Novel Telechelic 2-Methyl-2-Bromopropionate Terminated Polyurethane Macroinitiator for the Synthesis of ABA type Tri-block Copolymers through Atom Transfer Radical Polymerization of Methyl Methacrylate

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Novel telechelic 2-methyl-2-bromopropionate terminated polyurethane macroinitiator was synthesized and used further to polymerize methyl methacrylate to yield poly(methyl methacrylate)-*block*-polyurethane-*block*-poly(methyl methacrylate) tri-block copolymers through atom transfer radical polymerization. Number-average molecular weight (M_n) was increased linearly with increasing polymerization time and conversion. Molecular weight distribution becomes narrower as the polymerization time increases and theoretical M_n values of the tri-block copolymers were comparable to the experimental M_n values. Structures of the macroinitiator and the tri-block copolymers were confirmed by ^1H NMR, ^{13}C NMR and FT-IR spectroscopic techniques. Mole percentage of poly(methyl methacrylate) in the triblock copolymers was calculated using ^1H NMR spectroscopy and was found to be comparable with the gel permeation chromatography results. Presence of two phases in the tri-block copolymers has been confirmed through differential scanning calorimetric studies.

KEY WORDS: ATRP / Block Copolymers / Poly(methyl methacrylate) / Polyurethanes /

Living anionic polymerization was first discovered by Szwarc,¹ where polymer chain propagation took place without chain breaking reactions such as chain transfer and chain termination. As a result polymers with defined molecular weight, narrow molecular weight distribution (MWD) and desired end groups were achieved through this method. But it requires stringent experimental conditions and highly pure monomers and solvents. On contrary, free radical polymerization is used widely to polymerize more than 70% of vinyl and acrylate monomers in industries but it has poor control over degree of polymerization, MWD and end functionalization during polymerization. In recent years, the idea of introducing livingness in free radical polymerization was proposed and it was termed as controlled radical polymerization (CRP).² As the conversion increases M_n also should increase linearly in any living polymerizations.² In conventional radical polymerization there is no linear increase of molecular weight with the conversion.² Hence in all CRP routes linear increase of molecular weight with conversion should takes place to show that they are following living polymerization mechanism.² Indeed different types of CRP techniques have been reported which facilitated the synthesis of broad variety of polymeric materials with predetermined molecular weight, narrow MWD and desired chain end groups. CRP was achieved through iniferter (initiation transfer termination),³ stable nitroxide radicals,⁴ triazolanyl radicals,⁵ organo-bismuthine,⁶ organo-tellurium,⁷ organo-cobalt,⁸ organo-stilbene,⁹ alkyl-9-BBN,¹⁰ reversible addition-fragmentation-chain transfer (RAFT),¹¹ degenerative chain transfer by alkyl iodide,¹² and atom transfer radical polymerization (ATRP).^{13,14} All the CRP methods

include activation and deactivation steps with their respective rate constants, k_{act} and k_{deact} respectively and k_{deact} is higher in all the cases to get controlled radical polymerization of monomers. ATRP exploits organic halide (haloalkanes,^{13,15} haloketones,¹⁶ halonitriles,¹⁷ haloamide,¹⁸ haloesters,¹⁶ and arenesulphonyl halides,¹⁹) as an initiator and transition metal in their lower oxidation state (Cu(I),²⁰ Fe(II),^{21,22} Ni(II),²³ Ru(II),¹³ Mo(III),²⁴ Ti(III),²⁵ Pd(II),²⁶ Os(II),²⁷ and Re(II),²⁸) complexed with suitable ligand as catalyst to polymerize different monomers. Variety of polymers with different structures and architectures have been prepared through ATRP which includes polymer brushes,²⁹ block copolymers,^{30,31} syndiotactic graft copolymers,³² star shaped copolymers,³³ immobilized-polymer,³⁴ to mention a few.

Tri-block copolymers have widespread applications in the field of drug delivery and gene targeting because of the high drug-loading capacity of the inner core as well as the unique disposition characteristics in the body. Micelles from these block copolymers form extraordinary core-shell structure. Variety of hydrophilic polymers with flexible nature can be selected as the shell forming segment. Various poly (ethylene glycol) based block copolymeric micelles have been reported in the field drug delivery particularly for the delivery of genes and cytotoxic agents.^{35–38} Here size of the block copolymeric micelles, viruses and lipoproteins are in mesoscopic size range (tens of nanometer size) which is the reason for the interaction. But viruses and lipoproteins have narrow size distribution and hence polymeric micelles should also have narrow size distribution for good interaction.³⁹ The narrow size distribution of the polymeric micelle can be achieved when the MWD of

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the polymer or block copolymer is narrow. Narrow MWD can be achieved through controlled radical polymerization. As polyurethanes are important class of polymers that have found many applications as biomaterials on account of their excellent physical properties and relatively good biocompatibility,⁴⁰ synthesis of polyurethane-based tri-block copolymers are attempted in this study. By changing different commercially available polyols, diisocyanates and chain extenders, molecular weight of polyurethanes and their properties can easily be altered. Similarly, by using bromo-terminated polyurethane, controlled incorporation of polymeric blocks at the both the ends of polyurethane can be achieved through ATRP mechanism. The controlled incorporation of vinyl blocks into polyurethane was already achieved through iniferters.^{41,42} Polyurethane-polystyrene multi-block copolymers were synthesized through nitroxide radical mediated CRP, but broad MWD was obtained.⁴³ Very recently, polystyrene-*block*-polyurethane-*block*-polystyrene⁴⁴ (PSt-*b*-PU-*b*-PSt) tri-block copolymers have been reported through ATRP mechanism in our lab. However, the radicals generated from polyurethane with -CH₂Br end groups were not more stable and hence broad MWD values were obtained. Therefore in the present investigation, we have synthesized novel telechelic 2-methyl-2-bromopropionate terminated polyurethane (MBP-PU-MBP) and used it further as a ATRP macroinitiator to synthesize PMMA-*b*-PU-*b*-PMMA tri-block copolymers using CuBr as a catalyst and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) as a ligand. This is a basic study and if this is successful, this method can be used to prepare micelles forming polyurethane-based tri-block copolymers which can be used for drug delivery.

EXPERIMENTAL

Materials and Methods

Dibutyltin dilaurate, α -bromoisobutyryl bromide, toluene diisocyanate (TDI; mixture of 80% 2,4 and 20% 2,6 isomers), calcium hydride, and PMDETA were used as received from Aldrich, U.S.A. Analytical grade ethylene glycol was purchased from Merck, India refluxed with calcium hydride and then vacuum distilled. The middle portion was used after storing over type 4 Å molecular sieves. Poly(tetramethyleneoxide) glycol (PTMG) of molecular weight 1000 (Aldrich, U.S.A.) was used after drying it by heating at 105 °C under vacuum for 3 h just before use. Analytical grade *N,N*-dimethylformamide (DMF; CDH, India) was distilled under reduced pressure and the middle portions were used after storing over type 4 Å molecular sieves. The inhibitor present in methyl methacrylate (MMA; Aldrich, U.S.A.; 99%) was removed, using conventional method. It was then distilled at reduced pressure and the middle portion was stored at 0–4 °C until use. CuBr (Aldrich, U.S.A.; 98%) was purified using a reported procedure,⁴⁵ and stored under argon atmosphere. All other chemicals used were of analytical grades and were used as received.

Synthesis of 2-hydroxyethyl-2'-methyl-2'-bromopropionate and MBP-PU-MBP

2-Hydroxyethyl-2'-methyl-2'-bromopropionate (HMB) was prepared from α -bromoisobutyryl bromide and ethylene glycol as described previously.⁴⁶

¹H NMR (CDCl₃, ppm): δ = 4.3 (t, 2H), 3.85 (t, 2H), 3 (s, 1H), 1.9 (s, 6H).

¹³C NMR (CDCl₃, ppm): δ = 172.93, 68.33, 61.46, 56.90, 31.67.

MBP-PU-MBP was prepared as follows. Dried PTMG of molecular weight 1000 (20 g, 0.02 mol) was placed in 250 mL three necked round bottom flask, fitted with a mechanical stirrer, nitrogen inlet, a dropping funnel and heated in an oil bath. When the temperature reached 65 °C, TDI (6.96 g, 0.04 mol) was added drop by drop with stirring. The temperature was then raised to 70 °C and the reaction was allowed to proceed until the isocyanate content reached half of the initial value (as determined by dibutylamine titration). Then HMB (8.44 g, 0.04 mol) in 15 mL DMF was added followed by dibutyltin dilaurate (2 mol % of NCO, 0.25 g). The reaction was allowed to proceed until complete disappearance of isocyanate group, which was monitored by the Fourier-transform infrared (FT-IR) spectroscopy.

Synthesis of PMMA-*b*-PU-*b*-PMMA Tri-block Copolymers

For the synthesis of PMMA-*b*-PU-*b*-PMMA tri-block copolymers, first MBP-PU-MBP was dissolved in DMF and known quantities 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, 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 acetonitrile to remove homo PMMA, if any, from the block copolymers, dried in vacuum, and weighed.

Measurement and Characterization

Experimental number average (M_n), weight-average (M_w) molecular weights and MWD were determined by gel permeation chromatography (GPC) using polymer laboratories GPC 50 integrated system equipped with differential refractometer (RI Detector) and PLgel 5 μ m MIXED-C column. 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. Fourier-transform nuclear magnetic resonance (FT NMR) spectra were recorded on a Bruker DPX-300 NMR instrument using deuterated dimethyl sulfoxide as the solvent and tetramethylsilane as an internal standard. FT-IR spectra were recorded as a KBr pellet on a Nicolet Impact 400 FT-IR spectrophotometer. Differential scanning calorimeter (DSC) was carried out using DSC Q200 instrument (TA

Scheme 1. Synthesis of telechelic 2-methyl-2-bromopropionate terminated polyurethane and PMMA-*b*-PU-*b*-PMMA tri-block copolymers.

Table I. Effect of time on ATRP of MMA at 100 °C

Code No.	Time (min.)	Conv. ^a (%)	Molar content of PMMA ^b (%)	Molar content of PMMA ^c (%)	$M_n \times 10^{-3}$ (th) ^d	GPC results			f^e
						$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	
MBP-PU-MBP	0	0	—	—	—	3.2	4.8	1.50	—
POLY 1	15	6.4	118.7	134.3	5.1	7.5	12.3	1.65	0.68
POLY 2	30	11.7	298.5	312.5	6.7	13.2	21.3	1.62	0.50
POLY 3	60	21.4	452.6	478.1	9.6	18.5	29.2	1.58	0.52
POLY 4	120	39.5	723.8	762.5	15.0	27.6	41.6	1.51	0.54
POLY 5	180	53.4	821.2	840.6	19.2	30.1	44.5	1.48	0.63
POLY 6	240	65.2	903.8	918.7	22.7	32.6	47.2	1.45	0.69

^aConversion was determined gravimetrically. ^bMolar content of PMMA was calculated by comparing integration values of the peaks derived for $-\text{CH}_2-\text{CH}_2-$ protons of PTMO and $-\text{CH}_3$ protons of PMMA blocks in ^1H NMR spectra.⁴³ ^cMolar content of PMMA was calculated by using M_n values of MBP-PU-MBP and

PMMA-*b*-PU-*b*-PMMA derived from GPC. ^d $M_{n,th} = \left(\frac{[\text{MMA}]_0}{[\text{MBP-PU-MBP}]_0} \times \text{Conversion} \right) + M_n$ of MBP-PU-MBP. ^e $f = M_{n,th}/M_{n,GPC}$. Polymerization conditions: $[\text{MBP-PU-MBP}]_0 = 0.5 \text{ g}$ ($0.5/3200 = 0.156 \text{ mmol}$) $[\text{PMDETA}]_0 = [\text{CuBr}]_0 = 0.313 \text{ mmol}$; $\text{DMF} = 10 \text{ mL}$; $[\text{MMA}]_0 = 0.0468 \text{ mol}$.

instruments, USA) at a heating rate of 10 °C/min under N_2 atmosphere and thermogravimetric analysis (TGA) was carried out using DTG-60 instrument (Shimadzu, Japan) at a heating rate of 10 °C/min under N_2 atmosphere.

RESULTS AND DISCUSSIONS

Scheme 1 shows the synthetic route for the preparation of novel MBP-PU-MBP and PMMA-*b*-PU-*b*-PMMA tri-block copolymers. When HMB, was reacted with isocyanate terminated polyurethane, novel 2-methyl-2-bromopropionate terminated polyurethane, MBP-PU-MBP is formed as shown in Scheme 1. When MBP-PU-MBP/CuBr/PMDETA initiating system was used for the polymerization of MMA, ABA type tri-block copolymers were formed where A is PMMA block and B is PU block. Here the concentration of MBP-PU-MBP

was calculated using molecular weight of MBP-PU-MBP obtained through GPC (*cf.* Table I). Since MBP-PU-MBP has two Br in its structure, the ratio of MBP-PU-MBP, CuBr, and PMDETA was maintained at 1:2:2 respectively. To select the polymerization temperature, initially the polymerization was carried out at 80 °C, but there was no polymerization and at 90 °C, the polymerization was sluggish. However, in the case of the polymerization at 100 °C, the reaction was not sluggish and hence, 100 °C was chosen as a reaction temperature for the polymerization.

Controlled Radical Polymerization Studies

To understand the mechanism of polymerization, effect of changing time on the polymerization of MMA was carried out and the results are presented in Table I. Here, for the calculation of conversion, weight of $[\text{MMA}]_0$ was considered

Figure 1. Time-conversion and time- $\ln([M]_0/[M])$ plots for the polymerization of MMA at 100°C using MBP-PU-MBP/PMDETA/CuBr initiating system. $[\text{MBP-PU-MBP}]_0 = 0.5 \text{ g}$ ($0.5/3200 = 0.156 \text{ mmol}$) $[\text{PMDETA}]_0 = [\text{CuBr}]_0 = 0.313 \text{ mmol}$; DMF = 10 mL; $[\text{MMA}]_0 = 0.0468 \text{ mol}$.

and weight of $[\text{MBP-PU-MBP}]_0$ was not considered. The weight of MBP-PU-MBP will be same as the polymerization time was increased, so to get the accurate conversion in percentage, the weight of MBP-PU-MBP was not considered. Figure 1 shows polymerization time-conversion and polymerization time- $\ln([M]_0/[M])$ plots for MMA polymerization. As the time increases both conversion and $\ln([M]_0/[M])$ increased which is a typical result in any controlled radical polymerization. The linear increase of $\ln([M]_0/[M])$ shows that the radical concentration is steady throughout the polymerization. Figure 2 shows conversion- M_n and conversion-MWD plots for the polymerization of MMA. As the conversion increases M_n also increases which is clear evidence that the present system follows ATRP mechanism. But the increase of M_n with

Figure 2. Conversion- M_n and conversion- M_w/M_n plots for the polymerization of MMA at 100°C using MBP-PU-MBP/PMDETA/CuBr initiating system. $[\text{MBP-PU-MBP}]_0 = 0.5 \text{ g}$ ($0.5/3200 = 0.156 \text{ mmol}$) $[\text{PMDETA}]_0 = [\text{CuBr}]_0 = 0.313 \text{ mmol}$; DMF = 10 mL; $[\text{MMA}]_0 = 0.0468 \text{ mol}$.

conversion is not linear. Due the presence of inevitable radical-radical termination reactions,⁵ it leads to the loss of linearity in the curves. Similar type curves have been reported in case of ATRP.^{47–49} However, it is interesting to note that MWD decreases with increasing conversion which indicates that the controlled incorporation nature of MMA units take place as the conversion increases. The controlled polymerization nature of the present system can also be understood from the less deviation between $M_{n,\text{GPC}}$ and $M_{n,\text{th}}$ in Figure 2. It is interesting to note that when $-\text{CH}_2\text{Br}$ terminated polyurethane was used in our earlier investigation,⁴⁴ $M_{n,\text{GPC}}$ and $M_{n,\text{th}}$ values were nowhere near, but in the present case it is comparable. This result shows that 2-methyl-2-bromopropionate terminated polyurethane is better macroinitiator than $-\text{CH}_2\text{Br}$ terminated polyurethane. In addition, apparent initiator efficiency ($f = M_{n,\text{th}}/M_{n,\text{GPC}}$) was also calculated and it is high for POLY 1 and 6 (Table I; 0.68 and 0.69) and low for POLY 2 (0.50). These f values are in agreement with the reported f values of ATRP.¹⁵ As shown in Table I and Figure 2, the experimental M_n is not exactly matching with the theoretical M_n . This may be due to the poor deactivation by CuBr_2 which lead to the unavoidable radical-radical termination as side reactions. Similar types of results have been discussed thoroughly by Steenbock *et al.*⁵ and large deviation of experimental M_n with theoretical M_n has also been reported in the polymerization of MMA through ATRP mechanism.⁵⁰ However the initiator efficiency, f , is more or less high in all the cases. These observations imply that high blocking efficiency ($f = M_{n,\text{th}}/M_{n,\text{GPC}}$) was achieved by the effective transfer of bromine atom from terminal 2-methyl-2-bromopropionate groups of polyurethane to CuBr-PMDETA complex.

Spectral Studies

The ABA tri-block copolymers synthesized were further characterized by FT-IR spectroscopy to confirm the structure. Figure 3 shows the FT-IR spectra of the MBP-PU-MBP and

Figure 3. FT-IR spectra of (a) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, POLY 5 and (b) MBP-PU-MBP.

Figure 4. ^1H NMR spectra of (a) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, POLY 5 and (b) MBP-PU-MBP.

PMMA-*b*-PU-*b*-PMMA tri-block copolymer obtained at 180 min. (POLY 5 in Table I). In the FT-IR spectrum of MBP-PU-MBP (Figure 3(b)), the stretching vibrations of urethane carbonyl group is at 1721 cm^{-1} and bands at $2787\text{--}2949\text{ cm}^{-1}$ are associated with C-H asymmetric and symmetric stretching of CH_2 groups. The band at $1073\text{--}1107\text{ cm}^{-1}$ is due to the stretching of ether C-O-C groups. Stretching and bending vibrations of -N-H are observed at 3296 cm^{-1} and 1532 cm^{-1} respectively. In the FT-IR spectrum of PMMA-*b*-PU-*b*-PMMA tri-block copolymers (Figure 3(a)), the stretching vibrations of urethane groups and ester carbonyl groups of PMMA blocks are merged and observed at 1721 cm^{-1} . The C-H stretching vibrations of methylene groups in PU and PMMA are observed in the region $2787\text{--}2949\text{ cm}^{-1}$ and N-H stretching vibrations are observed at 3300 cm^{-1} . The C-H bending vibrations of methylene groups present in PU and PMMA are observed from 1445 cm^{-1} to 1595 cm^{-1} . The C-H bending peak of - CH_3 groups present in PU blocks (from TDI) and PMMA blocks is observed at 1370 cm^{-1} in Figure 3(a). The presence of all peaks which corresponds to MBP-PU-MBP in tri-block copolymer and new peaks of PMMA blocks further support the formation of PMMA-*b*-PU-*b*-PMMA tri-block copolymers.

FT NMR spectroscopy was also used to confirm the structure of MBP-PU-MBP and ABA tri-block copolymers. Figure 4(b) and Table II show ^1H NMR spectrum and spectral data for MBP-PU-MBP respectively. Phenyl protons and

Figure 5. ^{13}C NMR spectra of (a) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, POLY 5 and (b) MBP-PU-MBP.

methyl protons in TDI resonate at $7.03\text{--}7.47\text{ ppm}$ and $2.04\text{--}2.11\text{ ppm}$ respectively. The -N-H protons and the terminal methyl protons of 2-methyl-2-bromopropionate groups present in MBP-PU-MBP appeared at $8.75\text{--}9.53\text{ ppm}$ and 1.86 ppm respectively. The peaks correspond to - CH_2 and - OCH_2 protons of PTMG resonate at 1.5 ppm and 3.15 ppm respectively. The - OCH_2 groups present in HMB and - OCH_2 of PTMG which is attached to urethane group appeared at $4.33\text{--}4.36\text{ ppm}$ and 4.13 ppm respectively. Figure 5(b) and Table III shows ^{13}C NMR spectrum and spectral data for MBP-PU-MBP respectively. The - CH_2 and - OCH_2 groups of PTMG appeared at $25.83\text{--}26.16$ and 69.80 ppm respectively. Aromatic carbons, - CH_3 carbons (from TDI) and - C=O (from urethane) resonate at $115.14\text{--}137.30$, 17.16 and $155.56\text{--}154.33\text{ ppm}$ respectively. The carbon atoms present in CH_3 , C-Br, - C=O and - CH_2 of terminal 2-methyl-2-bromopropionate groups resonate at 31.40 , $56.95\text{--}58.75$, 170.81 and 61.83 ppm respectively. These results show that MBP-PU-MBP was successfully synthesized.

In the ^1H NMR spectrum of the ABA tri-block copolymer (Figure 4(a)), the -N-H protons of urethane and aromatic protons from TDI appeared at $8.50\text{--}9.25$ and $7.10\text{--}7.53\text{ ppm}$ respectively. The - CH_3 protons of PMMA were resonate at 0.84 ppm , 1.01 ppm and 1.21 ppm which correspond to syndiotactic (rr), atactic (mr) and isotactic (mm) PMMA respectively.⁵¹ The - OCH_3 protons of PMMA were appeared at 3.6 ppm . The protons correspond to - CH_2 and - OCH_2 groups of PTMG were appeared at 1.5 and 3.3 ppm respectively. The

Table II. ^1H NMR data of MBP-PU-MBP and PMMA-*b*-PU-*b*-PMMA tri-block copolymers

MBP-PU-MBP		PMMA- <i>b</i> -PU- <i>b</i> -PMMA tri-block copolymers	
^1H	Chemical Shift (ppm)	^1H	Chemical Shift (ppm)
Terminal Br-(CH ₃) ₂	1.86	N-H	8.50–9.27
CO-O-CH ₂ -CH ₂ -	4.33–4.36	C ₆ H ₃ (CH ₃)NH-	7.10–7.53
N-H	8.75–9.53	C ₆ H ₃ (CH ₃)NH- & -CH ₂ - of PMMA	1.82–1.90
C ₆ H ₃ (CH ₃)NH-	7.03–7.47	-CH ₂ , of PTMG	1.56
C ₆ H ₃ (CH ₃)NH-	2.04–2.11	-O-CH ₂ - of PTMG	3.18
-CH ₂ , of PTMG	1.5	-O-CH ₂ -NHCOO	4.08
-O-CH ₂ -, of PTMG	3.41	-OCH ₃ of PMMA	3.61
-CH ₂ -O-CO-NH-	4.05–4.13	CO-O-CH ₂ -CH ₂ -	4.27–4.31
		-CH ₂ -O-CO-NH-CH ₃ of PMMA	4.1185–1.21
		-CH ₃ of PMMA (rr)	0.84
		-CH ₃ of PMMA (mr)	1.01
		-CH ₃ of PMMA (mm)	1.21

Table III. ^{13}C NMR data of MBP-PU-MBP and PMMA-*b*-PU-*b*-PMMA tri-block copolymers

MBP-PU-MBP		PMMA- <i>b</i> -PU- <i>b</i> -PMMA tri-block copolymers	
^{13}C	Chemical Shift (ppm)	^{13}C	Chemical Shift (ppm)
Terminal Br-(CH ₃) ₂	31.40	C ₆ H ₃ (CH ₃)NH-	17.63
CO-O-CH ₂ -CH ₂ -	64.20	-CH ₂ , of PTMG	43.91–44.77
C ₆ H ₃ (CH ₃)NH-	115.14–137.30	-O-CH ₂ - of PTMG	69.49
C ₆ H ₃ (CH ₃)NH-	17.16	-CH ₂ - of PMMA	17.63
-CH ₂ , of PTMG	25.83–26.16	>C< of PMMA	38.95–40.05
-O-CH ₂ - of PTMG	69.80	>C=O of PMMA	175.8–176.8
-CH ₂ -O-CO-NH-	61.83	-OCH ₃ of PMMA	50.16–53.42
Br-C(CH ₃) ₂ -CO-O-	56.95–58.75	-OCH ₃ of PMMA (rr)	50.16
O-CO-NH- of urethane	153.56–154.33	-OCH ₃ of PMMA (mr)	51.17
Br-(CH ₃) ₂ -CO-O- of HMB	170.81	-OCH ₃ of PMMA (mm)	53.42
		-CH ₃ of PMMA	16.42–20.68
		-CH ₃ of PMMA (rr)	16.42
		-CH ₃ of PMMA (mr)	17.63
		-CH ₃ of PMMA (mm)	20.68

-CH₃ protons of TDI and -CH₂ protons of PMMA blocks were appeared in the region 1.8–1.9 ppm. Two -OCH₂ groups attached to -O-CONH and -O-CO present in 2-methyl-2-bromopropionate end groups resonate at 4.11 and 4.31 ppm respectively. The tacticity ratio of PMMA prepared in the present investigation is *rr:rm:mm* = 56:37:7 which is similar to the reported tacticity ratio (*rr:rm:mm*, 58:37:5) of PMMA prepared by ATRP of MMA.⁵² In the ^{13}C NMR spectrum of ABA tri-block copolymer (Figure 5(a)), the -C=O and >C< groups of PMMA were appeared in the region 175.8–176.8 ppm and 38.95–40.05 ppm respectively. The -CH₃ groups of PMMA resonate at 16.4, 17.6 and 18.4 ppm which correspond to rr, mr and mm respectively.⁵¹ The -CH₃ groups of TDI was merged with -CH₃ groups (rr) of PMMA at 17.6 ppm and -CH₂ groups of PMMA block was appeared at 43.91–44.77 ppm. The -OCH₃ groups of PMMA were appeared at 50.16, 51.17 and 53.42 ppm which correspond to rr, mr and mm respectively.⁵¹ As the ratio of phenyl carbons from TDI, carbonyl carbons of urethane and ester groups are lower than the PMMA and PTMG blocks, the peaks correspond to these groups are not appeared in the ^{13}C NMR of the block copolymer. However the peaks correspond to CH₂ and OCH₂

carbon present in PTMG are appeared at 25.8 and 69.4 ppm respectively. In addition to this, all the peaks correspond to polyurethane and PMMA blocks are present in the ^1H NMR, which is a clear evidence for the formation of ABA type tri-block copolymers. The molar content of PMMA in the tri block copolymers can easily be found out by comparing molecular weights (obtained by GPC) of MBP-PU-MBP and ABA tri-block copolymers which are given in Table I. It can also be found out by peak integration ratio of -CH₂-CH₂- group of PTMG at 1.5 ppm and -CH₃ protons of PMMA blocks at 0.84–1.21 ppm through ^1H NMR technique, as reported in the literature⁴³ and the results are given in Table I. The molar content of PMMA from GPC and ^1H NMR techniques are comparatively similar.

Thermal Studies

The PMMA-*b*-PU-*b*-PMMA tri-block copolymer obtained at 180 min (POLY 5 of Table I) was further characterized by DSC and the results are presented in Figure 6. All the glass transition temperatures (T_g) considered in this investigation is the middle point between onset and offset points. The T_g of the polyol segment present in MBP-PU-MBP and PMMA-*b*-PU-*b*-

Figure 6. DSC curves of (a) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, POLY 5 and (b) MBP-PU-MBP.

Figure 7. TGA curves of (a) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, POLY 5 and (b) MBP-PU-MBP.

PMMA tri-block copolymers was appeared at -42°C and -48°C respectively. The T_g of the PMMA block was observed at 112°C which is similar to the literature value for the tacticity ratio of *rr:rm:mm* = 56:37:6.⁵³ Thermal stability of MBP-PU-MBP and PMMA-*b*-PU-*b*-PMMA tri-block copolymer (POLY 5 in Table I) was also studied using TGA and the results are presented in Figure 7. MBP-PU-MBP undergoes two-stage decomposition; one is around 284°C which is due to the decomposition of the NHCOO groups and another is around 404°C which is due to the decomposition of PTMG blocks. In the case of tri-block copolymers, the decomposition is not in stages but the overall thermal stability of PMMA-*b*-PU-*b*-PMMA tri-block copolymers is higher than the MBP-PU-MBP. Thermal degradation of standard radically prepared PMMA under nitrogen atmosphere proceeds in three steps correspond-

ing to the head-to-head linkage ($\sim 165^{\circ}\text{C}$), the chain-end initiation from the vinylidene ends ($\sim 270^{\circ}\text{C}$), and the step referred to as random scission within the polymer chain ($\sim 360^{\circ}\text{C}$).⁵⁴ Thermal degradation of the polymers synthesized with MBP-PU-MBP/CuBr/PMDETA initiating system occurred around 380°C only originating from random scission. This result is a further indication of the absence of abnormal linkages therefore confirming the high regioselectivity and absence of unwanted irreversible termination or transfer reactions.²³

CONCLUSIONS

For the first time telechelic 2-methyl-2-bromopropionate terminated polyurethane was successfully synthesized and used further as a macroinitiator to synthesize PMMA-*b*-PU-*b*-PMMA tri-block copolymers through ATRP mechanism. ATRP mechanism during the polymerization was confirmed from the linear increase of time-conversion and time- $\ln([M]_0/[M])$ plots. Furthermore, the lack of linearity was observed for M_n Vs conversion curve that may be due to the presence of inevitable termination reactions. $M_{n,th}$ of the ABA type tri-block copolymers was found to be more or less similar to $M_{n,GPC}$. The molar percentage of PMMA calculated through ^1H NMR is matching with GPC results. The results from spectral and thermal methods also confirmed the formation of novel 2-methyl-2-bromopropionate terminated PU and PMMA-*b*-PU-*b*-PMMA tri-block copolymers. As MBP-PU-MBP generated narrow MWD tri-block copolymers, this macroinitiator can be used to synthesis different hydrophilic-*b*-hydrophobic-*b*-hydrophilic tri-block copolymers. These results will be communicated in near future as a separate article.

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