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Atom Transfer Radical Polymerization of Methyl Methacrylate Using Telechelic Tribromo Terminated Polyurethane Macroinitiator

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Novel telechelic tribromo terminated polyurethane (Br_3-PU-Br_3) was used as a macroinitiator in atom transfer radical polymerization (ATRP) of methyl methacrylate using CuBr as a catalyst and *NN,N',N",N"*-pentamethyldiethylenetriamine (PMDETA) as a ligand. During the course of polymerization, poly(methyl methacrylate)-*b*-polyurethane-*b*-poly(methyl methacrylate) (PMMA-*b*-PU-*b*-PMMA) tri-block copolymers were formed. The resulting tri-block copolymers were characterized by gel permeation chromatography (GPC) and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Molecular weight of the tri-block copolymers increases with increasing conversion. This result shows Br_3-PU-Br_3/CuBr/PMDETA initiating system polymerized methyl methacrylate through ATRP mechanism. NMR spectroscopy results revealed that apart from bromine atom transfer from Br_3-PU-$Br_3$to PMDETA-CuBr complex, bromine atom transfer from the initially formed tri-block copolymer to PMDETA-CuBr complex also takes place, and, as a result, double bond terminated copolymer formed. Mole ratio of polyurethane and poly(methyl methacrylate) present in the PMMA-*b*-PU-*b*-PMMA tri-block copolymers was calculated using ^{1}H-NMR spectroscopy and it was found to be comparable with the mole ratio calculated through GPC results. Differential scanning calorimetric results confirmed the presence of two different phases in the tri-block copolymers.

Keywords: Atom transfer radical polymerization, multifunctional macroinitiator, polyurethane, β-scission, poly(methyl methacrylate)

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1 Introduction

The poor control over degree of polymerization, molecular weight distribution (MWD) and end groups of the polymers obtained in conventional radical polymerization can be improved by replacing it with controlled radical polymerization (CRP) (1–5). Atom transfer radical polymerization (ATRP) (6, 7) is one of the most promising CRP routes, where organic halide and copper halide are used as an initiator and a catalyst respectively with suitable ligands. Bromo (8) and chloro (9) functionalized polymers were effectively used in ATRP to prepare star, block and graft copolymers. As polyurethane (PU) is a versatile polymer which can be synthesized according to the need of the end users, PU based macroinitiator for ATRP would generate interesting block copolymers. In this point of view, telechelic polyurethane with -CH_2Br functional group at both ends was successfully synthesized in our lab and used as a ATRP macroinitiator to prepare tri-block copolymers (10, 11). But, during the initiation, polyurethane with -CH_2 radical at both ends was formed and this radical is less stable, as it is a primary radical. As a result, tri-block copolymers with broader MWD were formed. To overcome this, telechelic polyurethane with –$(CH_3)_2$Br end groups was effectively used to prepare tri-block copolymers with narrow MWD (12). As Br terminated PU was used effectively in ATRP as macroinitiator, in the next step, we prepared, for the first time, novel telechelic tribromo-terminated polyurethane macroinitiator (Br_3-PU-Br_3) and effectively used to polymerize styrene (13). During the polymerization of St using Br_3-PU-Br_3, we expected six polystyrene chains out of six Br atoms attached at the end of Br_3-PU-Br_3 macroinitiator. Interestingly, after one bromine atom was transferred from one side of Br_3-PU-Br_3 during polymerization, other two bromine atoms become less reactive and hence only one polystyrene chain was formed at the one side of Br_3-PU-Br_3. As a result, polystyrene-*b*-PU-*b*-polystyrene tri-block copolymers were formed and no other reactions were found. However, when MMA was polymerized using this multifunctional initiator, interesting results are obtained

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and, hence, it is presented in this paper as a separate report. It is important here to mention that 2,2,2-tribromoethanol itself was used as an ATRP initiator for the polymerization of MMA, but there was no side reactions during the polymerization (14). But, in the present case, when tribromo terminated polyurethane macroinitiator is used in ATRP on methyl methacrylate, some interesting reactions occurred and these reactions were not discussed in detail by any research group. Hence, detailed discussion on ATRP of MMA using tribromo terminated macroinitiator is presented in this report.

2 Experimental

2.1 Materials

Toluene diisocyanate (TDI, mixture of 80% 2,4 and 20% 2,6 isomers), dibutyltin dilaurate, 2,2,2-tribromoethanol (TBE, 97%) and PMDETA were used as received from Aldrich, U.S.A. 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. Poly (tetramethyleneoxide) glycol of molecular weight 1000 (PTMG, Aldrich, USA) was used after drying for 3 h at 105°C under reduced pressure. CuBr (CDH, India) was purified as described in the reported procedure (15) just prior to use. The inhibitor present in MMA (CDH, India) was removed by washing with 5% aqueous NaOH, washed again with distilled water, and stored over anhydrous sodium sulfate for 24 h. It was then distilled at reduced pressure and the middle portion was stored at 0–4°C until use. All other chemicals were of analytical grades and were used as received.

2.2 Characterization Methods

Fourier-transform nuclear magnetic resonance (FT-NMR) spectra were recorded on a Bruker DPX-300 NMR instrument using deuterated dimethyl sulfoxide as a solvent and tetramethylsilane as an internal standard. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet Impact 400 FTIR spectrophotometer. MWD, number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights were determined by gel permeation chromatography (GPC) using Polymer Laboratories GPC 50 integrated system equipped with differential refractometer (RI Detector) and PLgel 5μm MIXED-C column. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL/min and the molecular weights were calibrated using polystyrene standards. Glass transition temperatures were determined using differential scanning calorimeter (DSC) Q200 (TA 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.

2.3 Synthesis of Br_3-PU-Br_3 and Polymerization of MMA using Br_3-PU-Br_3/CuBr/PMDETA Initiating System

Tribromo terminated polyurethane, Br_3-PU-Br_3, was synthesized as described in our previous report (13). For the polymerization of MMA, first accurately weighed Br_3-PU-Br_3 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 period of time. At the end of the stipulated period, the sealed polymerization tube was removed from the oil bath and the reaction was arrested by dipping the sealed tube in an ice–salt mixture. The resulting solution was poured into a 10-fold excess of methanol and the resulting precipitate was filtered using sintered-glass crucible, washed with methanol, dried in vacuum, and weighed. The dried PMMA-*b*-PU-*b*-PMMA tri-block copolymer samples were washed thoroughly with acetonitrile to remove homo PMMA, if any, from the block copolymers, dried in vacuum, and weighed.

3 Results and Discussion

3.1 Polymerization of MMA using Br_3-PU-Br_3/CuBr/PMDETA Initiating System

To check the efficiency of Br_3-PU-Br_3, MMA polymerization was carried out using Br_3-PU-Br_3/CuBr/PMDETA initiating system as outlined in Scheme 1. During the polymerization, PMMA-*b*-PU-*b*-PMMA tri-block copolymers are formed as a major product as shown in Scheme 1. In general, multifunctional ATRP initiators tend to undergo side reactions such as branching and β-scission (16). The effect of changing initiator concentration is necessary to understand these side reactions. As Br_3-PU-Br_3 is also a multifunctional macroinitiator, two different initiator concentrations (1:1:1 and 0.5:1:1 mole ratios of Br_3-PU-Br_3/CuBr/PMDETA) were used in the present investigation. Here the concentration of Br_3-PU-Br_3 was calculated based on its number average molecular weight derived from GPC (cf. Tables 1 and 2). To select the polymerization temperature, initially, the polymerization was carried out at 80°C, but there was no polymerization and the polymerization at 90°C was sluggish. However, the polymerization at 100°C was not sluggish and, hence, 100°C was chosen as the polymerization temperature.

Though Br_3-PU-Br_3 initiated MMA, it is important to understand mechanism of polymerization. For this, effect of changing polymerization time on MMA polymerization was carried out. Tables 1 and 2 show the effect of time on MMA polymerization using 1:1:1 and 0.5:1:1 mole ratios of Br_3-PU-Br_3/CuBr/PMDETA respectively. Here, for the calculation of conversion, weight of $[MMA]_0$ was considered and weight of $[Br_3\text{-PU-}Br_3]_0$ was not considered, as

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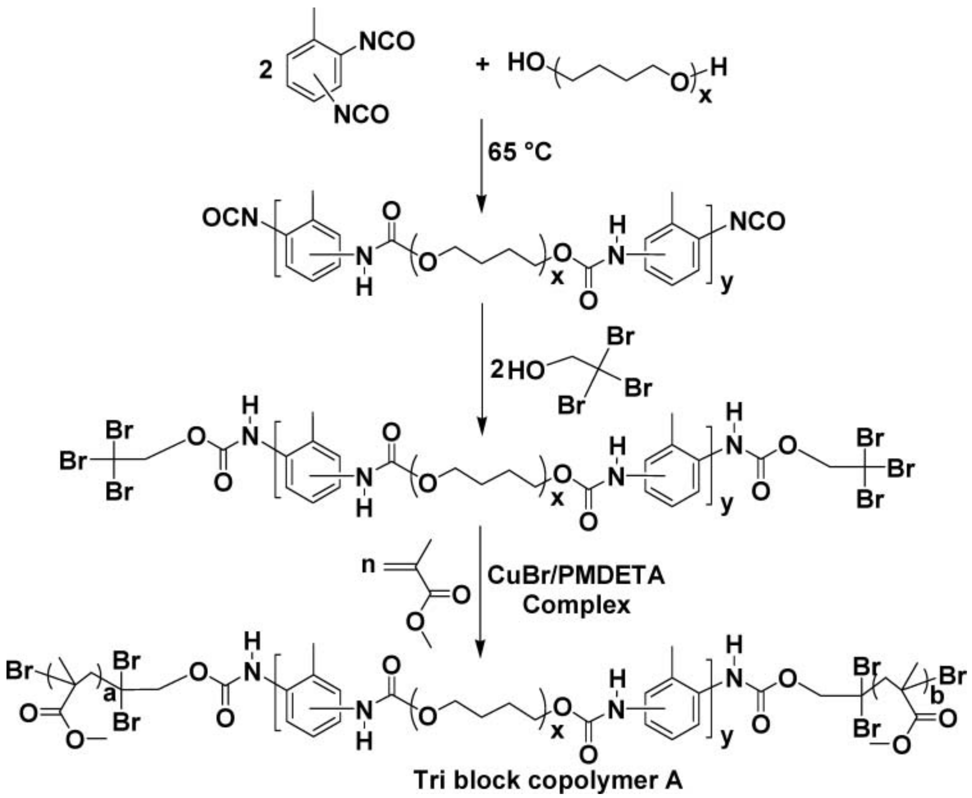

Sch. 1. Synthesis of PMMA-*b*-PU-*b*-PMMA tri-block copolymers.

chain length of Br_3-PU-Br_3 is same in the initiator as well as in the final tri-block copolymers. Time-conversion and time-ln ($[M]_0/[M]$) plots for MMA polymerization using 1:1:1 mole ratio are shown in Figure 1 and the same plots for 0.5:1:1 mole ratio are shown in Figure 2. The linear increase of ln ($[M]_0/[M]$) in Figures 1 and 2 shows both mole ratios generated and maintained constant concentration of propagating radicals throughout studied period of time. Figure 3 shows conversion-$\bar{M}_n$ and conversion-MWD plots for the polymerization of MMA using 1:1:1 mole ratio of Br_3-PU-Br_3/CuBr/PMDETA initiating system. Similarly conversion-$\bar{M}_n$ and conversion-MWD plots for MMA polymerization using 0.5:1:1 mole ratio are given in Figure 4. In both the cases, as the conversion increases, $\bar{M}_n$ also increases. This result shows that the present initiating system polymerized MMA through ATRP mechanism.

Table 1. Effect of time on ATRP of MMA using 1:1:1 mole ratio of Br_3-PU-Br_3/CuBr/PMDETA at 100°C

						GPC results			
Code No.	*Time (h)*	*Conv.*[a] *(%)*	*Molar content of PMMA*[b] *(%)*	*Molar content of PMMA*[c] *(%)*	$M_n \times 10^{-3}$ *(th)*[d]	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	*f*[e]
Br_3-PU- Br_3	0	0.0	–	0.0	–	6.1	8.1	1.33	–
TBCP 1	3	7.4	42.0	54.8	7.9	13.5	19.7	1.46	0.58
TBCP 2	7	17.2	67.8	83.2	10.4	36.4	57.5	1.58	0.28
TBCP 3	11	27.0	73.2	88.1	12.8	51.6	86.6	1.68	0.24
TBCP 4	15	36.8	77.0	90.0	15.3	61.1	95.3	1.56	0.25
TBCP 5	18	44.2	81.1	91.0	17.1	68.0	95.2	1.40	0.25

[a] Conversion determined gravimetrically.

[b] Molar content of PMMA was calculated by comparing integration values of the peaks derived from -CH_2-CH_2 protons of PTMO and -CH_3 protons of PMMA blocks in ^{1}H-NMR spectra (19).

[c] Molar content of PMMA was calculated by using $\bar{M}_n$ values of Br_3-PU-Br_3 and PMMA-*b*-PU-*b*-PMMA derived from GPC.

[d] $M_{n,th} = z + \bar{M}_n$ of Br_3-PU-Br_3 (16) where $z = ([MMA]_0/[Br_3\text{-PU-}Br_3]_0) \times$ MMA.

[e] $f = M_{n,th}/\bar{M}_{n,GPC}$ (16).

Polymerization conditions: $[Br_3\text{-PU-}Br_3]_0 = 1.0$ g ($1.0/6100 = 0.164$ mmol), $[PMDETA]_0 = [CuBr]_0 = 0.164$ mmol, DMF = 10 ml, $[MMA]_0 = 0.04075$ mol.

Table 2. Effect of time on ATRP of MMA using 0.5:1:1 mole ratio of Br_3-PU-Br_3/CuBr/PMDETA at 100°C.

						GPC results			
Code No.	*Time (h)*	*Conv.*[a] *(%)*	*Molar content of PMMA*[b] *(%)*	*Molar content of PMMA*[c] *(%)*	$M_n \times 10^{-3}$ *(th)*[d]	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	f^e
Br_3-PU-Br_3	0	0.0	–	0.0	–	6.1	8.1	1.33	–
POLY 1	3	7.4	51.2	62.5	7.6	16.3	29.6	1.82	0.46
POLY 2	7	14.7	63.7	78.0	9.0	27.8	55.0	1.98	0.32
POLY 3	11	22.1	71.2	85.5	10.6	42.3	87.9	2.08	0.25
POLY 4	15	29.4	76.3	89.8	12.0	59.9	103.6	1.73	0.20
POLY 5	18	35.6	89.9	91.5	13.3	72.5	116.7	1.61	0.18

[a] Conversion determined gravimetrically.

[b] Molar content of PMMA was calculated by comparing integration values of the peaks derived from -CH_2-CH_2 protons of PTMO and -CH_3 protons of PMMA blocks in ^{1}H-NMR spectra (19).

[c] Molar content of PMMA was calculated by using $\bar{M}_n$ values of Br_3-PU- $Br_3$and PMMA-*b*-PU-*b*-PMMA derived from GPC.

[d] $M_{n,th}$ = ([MMA]$_0$/[Br_3-PU-Br_3]$_0$)× monomer conversion + $\bar{M}_n$ of Br_3-PU-Br_3 (16).

[e] f = $M_{n,th}/\bar{M}_{n,GPC}$ (16).

Polymerization conditions: [Br_3-PU-Br_3]$_0$ = 0.5 g (0.5/6100 = 0.082 mmol), [PMDETA]$_0$ = [CuBr]$_0$ = 0.164 mmol, DMF = 10 ml, [MMA]$_0$ = 0.04075 mol.

In any living polymerization, $\bar{M}_{n,th}$ should be comparable to $\bar{M}_{n,GPC}$. In the present investigation, as it is shown in Tables 1 and 2, as well as Figures 3 and 4, there is a discrepancy between $\bar{M}_{n,th}$ and $\bar{M}_{n,GPC}$. This may be due to the involvement of second bromine atom present in the tri-block copolymer A of Scheme 2 that leads to the formation of branched copolymer C, PMMA radical D and double bond terminated block copolymer E. Due to these side reactions, MWD values of the tri-block copolymers from both the mole ratios are not narrow enough. Apparent initiator efficiency (f = $M_{n,th}/\bar{M}_{n,GPC}$) is also calculated for different polymerization time and it is high for TBCP 1 and POLY 1 and low for TBCP 3 and POLY 5. The discrepancy between $M_{n,th}$and $\bar{M}_{n,GPC}$ is the main reason for the low f values. But, similar range of f values was also reported during the synthesis of poly (hydroxyethyl methacrylate)-*b*-poly (ethylene oxide)-poly (hydroxyethyl methacrylate) tri-block copolymers through ATRP (17).

3.2 Spectral Characterization of PMMA-*b*-PU-*b*-PMMA Tri-Block Copolymers

The tri-block copolymers were characterized, first, by FTIR spectroscopy to confirm their structure. Figure 5(b) shows the FTIR spectrum of PMMA-*b*-PU-*b*-PMMA tri-block copolymer obtained at 7 h. (TBCP 2 in Table 1). For better comparison FTIR of Br_3-PU-$Br_3$is also included in Figure 5. The stretching vibrations of carbonyl groups

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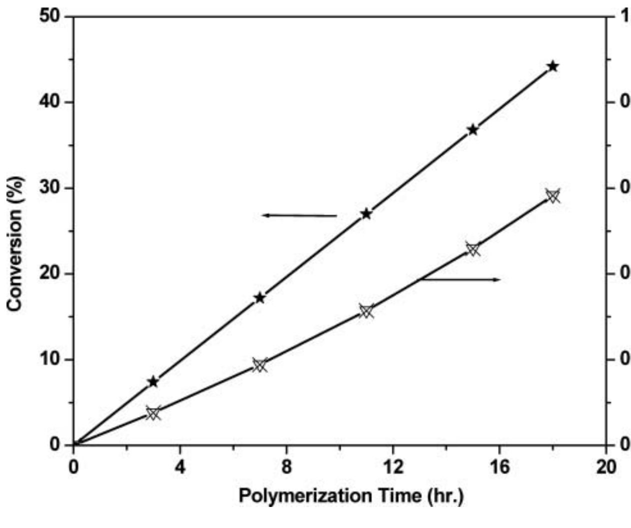

Fig. 1. Time-conversion and time-ln([M]$_0$/[M]) plots for the polymerization of MMA at 100°C using 1:1:1 mole ratio of Br_3-PU-Br_3/PMDETA/CuBr initiating system. [Br_3-PU-Br_3]$_0$ = 1.0 g (1.0/6100 = 0.164 mmol), [PMDETA]$_0$ = [CuBr]$_0$ = 0.164 mmol, DMF = 10 ml, [MMA]$_0$ = 0.04075 mol.

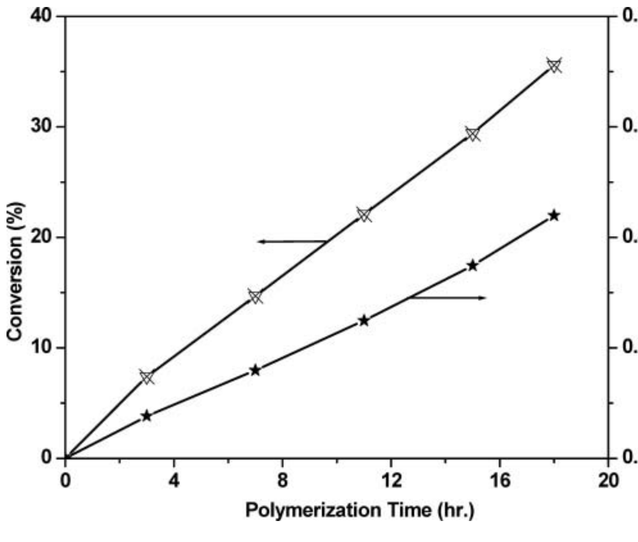

Fig. 2. Time-conversion and time-ln([M]$_0$/[M]) plots for the polymerization of MMA at 100°C using 0.5:1:1 mole ratio of Br_3-PU-Br_3/PMDETA/CuBr initiating system. [Br_3-PU-Br_3]$_0$ = 0.5 g (0.5/6100 = 0.082 mmol), [PMDETA]$_0$ = [CuBr]$_0$ = 0.164 mmol, DMF = 10 ml, [MMA]$_0$ = 0. 04075 mol.

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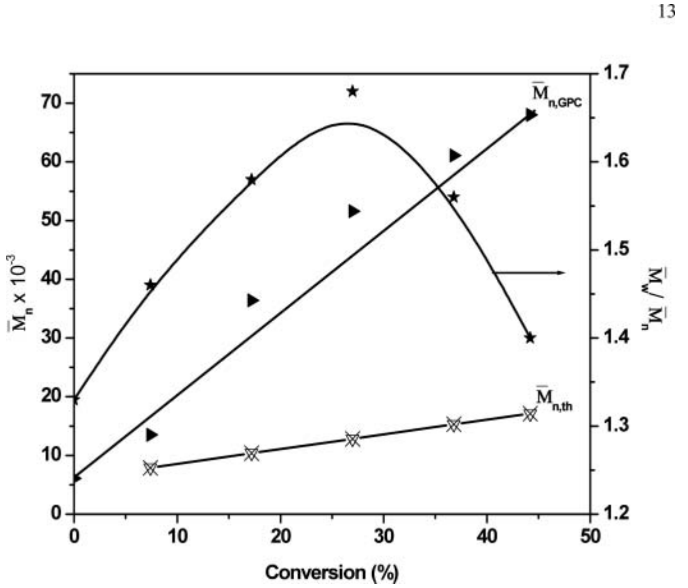


Fig. 3. Conversion-$\bar{M}_n$ and conversion-$\bar{M}_w/\bar{M}_n$ plots for the polymerization of MMA at 100°C using 1:1:1 mole ratio of Br_3-PU-Br_3/PMDETA/CuBr initiating system. $[Br_3\text{-PU-}Br_3]_0 = 1.0$ g ($1.0/6100 = 0.164$ mmol), $[PMDETA]_0 = [CuBr]_0 = 0.164$ mmol, DMF = 10 ml, $[MMA]_0 = 0.04075$ mol .

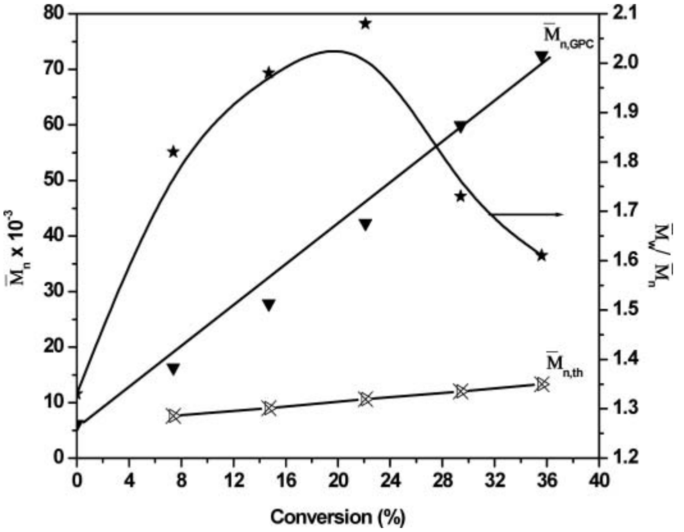
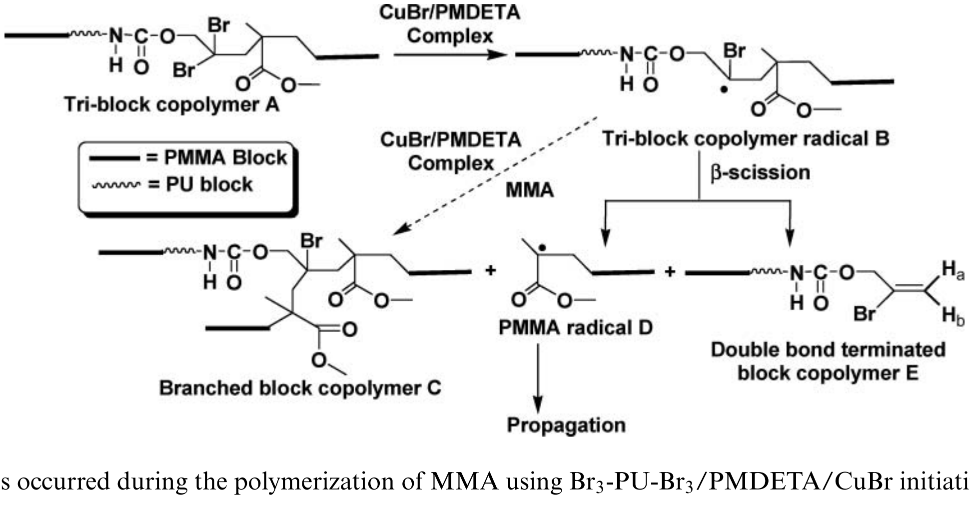


Fig. 4. Conversion-$\bar{M}_n$ and conversion-$\bar{M}_w/\bar{M}_n$ plots for the polymerization of MMA at 100°C using 0.5:1:1 mole ratio of Br_3-PU-Br_3/PMDETA/CuBr initiating system. $[Br_3\text{-PU-}Br_3]_0 = 0.5$ g ($0.5/6100 = 0.082$ mmol), $[PMDETA]_0 = [CuBr]_0 = 0.164$ mmol, DMF = 10 ml, $[MMA]_0 = 0.04075$ mol.

present in urethane and ester groups of PMMA blocks are observed as a single peak at 1722 cm^{-1}. The C-H stretching vibrations of methylene groups present in PU and PMMA are observed in the region 2787–2949 cm^{-1} and N-H stretching vibrations are observed at 3190–3390 cm^{-1}. The C-H bending vibrations of methylene groups present in PU and PMMA are observed at 1428–1595 cm^{-1}. The C-H bending vibrations of $-CH_3$ groups present in PU blocks (derived from TDI) and PMMA blocks are observed at 1355–1388 cm^{-1}. All the peaks corresponding to Br_3-PU-$Br_3$and new peaks corresponding to PMMA blocks are present in the FTIR spectrum of the tri-block copolymer further support the formation of PMMA-*b*-PU-*b*-PMMA tri-block copolymers. The stretching vibrations of C-H and C=C groups present in the double bond terminated block copolymer E (cf. Scheme 2) appeared as little peaks at 3007 cm^{-1} and 1601 cm^{-1}respectively. PMMA-*b*-PU-*b*-PMMA tri-block copolymers were also characterized by ^{1}H-NMR spectroscopy. Figure 6(b) shows ^{1}H-NMR spectrum of the tri-block copolymer obtained at 7 h (TBCP 2 in Table 1) and the spectral data for the tri-block copolymer is given in Table 3 along with the spectral data of Br_3-PU-Br_3. In the ^{1}H-NMR spectrum of the tri-block copolymer, the -CH_3 protons of PMMA gives three different peaks and presence of these three peaks indicates the presence of PMMA with three different tacticities. Syndiotactic (rr), atactic (mr) and isotactic (mm) PMMA show peaks at 0.78 ppm, 0.98 ppm and 1.20 ppm, respectively. The pro-



Sch. 2. Side reactions occurred during the polymerization of MMA using Br_3-PU-Br_3/PMDETA/CuBr initiating system.

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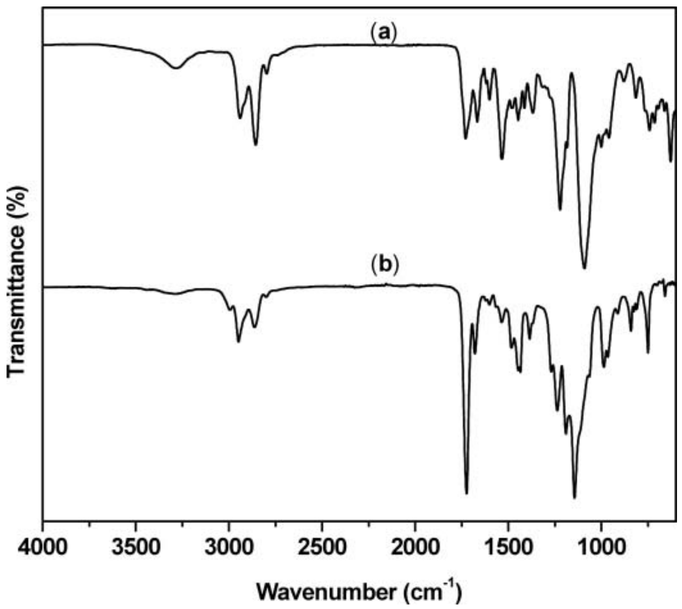

Fig. 5. FTIR spectra of (a) Br_3-PU-Br_3 and (b) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, TBCP 2.

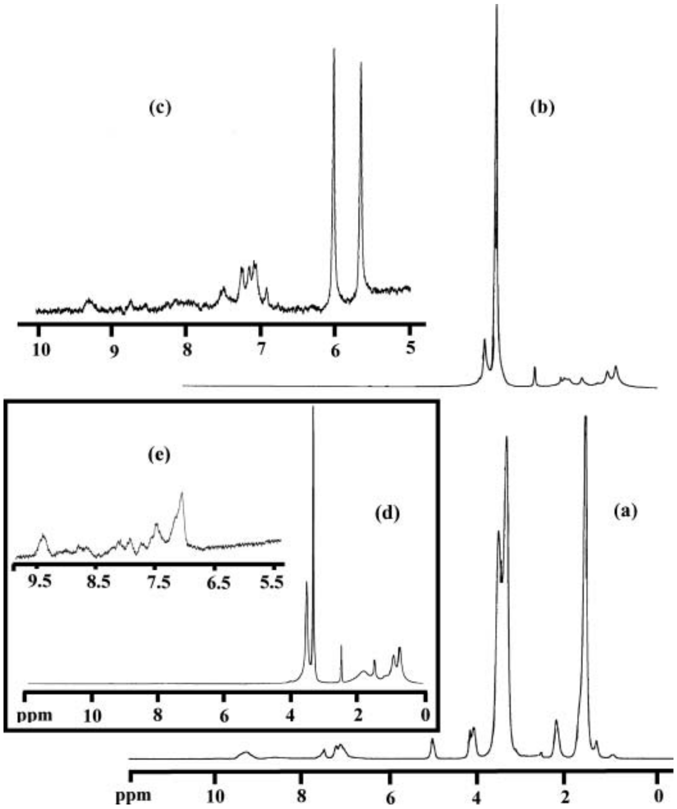

Fig. 6. ^{1}H-NMR spectra of (a) Br_3-PU-Br_3, (b) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, TBCP 2, (c) expanded spectrum of TBCP 2, (d) TBCP 5 and (e) expanded spectrum of TBCP 5.

tons of -OCH_3 protons of PMMA blocks appeared at 3.68 ppm. The -CH_2 and -OCH_2 groups of PTMG were appeared at 1.51 ppm and 3.31 ppm, respectively. The peak for -CH_2 protons of PMMA blocks is appeared in the region 1.88–1.95 ppm along with -CH_3protons of TDI. The terminal methylene protons present in CH_2-$CBr_3$of Br_3C-PU-CBr_3 appeared at 4.99 ppm (13). The disappearance of the peak at 4.99 ppm in the ^{1}H-NMR spectrum of tri-block copolymers suggest that bromine atom from Br_3-PU-Br_3 was effectively transferred to CuBr/PMDETA complex. The tacticity ratio of PMMA prepared in the present investigation is $rr{:}rm{:}mm = 56{:}37{:}7$ and this ratio is more or less similar to the reported tacticity ratio ($rr{:}rm{:}mm = 58{:}37{:}5$) of PMMA prepared by ATRP of MMA (18). The molar content of PMMA in tri block copolymers can easily be found out by comparing molecular weights (obtained by GPC) of Br_3-PU-Br_3 and tri-block copolymers which are given in Tables 1 and 2. It can also be found from the integration values of the peaks corresponding to -CH_2-CH_2- group of PTMO at 1.5 ppm and -CH_3 protons of PMMA blocks at 0.78-1.20 ppm as reported in the literature (19). The molar contents of PMMA in the tri-block copolymers were calculated using ^{1}H-NMR spectra and the results are given in Tables 1 and 2. The

Table 3. ^{1}H-NMR data of Br_3-PU-Br_3 and PMMA-*b*-PU-*b*-PMMA tri-block copolymers

Br_3-PU- Br_3		PMMA-*b*-PU-*b*-PMMA tri-block copolymers	
^{1}H	Chemical Shift (ppm)	^{1}H	Chemical Shift (ppm)
Terminal Br_3C-$C\underline{H}_2$-	4.99	-N-$\underline{H}$	8.63–9.30
-N-$\underline{H}$	8.63-9.28	$C_6\underline{H}_3$ (CH_3)NH-	7.10–7.53
$C_6\underline{H}_3$ (CH_3)NH-	7.10-7.48	C_6H_3 ($C\underline{H}_3$)NH-	1.88–1.95
C_6H_3 ($C\underline{H}_3$)NH-	2.16	-$C\underline{H}_2$ of PTMG	1.51
-$C\underline{H}_2$- of PTMG	1.50	-$OC\underline{H}_2$ of PTMG	3.31
-O-$C\underline{H}_2$- of PTMG	3.32	-$OC\underline{H}_3$ of PMMA	3.68
-$C\underline{H}_2$-O-CO-NH-	4.06-4.14	-CO-O-$C\underline{H}_2$-CH_2-	4.11
		-$C\underline{H}_3$ of PMMA	0.78-1.20
		-$C\underline{H}_3$ of PMMA (rr)	0.78
		-$C\underline{H}_3$ of PMMA (mr)	0.99
		-$C\underline{H}_3$ of PMMA (mm)	1.20

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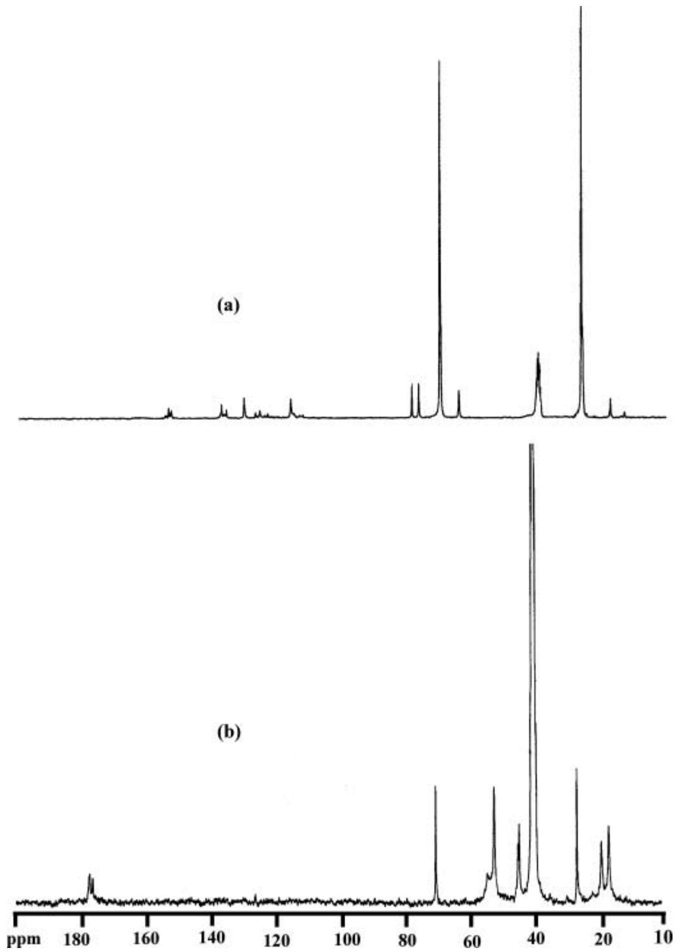

Fig. 7. ^{13}C-NMR spectra of (a) Br_3-PU-$Br_3$and (b) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, TBCP 2.

molar content values of PMMA from GPC and ^{1}H-NMR spectra are comparatively similar.

Figure 7 shows ^{13}C-NMR spectra of tri-block copolymer TBCP 2 and Br_3-PU-Br_3. The C=O groups of PMMA resonate in the region 176.22–177.16 ppm. The peaks corresponding to CH_2 and OCH_2 groups of PTMG appeared at 26.11 and 69.76 ppm respectively. The -CH_3 groups of PMMA resonate at 16.24 ppm, 18.55 ppm and 21.50 ppm which correspond to syndiotactic (rr), atactic (mr) and isotactic (mm) PMMA respectively (20). The -CH_3 groups present in PU and PMMA blocks appeared in the region 16.24–18.55 ppm. The -OCH_3 groups of PMMA generated three peaks at 43.96 ppm, 44.33 ppm and 44.40 ppm and these three peaks are due to syndiotactic (rr), atactic (mr) and isotactic (mm) PMMA, respectively (20).

3.3 Side Reactions Occurred During ATRP of MMA

In addition to the peaks corresponding to the polyurethane and PMMA blocks there are two additional peaks at 5.60 ppm and 6.01 ppm in Figure 6(c). If this is due to the presence of protons attached to the double bond of unreacted MMA, then, the methyl protons present in MMA should be present at 1.946 ppm. As there is no peak at 1.946 ppm in Figure 6(b), these additional peaks are not due to the unreacted MMA and they should be due to some other double bond. Literature survey shows that branching and β-scission are some of the side reactions which may take place when polyhaloalkane initiators are used in ATRP (16). Based on this observation, the probable side reactions that may take place in the present system are shown in Scheme 2. When Br_3-PU-Br_3 is used as an initiator, it forms tri-block copolymer A (cf. Scheme 2) with two bromine atoms at the junction of PU and PMMA blocks. When one of the above mentioned bromine atom is also transferred, tri-block copolymer radical B is formed and this radical is less reactive towards MMA due to the steric hindrance induced by adjacent neopentyl-like groups (16). As a result, branched block copolymer C is a less probable side product. The more probable side reaction is β-scission in tri-block copolymer radical B. This side reaction lead to a new PMMA radical D and double bond terminated block copolymer E as given in Scheme 2. This mechanism is very well matching with the ^{1}H-NMR results. The presence of two peaks at 5.60 ppm and 6.01 ppm in Figure 6(c) are due the H_a and H_b respectively (cf. Scheme 2). Another possibility of double bond formation is through conventional disproportionation reaction. But according to Koichi Hatada et al., the double bond from disproportionation in PMMA radical shows two peaks at 5.40 ppm and 6.14 ppm (21). But, in the present case, it is 5.60 ppm and 6.01 ppm. This result clearly shows that the peaks correspond to double bond are not due to the disproportionation, but, they are due to the β-scission (cf. Scheme 2). Here H_a(5.60 ppm) resonates more downfield than the hydrogen (5.40 ppm) of the double bond formed through conventional disproportionation. This is due to the simple reason that the H_a is *cis* to urethane group which is an electron withdrawing group whereas the hydrogen from the disproportionated PMMA is *cis* to –CH_2 group which is electron donating group. Similarly, H_b(6.01 ppm) resonates more upfield than the hydrogen (6.14 ppm) of the double bond formed through conventional disproportionation. This is because of the reason that the H_b is *cis* to Br whereas the other hydrogen is *cis* to ester group. It is well known that due to the anisotropic effect present in ketone, hydrogen *cis* to ester group resonate more downfield than the H_b *cis* to Br atoms where only isotropic effect is present. The formation of double bond block copolymer, E (Scheme 2) was further investigated for both the mole ratios (1:1:1 and 0.5:1:1 mole ratios of Br_3-PU-Br_3/CuBr/PMDETA) at different polymerization time. The intensity of peaks at 5.60 ppm and 6.01 ppm is high for TBCP 2 and POLY 2 as shown in Figure 6(c) and 8(a), respectively. However, as the conversion increases the intensity decreases and at 18 h, the block copolymer, POLY 5 has no double bond in its structure as shown in Figure 8(b). The disappearance of double bond may be due the less intensity of H_a and

H_b protons at 18 h or all the H_a and H_b protons might have been reacted already as 18 h is too long time for any double bond to exist at ATRP conditions. But, these results confirm that the additional signals at 5.60 ppm and 6.01 ppm are due the atom transfer reaction and not due to the conventional disproportionation reaction. The presence of this side reaction may be additional reason for the inconsistent relationship between $M_{n,th}$ and $\bar{M}_{n,GPC}$ as shown in Figures 3 and 4. However these types of results were not occurred during the polymerization of styrene under the same conditions (13). The reason for this discrepancy might be due the presence of less hindered styrene groups as compared to the more hindered neopentyl like groups present in PMMA-*b*-PU-*b*-PMMA tri-block copolymers. Similar types of results has been reported for the polymerization of meth (acrylates) using polychloroalkanes through ATRP mechanism (16).

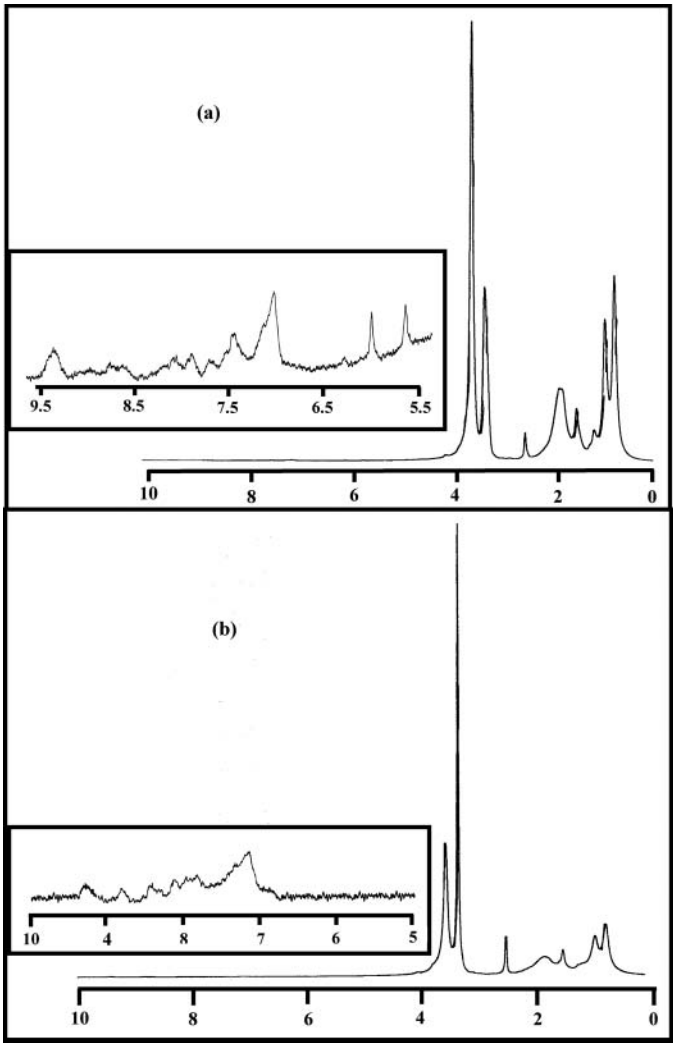

Fig. 8. ^{1}H-NMR spectra of (a) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, POLY 2 and (b) POLY 5.

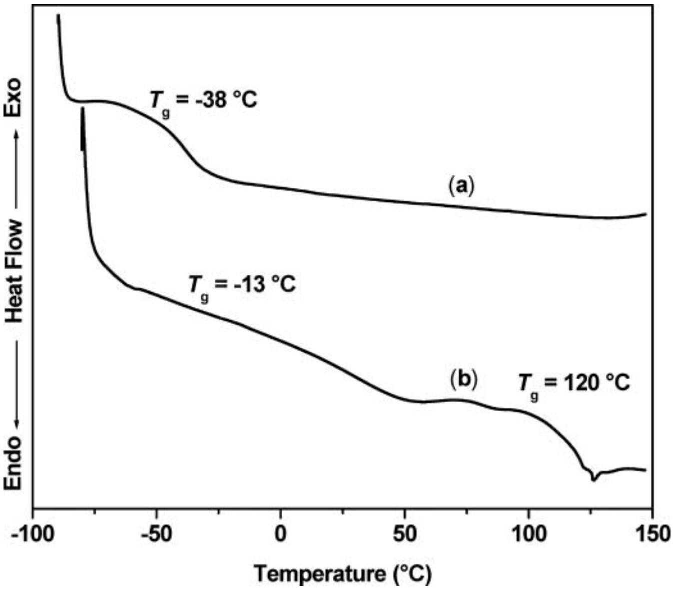

Fig. 9. DSC curves of (a) Br_3-PU-$Br_3$and (b) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, TBCP 2.

3.4 Thermal Studies

PMMA-*b*-PU-*b*-PMMA tri-block copolymer obtained at 7 h (TBCP 2 of Table 2) was characterized by DSC and the results are presented in Figure 9 along with the DSC curves of Br_3-PU-Br_3. All the glass transition temperatures (T_g) considered in this investigation are the middle point between onset and offset points. The $T_g$of the polyol segment present in Br_3-PU-Br_3 appeared at −38°C. The glass transition temperatures of polyol and PMMA segments in PMMA-*b*-PU-*b*-PMMA tri-block copolymers are appeared at −13°C and 120°C, respectively. The T_g of the PMMA block is similar to the literature value of PMMA with tacticity ratio of *rr*:*rm*:*mm* = 56:37:6 (22). The two glass transition temperatures present in the DSC curves of PMMA-*b*-PU-*b*-PMMA tri-block copolymers show that the block copolymers exist in phase separated nature.

The TGA curve for PMMA-*b*-PU-*b*-PMMA tri-block copolymer (TBCP 2 in Table 2) is given in Figure 10(b). Thermal stability of Br_3-PU-$Br_3$was also studied and the TGA curve of Br_3-PU-Br_3along with its derivative curve is given in Figure 10(a). Br_3-PU-Br_3undergoes two-stage decomposition, one is at 259°C which is due to the decomposition of the -NHCOO groups and another is at 336°C which is due to the decomposition of PTMG blocks. In the case of tri-block copolymer, the decomposition is not in stages but the overall thermal stability of PMMA-*b*-PU-*b*-PMMA tri-block copolymers is higher than the Br_3-PU-Br_3. Thermal degradation of standard radically prepared PMMA under nitrogen atmosphere proceeds in three steps. First decomposition is at 165°C which corresponds to the cleavage of head-to-head linkage, second step is at 270°C which corresponds to the chain-end initiation from the vinylidene ends and last degradation is at 360°C which is due to the

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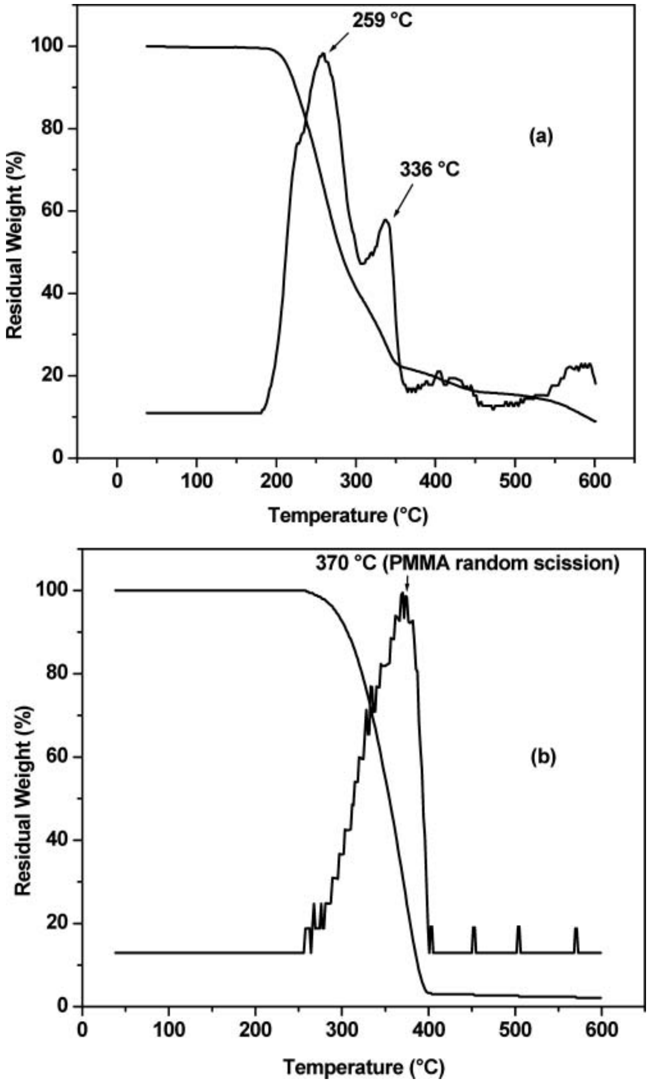

Fig. 10. TGA curves of (a) Br_3-PU-$Br_3$and (b) PMMA-*b*-PU-*b*-PMMA tri-block copolymer, TBCP 2.

random scission of PMMA chain (21, 23). Major thermal degradation of the tri-block copolymers synthesized with Br_3-PU-Br_3/CuBr/PMDETA initiating system occurred around 370°C originating from random scission. This result is a further indication of the absence of abnormal linkages therefore confirming the high regioselectivity and virtual absence of unwanted termination reactions.

4 Conclusions

For the first time, telechelic tribromo-terminated polyurethane, Br_3-PU-Br_3, was successfully used to polymerize MMA. Br_3-PU-Br_3/CuBr/PMDETA initiating system follows ATRP mechanism which was confirmed from the linear increase of conversion-$\bar{M}_n$ plots. Discrepancy between$\bar{M}_{n,th}$and $\bar{M}_{n,GPC}$ values is due to the side reactions. The presence of double bonds at the end of tri-block copolymers was confirmed by NMR spectroscopic analysis. Apparent initiator efficiency was found to be less because of the side reactions. However, linear increase of $\bar{M}_n$ with increase of conversion is the clear evidence to confirm the formation of block copolymers was through ATRP mechanism. The molar percentage of PMMA was calculated using ^{1}H-NMR spectra and it is matching with GPC results. Spectral and thermal studies also confirmed the formation of PMMA-*b*-PU-*b*-PMMA tri-block copolymers.

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