Novel Poly(Methyl Methacrylate)-*block*-Polyurethane-*block*-Poly(Methyl Methacrylate) Tri-block Copolymers through Atom Transfer Radical Polymerization

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ABSTRACT: Poly(methyl methacrylate)-*block*-polyurethane-*block*-poly(methyl methacrylate) tri-block copolymers have been synthesized successfully through atom transfer radical polymerization of methyl methacrylate using telechelic bromo-terminated polyurethane/CuBr/N,N,N,N'',N''-pentamethyldiethylenetriamine initiating system. As the time increases, the number-average molecular weight increases linearly from 6400 to 37,000. This shows that the poly methyl methacrylate blocks were attached to polyurethane block. As the polymerization time increases, both conversion and molecular weight increased and the molecular weight increases linearly with increasing conversion. These results indicate that the formation of the tri-block copolymers was through atom transfer radical polymerization mechanism. Proton nuclear magnetic resonance spectral results of the triblock copolymers show that the molar ratio between polyurethane and poly (methyl methacrylate) blocks is in the range of 1 : 16.3 to 1 : 449.4. Differential scanning calorimetry results show T_g of the soft segment at $-35°C$ and T_g of the hard segment at $75°C$. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1538–1544, 2008

Key words: atom transfer radical polymerization; living polymerization; polyurethanes; block copolymers; telechelic

INTRODUCTION

Controlled radical polymerization (CRP) was introduced to synthesize polymers with controlled molecular weight, molecular weight distribution, and end groups.[1,2] Elimination of irreversible reactions such as irreversible termination and/or irreversible transfer reactions is the main aim of the CRP. Reversible deactivation which is the main step in CRP, can be achieved through (i) reversible cleavage of covalent bonds such as iniferters-based radical polymerization,[3–6] stable nitroxide mediated radical polymerization (NMP),[7] organo-tellurium,[8] and organo-cobalt[9] based radical polymerization; (ii) reversible addition-fragmentation chain transfer (RAFT) polymerization[10]; (iii) degenerative chain transfer using alkyl iodides[11]; (iv) persistent radicals; and[12] (v) metal-catalyzed[13] or atom transfer radical polymerization (ATRP).[14] ATRP was first introduced in 1995 using copper halide as a catalyst.[15] Similar to ATRP, metal catalyzed radical polymerization was also introduced in the same year but in that case, ruthenium halide was used as a catalyst.[16] ATRP exploits organic halides as an initiators and transition metals in their lower oxidation state complexed with suitable ligand as a complexing agent to polymerize different type of monomers. It also provides halogen terminated polymers that can be used further to synthesize various polymers and copolymers of different functionality, composition, and topology.

Variety of polymers with different structures and architectures have been prepared through ATRP which includes hollow spherical nanoparticals,[17] amphiphilic block copolymers,[18] syndiotactic graft copolymers,[19] star shaped copolymers,[20] dendronized polymers,[21] novel electro-active nanoparticles,[22] to mention a few. Tri-block copolymers have sparked much interest and their potential has been realized in many areas. These block copolymers have been used as thermoplastic elastomer,[23] adhesives,[24] hot-melt adhesives,[25] blend compatibilizers,[26] membranes,[27] drug delivery polymers,[28] and biodegradable polymers.[29] Synthesis of polyurethane-polyvinyl multiblock copolymers through polyurethane-based iniferters[30,31] were reported already and it was found that these block copolymers have been synthe-

sized through CRP mechanism. Recently, NMP was used to synthesize polyurethane-polystyrene multi-block copolymers.[32] ATRP was also used recently to synthesis novel polystyrene-*block*-polyurethane-*block*-polystyrene tri-block copolymers.[33] Reverse ATRP is generally used for the polymerization of methyl methacrylate (MMA).[34] To check whether MMA polymerizes in controlled manner, in the present investigation, atom transfer radical polymerization of MMA was carried out using telechelic bromo-terminated polyurethane (Br-PU-Br) as a macroinitiator, CuBr as a catalyst and *N,N,N,N″,N″*-pentamethyldie-thylenetriamine (PMDETA) as a complexing agent. It is important here to mention that the resulting poly (methyl methacrylate)-*block*-polyurethane-*block*-poly (methyl methacrylate) (PMMA-*b*-PU-*b*-PMMA) tri-block copolymers is reported now for the first time.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI) (mixture of 80% 2,4 and 20% 2,6 isomers), dibutyltin dilaurate, 2-bromoethanol, and PMDETA were used as received from Aldrich (St. Louis, MO). Analytical grade *N,N*-dime-thylformamide (DMF; CDH, India), dimethyl sulfox-ide (DMSO; CDH, New Delhi, India), and *N,N*-dime-thylacetamide (DMAc; CDH, New Delhi, India) were distilled and the middle portions were used after storing over type 4A° molecular sieves. Poly(tetrame-thylene)oxide glycol of molecular weight 1000 (PTMG) (Aldrich, St. Louis, MO) was used as received after drying it by heating at 105°C under a vacuum for 3 h. Just before use, CuBr (CDH, New Delhi, India) was purified using a reported proce-dure by Keller and Wycoff.[35] The inhibitor present in MMA (CDH, New Delhi, India) was removed by washing with 5% aqueous NaOH, washed again with distilled water, and stored over anhydrous so-dium sulfate. It was then distilled at reduced pres-sure and the middle portion was stored at 0–4°C until use. All other chemicals used were of analytical grades and were used as received.

Characterization techniques

Fourier transform infrared (FTIR) spectra were recorded as a KBr pellet on a JASCO 460 plus FTIR spectrophotometer. Fourier-transform nuclear mag-netic resonance (FT-NMR) spectra were recorded on a Bruker DPX-300 NMR instrument using deuterated dimethyl sulfoxide as the solvent and tetramethylsi-lane as the internal standard. Differential scanning calorimetry (DSC) was carried out using DSC Q10 instrument (TA instruments, USA) at a heating rate of 10°C/min under N_2 atmosphere and thermo gravi-

metric analysis (TGA) was carried out using TGA Q50 instrument (TA instruments, USA) at a heating rate of 10°C/min under N_2 atmosphere. Number-average (M_n) and weight-average (M_w) molecular weights and molecular weight distribution (MWD) were determined by gel permeation chromatography (GPC) using a Viscotek GPC system equipped with a TDA302-triple detector and four ViscoGEL™ col-umns. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL/min and the molecular weight calibrations were done using polystyrene standards.
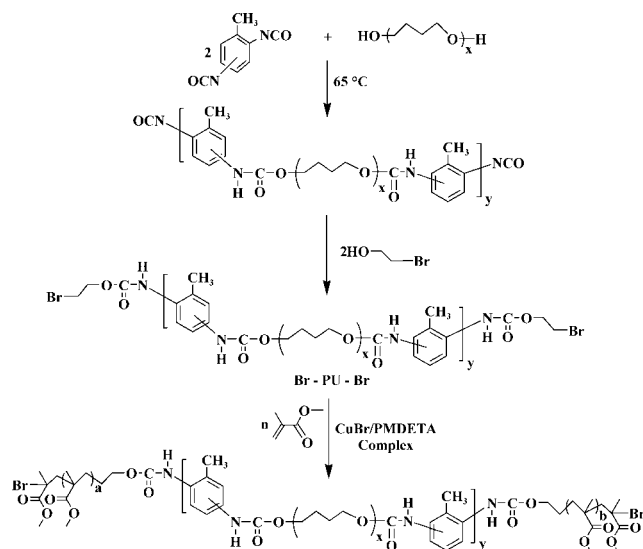
Polymerization procedures

Br-PU-Br was synthesized using already reported method[36] from one mole of PTMG, two moles of TDI, and two moles of 2-bromoethanol. For the syn-thesis of PMMA-*b*-PU-*b*-PMMA tri-block copolymers, first Br-PU-Br was dissolved in DMF and known quantity of PMDETA, CuBr and MMA were added successively. The homogeneous reaction mixture was degassed by three alternate freeze-pump-thaw cycles, sealed under vacuum, and placed in a thermo-stated oil bath controlled to ± 0.01°C for selected time. At the end of the stipulated period of time, the reaction mixture was removed from the oil bath and the reaction was arrested by dipping in an ice–salt mixture. The resulting solution was poured into a 10-fold excess of methanol and the precipitate was filtered, using sintered-glass crucible, washed with methanol, dried in vacuum, and weighed. The dried samples were washed thoroughly with aceto-nitrile to remove homo PMMA, if any, from the block copolymers, dried in vacuum, and weighed.

RESULTS AND DISCUSSION

ATRP has potential to synthesize variety of polymers with different type of architectures.[18,20,21,37,38] In an attempt to synthesis novel tri-block copolymers through ATRP mechanism, PMMA-*b*-PU-*b*-PMMA tri-block copolymers were synthesized for the first time and the results are presented in this article. Scheme 1 shows schematic representation of the syn-thesis of PMMA-*b*-PU-*b*-PMMA tri-block copolymers. When bromo-terminated telechelic polyurethane is used as an initiator and CuBr is used as a catalyst along with PMDETA as a complexing agent for the polymerization of MMA, PMMA-*b*-PU-*b*-PMMA tri-block copolymers are formed.

Synthesis of PMMA-*b*-PU-*b*-PMMA tri-block copolymers

To synthesize PMMA-*b*-PU-*b*-PMMA tri-block copoly-mers, first Br-PU-Br was synthesized from PTMG,

Scheme 1 Synthesis of PMMA-*b*-PU-*b*-PMMA tri-block copolymers through ATRP.

TDI and 2-bromoethanol using the known procedure.[36] This Br-PU-Br was used as a macroinitiator for the polymerization of MMA as mentioned above. To select the polymerization temperature, effect of temperature was studied first. Table I shows the effect of temperature on ATRP of MMA. At 90°C, there was no polymerization and at 100°C, the polymerization was sluggish. In the case of the polymerization at 140°C, the reaction was fast. But in the case of the polymerization at 130°C, the reaction was not sluggish and at the same time the polymerization was not also too fast. Hence 130°C was chosen as a reaction temperature for the polymerization. To select the solvent for the polymerization, different solvents were used and the results are presented in Table II. In the case of DMSO, the reaction is too fast and the MWD is also higher than the polymers obtained through DMF. The polymerization in DMAc is not fast, but the molecular weight is abnormally low. Hence, DMF was chosen as a solvent as it is giving better results compared to other solvents.

TABLE II
Effect of Solvent on ATRP of MMA at 130°C

Sl. No.	Solvent	Conversion[a] (%)	GPC results		
			$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
1.	DMSO	95.8	23.8	97.3	4.08
2.	DMAc	48.1	10.1	35.7	3.53
3.	DMF	23.9	25.9	94.5	3.64

Polymerization conditions: Polymerization time = 6 h; Solvent = 10 mL; $[Br\text{-}PU\text{-}Br]_0$ = 0.5 g (0.5/6400 = 7.8 × 10^{-5} mol Br); $[PMDETA]_0$ = $[CuBr]_0$ = 0.16 mmol; $[MMA]_0$ = 5.23 M/L.
[a] Conversion determined gravimetrically.

Mechanism of polymerization

To understand the mechanism of polymerization, effect of time on the polymerization of MMA was carried out and the results are presented in Table III. As the polymerization time increases, there is an increase in conversion and number average molecular weight. Here the concentration of Br in Br-PU-Br was calculated using molecular weight of Br-PU-Br obtained through GPC. As Br-PU-Br has two Br in its structure, the ratio of Br-PU-Br, CuBr, and PMDETA used was at 1 : 2 : 2, respectively. Figure 1 shows time-conversion and time-ln($[M_0]/[M]$) plots for the polymerization of MMA at 130°C. The straight line obtained in semi-logarithmic plot of time versus ln($[M_0]/[M]$) shows that the concentration of propagating radical is constant. Figure 2 shows conversion versus M_n and conversion versus MWD plots for the polymerization of MMA. Here, for the calculation of conversion, $[MMA]_0$ was considered and $[Br\text{-}PU\text{-}Br]_0$ was not considered. As the conversion increases, M_n also increases. These results show that the present Br-PU-Br/CuBr/PMDETA initiating system is following ATRP mechanism.[15]

The GPC curves of PMMA-*b*-PU-*b*-PMMA tri-block copolymers obtained at various polymerization times are shown in Figure 3. As the time increases, the unimodal peak of Br-PU-Br is converted into bimodal peak and finally it becomes unimodal peak.

TABLE I
Effect of Temperature on ATRP of MMA

Sl. No.	Temperature (°C)	Conversion[a] (%)	GPC results		
			$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
1	90	–	–	–	–
2.	100	1.0	6.3	18.4	2.92
3.	130	23.9	25.9	94.5	3.64
4.	140	86.8	41.2	84.1	2.04

Polymerization conditions: Polymerization time = 6 h; DMF = 10 mL; $[Br\text{-}PU\text{-}Br]_0$ = 0.5 g (0.5/6400 = 7.8 × 10^{-5} mol Br); $[PMDETA]_0$ = $[CuBr]_0$ = 0.16 mmol; $[MMA]_0$ = 5.23 M/L.
[a] Conversion determined gravimetrically.

TABLE III
Effect of Time on ATRP of MMA at 130°C

Code No.	Time (h)	Conversion[a] (%)	Molar content of PMMA[b] (%)	GPC results		
				$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
Poly 1	0	0	0	6.4	15.0	2.35
Poly 2	0.5	2.9	16.3	7.6	24.4	3.22
Poly 3	1	5.9	36.2	8.9	31.2	3.51
Poly 4	3	13.7	111.7	14.2	51.1	3.60
Poly 5	4.5	19.5	202.8	20.2	63.4	3.14
Poly 6	6	23.9	288.4	25.9	73.0	2.82
Poly 7	7.5	29.6	389.9	32.6	85.0	2.61
Poly 8	9	33.4	449.4	37.1	91.6	2.47

Polymerization conditions: DMF = 10 mL; [Br-PU-Br]$_0$ = 0.5 g (0.5/6350 = 7.87402 × 10^{-5} mol Br) [PMDETA]$_0$ = [CuBr]$_0$ = 0.15748 mmol; [MMA]$_0$ = 5.23 M/L.
[a] Conversion determined gravimetrically.
[b] Molar content of PMMA was calculated by comparing integration values of the peaks derived from PTMO and PMMA on ^{1}H NMR spectra[32].

The broad MWD and bimodal peaks are due to the presence of —CH$_2$-Br groups in Br-PU-Br. Since Br is attached to primary methyl groups, the stability of radicals is not high enough. This leads to slow initiation. As a result the radicals from the CH$_2$Br groups of Br-PU-Br have low stability which leads high MWD and bimodal peaks. This type of slow initiations leading to bimodal peaks and broad molecular weight distributions has been reported in ATRP.[39] In general MWD of the polymers synthesized through ATRP is nearly one. However, in the present case polydispersity is high which is due to the high MWD value of the basic macroinitiator (Br-PU-Br; cf. Table III). Moreover due to the primary radical formed from —CH$_2$—Br undergoes more side reaction and this may also be the reason for the high polydispersity index. Another important fact is that

the ATRP of MMA is itself difficult to control.[34] Comparison of polymerization using α-halopropionate and α-halobutyrate is a good example to explain the broad molecular weight distribution of the present system. Initiation by α-halopropionate is slower than the initiation by α-halobutyrate due to the low stability of the radicals from the former case than the later case.[40] Similar to our system, polystyrene-polyurethane multi-block copolymers prepared through nitroxide mediated radical polymerization are also having high polydispersity index.[32] Similar type of results was also obtained during the synthesis of PSt-*b*-PU-*b*-PSt tri-block copolymers.[33] To get good MWD and to avoid bimodal peaks, polyurethane macroinitiators with tertiary methyl bromide terminal groups are being used for the polymerization of different monomers and these results will be
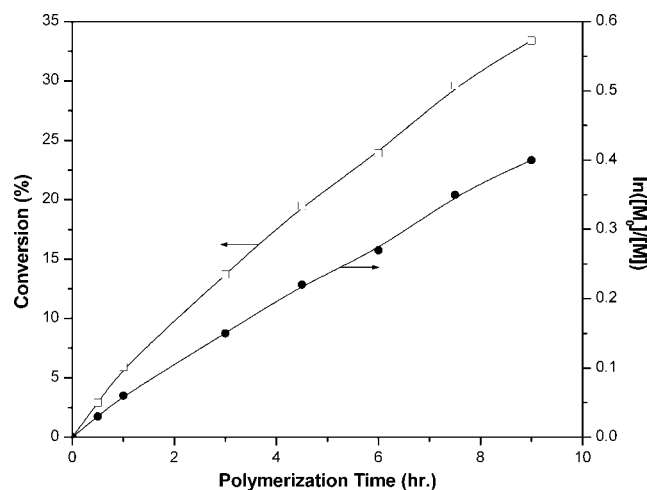

Figure 1 Time versus conversion and time versus ln([M]$_0$/[M]) plots for the polymerization of MMA at 130°C using Br-PU-Br/PMDETA/CuBr initiating system. [Br-PU-Br]$_0$ = 0.5 g (0.5/6400 = 7.8 × 10^{-5} mol Br); [PMDETA]$_0$ = [CuBr]$_0$ = 0.16 mmol; DMF = 10 mL; [MMA]$_0$ = 5.23 M/L.
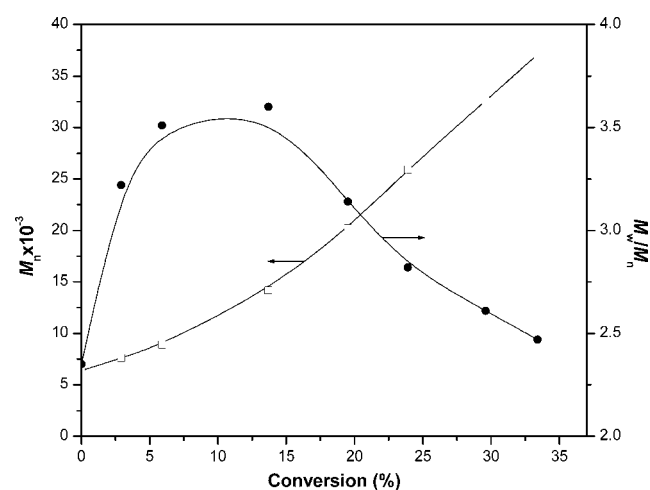
Figure 2 Conversion versus M_n and conversion versus M_w/M_n plots for the polymerization of MMA at 130°C using Br-PU-Br/PMDETA/CuBr initiating system. [Br-PU-Br]$_0$ = 0.5 g (0.5/6400 = 7.8 × 10^{-5} mol Br); [PMDETA]$_0$ = [CuBr]$_0$ = 0.16 mmol; DMF = 10 mL; [MMA]$_0$ = 5.23 M/L.
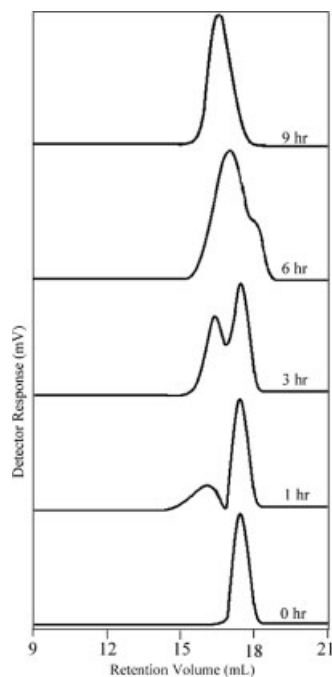
Figure 3 GPC curves for the polymerization of MMA at 130°C using Br-PU-Br/PMDETA/CuBr initiating system. $[Br\text{-}PU\text{-}Br]_0 = 0.5$ g $(0.5/6400 = 7.8 \times 10^{-5}$ mol Br); $[PMDETA]_0 = [CuBr]_0 = 0.16$ mmol; DMF = 10 mL; $[MMA]_0 = 5.23$ M/L.

communicated as a separate paper. Though the initiation is slow, the controlled polymerization of the present initiating system and the formation block copolymers can be confirmed by time-conversion, conversion-M_n, and spectral results.

Characterization of PMMA-b-PU-b-PMMA tri-block copolymers

The tri-block copolymers were further characterized by FTIR spectroscopy to confirm their structure. Figure 4 shows the FTIR spectra of the Br-PU-Br and PMMA-b-PU-b-PMMA tri-block copolymer obtained at 6 h. (Poly 6 in Table III). In the FTIR spectrum of Br-PU-Br [Fig. 4(b)], the stretching vibrations of urethane carbonyl group, C-H stretching vibrations and —N—H stretching vibrations are observed at 1726 cm^{-1}, 2935–2791 cm^{-1}, and 3291 cm^{-1}, respectively. In the FTIR spectrum of PMMA-b-PU-b-PMMA tri-block copolymer [Fig. 4(a)], the stretching vibrations of urethane groups and ester carbonyl groups of PMMA blocks are merged and observed at 1726 cm^{-1}. The C—H stretching vibrations of methylene groups in PU and PMMA are observed from 2852 to 3059 cm^{-1} and N—H stretching vibrations are observed at 3427 cm^{-1}. The C—H bending vibrations of methylene groups present in PU and PMMA observed from 1446 to 1597 cm^{-1}. The C—H bending peak of —CH$_3$ group present in PU block (from TDI) and PMMA block is observed at 1372 cm^{-1} in

Figure 4(a). The presence of N—H stretching vibrations and increased intensity of the —CH$_2$— and —CH$_3$ stretching as well as bending vibrations in Figure 4(a) confirm the formation of PMMA-b-PU-b-PMMA tri-block copolymers.

Table IV and Figure 5 shows ^{1}H NMR data and ^{1}H NMR spectra of Br-PU-Br and PMMA-b-PU-b-PMMA block copolymer, Poly 4 (cf. Table III), respectively. Both the protons of PU and PMMA blocks are present in Figure 5(b) which is a clear evidence of the formation of the block copolymer. The protons of terminal —CH$_2$—Br present in Br-PU-Br disappeared due to the atom transfer reaction and hence there is no peak at 3.63 ppm in the ^{1}H NMR spectrum of the tri-block copolymers. As reported in the literature, the methyl protons present in PMMA shows three peaks from 0.81 to 1.17 ppm.[41] The tacticity of PMMA can be identified using the integration values of these peaks at 0.81, 0.98, and 1.17 ppm which correspond to syndiotactic (rr), atactic (mr), and isotactic (mm) PMMA, respectively. The ratio among rr, mr, and mm in our study for Poly 4 is 54 : 37 : 11. The peaks appeared in this study for isotactic, atactic, and syndiotactic PMMA are similar to the already reported data[41] which shows that polymerization of MMA followed ATRP mechanism. The molar content of PMMA in tri block copolymers can easily be found out by comparing molecular weights (obtained by GPC) of Br-PU-Br and tri-block copolymers, which are given in Table III. It can also be found out using ^{1}H NMR technique as described by Higaki et al.[32] and the results are included in Table III. The molar content of PMMA from GPC and ^{1}H NMR technique are comparatively similar.

The PMMA-b-PU-b-PMMA tri-block copolymers were further characterized by thermal studies. The DSC curves for Br-PU-Br and PMMA-b-PU-b-PMMA

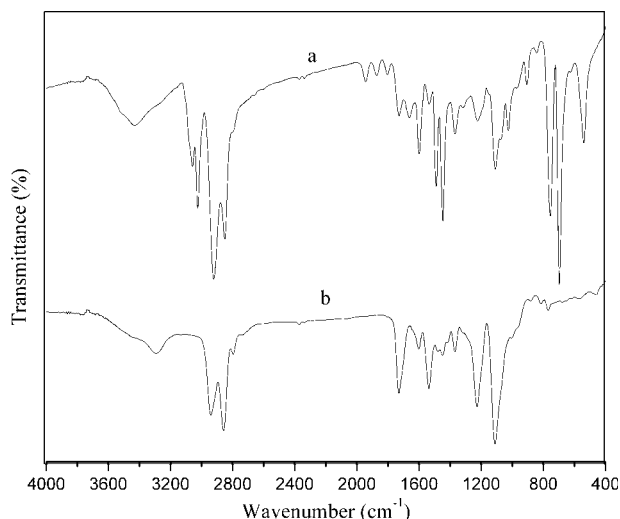**Figure 4** FTIR spectra of (a) PMMA-b-PU-b-PMMA tri-block copolymer, Poly 6 and (b) Br-PU-Br.

TABLE IV
^{1}H NMR Data of Br-PU-Br and PMMA-*b*-PU-*b*-PMMA Tri-Block Copolymers

Br-PU-Br		PMMA-*b*-PU-*b*-PMMA tri-block copolymers	
^{1}H	Chemical shift (ppm)	^{1}H	Chemical shift (ppm)
Br—CH$_2$—	3.63	N—H	8.08–9.25
Br—CH$_2$—CH$_2$—O—	4.49	C$_6$H$_3$(CH$_3$)NH—	6.59–7.5
N—H	8.08–9.25	C$_6$H$_3$(CH$_3$)NH—	2.20
C$_6$H$_3$(CH$_3$)NH—	7.06–7.5	—CH$_2$ of PTMG	1.42–1.52
C$_6$H$_3$(CH$_3$)NH—	2.20	—O—CH$_2$— of PTMG	3.35
—CH$_2$, of PTMG	1.42–1.52	—O—CH$_2$—NHCOO	4.08
—O—CH$_2$—, of PTMG	3.35	—CH$_2$— of PMMA	1.80–1.87
—O—CH$_2$—NHCOO	4.08	—OCH$_3$ of PMMA	3.5
		—CH$_3$ of PMMA	0.81–1.17
		—CH$_3$ of PMMA (rr)	0.81
		—CH$_3$ of PMMA (mr)	0.98
		—CH$_3$ of PMMA (mm)	1.17

tri-block copolymer, (Poly 6 in Table III) are presented in Figure 6. All the glass transition temperatures considered here are the middle point between onset and offset points. The T_g of the polyol segments is shifted from −54 to −35°C when Br-PU-Br is converted to PMMA-*b*-PU-*b*-PMMA tri-block copolymers. There is no change in melting point of the PTMG block when Br-PU-Br is converted to PMMA-*b*-PU-*b*-PMMA tri-block copolymer. The T_g of the

PMMA block is observed at 75°C which is less than the reported T_g of the PMMA block. The reason may be due to the presence of polyol and PU segments which act as plasticizers to PMMA segments. Similar type of results was also obtained in PU-vinyl block copolymers.[42] The presence of glass transition temperatures for PU and PMMA blocks in Figure 6(b) again confirms the formation of PMMA-*b*-PU-*b*-PMMA tri-block copolymers. Figure 7 gives the thermal stability of Br-PU-Br and PMMA-*b*-PU-*b*-PMMA tri-block copolymer (Poly 6 in Table III). The Br-PU-Br undergoes two-stage decomposition; one is around 250°C which is due to the decomposition of the NHCOO groups and other is around 380°C which is due to the decomposition of PTMG blocks. The overall thermal stability of PMMA-*b*-PU-*b*-PMMA tri-block copolymers is higher than the Br-PU-Br.
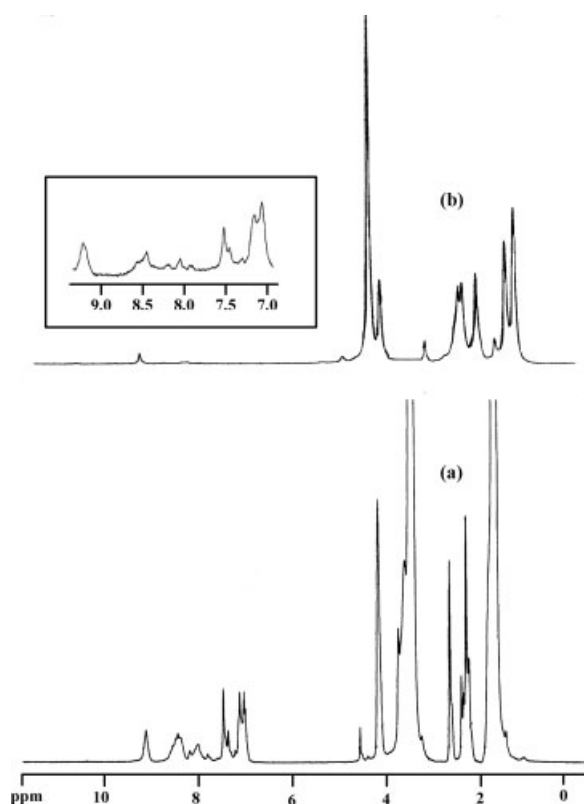

Figure 5 ^{1}H NMR spectra of (a) Br-PU-Br and (b) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, Poly 4.
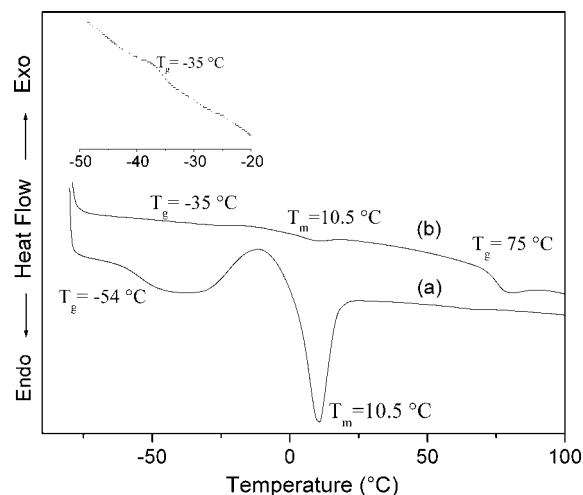

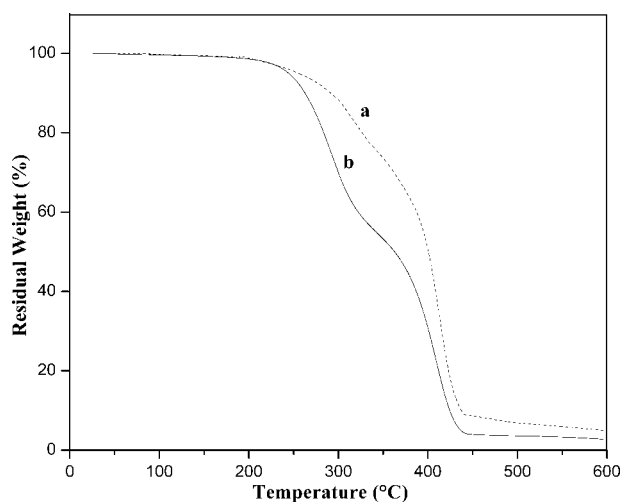**Figure 6** DSC curves of (a) Br-PU-Br and (b) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, Poly 6.

Figure 7 TGA curves of (a) PMMA-*b*-PU-*b*-PMMA triblock copolymer, Poly 6 and (b) Br-PU-Br.

CONCLUSIONS

Novel PMMA-*b*-PU-*b*-PMMA tri-block copolymers were successfully synthesized for the first time using Br-PU-Br as a macorinitiator, CuBr as a catalyst and PMDETA as a complexing agent. The linear increase of conversion and $\ln([M]_0/[M])$ during the increase of polymerization time confirms that the formation of tri-block copolymers was through controlled radical polymerization. Moreover, the linear increase of molecular weight with increase of conversion is also the clear evidence to prove the controlled radical polymerization mechanism. The presence of PU and PMMA blocks were further confirmed by spectral methods and DSC.

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