

Synthesis and Characterization of Amphiphilic Block Copolymers of Methyl Methacrylate with Poly(ethylene oxide) Macroinitiators Formed by Atom Transfer Radical Polymerization

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ABSTRACT: Amphiphilic ABA triblock copolymers of poly(ethylene oxide) (PEO) with methyl methacrylate (MMA) were prepared by atom transfer radical polymerization in bulk and in various solvents with a difunctional PEO macroinitiator and a Cu(I)X/*N,N,N',N'',N''*-pentamethyldiethylenetriamine catalyst system at 85°C where X=Cl or Br. The polymerization proceeded via controlled/living process, and the molecular weights of the obtained block copolymers increased linearly with monomer conversion. In the process, the polydispersity decreased and finally reached a value of less than 1.3. The polymerization followed first-order kinetics with respect to monomer concentration, and increases in the ethylene oxide repeating units or chain length in the macroinitiator decreased the rate of polymerization. The rate of polymerization of MMA with the PEO chloro macroinitiator and CuCl proceeded at approximately half the rate of bromo analogs. A faster rate of polymerization and controlled molecular weights with lower polydispersities were observed in bulk polymerization compared with polar and nonpolar solvent systems. In the bulk polymerization, the number-average molecular weight by gel permeation chromatography ($M_{n,GPC}$) values were very

close to the theoretical line, whereas lower than the theoretical line were observed in solution polymerizations. The macroinitiator and their block copolymers were characterized by Fourier transform infrared spectroscopy, ¹H-NMR, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, thermogravimetry (TG)/differential thermal analysis (DTA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). TG/DTA studies of the homo and block copolymers showed two-step and multistep decomposition patterns. The DSC thermograms exhibited two glass-transition temperatures at -17.7 and 92°C for the PEO and poly(methyl methacrylate) (PMMA) blocks, respectively, which indicated that microphase separation between the PEO and PMMA domains. SEM studies indicated a fine dispersion of PEO in the PMMA matrix. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 989–1000, 2005

Key words: atom transfer radical polymerization (ATRP); block copolymers; differential scanning calorimetry (DSC); living polymerization

INTRODUCTION

The synthesis of block copolymers is one prospective approach in polymer modification because the appropriate design of block copolymer architecture with segments of various chemical composition results in interesting physicochemical properties. Poly(ethylene glycol) (PEG) is one of the common hydrophilic polymers studied, which has potential applications in variety of fields,^{1,2} including biology, biomedical science, surface chemistry, and electrochemistry, due to its unique properties, such as solubility and flexibility of the chains and basicity of the ether oxygen in the main chain. It is used as a carrier polymer because of its

biocompatibility, solubility in water and organic solvents, and its availability in a wide range of molecular weights. Block copolymers comprising both hydrophilic and hydrophobic blocks are of considerable interest for various applications, and these materials could be used as surfactants, dispersion stabilizers, and compatibilizers.^{3,4}

Among several techniques available for the synthesis of block copolymers, anionic,^{5,6} cationic,⁷ ring-opening metathesis polymerization,⁸ and redox polymerization^{9,10} have been studied extensively. A need for high purity of monomers, solvents, and reagents and low temperatures are usually required, and hence, ionic polymerization has to meet with relatively stringent requirements for the preparation of well-defined polymers for commercial applications. Recent developments in controlled/living radical polymerization^{11–13} (CRP) have made it possible to synthesize controlled polymer architectures, usually only accessible by living ionic polymerization. CRP meth-

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ods offer an efficient way to prepare well-defined polymers with predetermined molecular weights, narrow molecular weight distributions, and well-controlled architectures, compositions, and terminal functionalities in systems where the contributions of side reactions are negligible.

Much progress in CRP has been made toward better control of polymerization in (a) nitroxide-mediated radical polymerization^{14,15} (stable free-radical polymerization), (b) metal-mediated polymerization,¹⁶ (c) reversible addition and fragmentation chain-transfer processes,¹⁷ and (d) atom transfer radical polymerization (ATRP).^{18–21} Controlled polymerization of ATRP is achieved by the establishment of a dynamic equilibrium between the propagating and dormant species with copper complexes acting as reversible halogen atom-transfer agents.^{18,19} As a result, the concentration of the propagating species is greatly lowered, and the contribution of termination to the overall reaction is suppressed.

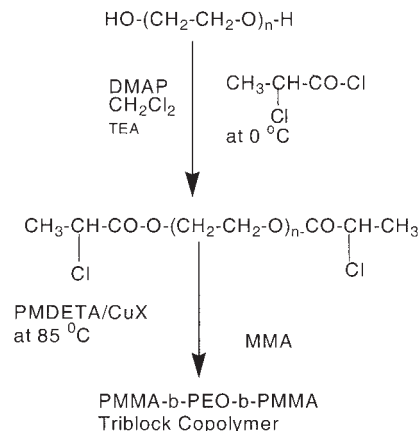
ATRP is a convenient method for the preparation of block copolymers because the macroinitiator can initiate the polymerization of a second monomer in the presence of a catalyst to form an AB- or ABA-type block copolymer.^{22–24} The 2-halopropionate end group is one efficient initiator for forming block copolymers in CRPs. Several research groups have reported the synthesis by this technique of AB- and ABA-type block copolymers with monofunctional and bifunctional poly(ethylene oxide) (PEO) macroinitiators with styrene,^{25,26} tert-butyl acrylate,²⁷ 2-hydroxyethyl methacrylate,²⁸ methyl methacrylate,^{29,30} and other hydroxyl-terminated oligomers^{31,32} as precursors.

The article deals with the detailed synthesis, kinetics, and characterization of amphiphilic ABA poly(methyl methacrylate) (PMMA)-*b*-PEO-*b*-PMMA triblock copolymers with varying number-average molecular weights (M_n 's) of PEO bifunctional macroinitiators in conjunction with Cu(I)X/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), where X=Cl or Br, as a catalyst in bulk or in solution under ATRP conditions.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA; E. Merck, Bombay, India) was purified by washing with 5% sodium hydroxide solution and then with distilled water. MMA was then dried over anhydrous sodium sulfate overnight, fractionally distilled at a reduced pressure over CaH₂, and stored in a refrigerator under nitrogen. PEG (M_n = 1000–10,000) (Aldrich, and S. D. Fine, Bombay, India) were dried by the removal of residual water by azeotropic distillation with toluene before use. Traces of residual toluene were removed under high vacuum. 4-(Dimethylamino) pyridine (DMAP; 98%, Fluka, Switzerland) was recrystallized from toluene. 2-Chloropropionyl chloride (97%, Fluka, Switzerland), 2-bromopropionyl



Scheme 1

chloride (technical grade, Aldrich, Milwaukee, WI), PMDETA (99%, Aldrich, Milwaukee, WI), Cu(I)Cl (>99%, Aldrich, Milwaukee, WI), and CuBr (99%, Fluka) were received and used without further purification. Triethylamine (TEA; SRL, Bombay, India) was refluxed with *p*-toluenesulfonyl chloride distilled and stored over CaH₂. All other solvents were purchased from commercial sources and used after standard purification procedures.

Preparation of PEO macroinitiators

PEO macroinitiators were prepared from commercially available PEG of varying M_n 's and 2-halopropionyl chloride according to a literature procedure²⁵ with TEA as a base.

Polymerization procedure: ATRP of MMA with a PEO bifunctional macroinitiator

PMMA-*b*-PEO-*b*-PMMA triblock copolymers were synthesized by either bulk or solution polymerization, as represented in Scheme 1. In a typical bulk polymerization, a dry glass tube was charged with 2 equiv of Cu(I)X, 2 equiv of PMDETA, and 1 equiv of PEO telechelic macroinitiator and subsequently evacuated and filled with nitrogen. MMA (5 mL, 0.047 mol) was added under a nitrogen atmosphere, and the reaction mixture was degassed via three freeze-thaw cycles. The polymerization was carried out at 85°C and terminated by rapid cooling to room temperature. In the kinetic studies, at various time intervals, the tube was removed from the oil bath, and the polymer was dissolved in dichloromethane and passed through a basic alumina column to remove the copper catalyst. The polymer solution was precipitated in an excess of hexane and dried *in vacuo* at room temperature.

Purification of block copolymers

The precipitated polymer was extracted twice with distilled water at room temperature to remove possi-

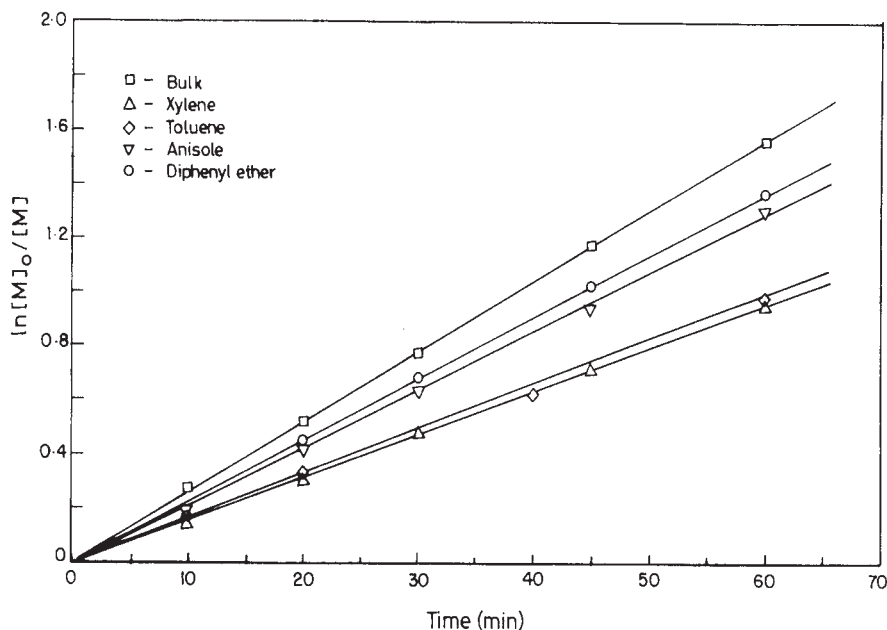


Figure 1 First-order kinetic plots of the ATRP of MMA initiated by a bifunctional PEO 1500 chloro macroinitiator with a CuCl/PMDETA catalyst in various solvent systems at 85°C ($[M] = 9.4M$; $[M]/[I]_0 = 141$, where $[I]_0$ = initiator concentration at $t = 0$ $[I]/[CuCl]/[PMDETA] = 1:2:2$; monomer/solvent ratio = 50% v/v).

ble unreacted PEO macroinitiator, and the purified product was dried *in vacuo* at room temperature, and the yield was determined gravimetrically.

Characterization

The structures of the reactants, macroinitiators, and block copolymers were characterized by Fourier trans-

form infrared (FTIR) spectroscopy on a Nicolet Impact 400 FTIR spectrometer (Madison, WI) with the KBr pellet technique. 1H -NMR spectra were recorded on a 300-MHz Bruker MSL Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer (Karlsruhe, Germany). $CDCl_3$ was used as a solvent, and tetramethylsilane served as an internal standard. The M_n and molecular weight distribution [polydispersity (M_w/M_n), where

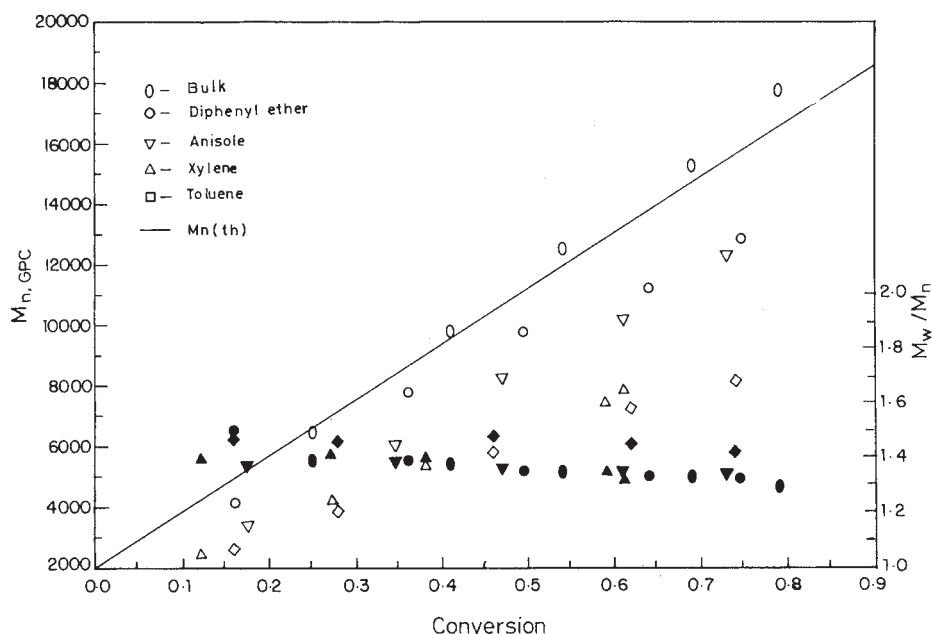


Figure 2 M_n (open symbols) and M_w/M_n (filled symbols) as a function of monomer conversion for the ATRP of MMA initiated by a bifunctional PEO 1500 chloro macroinitiator in various solvent systems at 85°C ($[M] = 9.4M$; $[M]/[I]_0 = 141$; $[I]/[CuCl]/[PMDETA] = 1:2:2$; monomer/solvent ratio = 50% v/v).

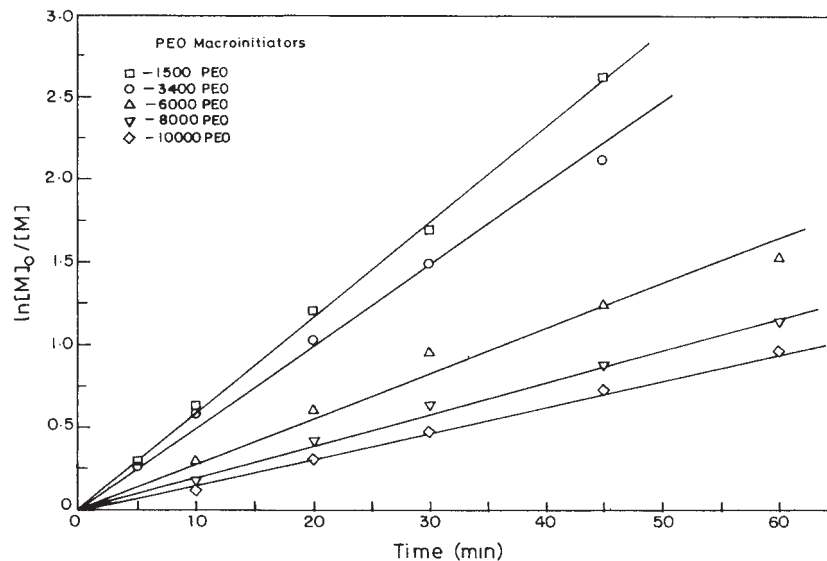


Figure 3 First-order kinetic plots of the bulk polymerization of MMA initiated by various molecular weights [1500, 3400, 6000, 8000, and 10,000] of bifunctional PEO chloro macroinitiators with a CuCl/PMDETA catalyst ($[M] = 9.4M$; $[I]/[CuCl]/[PMDETA] = 1:2:2$).

M_w is the weight-average molecular weight]) of the PEO macroinitiators and their block copolymers were determined by gel permeation chromatography (GPC) with a Waters 515 liquid chromatograph (Milford, MA) equipped with four Ultrastaygel columns (guard and 10^3 , 10^4 , and 10^5 Å) and a 410 RI detector. Measurements were performed in tetrahydrofuran as the eluent at $40^\circ C$ with a flow rate of 1 mL/min, and the calibration was based on linear polystyrene standards.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS, Kyoto, Japan) were recorded with a KRA TOS PC, Kompact SEQ analytical mass spectrometer, with the incorporation of a 337-nm nitrogen laser with a desorption/ionization pulse-width duration of 3 ns and a multiplier detector. The instrument was operated in delayed-extraction mode with an accelerating potential of 20 kV, and 2,5-dihydroxybenzoic acid was used as the matrix.

A Seiko model SSC5200H system (Nagano, Japan) attached to a differential scanning calorimeter and a thermogravimetric analysis module was used to determine the thermograms. The measurements were carried out at heating rates of 5 and $20^\circ C/min$ in a nitrogen atmosphere. The equipment was calibrated with indium and tin standards. The surface morphologies of the homo and block copolymers were examined with a Jeol JSM-35CF scanning electron microscope (Yamagata, Japan). The samples were dried *in vacuo*. Each sample was sputter-coated with gold under argon at 2.5 kV and 20 mA before analysis, and scanning electron microscopy (SEM) scans were taken at 10 kV.

RESULTS AND DISCUSSION

A series of ABA triblock copolymers of PEO with MMA was synthesized by means of ATRP. The synthesis of macroinitiator was achieved by the reaction of 2-chloropropionyl chloride or 2-bromopropionyl chloride with PEG in the presence of a base. The macroinitiator and its block copolymer were characterized by spectroscopic methods, and the kinetics of block copolymers were performed in bulk and various solvents.

Kinetics: Polymerization of MMA with a bifunctional PEO macroinitiator and a Cu(I)X/PMDETA catalyst system

ATRP is based on reversible halogen transfer between alkyl halides and transition metal complexes in the lower oxidation state to form radicals and transition metal complexes in a higher oxidation state. The dynamic equilibrium between the active radicals and dormant alkyl

TABLE I
 k^{app} Values for the MMA Polymerization with Bifunctional PEO Macroinitiators

Initiator	$[MMA]/[initiator]^a$	k^{app} ($10^{-4} s^{-1}$)
PEO 1500	40	9.415
PEO 3400	80	6.656
PEO 6000	144	3.921
PEO 8000	195	3.123
PEO 10,000	493	2.708

$[M] = 9.4M$, initiator/CuCl/PMDETA = 1/2/2, temperature = $85^\circ C$.

^a Molar ratio.

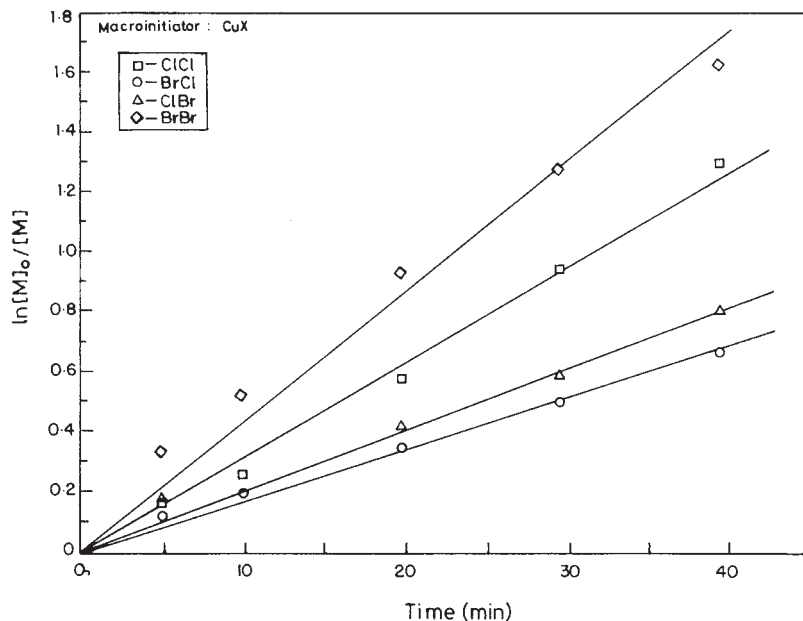


Figure 4 First-order kinetic plots for the bulk polymerization of MMA initiated by a PEO 1500 Cl/Br macroinitiator combination of CuCl and CuBr at 85°C ($[M]/[I]_0 = 141$; $[I]/[CuX]/[PMDETA] = 1:2:2$).

halides leads to control over the polymerization by the maintenance of a low concentration of active radicals and a predetermined concentration of total propagating species (active radicals plus dormant species) and to insignificant termination reactions.

Linear multidentate amines, such as PMDETA and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) in conjunction with cuprous halides, are efficient and are the most widely studied ATRP catalyst systems. The stronger catalytic activity of these amines is due to the lower redox potential value than the (substituted) bipyridine ligands.

Effect of solvents

ATRP can be carried out in bulk, in solution, or in a heterogeneous system. Various solvents, such as protic, aprotic, and nonpolar solvents, are used, depending on the monomer and catalyst system. Solvents such as xylene, toluene, anisole, and diphenyl ether were investigated for the ATRP of MMA with a CuCl/PMDETA catalyst at 85°C; this was initiated by a bifunctional PEO 1500 chloro macroinitiator, with a monomer concentration of 50% v/v for all reactions. The first-order kinetic plots of the poly-

TABLE II
Bulk Polymerization of MMA with PEO Bifunctional Chloro Macroinitiators

Sample	Macroinitiator (M_w/M_n) ^a	Conversion (%) ^b	$[M]/[I]$ ratio	$M_{n,th}$ ^c	$M_{n,GPC}$	M_w/M_n
1	PEO(CIP) ₂ -1030 (1.11)	68	48	4,300	24,100	1.33
2	PEO(CIP) ₂ -1710 (1.07)	44	80	5,260	19,500	1.38
3	PEO(CIP) ₂ -2360 (1.11)	83	110	11,500	41,080	1.34
4	PEO(CIP) ₂ -3420 (1.07)	67	161	14,200	159,00	1.38
5	PEO(CIP) ₂ -4120 (1.09)	90	195	21,700	13,650	1.20
6	PEO(CIP) ₂ -6150 (1.08)	86	290	31,200	66,900	1.40
7	PEO(CIP) ₂ -8290 (1.07)	45	195	17,000	42,400	1.25
8	PEO(CIP) ₂ -9450 (1.11)	54	223	21,500	24,690	1.39
9	PEO(CIP) ₂ -10500 (1.09)	76	493	48,100	26,700	1.31
10	PMMA homopolymer ^d	92	100	9,210	14,120	1.20

$[M] = 9.4M$, initiator/CuCl/PMDETA = 1/2/2, temperature = 85°C; CIP = 2-chloropropionate

^a The number indicates the M_n of the PEO bifunctional chloro macroinitiator with polydispersities. Reaction time = 1 h.

^b Conversion determined by gravimetry.

^c $M_{n,th} = [M]/[I]_0 \times MW_{MMA} \times \text{Conversion} + M_{n,GPC}$, where $M_{n,th}$ is the number-average molecular weight (theoretical) and MW_{MMA} is the molecular weight of methyl methacrylate.

^d Synthesized by ATRP. MMA/CuCl/PMDETA/2-bromopropionitrile (BPN) = 100/1/1/1.

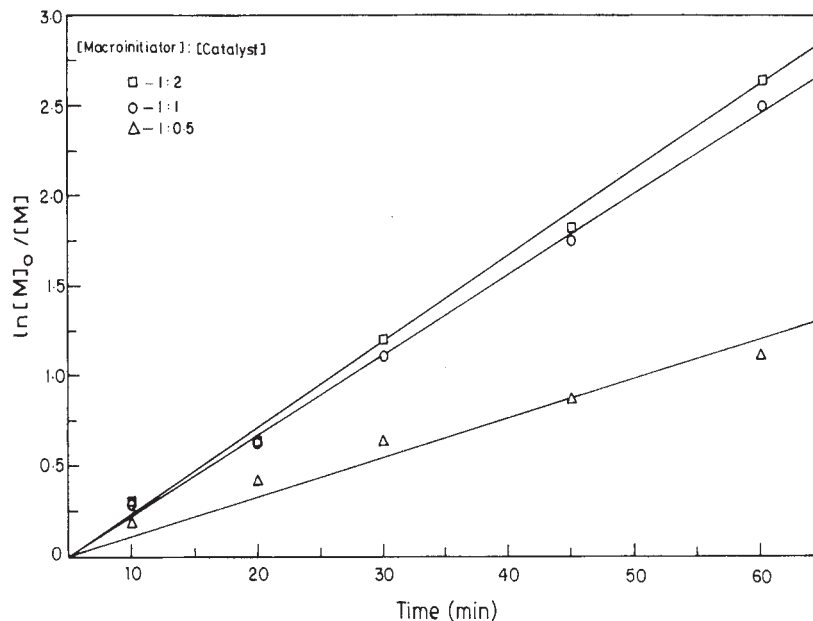


Figure 5 First-order kinetic plots for the bulk polymerization of MMA initiated by a PEO 1500 chloro macroinitiator at various catalyst ratios ($[M] = 9.4M$; $[M]/[I]_0 = 141$ at 85°C).

merization are shown in Figure 1. Bulk polymerization gave a faster rate of polymerization than the solvent system, and the first-order kinetic plots showed a straight line, which indicated that the concentration of the active species was constant during the polymerization. Polar solvents, such as anisole and diphenyl ether, gave a slower rate of polymerization than in the bulk, and less polar solvents,

such as xylene and toluene, gave much slower rates of polymerization than the polar systems. In agreement with the reported rate laws, bulk polymerization was expected to proceed at a faster rate than the polymerization in 50% solution. The resulting straight lines indicated that the polymerization proceeded in a controlled/living process, and the contribution of side reactions was insignificant.

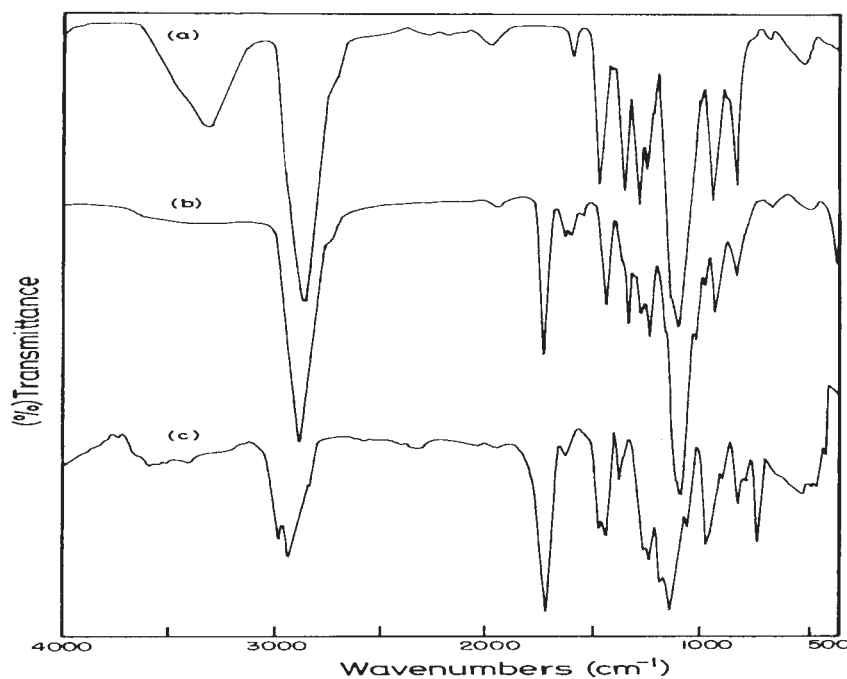


Figure 6 FTIR spectra of (a) PEG 1500, (b) PEO 1500 chloro macroinitiator, and (c) PMMA-*b*-PEO-*b*-PMMA triblock copolymer.

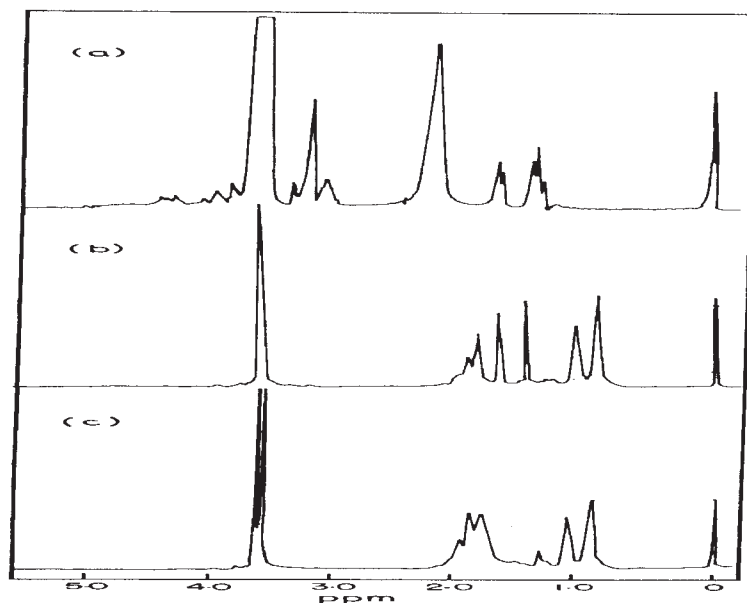


Figure 7 $^1\text{H-NMR}$ spectra of (a) PEO macroinitiator, (b) PMMA homopolymer, and (c) PMMA-*b*-PEO-*b*-PMMA triblock copolymer.

The plots of molecular weight evolution (M_n) and molecular weight distribution (M_w/M_n) as a function of monomer conversion in bulk and in different solvent systems are shown in Figure 2. In bulk polymerization, the molecular weights increased linearly with conversion, and the number-average

molecular weight by gel permeation chromatography ($M_{n,GPC}$) values were close to the theoretical line. However, the polymerization in solution systems gave values lower than the theoretical line. The M_w/M_n values of 1.2–1.5 showed an expected trend, and those values decreased with in-

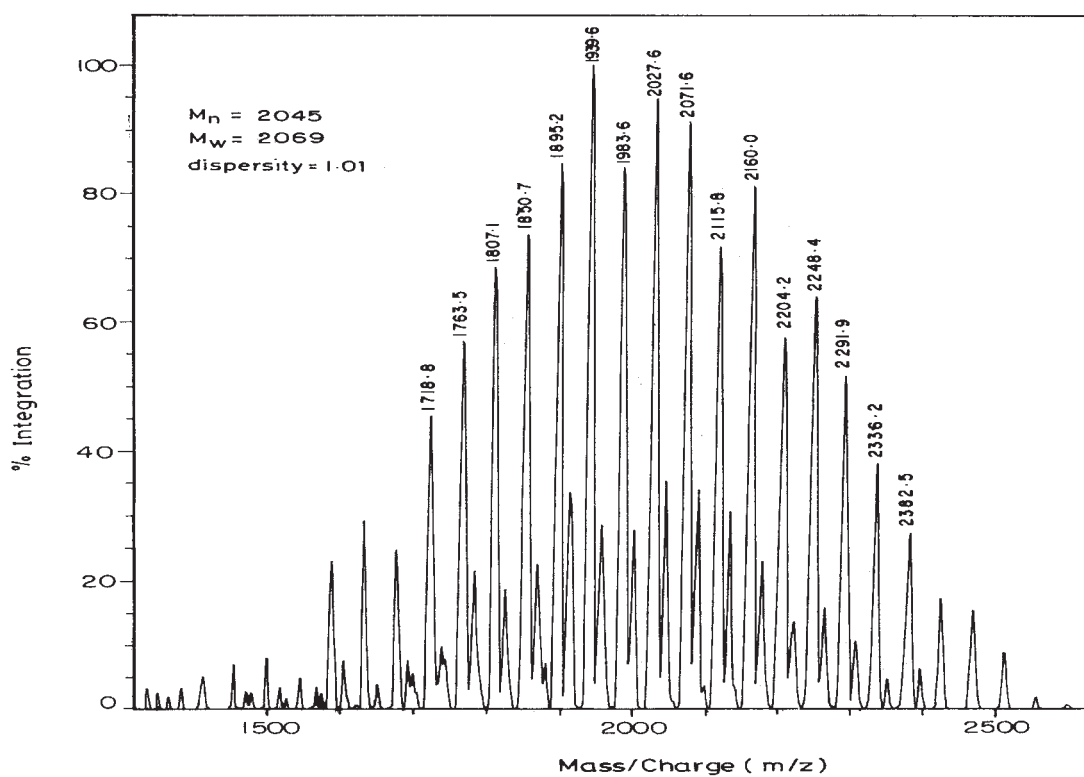
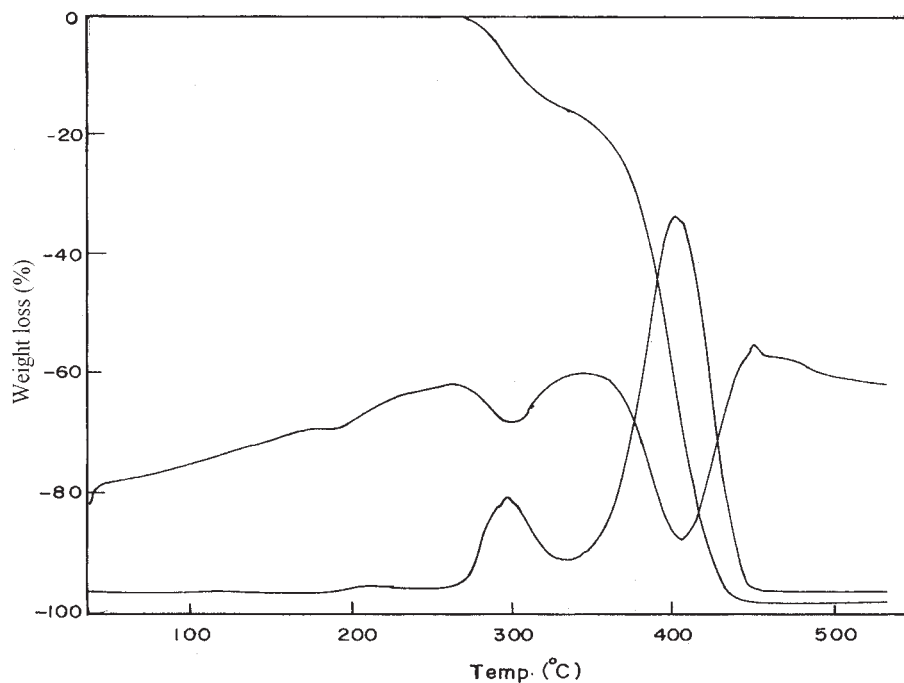
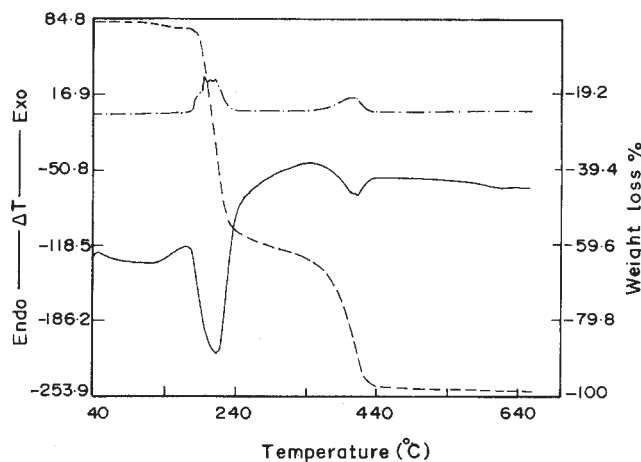


Figure 8 MALDI-TOF MS PEO 2000 bromo macroinitiator.



(a)



(b)

Figure 9 TG/DTA traces of the (a) PMMA homopolymer and (b) PMMA-*b*-PEO 8000-*b*-PMMA block copolymer.

creasing conversion in all of the polymerization systems.

Effect of PEO molecular weight

The first-order kinetic plots of the polymerization of MMA with the varying M_n 's of bifunctional initiators, such as PEO 1500, 3400, 6000, 8000, and 10,000, are shown in Figure 3. The plots are straight lines and show that the rate of polymerization decreased with increasing number of ethylene oxide (EO) repeating units in the PEO macroinitiator. This could have been due to the decrease in the initiator concentration with

increasing molecular weight of PEO macroinitiator. The apparent rate constants (k^{app} 's)²⁸ were calculated from the equation $k^{app} = k_p[P^0]$, where k_p is the polymerization rate constant and P^0 is the polymer radical concentration, and the values are summarized in Table I.

Effect of a mixed halide system

The effects of the leaving group X on atom transfer radical block copolymerization are shown in Figure 4. Because the atom transfer process reflects the strength of the bond breaking and forming in M_n-X , it was

expected that the leaving group X could also strongly affect the rate of polymerization. As shown in Figure 4, the ATRP of the PEO-Br/CuBr system showed a faster rate of polymerization than the PEO-Cl/CuCl system and other mixed halide systems. This could be explained by the enhanced contribution of growing radicals in the former polymerization process compared to the latter. Br was a better leaving group for the production of a high concentration of radicals than the mixed halide systems, and C—Br bond breaking was much easier than C—Cl bond breaking. It has been previously reported that the presence of chlorine originating from either the initiator or the catalyst becomes the ω -terminal end of the polymers.^{33,34} For mixed halide systems, the rate of polymerization at equilibrium concentration indicated that Cu—Br predominated over the Cu—Cl as C—Cl was formed in preference to C—Br.

A series of block copolymers prepared with varying M_n 's of PEO macroinitiators and their results are summarized in Table II.

Effect of catalyst concentration

The dependence of the rate of polymerization with respect to the macroinitiator-to-catalyst concentration ratios are shown in Figure 5. The optimum ratio was found to be 1:1 with the rate of polymerization increasing significantly as the catalyst concentration was raised from a ratio of 1:0.5. With a further increase in the catalyst concentration (to 1:2), there was no appreciable change in the rate of polymerization.

Structural characterization of the macroinitiators and their block copolymers

FTIR and ¹H-NMR studies

Representative FTIR spectra of PEG 1500, PEO chloro macroinitiator, and their block copolymers are shown in Figure 6. In the spectrum of PEG, the —C—O—C— and O—H stretching peaks were observed at 1113 and 3313 cm^{-1} . After the acetylation reaction, the O—H peaks disappeared, and the absorption of the C=O peak at 1743 cm^{-1} was observed correspondingly in the spectrum. The results further prove that O—H end groups were converted to the telechelic macroinitiator (substitution of 2-halopropionate end groups). The spectrum of the block copolymer exhibited characteristic peaks (2952, 1482, 1389, and 1113 cm^{-1}) of both PEO and PMMA blocks. PMMA methylene peaks at 2952, 1482, and 1389 cm^{-1} were also observed in the block copolymers.

¹H-NMR spectra of the PEO macroinitiator, PMMA, and the corresponding block copolymers are shown in Figure 7. In the PEO macroinitiator, the O—H signal (4.85 ppm) completely disappeared, and a new signal appeared at 4.32 ppm due to substitution of 2-halo-

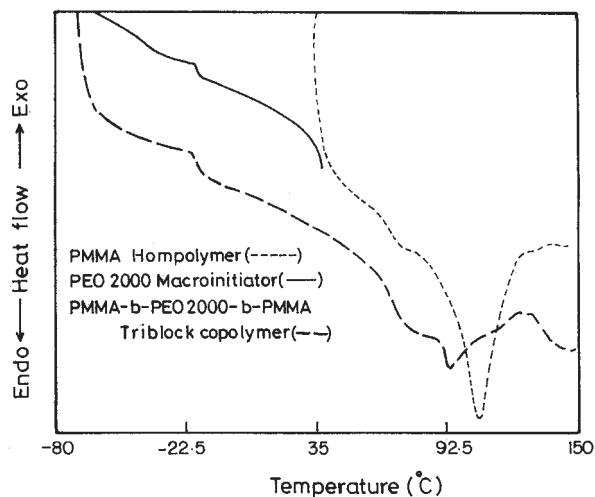


Figure 10 DSC thermograms of (a) PEO 2000 chloro macroinitiator, (b) PMMA homopolymer, and (c) PMMA-*b*-PEO 2000-*b*-PMMA triblock copolymer.

propionate end groups; the —CH₂—CH₂—O signal was observed at 3.66 ppm. PMMA showed a characteristic signal for the methoxy (OCH₃) group at 3.59 ppm in addition to the methylene protons at 1.88 ppm and α -methyl protons at 0.83 ppm [Fig. 7(b)]. The ¹H-NMR spectrum of a triblock copolymer showed characteristic signals of PEO (—CH₂—CH₂—O) at 3.66 ppm in addition to the PMMA methoxy (OCH₃) group at 3.59 ppm [Fig. 7(c)]. PMMA methylene protons at 1.88 ppm and α -methyl protons at 0.83 ppm were also observed in the block copolymer.

MALDI-TOF MS

End-group analysis of the PEO chloro telechelic macroinitiator was analyzed by MALDI-TOF MS, as shown in Figure 8. The M_n values determined by GPC and MALDI-TOF MS of the PEO 2000 bromo macroinitiator were GPC $M_n = 2160$ ($M_w/M_n = 1.07$) and MALDI-TOF MS $M_n = 2045$ ($M_w/M_n = 1.01$), respectively. After the substitution of 2-bromopropionate, the end groups showed narrow polydispersities. Two series of signals were observed in the spectra; within each series, the signals were separated by 44 molecular weight units, which corresponded to the molecular weight of the EO repeating units. The major series of peaks corresponded to [CH₃CH(Br)COO(CH₂—CH₂—O)_{*n*}—COCH(Br)CH₃ + Na⁺]. Thus, for the oligomer with degree of polymerization (DP_n) = 37, the calculated mass was equal to 1938.96 for Na⁺ ions, whereas the observed mass was 1939.6. The small peaks corresponded to K⁺ ions. This led to the conclusion that only Na⁺ ion peaks were more intensely observed in the spectra, and this was very close to the calculated mass values. The results of the MALDI-TOF MS analysis showed the complete substitution of PEG with 2-halopropionate end groups, and no frag-

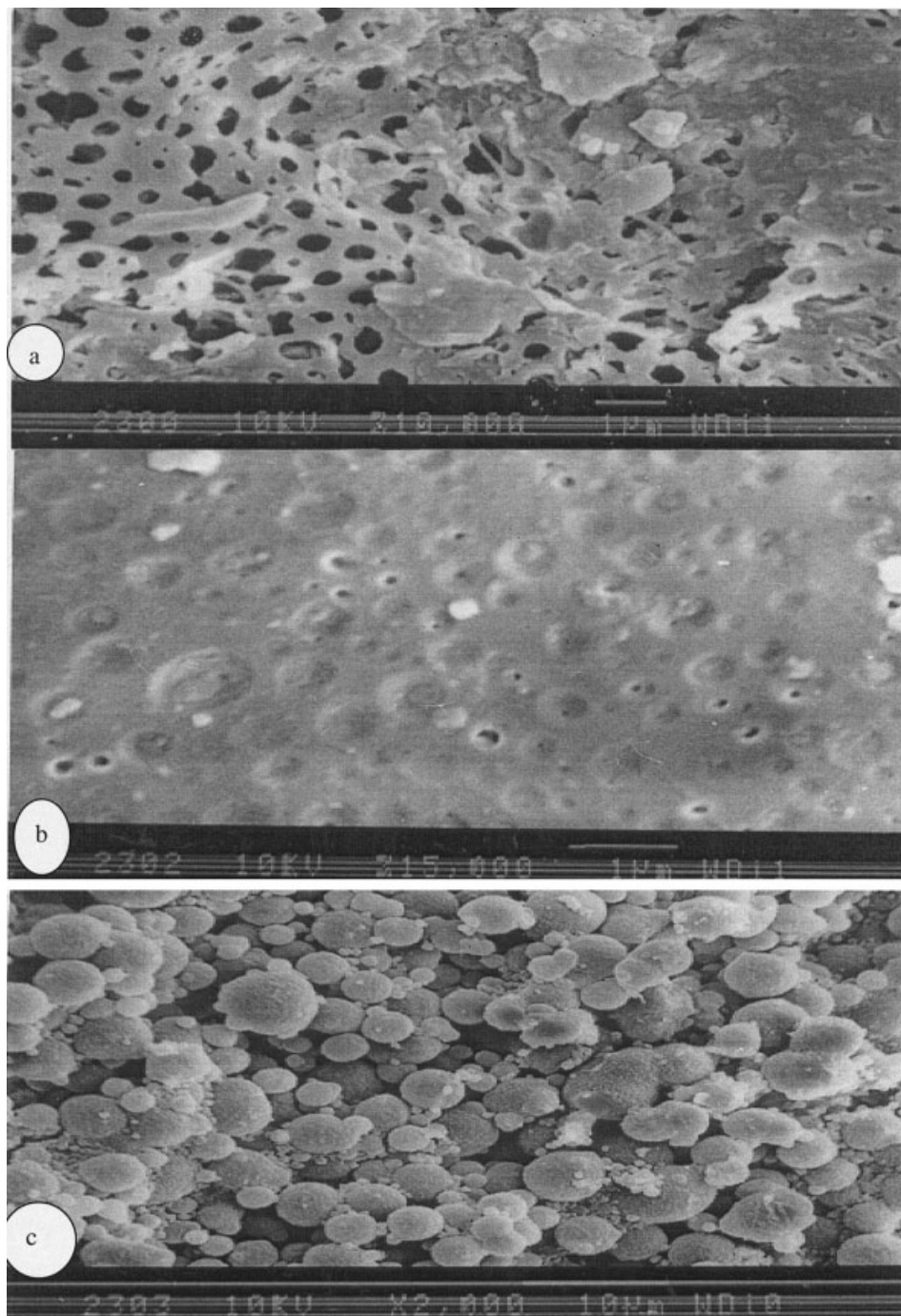


Figure 11 SEM photographs of (a) PMMA homopolymer, (b) PMMA-*b*-PEO 1000-*b*-PMMA triblock copolymer, and (c) PMMA-*b*-PEO 6000-*b*-PMMA triblock copolymer.

ments such as HCl were observed. The M_n and M_w/M_n values calculated from MALDI-TOF MS were very close to the values obtained by GPC measurements.

Thermal studies

Thermogravimetry (TG)/differential thermal analysis (DTA) studies

The simultaneous combination of TG and DTA is an extremely powerful tool for the study of many types

of reactions, particularly the decomposition of end groups, free-radical polymerization, and living polymerization patterns. In these cases, the TG curve indicates whether a DTA peak is due to a physical or a chemical change. The TG/DTA tracings of PMMA and the PMMA-*b*-PEO 8000-*b*-PMMA triblock copolymers are shown in Figures 9(a) and 9(b), respectively. It is evident from Figure 9(a) that PMMA exhibited a two-stage decomposition profile, with approximately 50% of the sample degrading at 395°C, whereas the

complete degradation was observed at 441°C. Actually, thermal degradation under nitrogen of the free-radically prepared PMMA proceeded in three steps corresponding to the head-to-head linkage (ca. 165°C), the chain-end initiation from the vinylidene ends (ca. 270°C), and the third step, referred to as *random scission within the polymer chain* (ca. 360°C).³⁵ Thermal degradation of the polymers synthesized by ATRP occurred around 375°C, which only originated from random scission and indicated the absence of linkages, such as head-to-head linkages and vinylidene ends, and thereby confirmed the high regioselectivity and the absence of termination reactions.³⁶ The PMMA synthesized by CuBr/PMDETA/M2-BP showed a two-step degradation, with steps corresponding to the (1) chain-end initiation from the vinylidene ends (ca. 271°C) and (2) random scission within the polymer chain (ca. 356°C). The presence of vinylidene ends showed that some termination reactions were possible in this initiation system. The DTA profile of PMMA [Fig. 9(a)] showed two endothermic peaks at 298 and 406°C. The block copolymer revealed a two-stage decomposition at 251 and 370°C, and its DTA profile displayed two endotherms at 238 and 381.5°C [Fig. 9(b)].

Differential scanning calorimetry (DSC) studies

The DSC thermograms of the PEO 2000 chloro macroinitiator, PMMA, and PMMA-*b*-PEO 2000-*b*-PMMA triblock copolymers are shown in Figure 10. The PEO macroinitiator and PMMA homopolymer exhibited glass-transition temperatures (T_g) at -18.2 and 104°C, respectively. In the DSC thermogram of the block copolymer, the T_g of PEO was observed at -17.7°C in addition to the T_g of PMMA at 92°C. Melting of PEO was not observed in the block copolymer, which indicated a finer dispersion of PEO in the block copolymer. This observation was consistent with that in the literature,³⁷ which showed that at low PEO compositions (<25% PEO), PEO/PMMA exists as a single phase, and the PEO/PMMA system was compatible. The compatibility of PEG and PMMA chains in solutions of their blends and diblock and triblock copolymers were compared by Wohlfarth et al.,³⁸ and it was pointed out that the blends behaved differently from the block copolymers and the diblock and triblock copolymers behaved alike.

Morphological characteristics

The SEM photographs of PMMA, PMMA-*b*-PEO 1000-*b*-PMMA, and PMMA-*b*-PEO 6000-*b*-PMMA are shown in Figure 11(a-c). The high T_g values of the PMMA homopolymer exhibited a discontinuous phase or porous structure morphology, as shown in Figure 10(a). PMMA-*b*-PEO 1000-*b*-PMMA [Fig. 11(b)] exhibited a continuous phase, as a low- T_g PEO mate-

rial was incorporated in the block copolymer. The micrograph of the block copolymer PMMA-*b*-PEO 6000-*b*-PMMA showed a significant change with a fine dispersion of PEO in the PMMA matrix, as shown in Figure 11(c).

CONCLUSIONS

Well-defined amphiphilic triblock copolymers of PMMA-*b*-PEO-*b*-PMMA were synthesized by ATRP in bulk and in various solvents with varying M_n 's of bifunctional PEO macroinitiators with Cu(I)X/PMDETA as a catalyst system. The macroinitiator end groups were confirmed by MALDI-TOF MS. The rate of polymerization decreased with increasing EO repeating units in the macroinitiator. The rate of polymerization was first order with respect to monomer concentration, and the catalyst-to-macroinitiator concentration of 1:1 (molar ratio) showed an optimum rate of polymerization. In the bulk polymerization, the molecular weight of the obtained block copolymers increased linearly with conversion and was close to the theoretical line. In the solution polymerization, the molecular weights were found below the theoretical line. The first-order plots of \ln monomer concentration at $t = 0$ $[M]_0$ /monomer concentration $[M]$ versus time were linear, which indicated that the polymerization proceeded in a controlled/living process. The DSC thermogram of the block copolymer showed two T_g 's corresponding to the PEO and PMMA blocks.

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References

- Kim, Y. J.; Nagasaki, Y.; Kataoka, K.; Kato, M.; Yokoyama, M.; Okano, Y.; Sakurai, Y. *Polym Bull* (Berlin) 1994, 33, 1.
- PEG Chemistry; Harris, J. M., Ed.; Plenum: New York, 1993.
- Hillmyer, M. A.; Bates, F. S.; Almdal, K.; Mortensen, K.; Ryan, A. J.; Fairclough, J. P. *Science* 1996, 271, 976.
- Jianlanella, G. L.; Firer, E. M.; Piirma, I. *J Polym Sci Part A: Polym Chem* 1992, 30, 1025.
- Szwarc, M. *Nature* (London) 1956, 178, 1168.
- Heish, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
- Matyjaszewski, K. *Cationic Polymerizations: Mechanisms, Synthesis and Applications*; Marcel Dekker: New York, 1996.
- Novak, B. M.; Rise, W.; Grubbs, R. H. *Adv Polym Sci* 1992, 47, 102.
- Nagarajan, S.; Srinivasan, K. S. V. *J Polym Sci Part A: Polym Chem* 1995, 33, 2925.
- Nagarajan, S.; Srinivasan, K. S. V. *Macromol Rapid Commun* 1996, 17, 261.
- Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
- Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
- Hawker, C. J.; Bosmon, A. W.; Harth, E. *Chem Rev* 2001, 101, 3661.

14. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 2987.
15. Hawker, C. J. *J Am Chem Soc* 1994, 116, 11185.
16. Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J Am Chem Soc* 1994, 116, 7943.
17. 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.
18. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
19. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
20. Percec, V.; Barboiu, B. *Macromolecules* 1995, 28, 7970.
21. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7572.
22. Gao, B.; Chen, X.; Ivan, B.; Kops, J.; Batsberg, W. *Polym Bull (Berlin)* 1997, 39, 559.
23. Zhang, X.; Matyjaszewski, K. *Macromolecules* 1999, 32, 1763.
24. Kotani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1996, 29, 6979.
25. Jankova, K.; Chen, X.; Kops, J.; Batsberg, W. *Macromolecules* 1998, 31, 538.
26. Jankova, K.; Truelsen, J. H.; Kops, J.; Batsberg, W. *Polym Bull (Berlin)* 1999, 42, 153.
27. Bednarek, M.; Biedron, T.; Kubisa, P. *Macromol Rapid Commun* 1999, 20, 59.
28. Reining, B.; Keul, H.; Hocker, H. *Polymer* 2002, 43, 3139.
29. Reining, B.; Keul, H.; Hocker, H. *Polymer* 1999, 40, 3555.
30. Krishnan, R.; Srinivasan, K. S. V. *Eur Polym J* 2003, 39, 205.
31. Wang, X. S.; Luo, N.; Ying, S. K.; Liu, Q. *Eur Polym J* 2000, 36, 149.
32. Jankova, K.; Kops, J.; Chen, X.; Batsberg, W. *Macromol Rapid Commun* 1999, 20, 219.
33. Zeng, F.; Shen, Y.; Zhu, S.; Pelton, R. *Macromolecules* 2000, 33, 1628.
34. Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron* 1997, 53, 15445.
35. Hatada, K.; Kityama, T.; Fujimoto, N.; Nishiura, T. *Macromol Sci Pure Appl Chem* 1993, 30, 645.
36. Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* 1996, 29, 8576.
37. Liberman, S. A.; Des Gomes, A.; Macchi, E. M. *J Polym Sci Part A: Polym Chem* 1984, 22, 2809.
38. Wohlfarth, C.; Regener, E.; Raetzsch, M. T. *Makromol Chem* 1989, 190, 145.