Available online at www.sciencedirect.com
ScienceDirect
Polymer 49 (2008) 1483–1489
polymer
www.elsevier.com/locate/polymer

Chain extension and block copolymer synthesis using silane radical atom abstraction coupled with nitroxide mediated polymerization

Sona Thakur, Nicole A. Cohen, Eric S. Tillman*

Department of Chemistry, Bucknell University, Lewisburg, PA 17837, United States

Received 1 November 2007; received in revised form 16 January 2008; accepted 26 January 2008
Available online 1 February 2008

Abstract

Silane radicals were used to abstract bromine termini from monobrominated polystyrene (PStBr) in the presence of excess monomer and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), generating polymer radicals that underwent chain extension. Typically, 70–85% of the PStBr precursors were activated by silane radical atom abstraction (SRAA) and were elongated by nitroxide mediated polymerization (NMP), shifting to higher number-average molecular weight (M_n) values as observed by gel permeation chromatography (GPC). Chain extension did not occur until the temperature was elevated to 130 °C, with no increase in M_n values observed when the reaction was held at 80 °C, which is the temperature of the SRAA phase. The NMP phase of the reaction showed a linear correlation between M_n values and monomer consumption, along with first order kinetics with respect to styrene. SRAA/NMP was then applied to the synthesis of polystyrene-*b*-poly(*n*-butyl acrylate) and polystyrene-*b*-poly(*p*-methylstyrene), with analysis by GPC indicating the formation of block copolymers with a similar amount of unreacted PStBr remaining. Quantitative activation and elongation of the polymer precursors were prevented due to the ability of both the *t*-butoxy radicals and tris(trimethylsilyl)silane radicals to add across monomeric double bonds, competing with atom abstraction. Reactions were thus performed in which the monomer was added only after the transition to the higher temperature, which resulted in improved activation of the PStBr.

Keywords: Atom transfer radical polymerization; Block copolymers; Polystyrene

1. Introduction

The controlled radical polymerization process known as atom transfer radical polymerization (ATRP) is capable of producing a wide range of end-halogenated polymers, a consequence of halogen atom shuttling between the propagating polymer radical and metal catalyst [1–4]. The presence of this end group allows for chain extension [5–8] or block copolymer synthesis [9–12], with the halogen-terminated polymer serving as a macroinitiator in a second ATRP reaction. Using similar chemistry, these polymers can be coupled together in a process called atom transfer radical coupling (ATRC), which again relies on the transfer of the chain-end halogen to a metal catalyst but in this case radical–radical coupling is favored due to the lack of monomer [13].

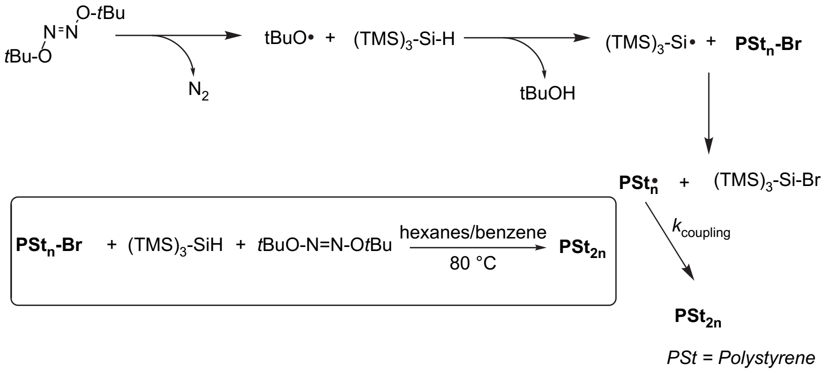
The bromophilicity of silane radicals has been exploited by others in reactions involving alkyl bromides, generating carbon-based radicals that can be trapped by persistent, oxygen-based radicals to produce a variety of alkoxyamines [14]. Our group has recently reported silane radical atom abstraction (SRAA) as a means to activate brominated polystyrene (PStBr), forming polymer radicals that undergo radical–radical coupling reactions to give polystyrene (PSt) of controllable molecular weight values and low polydispersity indices (PDIs) (Scheme 1) [15]. Activation by silane radicals, in contrast to activation by atom transfer to a metal–ligand catalyst, does not require the addition of metals to the reaction mixture.

In an attempt to extend the utility of SRAA into other areas of polymer synthesis, we report here the combination of SRAA with nitroxide mediated polymerization (NMP) as a method to perform chain elongation, leading to either higher molecular weight homopolymers (chain extension) or block copolymers depending on the choice of the second monomer.

---

* Corresponding author. Tel.: +1 570 577 3265; fax: +1 570 577 1739.
E-mail address: etillman@bucknell.edu (E.S. Tillman).

0032-3861/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.01.060



Scheme 1. Silane radical atom abstraction, leading to PSt dimers. Box shows the condensed reaction.

NMP, like ATRP and other controlled radical polymerizations, relies on the equilibrium between a dormant species and an active polymer radical, with the dormant species in this case being an alkoxyamine at the polymer chain terminus [16–19]. Because SRAA and NMP can occur at different temperatures, the reaction sequence can be performed in one-pot with all the ingredients added together, with only a change in temperature used to signify the transition from the SRAA phase to the NMP phase (Scheme 2). Conversely, the reaction can be performed solely at the elevated temperature, which would allow both SRAA and NMP to occur immediately.

2. Experimental section

2.1. Materials

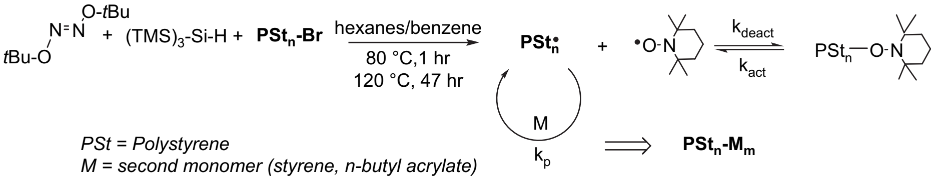
CuBr (98%, Aldrich), $CuBr_2$ (99%, Aldrich), (1-bromoethyl)benzene (97%, Aldrich), tris(trimethylsilyl)silane (TTMSS, 96%, Aldrich), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (98%, Aldrich), benzene-d_6 (99.6%, Aldrich), *t*-butyl bromide (≥97%, Fluka), zinc chloride (Acros), sodium *trans*-hyponitrite hydrate (Aldrich), and alumina (Aldrich) were used as received. Styrene (99%, Aldrich), *n*-butyl acrylate (99+%, Aldrich) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were distilled from calcium hydride under reduced pressure and stored in sealed glass ampoules at −15 °C prior to use. *p*-Methylstyrene (MSt, 98%, Acros) was passed through an alumina column prior to use. Benzene and hexanes were passed through a Grubbs-type purification column [20] before use.

2.2. Synthesis of monobrominated polystyrene (PStBr)

For [monomer]/[initiator] = 20:1, to a flamed 50-mL two-neck round bottom flask, CuBr (187 mg, 1.3 mmol) and $CuBr_2$ (72.6 mg, 0.32 mmol) were added and the reaction flask was placed on a Schlenk line with a septum on the remaining neck. The flask was evacuated, after which styrene (3.0 mL, 26 mmol) and (1-bromoethyl)benzene (177 μL, 1.3 mmol) were sequentially introduced into the reaction chamber via argon-flushed syringes. The reaction mixture was then subjected to three cycles of freeze–pump–thawing, after which the flask was sealed from the Schlenk line via a Teflon stopcock. The reaction vessel was then placed in an oil bath set at 80 °C and stirred for several minutes to allow the contents to reach the temperature of the bath, after which PMDETA (272 μL, 1.3 mmol) was added via an argon-flushed syringe to commence the polymerization. After approximately 2 h, the reaction mixture was diluted with THF, followed by precipitation in cold methanol. Conversions were allowed to reach between 50% and 70% in order to retain end group functionality. A THF solution of the polymer was passed through an alumina column, giving an ultra white powder. The polymer was characterized by GPC and ^1H NMR to ensure retention of the bromo end group.

2.3. Synthesis of trans t-butyl hyponitrite (tBHN)

The title compound was synthesized using procedures adapted from literature [21], and its synthesis was previously reported by our group [15]. Briefly, *t*-butyl bromide (4.0 mL, 35 mmol) and ether (4.0 mL) were added to a clean, dry flask and stirred at room temperature. Anhydrous zinc chloride (0.50 g, 3.7 mmol) was added to the swirling mixture and within 5 min sodium hyponitrite (0.40 g, 3.8 mmol) was introduced. The reaction mixture was allowed to stand for 75 min at room temperature and then left overnight at 5 °C. The solution was gravity filtered, washed several times with water, and dried with anhydrous sodium sulfate. The volatiles were removed under reduced pressure to produce an off-white solid, which was triturated with cold methanol (−20 °C) to give



Scheme 2. Silane radical atom abstraction coupled with nitroxide mediated polymerization, leading to chain extension.

the desired product as a white solid in 50% yield. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.3 (s, 18H).

2.4. Typical procedure for chain extension

A 50-mL round bottom flask was charged with PStBr ($M_n = 1250$ g/mol, PDI = 1.12; 0.325 g, 0.26 mmol), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (40.62 mg, 0.26 mmol) and *t*BHN (27.14 mg, 0.156 mmol) and placed on a Schlenk line with a septum on the remaining neck. After that, TTMSS (80 μL, 0.26 mmol), styrene (2.0 mL, 17.45 mmol), benzene (2.0 mL) and hexanes (3.0 mL) were sequentially added via argon-flushed syringes. Three freeze–pump–thaw cycles were performed, after which the flask was placed in an oil bath and stirred at 80 °C for 1 h (or as indicated) and then transferred to another oil bath at 130 °C and stirred for 47 h. The flask was removed from the oil bath and the reaction mixture was diluted with THF. Polymeric product was recovered by precipitation in cold methanol, dried to a constant weight, and characterized by GPC. Percent elongation was estimated by comparing the areas under the GPC traces.

Reactions were also performed in which the monomer was added only after the reaction temperature was raised. These reactions were run in an identical manner, but the monomer was introduced into the reaction chamber after the transfer to the 130 °C oil bath.

2.5. Monitoring M_n and PDI as a function of % monomer conversion and time

In a typical experiment, PStBr ($M_n = 1120$ g/mol, PDI = 1.13; 0.873 g, 0.78 mmol), TEMPO (121.86 mg, 0.78 mmol) and *t*BHN (81.42 mg, 0.468 mmol) were added to a 50-mL round bottom flask, which was previously flamed under reduced pressure. After sealing with a rubber septum, TTMSS (240 μL, 0.78 mmol), styrene (6.0 mL, 52.3 mmol), benzene-d_6 (6.0 mL) and hexanes (9.0 mL) were sequentially added via argon-flushed syringes. Three freeze–pump–thaw cycles were performed, after which the flask was placed in an oil bath and stirred at 80 °C for 1 h and then placed in an oil bath at 130 °C for 42 h. Approximately 0.75 mL aliquots were removed from the reaction mixture every 6 h via argon-flushed syringes and immediately cooled to quench the reaction. These samples were stored in NMR tubes at −15 °C prior to NMR and GPC analyses.

2.6. Determination of monomer conversion using NMR

Monomer conversion and $[M]_t$ values (Fig. 2a and b) were calculated using ^{1}H NMR data by comparing the area of the vinylic protons at the β-position of monomeric styrene to the entire area of the aromatic protons. By beginning at $t = 0$ (prior to the reaction, and thus monomer conversion = 0%), the aromatic region contains phenylic monomeric protons, phenylic PStBr protons, and vinylic α-protons from the monomeric styrene (these vinylic protons overlapped with phenylic PSt protons and thus were incorporated in the integration of the aromatic region). The area in the aromatic region due to the monomeric protons (both vinylic and phenylic) was calculated based on the average area of the vinylic β-protons (at 5.0 and 5.7 ppm), and was expressed as a percentage of the overall aromatic region.

For example, if the average integration of a β-proton at time = t was 1, and the overall integration of the aromatic region (between 6 and 8 ppm) was 11, the percentage of the aromatic region due to monomer would be 50. This is determined by multiplying 1 by 5 (to get the area in the aromatic region due to monomeric phenylic protons), while subtracting the monomeric α-proton from the aromatic region (which would be 1, the same area as the β-protons). At each reaction time, this calculation was repeated and compared to the initial percentage at $t = 0$, allowing for calculation of monomer conversion and at each time t. From these conversion values, $[M]_t$ could be calculated, taking into account the decrease in reaction volume for each calculation as styrene is converted into polymer.

2.7. Typical procedure for block copolymer synthesis

To a flamed 50-mL two-neck round bottom flask, PStBr ($M_n = 2270$ g/mol, PDI = 1.09; 0.28 g, 0.10 mmol), *t*BHN (6.0 mg, 0.06 mmol) and TEMPO (16.0 mg, 0.10 mmol) were added and the reaction vessel was placed on a Schlenk line with a septum on the remaining neck. TTMSS (31 μL, 0.10 mmol), benzene (2.0 mL), hexanes (3.0 mL), and *n*-butyl acrylate (1.47 mL, 0.010 mol) were sequentially introduced into the reaction vessel via argon-flushed syringes. The reaction mixture was then subjected to three freeze–pump–thaw cycles, after which the flask was sealed from the Schlenk line with a Teflon stopcock. The reaction was allowed to proceed at 80 °C for 1 h and then at 125 °C for an allotted time. To terminate the reaction, the contents of the vessel were diluted with THF and cooled to room temperature. Polymer was recovered by precipitation in cold methanol, dried to a constant weight, and characterized by GPC. Percent elongation was estimated by comparing the areas under the GPC traces. Analogous reactions using *p*-methylstyrene in place of *n*-butyl acrylate were also performed.

2.8. Characterization

The polymers were analyzed on a Waters Gel Permeation Chromatography (GPC) system connected to a PC running Waters Breeze software. The system consists of a Waters 1515 isocratic pump, a Waters 717 auto sampler, two Pl-gel 5 mm Mixed C columns (Polymer Labs), a Waters 2487 dual wavelength detector and a Waters 2414 RI detector. A 10-point calibration using polystyrene standards (Polymer Laboratories, Mp range: 5.0×10^2–3.05×10^6 Da) was used to obtain molecular weights and polydispersities, with THF as the mobile phase. NMR measurements were taken on a Varian 400 MHz FT-NMR at room temperature.

3. Results and discussion

3.1. Chain extension

Established ATRP methods were used to synthesize PStBr of controllable number-average molecular weight (M_n) and

PDI values [22–25], which were used as precursors for chain extension reactions using the SRAA/NMP reaction sequence (Scheme 2). Previous research in our group has shown that SRAA is capable of near-quantitative activation of PStBr chains, as verified by a doubling of M_n values and similarly low PDI values after a radical–radical coupling reaction had occurred (Scheme 1) [15]. In this study, PStBr was activated by SRAA in the presence of a second monomer and TEMPO at temperatures suitable for SRAA but not NMP, after which the reaction temperature was elevated to allow NMP to occur. Thus, the reaction sequence has two distinct steps: activation of the PStBr using SRAA, followed by polymerization of the second monomer using NMP.

In the initial reactions, styrene (St) was used as the second monomer, and the components (PStBr, St, TEMPO, *t*BHN, and TTMSS) were added together in a 5 mL hexanes/benzene (3:2 v/v) solution and allowed to react initially at 80 °C, before being placed in a separate oil bath held at 130 °C. We [15] and others [14] have previously had success using this mixed solvent system in reactions between silane radicals and halogens. A typical GPC trace of polymer formed by the SRAA/NMP combination and the corresponding PStBr precursor is shown in Fig. 1. Results of several of these SRAA/NMP chain extension reactions are summarized in Table 1 (entries 1–6). Because the refractive index of both the original PStBr and the extended PSt product should not change, the amount (by mass) of PStBr precursor remaining in the elongated product could be estimated by comparing the areas under the signals corresponding to each polymeric species. Appreciable extension was observed in each case (typically ~80% of the product corresponded to the elongated species). As shown in Fig. 1, a lower molecular weight peak or shoulder was typically present in the GPC chromatogram after the extension occurred, and its elution volume corresponded with that of the PStBr precursor. The length and necessity of the 80 °C phase of the reaction were also studied. As shown in Table 1 (entries 7 and 8), doubling the length of the SRAA phase (holding the temperature at 80 °C for 2 h rather than 1 h) did not impact the results when identical PStBr precursors were used. Likewise, omitting this phase altogether and simply performing the entire reaction at 130 °C had a negligible impact on the products (Table 1, entries 9 and 10).

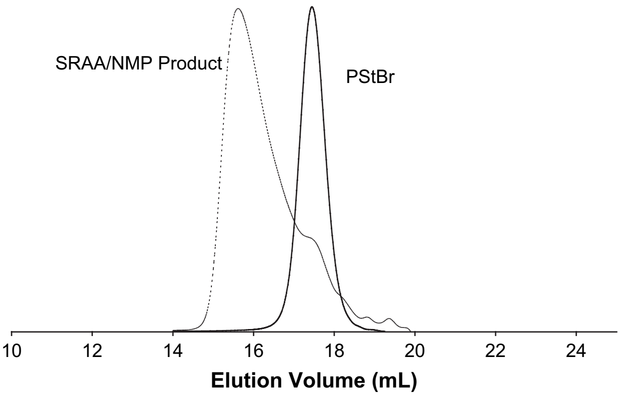


Fig. 1. Typical GPC traces of PSt formed by chain elongation using SRAA/NMP under varying reaction conditions (Scheme 2; Table 1, entry 4).

Table 1
Products obtained from the chain extension of PSt using SRAA/NMP (Scheme 2)

Entry	PStBr precursor[a]		Elongated PSt[b]		% Elongation[c]
	M_n	PDI	M_n	PDI	
1	1100	1.09	3170	1.82	75
2	1300	1.10	2160	1.78	75
3	1100	1.09	4010	1.81	70
4	1850	1.08	5890	1.70	85
5	1410	1.12	3100	1.75	80
6	1130	1.10	2350	1.81	70
7	1300	1.12	2120	1.71	85
8[d]	1300	1.12	2310	1.72	85
9	1220	1.12	3000	1.71	80
10[e]	1220	1.12	2860	1.76	80

Reactions were carried out in hexanes/benzene (3:2 v/v) at 80 °C for 1 h followed by 130 °C for 47 h. [PStBr]:[TEMPO]:[TTMSS]:[TTBON]:[St] = 1:1:1:0.6:67. See Section 2 for details.

[a] Characteristics of PStBr precursor obtained via ATRP, as determined by GPC calibrated with PSt standards.

[b] Characteristics of PSt obtained after SRAA and NMP, as determined by GPC.

[c] Amount of the original PStBr remaining in the chain elongation product, as estimated by the areas under the GPC traces of the PStBr precursor and PSt product.

[d] Reaction carried out at 80 °C for 2 h followed by 130 °C for 46 h.

[e] Reaction carried out at 130 °C for 48 h.

The chain elongation was further investigated to verify that it possessed characteristics consistent with a controlled radical polymerization. The NMP phase of the reaction was monitored by removing aliquots of the reaction mixture at various time intervals, and conversion of the monomer was calculated by integration of the vinylic monomer peaks with the aromatic peaks using ^{1}H NMR (see Section 2 for details). As shown in Fig. 2a, the M_n of the polymer was observed to increase linearly with monomer conversion, with PDI values slowly over the course of the reaction. At 0% monomer conversion, the M_n and PDI of the polymer are simply those of the PStBr precursor ($M_n = 1220$ g/mol; PDI = 1.13), since the % monomer conversion corresponds to the monomer participating in chain extension via SRAA/NMP. Because a portion of the PStBr precursor persists throughout the reaction and does not undergo elongation, the overall PDI of the polymeric species increases as the NMP phase of the reaction occurs. Fig. 2b shows a first order kinetic plot, with $\ln([M]_0/[M]_t)$, where $[M]_0$ is the initial St concentration and $[M]_t$ is the concentration at time t, plotted as a function of time (h). The kinetic data is consistent with the chain extension proceeding with a first order dependence on monomer concentration. GPC traces of the monitored reaction as a function of time are shown in Fig. 3, and clearly indicate the majority of the PStBr precursor undergoing extension and shifting to higher M_n values as the reaction progresses.

3.2. Block copolymer synthesis

Using a different monomer in the system would enable the synthesis of block copolymers, provided the second monomer was compatible with NMP. Two monomers were chosen in this study: one predicted to behave similarly to St in chain

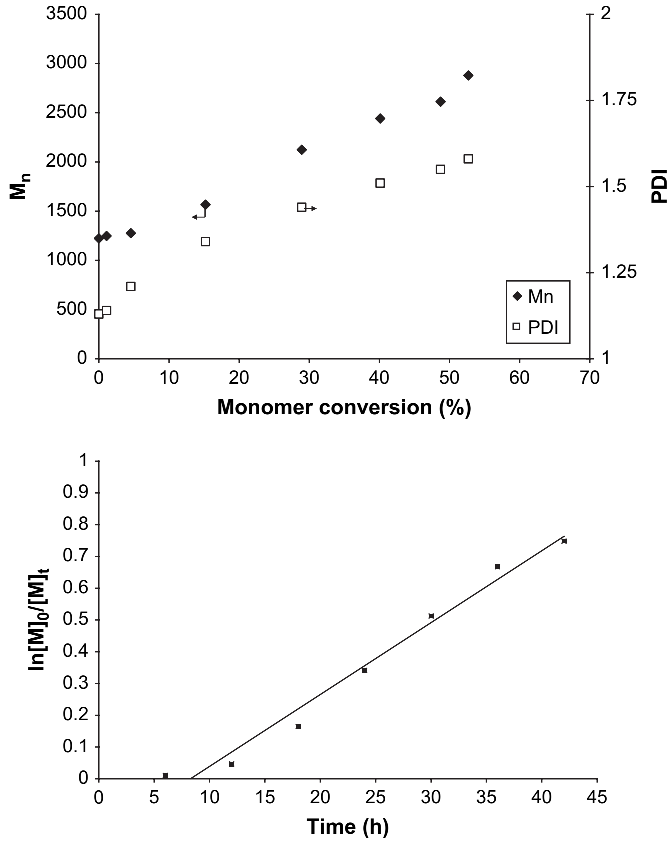


Fig. 2. (a) Number-average molecular weight (M_n) and PDI as a function of percent monomer conversion and (b) first order kinetic plot for the chain elongation of PSt performed by SRAA/NMP. $[M]_0$:$[PStBr]_0$:$[t\text{BHN}]_0$:$[TMSS]_0 = 67:1:0.6:1$. Note that $t = 0$ is defined as the beginning of the NMP phase (reaction vessel is placed in 125 °C bath).

elongation phase (*p*-methylstyrene, MSt), and one expected to behave in a substantially different manner (*n*-butyl acrylate, BA).

n-Butyl acrylate (BA) has previously been used in NMP reactions mediated by TEMPO or TEMPO derivatives by others [18,28,29]. Reactions were run in an analogous manner to the chain extension trials discussed above, with PStBr again used as the precursor. A typical GPC chromatogram of the block copolymers obtained from SRAA/NMP, along with the original PStBr, is shown in Fig. 4 and the results are summarized in Table 2 (entries 1 and 2). In all cases, M_n values were observed to shift to higher values while a portion of the PStBr precursor did not participate, which is similar to chain elongation using SRAA/NMP. The higher PDI values observed in the case of the synthesis of the PSt-*b*-PBA block compared to chain elongation (Table 2, entry 1) are consistent with reduced control over the NMP reaction when BA is used as the second monomer. This has been reported by others [30], and has been attributed to excess free nitroxide build-up due to termination reactions occurring throughout the polymerization, thus shifting equilibrium towards the TEMPO-capped PSt chains and inhibiting the polymerization of BA.

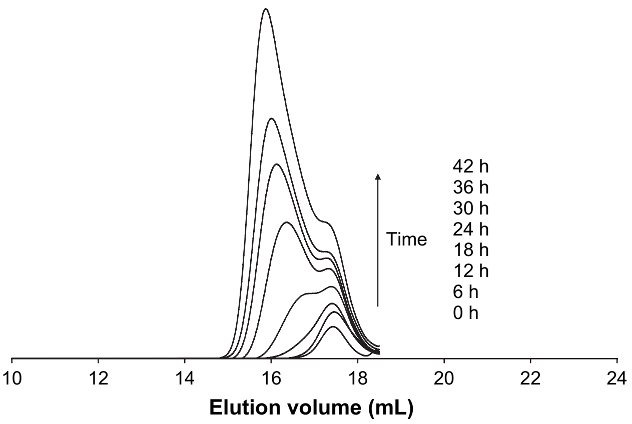


Fig. 3. GPC traces as a function of time for the chain extension of PStBr using SRAA/NMP.

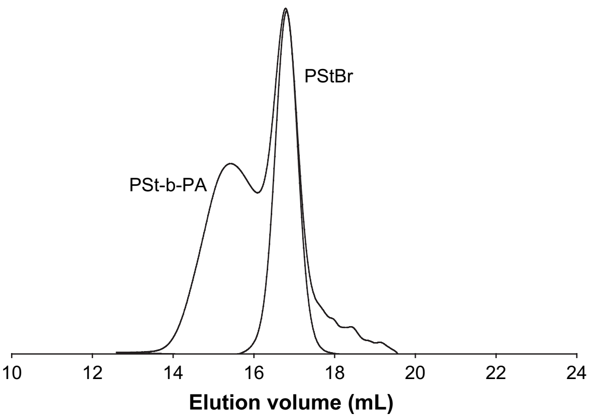


Fig. 4. Typical GPC trace of PSt-*b*-PBA formed by SRAA/NMP (Table 2, entry 1).

Table 2
PSt-*b*-PBA and PSt-*b*-PMSt diblock copolymers obtained using SRAA/NMP

Entry	Monomer[a]	PStBr precursor[b]		Diblock[c]		% Elongation[d]
		M_n	PDI	M_n	PDI	
1	BA	2270	1.09	3580	2.07	70
2	BA	2270	1.09	3380	1.81	70
3	MSt	1468	1.16	2750	1.63	80
4	MSt	1308	1.16	2500	1.59	85

Reactions were carried out in hexanes/benzene (3:2 v/v) at 80 °C for 1 h followed by 125 °C for 47 h. [PStBr]:[TEMPO]:[TTMSS]:[tBHN]:[BA or MSt] = 1:1:1:0.6:100 except where noted. See Section 2 for details.

[a] Monomer used in the NMP phase. BA = butyl acrylate; MSt = α-methylstyrene.

[b] Characteristics of PStBr precursor obtained via ATRP, as determined by GPC calibrated with PSt standards.

[c] Characteristics of diblock obtained after SRAA and NMP, as determined by GPC.

[d] Amount of the original PStBr remaining in the chain elongation product, as estimated by the areas under the GPC traces of the PStBr precursor and PSt product.

Analogous reactions were performed using MSt as the second monomer, forming PSt-*b*-PMSt. As shown in Fig. 5 and Table 2 (entries 3 and 4), a larger portion of the PStBr shifted to higher M_n values, which is consistent with behavior observed in chain extension reactions using St in the NMP phase (Fig. 1 and Table 1). Furthermore, the PDI of the diblocks formed in this case was generally narrower than the values

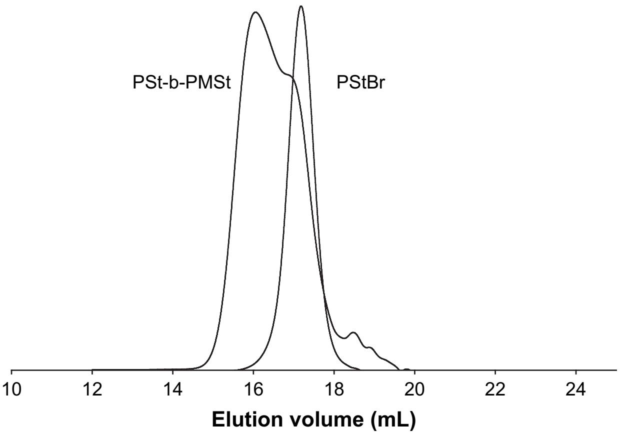
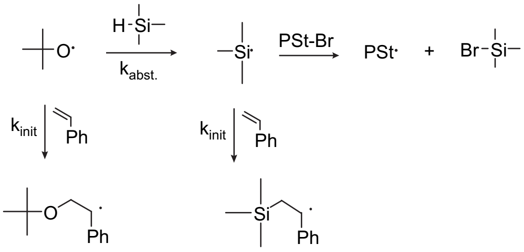


Fig. 5. Typical GPC trace of PSt-*b*-PMSt formed by SRAA/NMP (Table 2, entry 3).

of those when BA was used. These results highlight both the versatility and limitations of the SRAA/NMP reaction sequence in the synthesis of block copolymers. Both monomers were able to be incorporated into the block copolymer during the NMP phase, with the success mirroring the monomer's compatibility in NMP reactions mediated by TEMPO.

3.3. Mechanistic explanation

These results are consistent with some amount of the PStBr resisting activation by SRAA, and thus being unable to participate in chain elongation or block copolymer synthesis regardless of the length of the SRAA phase (80 °C). This appears to be inconsistent with our previously reported results that show near-quantitative activation and coupling of PStBr chains at this temperature (Scheme 1) [15]. In order to probe this discrepancy, reactions were performed in the presence of all reactants except PStBr, to observe if the *t*-butoxy radicals or tris(trimethylsilyl)silane radicals were alone capable of initiating PSt chains. In all cases, PSt was formed in reactions performed under identical reaction conditions (130 °C or 80 °C → 130 °C), with analysis by ^{1}H NMR indicating that both *t*-butoxy and tris(trimethylsilyl)silane end groups were present at the chain ends [26]. Integration of end groups on ^{1}H NMR spectra indicated that *t*-butoxy groups were much more likely to act as initiators, as they accounted for ~95% of the chain termini. As shown in Scheme 3, the radicals (both oxygen- and silane-based) essential for the SRAA phase can also act as initiators for styrene, making some portion of them unavailable for bromine abstraction. Thus, despite the ability of SRAA to lead to coupled PSt in near-quantitative yields as demonstrated previously (Scheme 1), the presence of monomer provides a competitive reaction pathway. If the radicals were formed and allowed to react with styrene at 80 °C in the absence of TEMPO, PSt possessing broad PDI values was formed [27]. This is consistent with these radical addition pathways (Scheme 3) also occurring during the low temperature (SRAA) phase.



Scheme 3. Competition between atom abstraction and initiation occurring during the silane atom abstraction phase. Note: TMS groups of silane not shown.

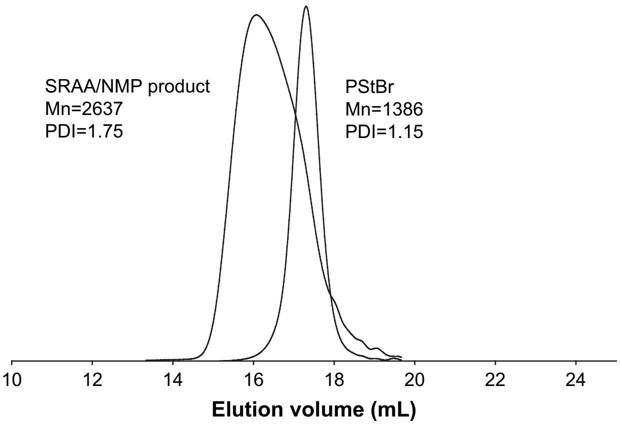


Fig. 6. Typical GPC traces of PSt formed by chain elongation using SRAA/NMP under varying reaction conditions with the monomer added after the SRAA phase. PStBr precursor: $M_n = 1390$; PDI = 1.15. SRAA/NMP product: $M_n = 2640$; PDI = 1.75.

To verify that propagation of polymer chains was not occurring during the SRAA phase of the reaction when TEMPO was present, aliquots were removed from the chain elongation reaction mixture at various time intervals while the temperature was held at 80 °C. Both the M_n and the PDI of the polymer precursor remained constant even after 2 h, consistent with only radical abstractions and radical addition to alkenes occurring at this temperature. These findings are consistent with a portion of the radicals needed for the SRAA phase being consumed by addition to monomer, and therefore non-quantitative activation of the PStBr.

To overcome these limitations and produce polymers that undergo elongation to a greater extent, reactions were run with monomer omitted during the SRAA phase of the reaction, in an attempt to shut down the competitive pathways outlined in Scheme 3. After 1 h at 80 °C, the reaction temperature was raised to 130 °C and styrene was added to the system. A typical GPC trace of both the PStBr precursor and the elongated (SRAA/NMP) product is shown in Fig. 6. The lack of a low molecular weight shoulder in the elongated product, in comparison to reactions with monomer present throughout, is consistent with a greater amount of the PStBr precursors being activated during the SRAA phase. Despite the overall improvement, as illustrated by the GPC traces shown in Fig. 6 compared to Fig. 1, a low molecular weight tail is still apparent in the elongated product even when monomer is withheld at the abstraction phase and quantitative activation and elongation of the PStBr precursor were not seen.

4. Conclusion

Silane radicals were used to activate PStBr at 80 °C, forming polymer radicals that underwent chain elongation in the presence of excess monomer and TEMPO when temperatures were elevated to 130 °C. This combination of SRAA and NMP was used to create homopolymers of PSt possessing higher M_n values, or block copolymers of PSt-*b*-PBA or PSt-*b*-PMSt when BA or MSt was used as the monomer. In all cases, a portion of the PStBr precursor remained in the reaction mixture, which is consistent with the radicals used in the SRAA phase being able to react with monomeric alkenes. When styrene was added only after the temperature was raised to that of the NMP phase, the activation of the PStBr was improved, as observed by GPC traces of the elongated product. Monitoring the extension indicated that the M_n values showed a linear correlation with monomer conversion, along with a first order dependence on the concentration of monomer.

Acknowledgements

This work was financially supported by Bucknell University and the Hobar Fund. The authors are grateful to Prof. David Rovnyak for his help in obtaining NMR data for kinetic studies.

References

[1] Matyjaszwski K, Xia J. Chem Rev 2001;101:2921.
[2] Patten TE, Matyjaszewski K. Acc Chem Res 1999;32(10):895.
[3] Matyjaszewski K. J Am Chem Soc 2006;128:16277.
[4] Wang J, Matyjaszewski K. Macromolecules 1995;28:7900.
[5] Pyun J, Matyjaszewski K. Macromolecules 2000;33:217.
[6] Mueller L, Jakubowski W, Tang W, Matyjaszewski K. Macromolecules 2007;40:6464.
[7] Brar AS, Saini T. Eur Polym J 2007;43:1046.
[8] Jewrajka SK, Mandal BM. Macromolecules 2003;36:311.
[9] Shipp DA, Wang J-L, Matyjaszewski K. Macromolecules 1998;31:8005.
[10] Muhlebach A, Gaynor SG, Matyjaszewski K. Macromolecules 1998; 31:6046.
[11] Zhao B, Brittain WJ. J Am Chem Soc 1999;212:3557.
[12] Sedjo RA, Mirous BK, Brittain WJ. Macromolecules 2000;33:1492–3.
[13] Sarbu T, Lin K, Ell J, Siegwart DJ, Spanswick J, Matyaszewski K. Macromolecules 2004;37:3120.
[14] Braslau R, Tsimelzon A, Gewandter J. Org Lett 2004;6:2233.
[15] Thakur S, Tillman ES. J Polym Sci Part A Polym Chem 2007;45:3488.
[16] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661.
[17] Hawker CJ, Barclay GG, Dao J. J Am Chem Soc 1996;118:11467.
[18] Listigovers NA, Georges MK, Odell PG, Keoshkerian B. Macromolecules 1996;29:8992.
[19] Mather BD, Lizotte JR, Long TE. Macromolecules 2004;37:9331.
[20] Pangborn AB, Giardello MA, Grubbs RH, Rosen RK, Timmers FJ. Organometallics 1996;15:1518.
[21] Mendenhall GD. Tetrahedron Lett 1983;24:451.
[22] Jankova K, Bednarek M, Hvilsted S. J Polym Sci Part A Polym Chem 2005;43:3748.
[23] Yu WH, Kang ET, Neoh KG, Zhu S. J Phys Chem 2003;107:10198.
[24] Ge Z, Cai Y, Yin J, Zhu Z, Rao J, Liu S. Langmuir 2007;23:1114.
[25] Zhang W, Shiotsuki M, Masuda T, Kumaki J, Yashima E. Macromolecules 2007;40:178.
[26] Georges MK, Hamer GK, Listigovers NA. Macromolecules 1998;31: 9087.
[27] Tang C, Kowalewski T, Matyjaszewski K. Macromolecules 2003;36: 1465.
[28] Georges MK, Lukkarila JL, Szkurhan AR. Macromolecules 2004;37: 1297.
[29] Typical reaction: *t*-butyl hyponitrite (0.23 g, 1.3 mmol), TEMPO (0.20 g, 1.3 mmol), styrene (3 mL, 26 mmol), tris(trimethylsilyl)silane (400 µL, 1.3 mmol), hexane (3 mL) and benzene (2 mL) were reacted at 80 °C for 1 h followed by 130 °C for 47 h in a manner identical to that of "Typical procedure for chain extension" (see Section 2). Characteristics of polymer: $M_n = 3930$ g/mol; PDI = 1.55. ^{1}H NMR indicates ∼95% of chain ends have *t*-butoxy rather than tris(trimethylsilyl)silyl groups.
[30] Performed identically as reaction described in Ref. [26], but with TEMPO omitted and reaction temperature held at 80 °C. Characteristics of polymer: $M_n = 4090$ g/mol; PDI = 1.81.