_3 protons at 3.58 ppm. The disappearance of CH-Br signal could not be confirmed for [poly(St)-*alt*-poly(MBr)]-g-poly(MMA), because of the overlapping of the signal resulting from —CH protons of maleimide (Fig. 3). But these protons were shifted to $\delta = 2.0$ –2.6 ppm by the consumption of bromine in ATRP.

Under typical reaction conditions, a linear semilogarithmic plot of monomer conversion versus time was observed, indicating that the apparent propagation rate constant was first-order in the monomer concentration; this implied that the concentration of the growing radicals stayed constant during the polymerization, regardless of the initial concentration of the initiator for 48 h reaction time (Fig. 4). Also, dependence of MW and polydispersities on conversion of copolymerization of MMA with C2 can be seen in Figure 5.

Theoretical MWs were calculated from ^1H NMR spectrum, according to the following equation³¹:

$$M_{n(\text{NMR})} = M_{n(\text{first monomer})} \left(1 + X \frac{MW_{2\text{nd monomer}}}{MW_{\text{first monomer}}} \right) + Y M_{n(\text{first monomer})}$$

X is the molar ratio of 2nd monomer units to 1st monomer units in copolymer, measured by ^1H NMR. Y is the percent of maleimide unit in alternating copolymer, measured by ^1H NMR. The $M_{n(\text{first monomer})}$ value is based on the apparent MW of poly(MBr)-*alt*-

poly(St) estimated by GPC, using polystyrene standards. The calculated values are in Table II.

GPC analysis showed that the MW of the copolymer increased after the graft copolymerization of MMA. The monomodal shape of the GPC trace of the obtained polymer suggests the formation of graft copolymer without homopolymerization (Fig. 6).

The polydispersities of the resulting graft copolymers were relatively low compared to that of the precursor copolymers. The precise MW of the copolymers could not be determined directly from the GPC data, because of the difference in hydrodynamic volumes between graft copolymers and linear PSt standards. This was confirmed by comparing the M_n of the polymers that were determined by GPC and ^1H NMR (Table II).

As shown in Table I, the average MW of C3 is 32,600 and the polydispersity is 5.2. During the graft copolymerization of C3 with MMA for 12, 24, and 48 h with the same ratios of macroinitiators, the average MWs increased to 74,000, 75,150, and 78,600 while polydis-

TABLE III
DSC and TGA Data for Precursor Polymers and Graft Copolymers

Polymers	T_g (°C)	$T_{50\%}$ (°C)	Residue at 500°C (%)
C1	170	398.4	16.0
C2	173	394.7	17.1
C3	157	388.2	13.0
C1-G1	218	398.4	13.7
C1-G2	225	400.2	14.2
C1-G3	231	399.8	15.9

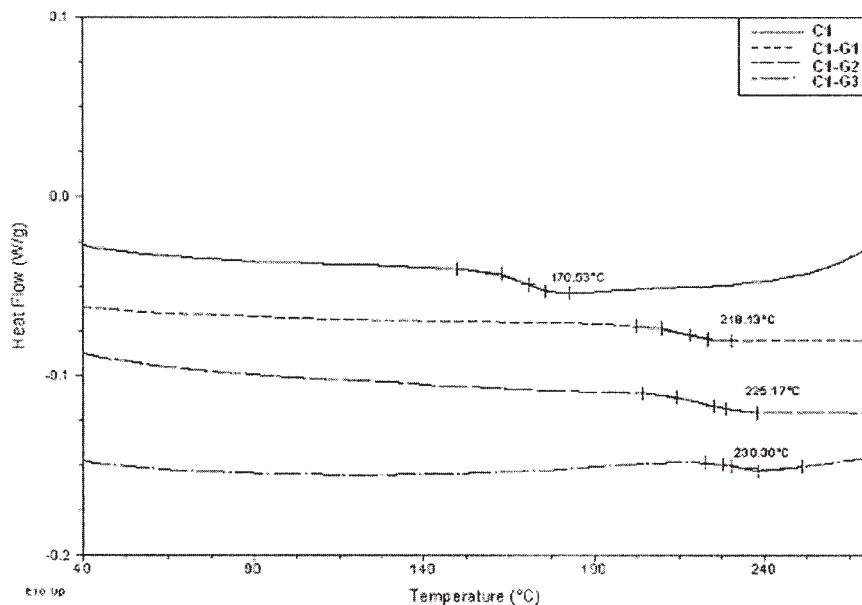


Figure 8 DSC thermograms of C1 and C1-G1, C1-G2, and C1-G3.

persities were decreased to 2.0, 1.9, and 1.5, respectively, (Table II). The polydispersity almost remains constant for the first two and decreases slightly for the last, whereas the MW increases in the graft copolymerization. Similar behavior was also observed for the other graft copolymers (Table II).

Effectiveness of the graft copolymerization was also proved by thermal analysis. DSC measurements were performed to know the behavior of phase separation on the graft copolymers as compared with precursor copolymer (C1-C3) samples (Fig. 7).

T_g values of the graft copolymers are listed in Table III. In the cases of C1, C2, and C3, only a single transition whose value changes from 157 to 170°C is detected in their respective DSC thermograms. Figure 8 shows a DSC thermogram of a representative graft copolymer, the T_g values of copolymers decreases with increasing content of MI in the copolymers.

Attachment of MMA groups to a polymer backbone will have opposing effects: the bulky MMA groups will severely hinder main chain motions slowing down the molecular dynamics and thus increasing the

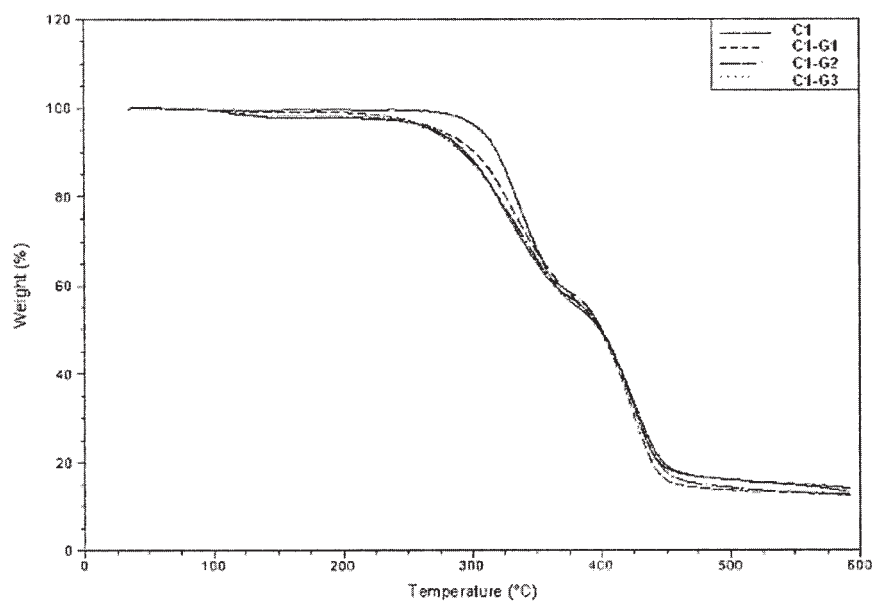


Figure 9 TGA thermograms of C1 and C1-G1, C1-G2, and C1-G3.

T_g .^{32,33} Additionally the increase in T_g values result from the rigidity of maleimide units and their ability to form hydrogen bonds.

The TGA results of the different graft copolymers and precursor copolymers are summarized in Table III and traces of some of them are shown in Figure 9. The 50% weight loss temperature has been assumed simply as a measurement of thermal stability, and in Table III represents the temperature of 50% mass loss, $T_{50\%}$. All the selected graft copolymers indicate a lower temperature for 50% weight loss relative to their precursor copolymers, and they leave residue in a lower ratio than their precursor copolymers. Obviously, it is the incorporated five member cyclic structure in the copolymer chain that improves the materials thermal stability. C1 and its graft copolymers C1-G1, C1-G2, and C1-G3 show good thermal stability. Initial thermal degradation temperature and $T_{50\%}$ are higher than those of neat PMMA, which means that the graft copolymer exhibits a better thermal stability than that of PMMA.

They did not show any change in appearance when heated up to 250°C. Furthermore, TGA was carried out in a nitrogen stream. From the thermograms, apparent loss could be observed below 225°C. Precursor copolymers and graft copolymers begin to degrade at around 225°C and perform a two-stage decomposition, losing about 50% of its weight at 400°C. The other 50% decomposes completely at about 500°C. It is known that PMMA is liable to degradation at high temperature.

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