ORIGINAL ARTICLE

A novel tertiary bromine-functionalized thermal iniferter for controlled radical polymerization

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A novel terminal tertiary bromine-containing thermal iniferter, 1,1,2,2-tetraphenylethane-1,2-diyl bis(2-bromo-2-methylpropanoate) (TPEBMP), was prepared from 1,1,2,2-tetraphenyl-1,2-ethanediol and α -bromoisobutyryl bromide. The controlled radical polymerization of methyl methacrylate and styrene was successfully carried out using TPEBMP at 70 °C. During the polymerization, the number average molecular weight increased linearly with increasing conversion. Number average molecular weight was determined by gel permeation chromatography, and was found to be similar to the theoretical molecular weight. The novel iniferter TPEBMP and the polymers prepared from this iniferter were characterized by spectral, thermal and chromatographic methods. The glass transition temperature (T_g) of the poly(methyl methacrylate) was observed at 127 °C, whereas the T_g of the polystyrene was observed at 102 °C. Because the resulting polystyrene and poly(methyl methacrylate) consist of tertiary bromine at both ends of the chains, these polymers can be used as macroinitiators for atom transfer radical polymerization to synthesize tri-block copolymers.

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INTRODUCTION

Living anionic polymerization can be used to synthesize the block copolymers of a desired molecular weight and end functionality,^{1,2} but this process requires rigorous polymerization conditions such as high vacuum and highly purified monomers and solvents. In addition, living anionic polymerization can only be used to polymerize hydrocarbon monomers, and the polymerization of polar monomers through anionic polymerization leads to unwanted side reactions. On the other hand, free radical polymerization is the preferred method for manufacturing a wide variety of polymers because it does not require rigorous polymerization conditions, and it tolerates trace impurities. However, the main drawback of radical polymerization is the uncontrolled molecular weight build-up, which results in polymers with a broad molecular weight distribution (MWD). Many controlled radical polymerization (CRP) methods have been proposed to date to control the molecular weight and MWD.^{3–5} A wide variety of polymers can be synthesized through CRP with controlled molecular weights, narrow MWDs and desired end groups that are difficult to achieve with conventional radical polymerization.⁴

One effective CRP method is controlled molecular weight build-up using the stable nitroxide radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl⁶ as a reversible capping agent. However, the high temperature (for example, 130 °C for the polymerization of styrene) that is required to reversibly cleave the bond between the 2,2,6,6-tetramethylpiperidine-*N*-oxyl moiety and the growing polymer chain confines the application of this route to very few monomers. Atom transfer radical

polymerization (ATRP)⁵ is another effective CRP method that has been proposed for the polymerization of a variety of vinyl monomers at a lower polymerization temperature (for example, 100–110 °C for the polymerization of styrene) than the 2,2,6,6-tetramethylpiperidine-*N*-oxyl system. Because ATRP is catalyzed by transition metal halides, such as copper (I) bromide, the presence of catalytic amounts of metal in the final polymers is the main drawback of this route.⁷ Polymerization through iniferters, proposed by Otsu *et al.*^{8,9} in 1982, is another CRP route. The iniferter approach does not have any metal recovery issues as in the case of ATRP, and hence, this route is more eco-friendly than the ATRP route. Therefore, this paper attempts to synthesize a novel iniferter for CRP.

Iniferters act as initiators as well as reversible radical chain transfer/terminating agents in radical polymerization. As a result, reversible primary radical termination or transfer reactions are generally observed more extent in this route. Iniferters can be classified as photoiniferters and thermal iniferters. Photoiniferters are mainly *N,N*-diethyldithiocarbamyl group-bearing compounds,^{9–12} whereas thermal iniferters, apart from phenylazotriphenylmethane,¹³ are usually carbon–carbon labile bond-containing compounds, such as tetraphenylsuccinodinitrile,¹⁴ hydroxy-2-(*p*-tolylaminocarbonyloxy)-1,1,2,2-tetraphenylethane,¹⁵ tetra(*p*-methoxy phenyl) succinodinitrile,¹⁶ pentaphenylethane,¹⁶ 1,1,2,2-tetraphenyl-1,2-bis(trimethylsilyloxy)-ethane¹⁷ and 1,1,2,2-tetraphenyl-1,2-bis(phenoxy)-ethane.¹⁸ 1,1,2,2-Tetraphenyl-1,2-ethanediol (TPED) has also been used as a radical initiator, but it does not proceed via the CRP mechanism^{19,20} due to

the occurrence of a side reaction during the initiation of the monomer. To avoid this side reaction, the OH groups of TPED were reacted with diisocyanate, and the resulting polyurethane iniferter was used to polymerize vinyl monomers via a 'living' radical mechanism.^{21–23} Similarly, in this study, the OH groups of TPED were modified. A novel thermal iniferter was synthesized by reacting TPED with α -bromoisobutyl bromide, and the resulting compound was used as a thermal iniferter for the polymerization of methyl methacrylate (MMA) and styrene.

EXPERIMENTAL PROCEDURE

Materials

Styrene (Aldrich, St Louis, MO, USA) and MMA (CDH, Delhi, India) were purified using conventional purification methods. The purified monomers were distilled under vacuum and the middle fractions were stored at 0–4 °C until they were used. α -Bromoisobutyl bromide was obtained from Aldrich and was used without further purification. Diethyl ether and tetrahydrofuran (THF) were purchased from S.D. Fine Chemicals, Mumbai, India and purified by distillation over sodium–benzophenone complex just before use. All other chemicals were of analytical grade and were used as received.

Synthesis of TPED

TPED was prepared according to a photochemical method as described in the literature.²⁴

Elemental analysis: C₂₆H₂₂O₂: (calculated, %) C=85.212, H=6.050, O=8.732. (Observed, %) C=85.220, H=6.132, O=8.648.

¹H nuclear magnetic resonance (NMR; δ in p.p.m., CDCl₃, 300 MHz): 3.02 (s, OH, 2 H), 7.00–7.30 (m, phenyl, 20 H).

¹³C NMR (δ in p.p.m., CDCl₃, 75 MHz): 83.00, 125.78, 125.88, 126.12, 126.38, 127.05, 127.44, 144.22.

Synthesis of 1,1,2,2-tetraphenylethane-1,2-diyl bis(2-bromo-2-methylpropanoate) (TPEBMP)

TPEBMP was synthesized from TPED and α -bromoisobutyl bromide. TPED (13.6 mmol) was added to a 500-ml three-necked round-bottom flask fitted with a reflux condenser, a magnetic stirrer, and a dropping funnel. To this, 300 ml of anhydrous diethyl ether was added under a nitrogen atmosphere. Then, *N,N'*-diethyl aniline (27.2 mmol) was added followed by α -bromoisobutyl bromide (27.2 mmol). The reaction mixture was refluxed, and after 30 min, diethyl aniline hydrobromide began to precipitate as a white solid. After the reaction reached completion (~6 h) as determined by thin layer chromatography, 100 ml of distilled water was added to the reaction mixture and stirring was continued until the diethyl aniline hydrobromide salt was dissolved. The ether layer was separated and washed three times with 5% aqueous hydrochloric acid followed by a saturated aqueous sodium hydrogen carbonate solution. Finally, the ether layer was again washed with distilled water until the solution reached neutral pH. The ether portion was dried over anhydrous sodium sulfate overnight. Ether was distilled under reduced pressure, yielding the novel iniferter as a white crystalline solid at a yield of 86%.

Elemental analysis for C₃₄H₃₂O₄Br₂: (Calculated, %) C=61.461, H=4.854, O=9.632, Br=24.053. (Observed, %) C=61.35, H=4.90, O=9.61.

Fourier-transform infrared (FT-IR) (KBr, cm⁻¹): 1715 (C=O str.), 2922 (Ar-H str.), 2854 (C-H str.).

¹H NMR (δ in p.p.m., CDCl₃, 300 MHz): 1.94 (-CH₃, 12 H), 7.14–7.31 (phenyl, 20 H).

¹³C NMR (δ in p.p.m., CDCl₃, 75 MHz): 30.60, 55.18, 88.11, 125.78, 125.88, 126.12, 126.38, 127.05, 127.44, 143.01, 176.80.

CRP of MMA and styrene

First, an appropriate amount of TPEBMP (6.02×10^{-4} mol l⁻¹) was added to a clean glass polymerization tube under a nitrogen atmosphere and was dissolved in dry THF. The required amount of monomer (0.903 mol l⁻¹; iniferter:monomer=1:1500) was then added to the reaction mixture and polymerization was carried out for a specified period of time at 70 °C in a thermostated oil bath. After the specified reaction time, the polymerization was stopped by removing the tube from the oil bath and cooling in an ice-salt

mixture. The resultant polymer solution was poured into a 10-fold excess of methanol to obtain the polymer as a white precipitate. The resulting precipitate was filtered using a glass crucible, dried in an oven at 50 °C and weighed. The conversion was determined by gravimetric method.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-300 NMR instrument (Bruker, Billerica, MA, USA), and FT-IR spectra were recorded from KBr pellets on a Nicolet Impact 400 FT-IR spectrophotometer (Nicolet, Madison, WI, USA). Number average ($\bar{M}_n$), weight average ($\bar{M}_w$), molecular weights and MWD were determined using a Waters gel permeation chromatography (GPC) instrument equipped with a 2414 differential refractive index detector and two (HR 2 and HR 4) Waters μ -styragel columns. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 ml min⁻¹, and the molecular weight calibrations were carried out using polystyrene standards. Differential scanning calorimetric studies were carried out using a TA Instruments DSC Q200 instrument (New Castle, DE, USA) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere, and thermogravimetric analysis was carried out using a TA Instruments TGA Q50 instrument at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

RESULTS AND DISCUSSION

TPED is a well known free radical initiator that is used in conventional radical polymerization,²⁰ but it neither acts as an iniferter nor follows a CRP mechanism, because of the presence of OH groups. When TPED is used to polymerize a vinyl monomer, benzophenone is formed as the side product.²² To avoid this reaction, the OH groups of TPED were reacted with diisocyanates and the resulting compounds were used as macroiniferters in CRP.^{22,23} If the hydroxyl groups of TPED are converted to halogen groups, the product can be used for surface initiated polymerization by anchoring the initiator onto the clay surface. Keeping this in mind, the OH groups of TPED were effectively modified with α -bromoisobutyl bromide, resulting in the novel bromine-containing thermal iniferter TPEBMP.

Synthesis and characterization of TPEBMP

As shown in Scheme 1a, TPED was reacted with α -bromoisobutyl bromide, and the resulting novel iniferter was characterized by NMR spectroscopy. Figure 1 shows the ¹H NMR spectrum of the novel iniferter, TPEBMP. The absence of a peak corresponding to OH protons and the appearance of a new peak at 1.94 p.p.m. corresponding to the methyl protons present in TPEBMP confirms the formation of the novel iniferter. In the FT-IR spectrum of TPEBMP, a new peak at 1715 cm⁻¹ is observed that corresponds to the carbonyl stretching vibrations of the newly formed ester groups. These results confirm the formation of the novel iniferter, TPEBMP.

CRP studies

The newly synthesized iniferter, TPEBMP, was used to polymerize MMA and styrene to study the mechanism of polymerization. Scheme 1b shows a possible mechanism for the polymerization of MMA using the novel iniferter, TPEBMP. Similar to other iniferter-based polymerizations, primary radical termination and transfer reactions were more prevalent, resulting in the attachment of iniferter fragments at both ends of the polymers. Tables 1 and 2 show the results of the polymerization of MMA and styrene, respectively. The novel iniferter successfully polymerizes both MMA and styrene, and conversion increases with polymerization time. Figure 2 shows the time vs conversion and time vs ln [M_0]/[M] plots for MMA polymerization, and similar plots for styrene polymerization are shown in Figure 3. Here, [M_0] and [M] represent the initial monomer concentration and the monomer concentration at time t , respectively. The linear time vs ln ([M_0]/[M]) plots show that the concentrations

Scheme 1 (a) Synthesis of TPEBMP and (b) controlled radical polymerization of MMA using TPEBMP.

of propagating radicals were constant throughout the studied period of time. In the case of styrene polymerization, time vs conversion and time vs $\ln([M]_0/[M])$ plots pass through the origin, which is a typical result of CRP. In the MMA polymerization, however, the time vs conversion and time vs $\ln([M]_0/[M])$ plots do not pass through the origin. As reported in the literature, this may be due to an initial delay in reaching equilibrium between propagating radicals and dormant species. During this delay, the irreversible termination of some of the primary radicals may occur in MMA polymerization, resulting in the deviations that are observed in both the time vs conversion and the time vs $\ln([M]_0/[M])$ plots. A similar result was reported for MMA polymerization through ATRP²⁵ and iniferter-based CRP.²⁶ To further confirm the presence of CRP mechanism, the $\bar{M}_n$ calculated through GPC was plotted against conversion. Figures 4 and 5 show the conversion vs $\bar{M}_n$ plots for the polymerizations of MMA and styrene, respectively. In these figures, molecular weight increased linearly with conversion. This is also a characteristic result of CRP. However, in the case of MMA polymer-

ization, the conversion vs $\bar{M}_n$ plot does not pass through the origin, which could be due to the presence of some amount of irreversible termination, as reported in the literature.^{25,26} Interestingly, in the case of styrene polymerization, the conversion vs $\bar{M}_n$ plot passes through the origin. The time vs $\ln([M]_0/[M])$ and conversion vs $\bar{M}_n$ plots demonstrate that the TPEBMP-initiated polymerization of MMA proceeds through a CRP mechanism, along with some irreversible termination reactions, whereas styrene polymerization undergoes CRP without significant amounts of irreversible termination reactions.

Figures 6 and 7 show GPC curves for the polymerization of MMA and styrene, respectively. As the polymerization time and conversion increase, the GPC curves shift from the lower molecular weight region to the higher molecular weight region. The MWD values of poly (methyl methacrylate) (PMMA) and polystyrene prepared through TPEBMP are also narrow. These results again confirm that the polymerizations of MMA and styrene that were initiated by the thermal iniferter TPEBMP occur through CRP mechanism.

 Figure 1 ^1H NMR spectrum of the iniferter TPEBMP.

Table 1 Polymerization of MMA using TPEBMP at 70 °C in THF

Code	Time (h)	Conversion ^a (%)	$\bar{M}_{n,th}^b \times 10^{-4}$	$\bar{M}_{n,NMR}^c \times 10^{-4}$	GPC results		
					$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
SM1	1	9.6	0.7296	1.0123	5.36	2.55	2.10
SM2	2	24.6	1.8538	1.7812	7.18	3.42	2.10
SM4	4	45.8	3.4428	5.9786	6.90	4.60	1.50
SM6	6	70.0	5.2566	6.9243	9.12	5.70	1.60

Abbreviations: GPC, gel permeation chromatography; MMA, methyl methacrylate; THF, tetrahydrofuran; TPEBMP, tetraphenylethane-1,2-diyl bis(2-bromo-2-methylpropanoate).

^aConversion was determined gravimetrically.

^b $\bar{M}_{n,th} = \left(\frac{[M]_0}{2[I]_0} \times \text{Monomer conversion} \right) + M$. Wt. of monomer.

^cCalculated by ^1H NMR.

Polymerization conditions: $[\text{TPEBMP}]_0 = 6.02 \times 10^{-4} \text{ mol l}^{-1}$; $[\text{MMA}]_0 = 0.903 \text{ mol l}^{-1}$.

Table 2 Polymerization of styrene using TPEBMP at 70 °C in THF

Code	Time (h)	Conversion ^a (%)	$\bar{M}_{n,th}^b \times 10^{-4}$	GPC results		
				$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
SS6	6	15.0	1.1346	3.01	1.01	2.98
SS12	12	31.1	2.3413	5.26	2.58	2.04
SS18	18	54.0	4.0577	7.96	3.67	2.17
SS24	24	65.8	4.9421	8.66	4.67	1.85

Abbreviations: GPC, gel permeation chromatography; MMA, methyl methacrylate; THF, tetrahydrofuran; TPEBMP, tetraphenylethane-1,2-diyl bis(2-bromo-2-methylpropanoate).

^aConversion was determined gravimetrically.

^b $\bar{M}_{n,th} = \left(\frac{[M]_0}{2[I]_0} \times \text{Monomer conversion} \right) + M$. Wt. of monomer.

Polymerization conditions: $[\text{TPEBMP}]_0 = 6.02 \times 10^{-4} \text{ mol l}^{-1}$; $[\text{Styrene}]_0 = 0.903 \text{ mol l}^{-1}$.

Spectral studies of polymers

^1H NMR spectra were recorded to understand the polymerization mechanism and the end groups that were present at both ends of the PMMA and polystyrene polymers synthesized here. Figure 8 shows the ^1H NMR spectrum of PMMA (SM6) synthesized through the novel iniferter, TPEBMP. The methylene protons of PMMA are observed at 1.77–1.82 p.p.m. The methyl protons of PMMA resonate at 0.80, 0.98 and 1.17 p.p.m., corresponding to syndiotactic (rr), atactic (rm) and isotactic (mm) PMMA, respectively. The tacticity ratio of PMMA synthesized in the present investigation is rr:rm:mm=59:33:8, which is similar to the reported tacticity ratio of PMMA synthesized through CRP.²⁷ The peak at 3.56–3.70 p.p.m. is due to the methyl protons of the ester unit present in the PMMA. The aromatic protons derived from the TPEBMP iniferter are observed at 7–7.3 p.p.m. The methyl

protons derived from the TPEBMP iniferter should be observed at 1.9 p.p.m. as in the case of the iniferter. However, these methyl protons are merged with the methylene protons of PMMA, which are observed at 1.77–1.82 p.p.m. The molecular weight of the PMMA was also determined from ^1H NMR spectra. These values were calculated from the peak intensity ratios between the methyl protons that are present in the ester groups of PMMA and the aromatic protons that are present in the TPEBMP fragments. In the ^1H NMR spectrum of polystyrene (SS12) that were prepared from TPEBMP iniferter, the methylene and methine protons of the polystyrene repeating unit are observed at 1.32 and 1.49 p.p.m., respectively. The aromatic protons on the phenyl rings of the iniferter fragments are merged with the aromatic protons of the phenyl rings that are present in the polystyrene repeating units, which are observed between 6.4 and 7.3 p.p.m.

Figure 2 Time vs conversion and time vs $\ln[M]_0/[M]$ plots for the polymerization of MMA using TPEBMP. Polymerization conditions: $[TPEBMP]_0 = 6.02 \times 10^{-4} \text{ mol l}^{-1}$; $[MMA]_0 = 0.903 \text{ mol l}^{-1}$.

Figure 3 Time vs conversion and time vs $\ln[M]_0/[M]$ for the polymerization of styrene using TPEBMP. Polymerization conditions: $[TPEBMP]_0 = 6.02 \times 10^{-4} \text{ mol l}^{-1}$; $[\text{styrene}]_0 = 0.903 \text{ mol l}^{-1}$.

Figure 4 Conversion vs $\bar{M}_n$ and conversion vs polydispersity index (PDI; $\bar{M}_w/\bar{M}_n$) plots for the polymerization of MMA using TPEBMP. Polymerization conditions: $[TPEBMP]_0 = 6.02 \times 10^{-4} \text{ mol l}^{-1}$; $[MMA]_0 = 0.903 \text{ mol l}^{-1}$.

Figure 5 Conversion vs $\bar{M}_n$ and conversion vs polydispersity index (PDI; $\bar{M}_w/\bar{M}_n$) for the polymerization of styrene using TPEBMP; $[TPEBMP]_0 = 6.02 \times 10^{-4} \text{ mol l}^{-1}$; $[\text{styrene}]_0 = 0.903 \text{ mol l}^{-1}$.

Figure 6 GPC curves for MMA polymerization using TPEBMP.

As the methyl protons and phenyl protons of iniferter fragments are merged with the repeating units of polystyrene, the molecular weight of polystyrene could not be determined by ^1H NMR spectroscopy. However, the polymerization of styrene through this iniferter is confirmed by the presence of $\text{C}=\text{O}$ stretching vibrations of terminal ester groups present in the FT-IR spectrum of polystyrene.

Thermal studies of polymers

Finally, polymers synthesized using TPEBMP were characterized by differential scanning calorimetric and thermogravimetric analysis. Figure 9 shows the differential scanning calorimetric curves of PMMA (SM6) and polystyrene (SS12), and the glass transition temperature (T_g) values were determined as the middle point between the onset and offset points. The T_g values of PMMA and polystyrene are 127°C and 102°C , respectively, which are similar to the values reported in the literature.^{28,29} In general, the thermal degradation of

PMMA that is prepared by conventional free radical polymerization under a nitrogen atmosphere proceeds in three steps corresponding to head-to-head linkage ($\sim 165^\circ\text{C}$), initiation of chain ends from the vinylidene ends ($\sim 270^\circ\text{C}$) and random scission within the PMMA chain ($\sim 360^\circ\text{C}$).³⁰ In contrast, the PMMA synthesized here undergoes two stages of decomposition, initially at around 170°C and later at 320°C , corresponding to the cleavage of head-to-head linkages

followed by the random scission of PMMA chains. The absence of vinylidene end cleavage shows that MMA polymerization through the TPEBMP iniferter does not proceed through conventional radical polymerization, but rather through CRP. Similarly, single stage decomposition was observed at around 390°C for polystyrene, which is also evidence of the absence of vinylidene end groups and the presence of CRP.

Figure 7 GPC curves for styrene polymerization using TPEBMP.

Figure 9 Differential scanning calorimetric curves of PMMA (SM6) and polystyrene (SS12) synthesized using TPEBMP.

Figure 8 ^1H NMR spectrum of PMMA (SM6) synthesized using TPEBMP.

CONCLUSIONS

A novel bromine-containing thermal iniferter was successfully prepared and used to polymerize MMA and styrene. A linear increase in the number average molecular weight was observed with increasing monomer conversion. Similarly, linear increases were observed in time vs conversion and time vs $\ln([M]_0/[M])$ plots. These results indicate that the novel iniferter polymerizes MMA and styrene via a CRP mechanism. Because the novel functional thermal iniferter polymerizes styrene and MMA through CRP, this iniferter can be incorporated into nano-clay, and the resulting nano-clay can be used to polymerize vinyl and acrylate type monomers to prepare polymer-clay nanocomposites.

Thermogravimetric analysis curves of PMMA and polystyrene prepared using TPEBMP and ^1H NMR spectrum of polystyrene prepared using TPEBMP are available as Supplementary Information.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)