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Poly(ethylene glycol) Block Copolymers by Atom Transfer Radical Polymerization-Synthesis, Kinetics and Characterization

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A series of block copolymers of poly(ethylene oxide) (PEO) with n-butyl methacrylate were prepared by atom transfer radical polymerization using varying number-average molecular weights of bifunctional PEO chloro macroinitiators and CuCl/HMTETA as a catalyst system at 85°C. The atom transfer radical polymerization of n-butyl methacrylate proceeds with a quantitative initiation, leading to ABA triblock copolymers. In bulk polymerization, the kinetic plot of $\ln[M]_0/[M]$ vs. time was linear showing that there is a constant concentration of active species present throughout the polymerization and follows the first-order kinetics with respect to monomer. Moreover, the experimental molecular weight of the block copolymers increased linearly with monomer conversion and polydispersities decrease from 1.4 to 1.3. There is no formation of homopolymer of n-butyl methacrylate, indicating that the blocking proceeds from the poly(ethylene oxide) macroinitiators. The structure of macroinitiators and their block copolymers were characterized by FTIR, ¹H NMR, MALDITOF MS and gel permeation chromatography. TG/DTA studies of the homo and block copolymers reveal single and multi-stage decomposition pattern. The DSC thermograms of block copolymer exhibited two glass transition temperatures (T_g) at -19.4 and 24.6°C due to the PEO block and P(nBMA) blocks, respectively indicating the micro-phase separation between the PEO and P(nBMA) domains.

SEM studies also indicated a fine dispersion of PEO in the P(nBMA) matrix.

Keywords ATRP, block copolymers poly(ethylene oxide) macroinitiator n-butyl methacrylate living polymerization

Introduction

Controlled/“living” polymerization methods offer an efficient way to prepare well-defined polymers in systems where the contribution of side reactions, such as irreversible chain transfer and chain termination is small or negligible (1, 2). Living polymerization can proceed via anionic, (1, 3) cationic, (2, 4, 5) group transfer, (6) metathesis, (7) Ziegler-Natta (8, 9) or radical mechanisms (10–15). These polymerization techniques give several advantages for the synthesis of block copolymers with well-defined structures; (1) sequential monomer addition (SMA) (2) coupling of living chains and (3) transformation of a growing chain end to a group capable of initiating polymerization of a second monomer.

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The development of controlled/"living" radical polymerization (CRP) method has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups, impurities and a leading industrial method to produce polymers. Further CRP technique is possible to control the polymerization to obtain polymers with predetermined molecular weights, narrow molecular weight distributions, well-defined compositions, architectures and end functionalities etc. (11–17).

Amphiphilic block copolymers are of considerable interest for various applications in which the combination of hydrophilic and hydrophobic properties of these materials may be utilized e.g., as emulsifiers, dispersion stabilizers and compatibilizers (18, 19). Poly(ethylene glycol) is one of the most common hydrophilic polymers studied, which has potential applications in a variety of fields, (20, 21) such as biology, biomedical science, surface chemistry, and electrochemistry, etc. 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.

Transition-metal mediated atom transfer radical polymerization (ATRP) is a convenient method to prepare block copolymers with various monomer classes (22, 23) because the 2-halopropionate end groups, which is an efficient initiator for ATRP polymerization, can easily be introduced as the end-group to different polymers obtained by ionic mechanism, either by direct termination of living ionic active species or by esterification of hydroxyl terminated polymers. The di and triblock copolymers of poly(ethylene oxide) with styrene, (24, 25) 2-hydroxyethyl methacrylate, (26) t-butyl acrylate (27) and methyl methacrylate, (28, 29) were obtained by the latter approach.

This paper deals with the synthesis and characterization of a series of amphiphilic ABA triblock copolymers of poly(ethylene oxide) with n-butyl methacrylate prepared by ATRP using varying number-average molecular weights of PEO bifunctional chloro macroinitiators in conjunction with CuCl/HMTETA as a catalyst at 85°C in bulk polymerization.

Experimental

Materials

n-Butyl methacrylate (BDH, India) was purified by washing with 5% sodium hydroxide solution, then with distilled water, and dried over anhydrous sodium sulfate overnight, then fractionally distilled at reduced pressure over CaH₂ and stored in a refrigerator under nitrogen. Poly(ethylene glycol) ($M_n = 1000$ to 10,000) (Aldrich, USA, and S. D. Fine, India) were dried by removing residual water by azeotropic distillation with toluene before use. Traces of residual toluene were removed in high vacuum. 4-(Dimethylamino)pyridine (DMAP, 98%, Fluka) was recrystallized from toluene. 2-Chloropropionyl chloride (97%, Fluka), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%, Aldrich), Cu(I)Cl (99 + %, Aldrich) was received and used without purification. Triethylamine (TEA, SRL, Bombay) was refluxed with p-toluenesulphonyl chloride, distilled and stored over CaH₂. All other chemicals were purchased from commercial sources and used after standard purification procedures.

Preparation of PEO Macroinitiators

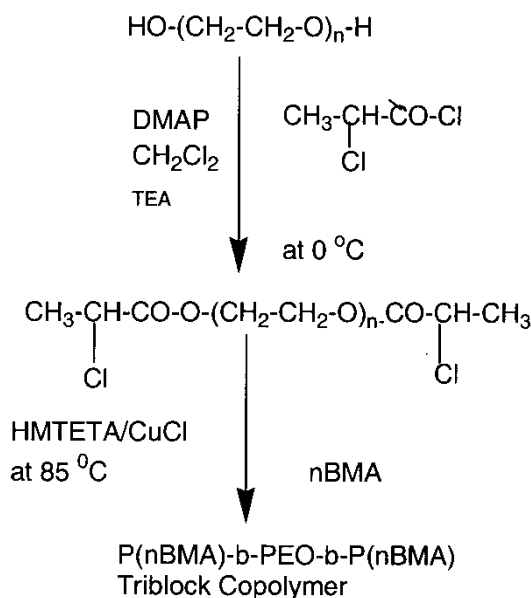
Poly(ethylene oxide) macroinitiators were prepared from commercially available poly(ethylene glycol) of varying number-average molecular weights and 2-chloropropionyl chloride according to a literature procedure (24) using triethylamine (TEA) as a base.

Polymerization Procedure

P(*n*BMA)-*b*-PEO-*b*-P(*n*BMA) block copolymers were synthesized in bulk polymerization as represented in Scheme 1. In a typical bulk polymerization, a dry glass tube was charged with two equivalents of Cu(I)Cl, two equivalents of HMTETA and one equivalent of poly(ethylene oxide) chloro telechelic macroinitiator and, subsequently evacuated and filled with nitrogen. *n*BMA (5 mL, 31.5 mmol) was added under nitrogen atmosphere and the reaction mixture is degassed via three-freeze-thaw cycles. The polymerization was carried out at 85°C and the polymerization was terminated by rapidly cooling to room temperature. At various time intervals, the tube was removed from the oil bath, and the polymer was dissolved in THF and passed through the basic alumina column to remove the copper catalyst. The polymer solution was precipitated in an excess of hexane. The precipitated polymer was extracted twice with distilled water at room temperature in order to remove the unreacted PEO macroinitiator and the purified product was dried in vacuum at room temperature and the yield was determined gravimetrically.

Characterization of Materials

The structure of reactants, macroinitiators and block copolymers were characterized by FTIR spectra on a Nicolet Impact 400 Fourier Transform Infrared spectrometer using the KBr pellet technique. ¹H NMR spectra were recorded on a 300 MHz Bruker MSL FT-NMR spectrometer. CDCl₃ was used as a solvent and tetramethylsilane (TMS) served as an internal standard. The number-average molecular weight (*M_n*) and molecular weight distribution (*M_w*/*M_n*), of PEO macroinitiators and their block copolymers were determined by gel permeation chromatography (GPC), using a Waters 515 liquid chromatograph equipped with four Ultrastaygel columns (guard, 10³, 10⁴, 10⁵ Å) and 410 RI detector. Measurements were performed in tetrahydrofuran (THF) as an eluent at 40°C with a flow rate of 1 mL/min and the calibration was based on linear polystyrene standards.



Scheme 1.

MALDITOF mass spectra were recorded with a KRATOS PC, Kompact SEQ analytical mass spectrometer, incorporating a 337 nm nitrogen laser with desorption/ionization pulse width duration 3 ns and a multiplier detector. The instrument was operated in a 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 attached to a differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) module was used to determine the thermograms. The measurements were carried out in nitrogen atmosphere at heating rates of 5 and 20°C/min. The equipment was calibrated with indium and tin standards. The surface morphologies of the homo and block copolymers were examined using a JEOL JSM-35CF scanning electron microscope. The samples were dried in vacuum. Each sample was sputter coated with gold under argon at 2.5 KV and 20 mA before analysis and SEM scans were taken at 10 KV.

Results and Discussion

A series of ABA triblock copolymers of PEO with *n*-butyl methacrylate (*n*BMA) were synthesized by atom transfer radical polymerization. The synthesis of macroinitiator was achieved by reaction of 2-chloropropionyl chloride with poly(ethylene glycol) in the presence of base. Macroinitiator and their block copolymers were characterized by spectroscopic methods and kinetics of block copolymers were performed in bulk polymerization.

Structural Characterization of Macroinitiator and their Block Copolymers FTIR and ¹H NMR Spectroscopic Studies

Representative FTIR spectra of PEG3400, PEO3400chloro macroinitiator and their block copolymers are shown in Figure 1. In the spectra of PEG, the -C-O-C- and O-H stretching

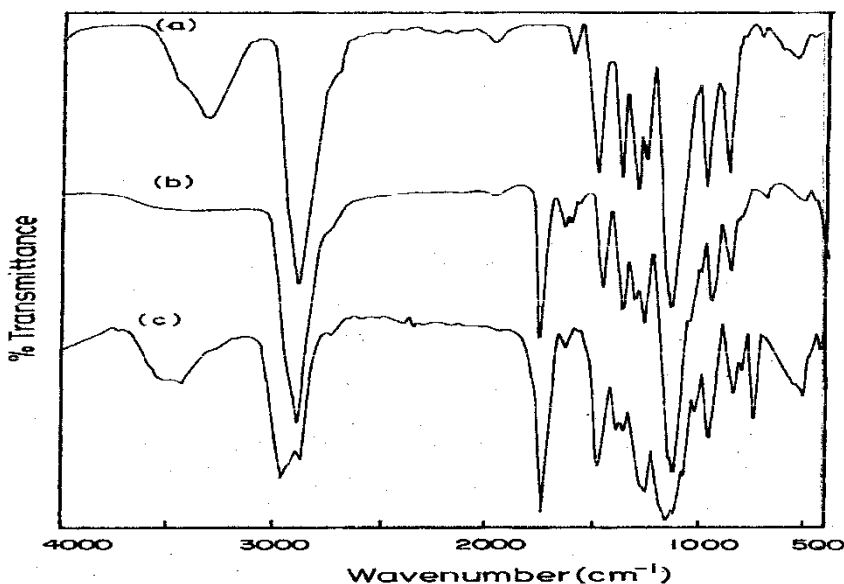


Figure 1. FT-IR spectra of (a) poly(ethylene glycol)3400; (b) poly(ethylene oxide)3400 chloro macroinitiator and; (c) *Pn*BMA-*b*-PEO3400-*b*-*Pn*BMA triblock copolymer.

peaks are observed at 1110 and 3313 cm^{-1} , respectively. After acetylation reaction the O-H peaks disappeared and the absorption of C=O peak at 1742 cm^{-1} was observed correspondingly in the spectrum. The disappearance of the O-H peak suggests that the O-H end groups have been converted quantitatively by 2-chloropropionate end groups. The results further proved that O-H end groups had been completely converted to the telechelic chloro macroinitiator. The spectrum of block copolymer exhibits characteristic peaks (2960, 1472, 1360, and 1110 cm^{-1}) of both PEO and P(*n*BMA) blocks. P(*n*BMA) methylene peaks at 2961, 1472, and 1389 cm^{-1} were also observed in the block copolymer.

The typical ^1H NMR spectra of PEO6000chloro macroinitiator, P(*n*BMA) homopolymer and the corresponding block copolymer are shown in Figure 2. In the PEO chloro macroinitiator, the OH signal (4.85 ppm) completely disappeared and a new signal has appeared at 4.32 ppm due to substitution of 2-chloropropionate end groups and $\text{CH}_2\text{-CH}_2\text{-O}$ signal is observed at 3.63 ppm. The P(*n*BMA) homopolymer shows characteristic signals for the butoxy ($\text{O-(CH}_2)_3\text{-CH}_3$) group at 3.93 ppm (singlet) in addition to the methylene protons at 1.80 ppm (doublet) and α -methyl protons at 0.86 ppm (quartet) (Figure 2b). ^1H NMR spectrum of a triblock copolymer shows characteristic signals of PEO ($\text{CH}_2\text{-CH}_2\text{-O}$) at 3.63 ppm in addition to the P(*n*BMA) butoxy protons ($\text{O-(CH}_2)_3\text{-CH}_3$) at 3.93 ppm (Figure 2c). P(*n*BMA) methylene protons at 1.80 ppm and α -methyl protons at 0.86 ppm were also observed in the block copolymer.

MALDITOF Mass Spectrometry

End group analysis of poly(ethylene oxide) chloro telechelic macroinitiator was carried out by matrix-assisted laser desorption ionization time-of-flight mass spectrometry

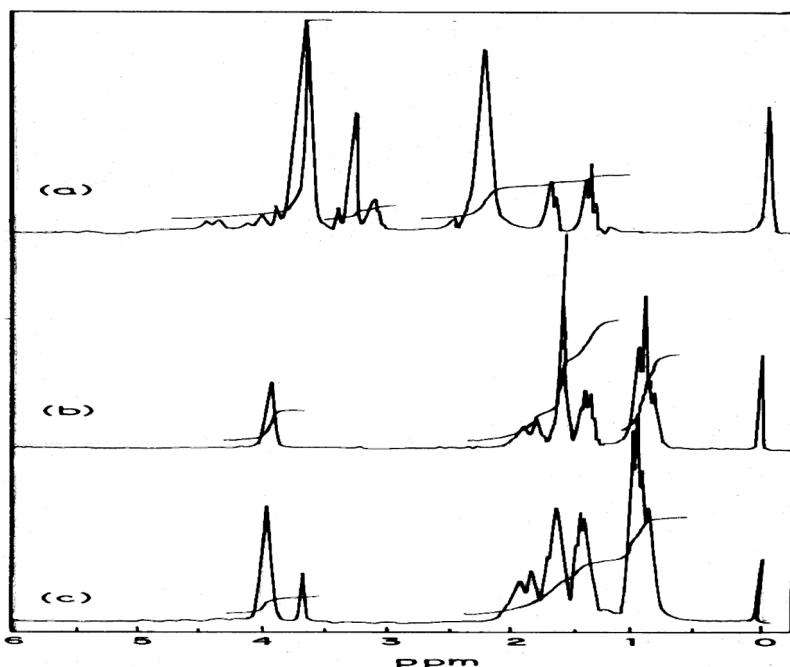


Figure 2. ^1H NMR spectra of (a) poly(ethylene oxide) macroinitiator; (b) P(*n*BMA) homopolymer and; (c) P(*n*BMA)-b-PEO-b-P(*n*BMA) triblock copolymer.

(MALDITOF MS) and the same is shown in Figure 3. Number-average molecular weights determined by GPC increased slightly (PEG $M_n = 1490$, $M_w/M_n = 1.07$, PEO $M_n = 1710$, $M_w/M_n = 1.07$) after substitution of 2-chloropropionate end groups, but there is no change of molecular weight distribution of PEG and PEO macroinitiator. Only one series of signals are observed in the spectra; with in each series, the signals are separated by 44 molecular weight units, which correspond to the molecular weight of the ethylene oxide repeating units. The major series of peaks correspond to $[\text{CH}_3\text{CH}(\text{Cl})\text{COO}(\text{CH}_2\text{-CH}_2\text{-O})_n\text{-COCH}(\text{Cl})\text{CH}_3 + \text{Na}^+]$. Thus, for the oligomer with $\text{DP}_n = 28$, the calculated mass is equal to 1453.98 for Na^+ ions, while the observed mass is 1453.1. This leads to the conclusion that only Na^+ ion peaks were observed in the spectra and this is very close to the calculated mass values.

Polymerization of n-butyl Methacrylate with Difunctional Poly(ethylene oxide) Chloro Macroinitiators with CuCl/HMTETA as a Catalyst System

The commercially available linear multidentate amines like 1,1,4,7,10, 10-hexamethyltriethylenetetramine (HMTETA) is an efficient ligand, in conjunction with copper halides mediated atom transfer radical polymerization processes (30). The kinetic study of the block copolymers was performed in bulk are shown in Figure 4. In bulk polymerization, a linear semilogarithmic kinetic plot of $\ln[M]_0/[M]$ vs. time was obtained, indicating that the number of propagating species remained constant throughout the polymerization (Figure 4). It shows a quantitative initiation efficiency of the telechelic chloro macroinitiator and follows the first-order kinetics with respect to monomer. It implies that the bulk polymerization proceeded in a controlled/“living” process for the synthesis of well-defined amphiphilic ABA triblock copolymers with predetermined

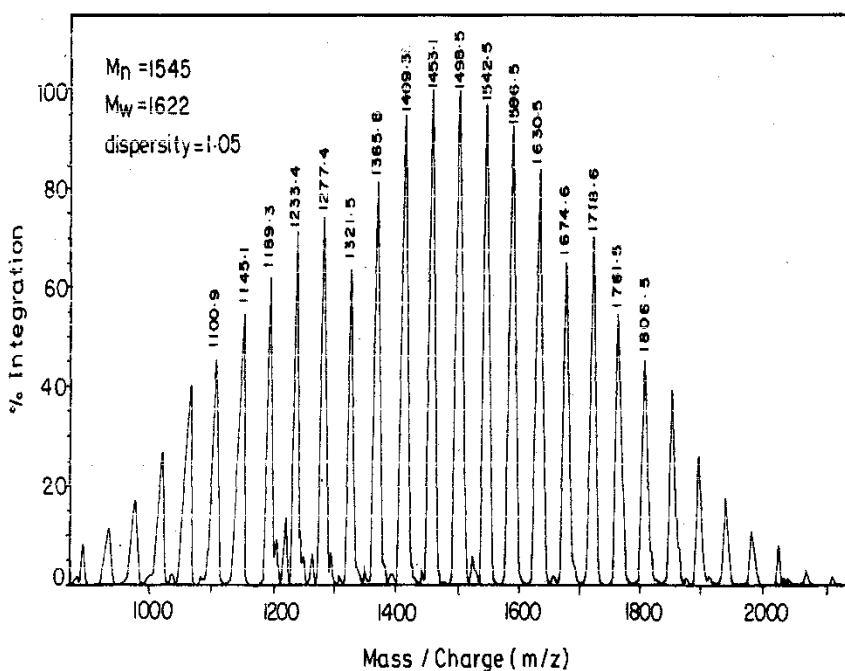


Figure 3. MALDITOF MS of poly(ethylene oxide)1500 chloro macroinitiator.

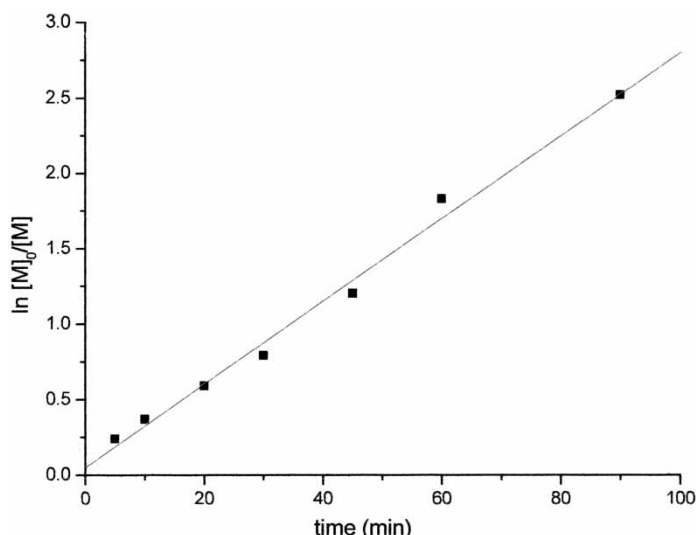


Figure 4. First-order kinetic plots of the ATRP of nBMA initiated by bifunctional PEO3400 chloro macroinitiator with a CuCl/HMTETA catalyst in bulk at 85°C. $[M] = 6.3 \text{ M}$, $[M]/[I]_0 = 141$ $[I]:[\text{CuCl}]:[\text{HMTETA}] = 1:2:2$.

molecular weights. The molecular weight evolution (M_n) and molecular weight distribution (M_w/M_n) as a function of monomer conversion are shown in Figure 5. In bulk polymerization, molecular weights of the block copolymers increase linearly with monomer conversion and polydispersity decreases with increasing conversion and reaches a value of $M_w/M_n < 1.3$.

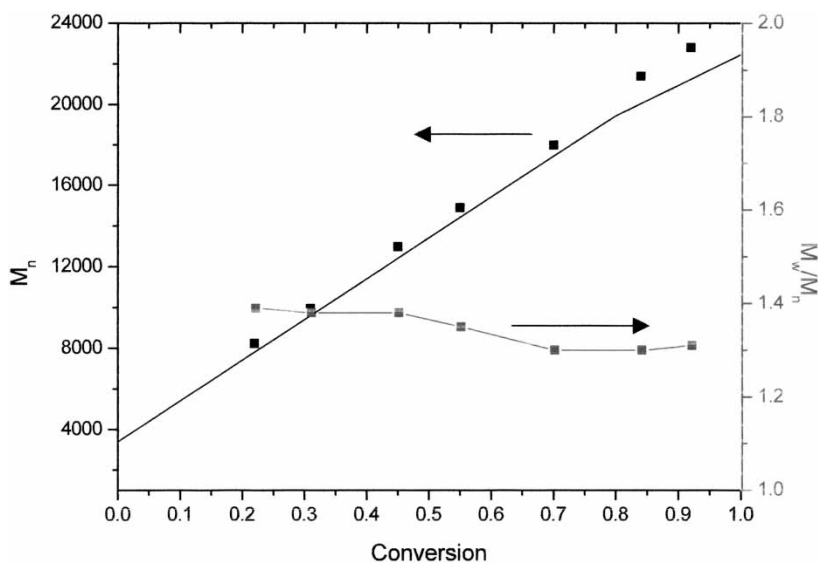


Figure 5. Number-average molecular weight (M_n) and polydispersity (M_w/M_n) as a function of monomer conversion for the ATRP of nBMA initiated by bifunctional PEO3400 chloro macroinitiator in bulk at 85°C. $[M] = 6.3 \text{ M}$, $[M]/[I]_0 = 141$ $[I]:[\text{CuCl}]:[\text{HMTETA}] = 1:2:2$.

A series of block copolymers prepared with varying number-average molecular weight of PEO macroinitiators from $M_n = 1000$ to 10,000 with varying $[M]/[I]_0$ ratios and the percent conversion are summarized in Table 1. All the results shows that $M_{n,GPC}$ values are higher than the $M_{n,th}$ indicating a low initiation efficiency of the macroinitiators and the polydispersities are lower than 1.5. The rate of the polymerization was observed to decrease with increasing molecular weight of the macroinitiators. This could probably due to the decrease of initiator concentration.

Thermal Analysis

The TG/DTA thermograms of PnBMA and PnBMA-b-PEO9000-b-PnBMA triblock copolymers are shown in Figure 6 (a) and (b). PnBMA homopolymer prepared by ATRP using CuCl/HMTETA/*p*-TSCl initiation system shows the single-step degradation. This result is a further indication of the absence of linkages, such as head-to-head and vinylidene ends, thereby confirming the high regioselectivity and the virtual absence of termination reactions (31, 32). The DTA profile of PnBMA shows one

Table 1
Bulk polymerization of *n*BMA with poly(ethylene oxide) bifunctional chloro macroinitiators $[M] = 6.3$ M, (initiator/CuCl/HMTETA = 1/2/2, at 85°C)

S. No.	Macroinitiator ^a (M_w/M_n)	%Con	Reaction time (min)	$[M]/[I]$ ratio	$M_{n,th}$ ^b	$M_{n,GPC}$	M_w/M_n
1	PEO(CIP) ₂ -1030 (1.11)	92	180	32	5210	19,400	1.36
2	PEO(CIP) ₂ -1710 (1.09)	96	180	54	9100	14,400	1.32
3	PEO(CIP) ₂ -2360 (1.11)	90	180	74	11,800	18,200	1.43
4	PEO(CIP) ₂ -3420 (1.07)	89	180	107	17,000	51,100	1.40
5	PEO(CIP) ₂ -4120 (1.09)	85	180	130	19,800	35,600	1.38
6	PEO(CIP) ₂ -6150 (1.08)	66	180	194	24,300	20,800	1.33
7	PEO(CIP) ₂ -8290 (1.07)	41	180	262	23,500	17,900	1.38
8	PEO(CIP) ₂ -9450 (1.05)	67	180	297	37,700	46,500	1.43
9	PEO(CIP) ₂ -10500 (1.09)	33	180	330	25,980	22,000	1.56
10	<i>n</i> BMA homopolymer ^c	82	120	150	17,500	10,500	1.24

^aThe number indicates the number-average molecular weights of PEO bifunctional macroinitiators with polydispersities.

^b $M_{n,th} = [M]/[I]_0 \times MW_{nBMA} \times \text{Conversion} + M_{n,GPC}$.

^cATRP conditions: Bulk polymerization: *n*BMA:*p*-TSCl:CuCl:HMTETA = 150:1:1:1 at 85°C.

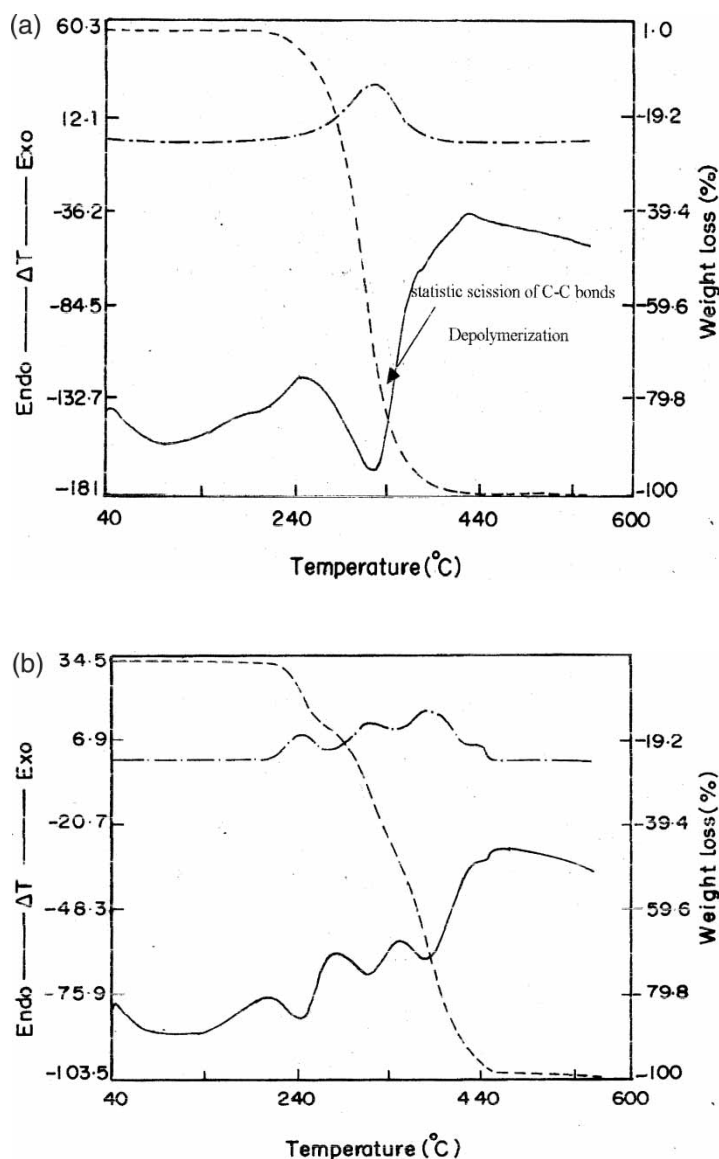


Figure 6. TG/DTA traces of (a) P(*n*BMA) homopolymer and (b) P(*n*BMA)-*b*-PEO9000-P(*n*BMA) block copolymer.

endothermic peak at 326°C. On the other hand, the block copolymer showed four-stage decomposition at 247, 319, 384, and 441°C. 100% decomposition was observed in P*n*BMA and P*n*BMA-*b*-PEO9000-*b*-P*n*BMA at 409 and 452°C, respectively.

Differential Scanning Calorimetry

The DSC thermograms of PEO3400chloro macroinitiator, P(*n*BMA) homopolymer and P(*n*BMA)-*b*-PEO3400-*b*-P(*n*BMA) triblock copolymers are shown in Figure 7.

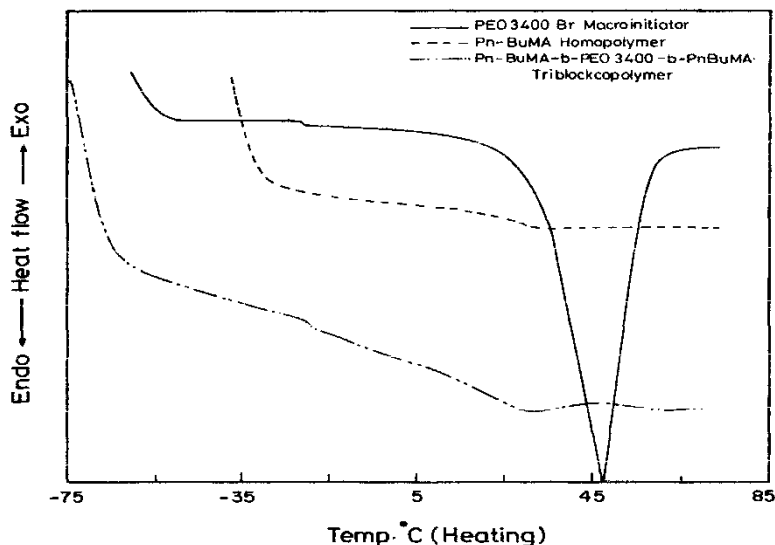


Figure 7. DSC thermograms of PEO3400 chloro macroinitiator, P(*n*BMA) homopolymer and P(*n*BMA)-*b*-PEO3400-*b*-P(*n*BMA) triblock copolymer.

PEO3400chloro macroinitiator and P(*n*BMA) homopolymer exhibit a glass transition temperatures (T_g) at -21.5 and 28.9°C , respectively. In the DSC thermogram of the block copolymer, T_g of PEO is observed at -19.4°C in addition to the T_g of P(*n*BMA) at 24.6°C . Melting of PEO is not observed in the block copolymer, indicating a finer dispersion of PEO in the block copolymer. This observation is consistent with those in the literature, (33) which have shown that at low PEO compositions ($<25\%$, PEO), PEO/P(*n*BMA) exist as a single-phase material and the system of PEO/P(*n*BMA) is compatible. The compatibility of PEG and P(*n*BMA) chains in solutions of their blends, diblock and triblock copolymers were compared by Wohlfarth et al. (34), and it was pointed out that the blends behaved differently from the block copolymers and the di and tri block copolymers behaved alike.

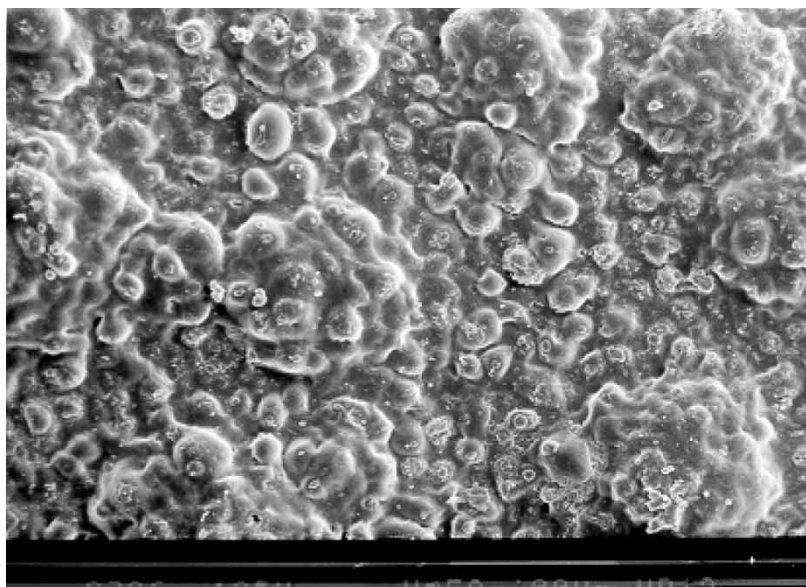
Morphological Characteristics

The surface morphologies of P*n*BMA homopolymer, P*n*BMA-*b*-PEO1000-*b*-P*n*BMA and P*n*BMA-*b*-PEO9000-*b*-P*n*BMA triblock copolymers are shown in Figure 8(a–d). P*n*BMA homopolymer exhibits a discontinuous phase as shown in Figure 8a. P*n*BMA-*b*-PEO1000-*b*-P*n*BMA, (Figure 8b and c) show the domains formed by both the blocks, where PEO blocks form a continuous phase. This could possibly be due to low T_g value of PEO block compared to P*n*BMA blocks. Due to this reason, the PEO block shows striation (relaxation lines) due to stretching. With an increase of molecular weight of PEO segment, which forms into a continuous phase, wherein the *n*BMA segments are embedded as could be seen from the micrograph (Figure 8d).

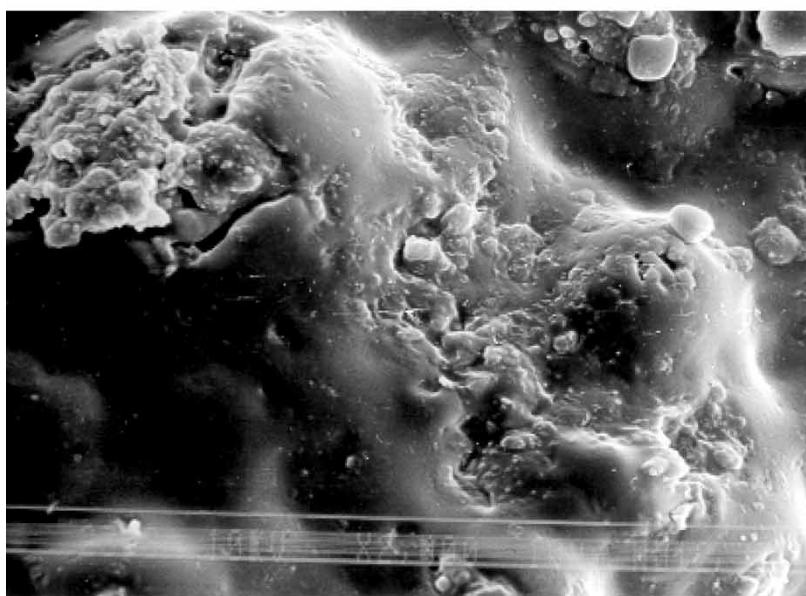
Conclusion

Well-defined P*n*BMA-*b*-PEO-*b*-P*n*BMA triblock copolymer was synthesized in bulk, using varying number-average molecular weights of bifunctional poly(ethylene oxide)chloro

macroinitiators and Cu(I)Cl/HMTETA as a catalyst system at 85°C. The rate of polymerization is first-order with respect to monomer concentration and the molecular weight of the obtained block copolymers increases linearly with conversion. The first-order kinetic plot of $\ln[M]_0/[M]$ vs. time was linear indicating that the polymerization proceeds in a



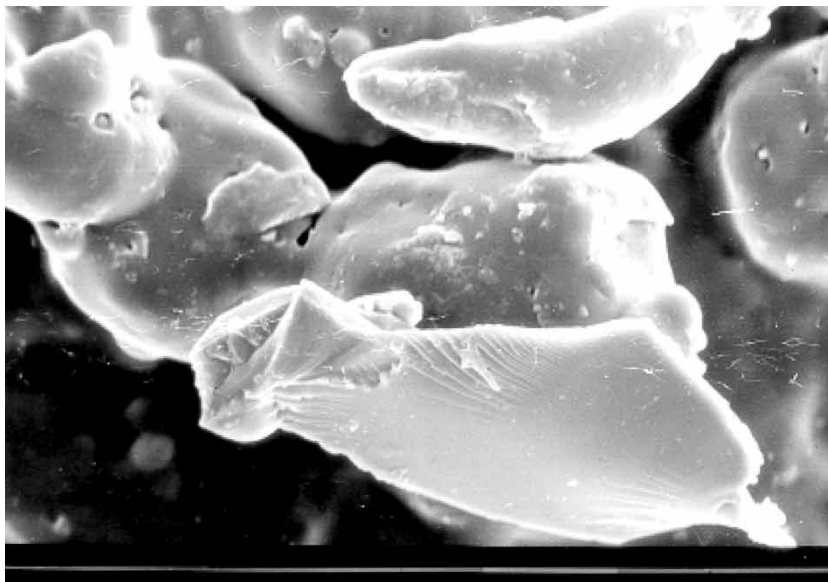
(a)



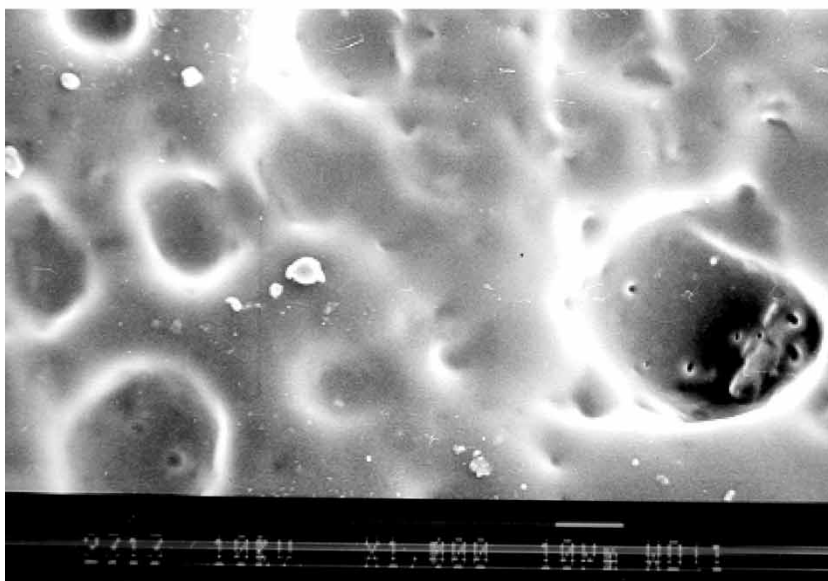
(b)

Figure 8. SEM photographs of (a) P(*n*BMA) homopolymer; (b) and (c) P(*n*BMA)-*b*-PEO1000-*b*-P(*n*BMA) triblock copolymer and (d) P(*n*BMA)-*b*-PEO9000-*b*-P(*n*BMA) triblock copolymer.

(continued)



(c)



(d)

Figure 8. Continued.

controlled/“living” process. The DSC thermogram of block copolymer shows two glass transition temperatures (T_g) corresponding to PEO and *Pn*BMA blocks. TG/DTA studies show that *Pn*BMA and *Pn*BMA-*b*-PEO-*b*-*Pn*BMA follow a single and multiple stage decomposition patterns, respectively. SEM studies indicate a fine dispersion of PEO in the continuous *Pn*BMA matrix.

Acknowledgment

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