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Telechelic Multifunctional Polyurethane-Based Macroinitiator for the Synthesis of Polystyrene-*block*-Polyurethane-*block*-Polystyrene Tri-Block Copolymers via Atom Transfer Radical Polymerization

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Atom transfer radical polymerization was successfully used to synthesize polystyrene-*b*-polyurethane-*b*-polystyrene tri-block copolymers (PSt-*b*-PU-*b*-PSt) using telechelic multifunctional polyurethane (Br₃C-PU-CBr₃) as a macroinitiator. Along with macroinitiator, CuBr and N,N,N',N'',N''-pentamethyldiethyltetramine (PMDETA) were also used as catalyst and ligand, respectively to polymerize styrene. The linear increase of \bar{M}_n with conversion shows that Br₃C-PU-CBr₃/CuBr/PMDETA initiating system polymerizes styrene through controlled radical polymerization mechanism. Mole ratio of polyurethane and polystyrene present in PSt-*b*-PU-*b*-PSt tri-block copolymers was calculated using proton nuclear magnetic resonance spectroscopy and the results were found to be comparable with the gel permeation chromatography results. Differential scanning calorimetric results confirmed the presence of polyurethane and polystyrene phases in the tri-block copolymers.

Keywords: atom transfer radical polymerization, differential scanning calorimeter, polyurethane, polystyrene, tri-block copolymers

1 Introduction

Radical polymerization is widely used for the production of a substantial amount of polymeric materials because of its mild polymerization conditions, compatibility with wide variety of solvents and monomers, and its high tolerance towards traces of impurities, water, functional groups, and additives. However, molecular weight control in radical polymerization is quite difficult due to the presence of inevitable irreversible termination. To avoid this occurrence of irreversible termination, different ways to introduce livingness in free radical polymerization were proposed and they were collectively termed as controlled radical polymerization (CRP) (1–7). CRP facilitated the synthesis of wide variety of polymeric materials with predetermined molecular weight, narrow MWD and desired chain end groups (8, 9). CRP based on ruthenium complexes and copper complexes are some of the well established CRP routes and these two routes have similar mechanism but the former one is called as metal catalyzed radical polymerization

(10, 11) and the latter one is called as atom transfer radical polymerization (ATRP) (12, 13). ATRP exploits organic halides as initiators and transition metals in their lower oxidation state complexed with suitable ligands as catalysts (14, 15). A variety of polymers and copolymers with different functionality, composition and end groups have been successfully prepared through ATRP (16, 17).

Polyurethanes are versatile polymers that have found many applications in various fields and their versatile nature is due to the simple variation of their properties by just changing the ratio and nature of diols and diisocyanates (18, 19). To prepare more versatile polymers, synthesis of tri-block copolymers based on polyurethane (PU) was attempted in our lab using –CH₂Br terminated PU as an ATRP macroinitiator. The radicals generated from this macroinitiator were only primary radicals and hence they were not stable enough to achieve controlled radical polymerization (20, 21). However, to control the polymerization and to get the narrow polydisperse polymers, novel 2-methyl-2-bromopropionate terminated polyurethane (22) and tetraphenylethane containing polyurethane (23) have been successfully used in ATRP and reverse ATRP, respectively. Many bifunctional macroinitiators have already been used for the polymerization of different monomers through ATRP mechanism (24, 25). In search of

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a macroinitiator which can generate stable tertiary radical, polymerization of styrene using telechelic tribromo terminated polyurethane macroinitiator ($\text{Br}_3\text{C-PU-CBr}_3$) is reported in this paper. Along with $\text{Br}_3\text{C-PU-CBr}_3$, CuBr and $\text{N, N, N', N'', N''}$ -pentamethyldiethylenetriamine (PMDETA) are used as catalyst and ligand, respectively. It is important here to mention that if predetermination of molecular weight of polyurethane and polystyrene is successful, then this method can be used to polymerize variety of monomers to get different types of tri-block copolymers.

2 Experimental

2.1 Materials

Dibutyltin dilaurate, 2, 2, 2-tribromoethanol (TBE; 97%), toluene diisocyanate (TDI; a mixture of 80% 2, 4-TDI and 20% 2, 6-TDI isomers), and PMDETA were used as received from Aldrich, USA. 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. Just before use, CuBr (Aldrich, USA) was purified as described in the literature (26). The inhibitor present in styrene (St; Aldrich, USA) 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. Poly(tetramethyleneoxide) glycol of molecular weight 1000 (PTMG; Aldrich, USA) was used as received after drying it by heating at 105°C under a vacuum for 3 h. All other chemicals used were of analytical grades and were used as received.

2.2 Synthesis of $\text{Br}_3\text{C-PU-CBr}_3$

For the preparation of $\text{Br}_3\text{C-PU-CBr}_3$, first dried PTMG of molecular weight 1000 (0.02 mol) was taken in a 250 ml three-necked round bottom flask, fitted with a mechanical stirrer, nitrogen inlet, dropping funnel and heated in an oil bath. When the temperature reached 65°C, TDI (0.04 mol) was added dropwise 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, TBE (0.04 mol) in 15 ml DMF was added, followed by dibutyltin dilaurate (2 mol% of NCO, 0.000396 mol). The reaction was allowed to proceed until complete disappearance of isocyanate group, which was monitored and confirmed by the Fourier-transform infrared (FTIR) spectroscopy. At the end of the reaction, the mixture was poured into 500 mL of methanol and the resulting viscous solid was washed repeatedly three times with methanol and dried under vacuum.

2.3 Synthesis of PSt-*b*-PU-*b*-PSt tri-block copolymers

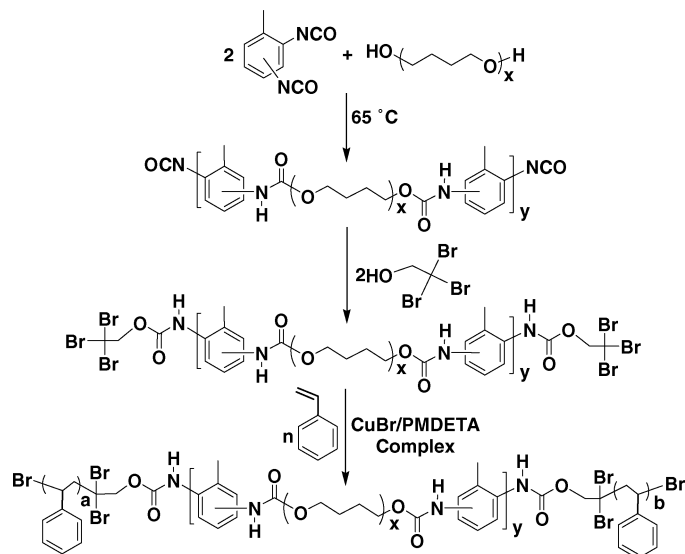
For the synthesis of PSt-*b*-PU-*b*-PSt tri-block copolymers, a first calculated amount of $\text{Br}_3\text{C-PU-CBr}_3$ was dissolved in DMF and known quantities of PMDETA, CuBr and St were added successively. Then, the homogeneous reaction mixture was degassed by three alternate freeze-pump-thaw cycles, sealed under vacuum and placed in a thermostated oil bath controlled to $\pm 0.01^\circ\text{C}$ for a 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 cyclohexane and acetone to remove homo PSt and PU, respectively, dried in vacuum, and weighed.

2.4 Characterization Techniques

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. FTIR spectra were recorded as a KBr pellet on a Nicolet Impact 400 FTIR spectrophotometer. Number-average (\bar{M}_n) and weight-average (\bar{M}_w) molecular weights and molecular weight distribution (MWD) were determined by gel permeation chromatography (GPC) using polymer laboratories GPC 50 integrated system equipped with differential refractometer (RI Detector) and PLgel 5 μm 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. Differential scanning calorimetry (DSC) was carried out using a DSC Q200 instrument (TA instruments, USA) at a heating rate of 10°C/min under N_2 atmosphere and thermo gravimetric analysis (TGA) was carried out using a DTG-60 instrument (Shimadzu, Japan) at a heating rate of 10°C/min under N_2 atmosphere.

3 Results and Discussion

Polystyrene and PU containing multi-block copolymers were already synthesized through iniferter and nitroxyl radical mediated CRP of styrene (27). However, polystyrene and PU containing tri-block copolymers were not reported and hence, these tri-block copolymers were prepared for the first time in our lab using $-\text{CH}_2\text{Br}$ terminated PU as an ATRP macroinitiator. As theoretical \bar{M}_n values of the tri-block copolymers from $-\text{CH}_2\text{Br}$ terminated macroinitiator were not close to experimental \bar{M}_n , we synthesized a novel multifunctional macroinitiator, $\text{Br}_3\text{C-PU-CBr}_3$ and ATRP of styrene using this macroinitiator is presented in



Sch. 1. Synthesis of $\text{Br}_3\text{C-PU-CBr}_3$ and $\text{PSt-}b\text{-PU-}b\text{-PSt}$ tri-block copolymers.

this paper. Scheme 1 shows synthesis of $\text{Br}_3\text{C-PU-CBr}_3$ and $\text{PSt-}b\text{-PU-}b\text{-PSt}$ tri-block copolymers. When $\text{Br}_3\text{C-PU-CBr}_3/\text{CuBr}/\text{PMDETA}$ initiating system was used for the polymerization of St, $\text{PSt-}b\text{-PU-}b\text{-PSt}$ tri-block copolymers were formed. The ratio of $\text{Br}_3\text{C-PU-CBr}_3$: CuBr : PMDETA initiating system was maintained at 1:1:1, respectively and the concentration of $\text{Br}_3\text{C-PU-CBr}_3$ was calculated using molecular weight of $\text{Br}_3\text{C-PU-CBr}_3$ obtained through GPC (cf. Table 1). 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 polymerization temperature.

3.1 Mechanism

To understand the mechanism of polymerization, the effect of changing polymerization time on the polymerization of St using $\text{Br}_3\text{C-PU-CBr}_3/\text{CuBr}/\text{PMDETA}$ initiating system was carried out. Table 1 shows polymerization of St using $\text{Br}_3\text{C-PU-CBr}_3/\text{CuBr}/\text{PMDETA}$ at 100°C . Time-conversion and $\ln([M]_0/[M])$ plots for St polymerization at 100°C is shown in Figure 1. The linear increase of $\ln([M]_0/[M])$ in Figure 1 shows that the concentration of propagating radicals is constant during the studied period of time. Figure 2 shows conversion- \bar{M}_n and conversion-MWD plots for the polymerization of St at 100°C . In this case, as the conversion increases, \bar{M}_n also increases. This result shows that the present initiating system polymerizes St through ATRP mechanism. In any living polymerization, $\bar{M}_{n,\text{th}}$ should be comparable to $\bar{M}_{n,\text{GPC}}$. In the present investigation, as shown in Table 1, it is interesting to note that $\bar{M}_{n,\text{th}}$ and $\bar{M}_{n,\text{GPC}}$ values were found to be more or less similar. These results further support the fact that the $\text{Br}_3\text{C-PU-CBr}_3/\text{CuBr}/\text{PMDETA}$ initiating system polymerizes styrene through a CRP mechanism. The apparent initiator efficiency ($f = \bar{M}_{n,\text{th}}/\bar{M}_{n,\text{GPC}}$) was also calculated for different time and it is high for PS-PU-PS 5 (Table 1, 0.81) and low for PS-PU-PS 2 (Table 1, 0.77). The low f value for the present initiating system indicates that more irreversible termination reactions were occurred during the polymerization. However the values of f in the present investigation are in the range of reported f values for ATRP. GPC analysis was performed to determine \bar{M}_n , \bar{M}_w and \bar{M}_w/\bar{M}_n of $\text{Br}_3\text{C-PU-CBr}_3$ and $\text{PSt-}b\text{-PU-}b\text{-PSt}$ tri-block copolymers. When $-\text{CH}_2\text{Br}$ terminated PU was used as an ATRP macroinitiator, bimodal peaks were observed in GPC whereas in the present investigation unimodal peaks are observed. This result shows the present initiating system is polymerizing styrene in a controlled manner. As shown in Table 1 and Figure 2, the

Table 1. Effect of time on ATRP of St for 1:1:1 mole ratio of $\text{Br}_3\text{C-PU-CBr}_3/\text{CuBr}/\text{PMDETA}$ at 100°C

Code No.	Time (h)	Conversion ^a (%)	Molar content of PSt ^b	Molar content of PSt ^c (%)	$\bar{M}_n \times 10^{-3}$ (th) ^d	GPC results			
						$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	M_w/M_n	f^e
$\text{Br}_3\text{C-PU-CBr}_3$	0	0.0	—	0.0	—	6.1	8.1	1.33	—
PS-PU-PS 1	3	3.0	26.3	29.8	6.9	8.7	17.2	1.98	0.79
PS-PU-PS 2	7	8.1	36.3	42.9	8.2	10.7	20.0	1.87	0.77
PS-PU-PS 3	11	12.8	44.9	48.7	9.5	11.9	21.5	1.81	0.80
PS-PU-PS 4	15	18.8	49.5	55.4	11.0	13.7	24.1	1.76	0.80
PS-PU-PS 5	18	23.4	52.3	59.8	12.3	15.2	25.5	1.68	0.81

^a Conversion = $[(\text{Weight of PS-PU-PS} - \text{Weight of } \text{Br}_3\text{C-PU-CBr}_3)/\text{Weight of styrene}] \times 100$.

^b Molar content of PSt was calculated by comparing integration values of the peaks derived from $-\text{CH}_2-\text{CH}_2$ protons of PTMO and PSt blocks in $^1\text{H-NMR}$ spectra (27).

^c Molar content of PSt = $[(\bar{M}_n \text{ of PS-PU-PS} - \bar{M}_n \text{ of } \text{Br}_3\text{C-PU-CBr}_3)/\bar{M}_n \text{ of PS-PU-PS}] \times 100$.

^d $\bar{M}_{n,\text{th}} = \{([St]_0/[Br_3C-PU-CBr_3]_0) \times \text{monomer conversion}\} + \text{molecular weight of } \text{Br}_3\text{C-PU-CBr}_3$ (30).

^e $f = \bar{M}_{n,\text{th}}/\bar{M}_{n,\text{GPC}}$ (30).

Polymerization conditions: $[Br_3C-PU-CBr_3]_0 = [PMDETA]_0 = [CuBr]_0 = 0.0164\text{m/L}$; $[St]_0 = 4.31\text{m/L}$; solvent = DMF.

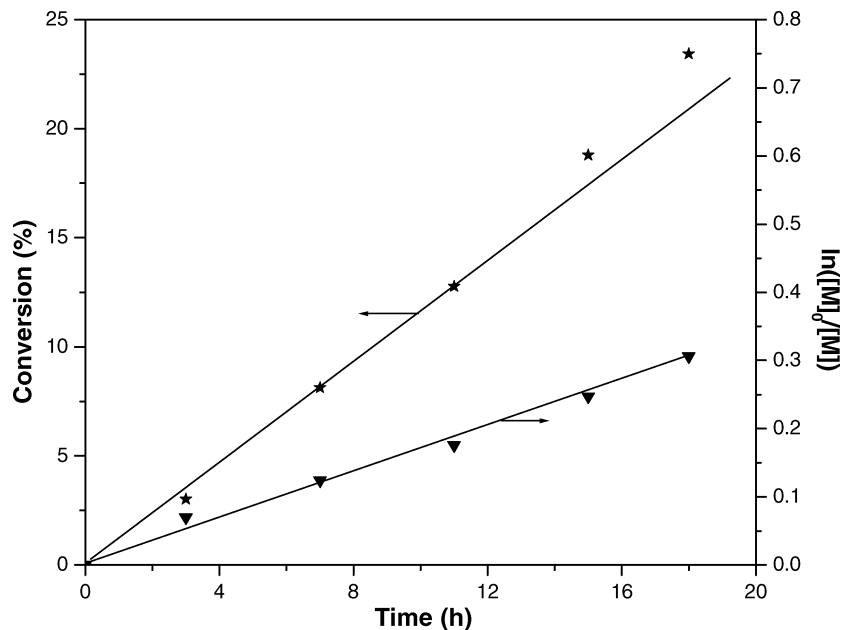


Fig. 1. Time-conversion and time- $\ln([M]_0/[M])$ plots for the polymerization of St at 100°C using 1:1:1 mole ratio Br in $\text{Br}_3\text{C-PU-CBr}_3/\text{PMDETA}/\text{CuBr}$ initiating system. Polymerization conditions: $[\text{Br}_3\text{C-PU-CBr}_3]_0 = [\text{PMDETA}]_0 = [\text{CuBr}]_0 = 0.0164\text{m/L}$; $[\text{St}]_0 = 4.31\text{ m/L}$; solvent = DMF.

experimental \bar{M}_n roughly agrees with the theoretical \bar{M}_n and initiator efficiency is in the range of reported values. These results confirm that the present initiating system, $\text{Br}_3\text{C-PU-CBr}_3/\text{CuBr}/\text{PMDETA}$, is more efficient and controlled in comparison to $\text{BrH}_2\text{C-PU-CH}_2\text{Br}/\text{CuBr}/\text{PMDETA}$ initiating system for the ATRP of styrene.

3.2 Spectral Studies

The tri-block copolymers synthesized were further characterized by FTIR spectroscopy to confirm the structure. Figure 3 shows the FTIR spectra of the $\text{Br}_3\text{C-PU-CBr}_3$ and $\text{PSt-}b\text{-PU-}b\text{-PSt}$ tri-block copolymer obtained at 7 h. (Table 1, PS-PU-PS 2). In the FTIR spectrum of $\text{Br}_3\text{C-}$

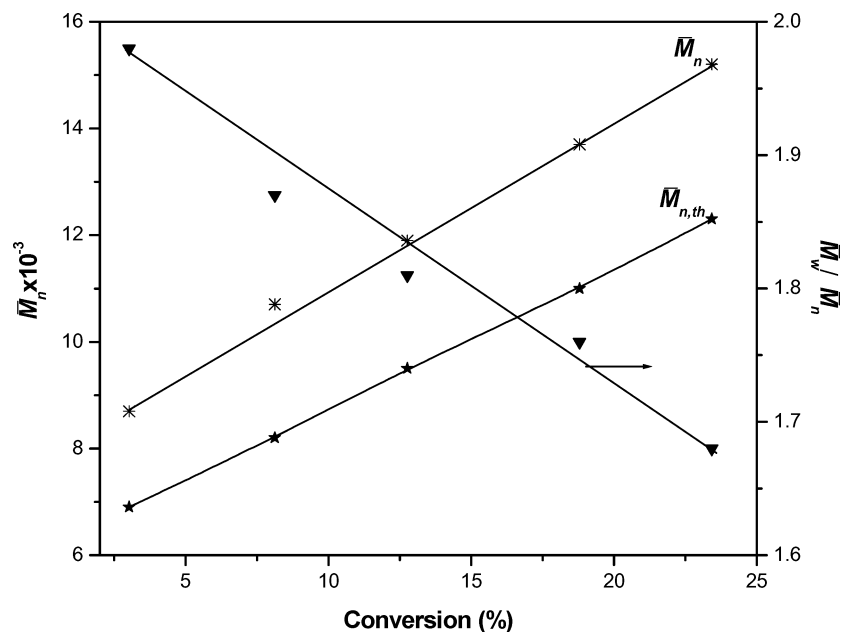


Fig. 2. Conversion- \bar{M}_n and conversion- \bar{M}_w/\bar{M}_n plots for the polymerization of St at 100°C using 1:1:1 mole ratio of Br in $\text{Br}_3\text{C-PU-CBr}_3/\text{PMDETA}/\text{CuBr}$ initiating system. Polymerization conditions: $[\text{Br}_3\text{C-PU-CBr}_3]_0 = [\text{PMDETA}]_0 = [\text{CuBr}]_0 = 0.0164\text{m/L}$; $[\text{St}]_0 = 4.31\text{ m/L}$; solvent = DMF.

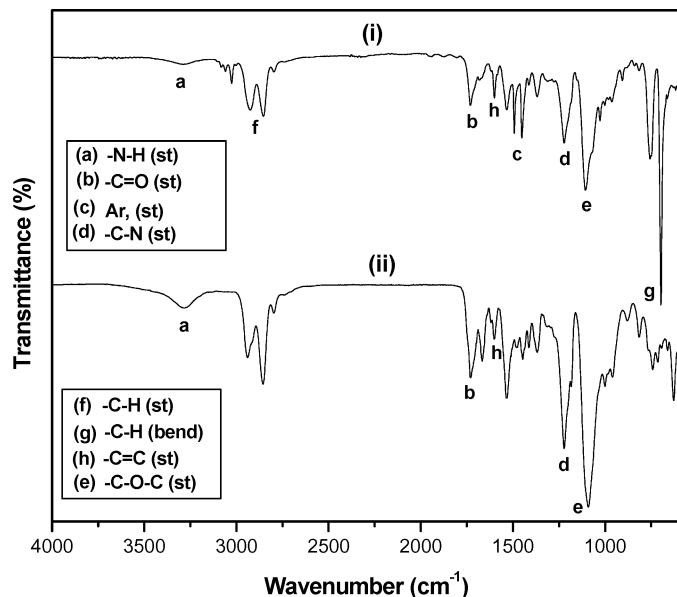


Fig. 3. FTIR spectra of (i) PSt-*b*-PU-*b*-PSt tri-block copolymer, PS-PU-PS 2 and (ii) Br₃C-PU-CBr₃.

PU-CBr₃ which is shown in Figure 3 (ii), the stretching vibrations of urethane carbonyl group is observed at 1735 cm⁻¹ and C-H asymmetric and symmetric stretching vibrations of -CH₂ groups are observed at 2856–2938 cm⁻¹. The band at 1100 cm⁻¹ is due the stretching vibrations of ether -C-O-C- groups. The peak at 1600 cm⁻¹ is due to the -C=C- stretching vibrations of aromatic ring. Stretching and bending vibrations of -N-H are observed at 3300 cm⁻¹ and 1532 cm⁻¹, respectively. The peak present at 1217 cm⁻¹ corresponds to C-N stretching vibrations present in urethane groups. Figure 3 (i) shows FTIR spectrum of PSt-*b*-PU-*b*-PSt tri-block copolymers. The stretching vibrations of urethane carbonyl, -N-H and C-O-C groups are present at the same frequencies as they were present in Br₃C-PU-CBr₃. The -C-H stretching vibrations of methylene groups in PU and PSt are observed in the region 2846–2929 cm⁻¹. Stretching vibrations of -C=C- from aromatic ring is appeared at 1604 cm⁻¹. The C-H bending peak of -CH₃ groups present in PU blocks (from TDI) is observed at 1369 cm⁻¹ in Figure 3 (i). In addition to this, new peaks at 3021–3088 cm⁻¹, 1601 cm⁻¹ and 701 cm⁻¹ are also observed in the FTIR spectrum of the block copolymers which correspond to the -C=C-H stretching, -C=C- stretching and out of plane -C=C-H bending of benzene ring present in PSt blocks (28). There are two new peaks at 1451 cm⁻¹ and 1495 cm⁻¹, which are due to the benzene ring stretching present in PSt blocks (28). These new peaks are not present in the FTIR spectrum of Br₃C-PU-CBr₃. The presence of all peaks which corresponds to Br₃C-PU-CBr₃ in tri-block copolymer and new peaks of PSt blocks further support the formation of PSt-*b*-PU-*b*-PSt tri-block copolymers.

FT-NMR spectroscopy was also used to confirm the structure of Br₃C-PU-CBr₃ and tri-block copolymers. Fig-

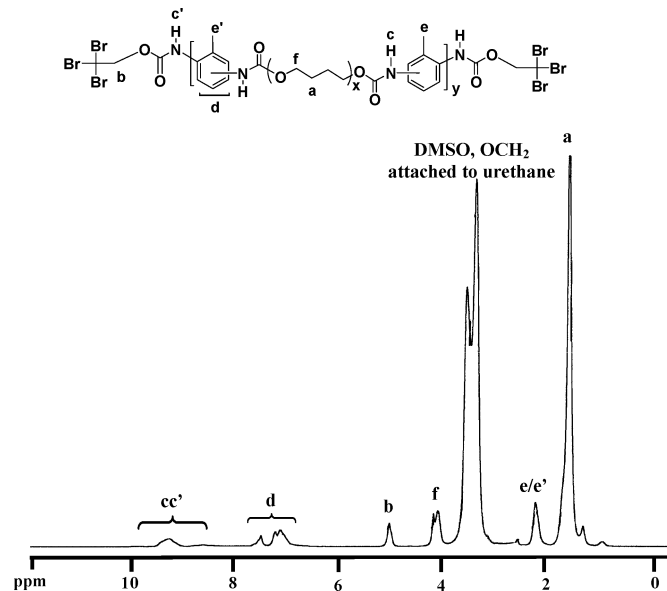


Fig. 4. ¹H-NMR spectra of Br₃C-PU-CBr₃.

ure 4 shows ¹H-NMR spectrum of Br₃C-PU-CBr₃. Phenyl protons and methyl protons present in TDI resonate at 7.10–7.48 ppm and 2.16 ppm, respectively. The -N-H protons and the terminal methylene protons present in CH₂-C(Br)₃ of Br₃C-PU-CBr₃ appeared at 8.63–9.28 ppm and 4.99 ppm, respectively. The peaks correspond to -CH₂ and -OCH₂ protons of PTMG resonate at 1.50 ppm and 3.32 ppm respectively. The -OCH₂ of PTMG which is attached to urethane group appeared at 4.06–4.14 ppm. To confirm the structure further, ¹³C NMR spectrum of Br₃C-PU-CBr₃ was obtained. The -CH₂ and -OCH₂ groups of PTMG appeared at 25.91–26.91 and 69.91 ppm respectively. The -OCH₂ groups attached to the urethane group was appeared at 64.15 ppm. The aromatic carbon atoms, -CH₃ carbon atoms (from TDI) and -C=O (from urethane) carbons resonate at 116.00–130.47, 17.25 and 152.95–153.76 ppm, respectively. The carbon atoms present in C-Br₃, and -OCH₂ of terminal 2,2,2-tribromoethane groups resonate at 78.56 and 76.46 ppm, respectively. These results show that Br₃C-PU-CBr₃ was successfully synthesized. In the ¹H-NMR spectrum of the tri-block copolymer (Figure 5), the -N-H protons of urethane and aromatic protons of TDI appeared at 8.63–9.28 and 7.05–7.50 ppm, respectively. The -OCH₂ protons of PTMG which is attached to the urethane group and -OCH₂ protons of PTMG appeared at 4.07 ppm and 3.32 ppm, respectively. The -CH protons of PSt and -CH₃ protons of TDI appeared at 1.86 ppm and 2.13–2.19 ppm, respectively. Appearance of a new peak at 4.50 ppm, which is due to the -CH₂-O-CO-NH- group adjacent to -CBr₂, confirms the effective transfer of one Br atom from the terminal Br₃-C groups of Br₃C-PU-CBr₃. The -CH₂ protons of PSt and -CH₂ protons of PTMG are appeared at 1.86 ppm and 1.52 ppm, respectively. The phenyl protons of PSt generally appear as two

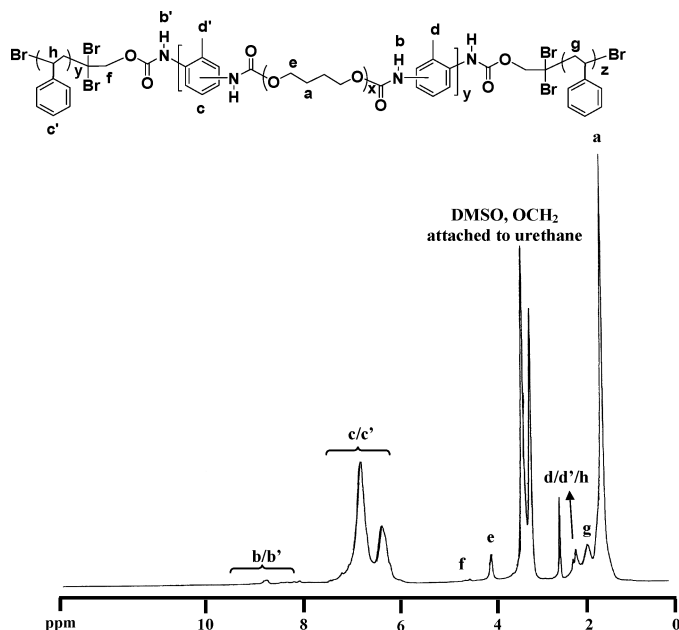


Fig. 5. $^1\text{H-NMR}$ spectra of PSt-*b*-PU-*b*-PSt tri-block copolymer, PS-PU-PS 2.

peaks, one at 6.58 ppm and the other at 7.05 ppm (29). In the present case, the 6.58 ppm peak clearly appeared, but the peak at 7.05 ppm merges with the peak of phenyl protons of TDI. All the peaks correspond to PU and PSt blocks are present in Figure 5, which is clear evidence of the formation of the block copolymers. The molar content of PSt in tri-block copolymers can easily be calculated by comparing molecular weights of $\text{Br}_3\text{C-PU-CBr}_3$ and tri-block copolymers which are determined by GPC (cf. Table

1). It can be calculated by comparing the peak integration ratio of $-\text{CH}_2-\text{CH}_2-$ group of PTMG at 1.52 ppm and aromatic protons of PSt blocks at 6.55–7.05 ppm through the $^1\text{H-NMR}$ technique as described in the literature (27) and the results are given in Table 1. These values are approximate only because the peak for aromatic protons of PSt is merging with the peak for aromatic protons of TDI in the $^1\text{H-NMR}$ spectrum of the block copolymers. The molar content of PSt from GPC and $^1\text{H-NMR}$ technique are comparatively similar.

3.3 Thermal Studies

The PSt-*b*-PU-*b*-PSt tri-block copolymer obtained at 7 h (Table 1, PS-PU-PS 2) 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 the onset and offset points. The T_g of the polyol segment present in $\text{Br}_3\text{C-PU-CBr}_3$ appears at -38°C . The glass transition temperatures of polyol and PSt segments in PSt-*b*-PU-*b*-PSt tri-block copolymers are appeared at -63°C and 73°C , respectively. The two glass transition temperatures in PSt-*b*-PU-*b*-PSt tri-block copolymers show there is phase separation in the block copolymers. Thermal stability of $\text{Br}_3\text{C-PU-CBr}_3$ and PSt-*b*-PU-*b*-PSt tri-block copolymer was also studied using TGA. $\text{Br}_3\text{C-PU-CBr}_3$ undergoes 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 copolymers (Table 1, PS-PU-PS 2), the decomposition is not in stages, but the overall thermal stability of PSt-*b*-PU-*b*-PSt tri-block copolymers is higher than $\text{Br}_3\text{C-PU-CBr}_3$.

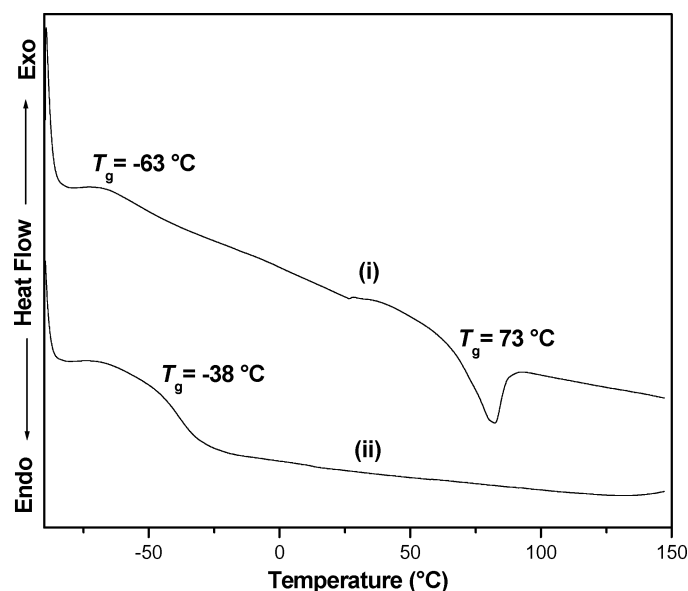


Fig. 6. DSC curves of (i) PSt-*b*-PU-*b*-PSt tri-block copolymer, PS-PU-PS 2 and (ii) $\text{Br}_3\text{C-PU-CBr}_3$.

4 Conclusions

For the first time, telechelic tribromo terminated polyurethane, $\text{Br}_3\text{C-PU-CBr}_3$ was successfully used to polymerize styrene and PSt-*b*-PU-*b*-PSt tri-block copolymers were synthesized. The $\text{Br}_3\text{C-PU-CBr}_3/\text{CuBr}/\text{PMDETA}$ initiating system follows the ATRP mechanism, which was confirmed from the linear increase of $\text{time} \cdot \ln([\text{M}]_0/[\text{M}])$ and conversion- \bar{M}_n plots. The molar percentage of PSt was calculated using $^1\text{H-NMR}$ and it matches GPC results. The results from spectral and thermal methods also confirmed the formation of novel tribromo terminated polyurethane and PSt-*b*-PU-*b*-PSt tri-block copolymers.

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