10304 *Macromolecules* **2010**, *43*, 10304–10310
DOI: 10.1021/ma102319r

Macromolecules
ARTICLE

An Easy and Efficient Route to Macrocyclic Polymers Via Intramolecular Radical−Radical Coupling of Chain Ends

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Received October 9, 2010; Revised Manuscript Received November 12, 2010

ABSTRACT: Macrocyclic polystyrene (PSt) was produced in high yields by an intramolecular atom transfer radical coupling reaction of the chain ends. The slow addition of the dibrominated polystyrene (BrPStBr) precursors, prepared by atom transfer radical polymerization, into a refluxing tetrahydrofuran solution of copper(I) bromide, tris[2-(dimethylamino)ethyl]amine, and copper (0) activated the alkyl bromides at the PSt chain ends, favoring an intramolecular ring closing reaction with only minor competition from intermolecular coupling. Comparison of the gel permeation chromatography traces of the BrPStBr precursor to the cyclic product showed a shift to lower apparent molecular weight values, consistent with the reduced hydrodynamic radius of the macrocycle. Quantitative activation of the chain ends was confirmed by ^{1}H NMR spectroscopy, with the resonance due to the C(H)Br methine termini on the BrPStBr precursor absent on the NMR spectrum of the cyclic product. The cyclic structure was directly confirmed by matrix-assisted laser desorption ionization−time-of-flight spectrometry.

Introduction

Macrocyclic vinyl polymers have long elicited interest due to their unique properties when compared to linear polymer analogues, yet efficient, straightforward synthetic routes toward their production are lacking. Beyond differences such as increased glass transition temperature and reduced viscosity,[1] cyclic vinyl polymers show improved energy transfer between pendant groups compared to linear analogues,[2] owing to their spatial orientation around the ring (especially pronounced at lower degrees of polymerization), making them potentially valuable in light harvesting systems. Early reports of the formation of macrocycles involved backbiting reactions occurring in poly(dimethylsiloxane), creating an equilibrium between the open chain and polymer cycle.[3] More recently, polyhomologation was reported capable of making macrocycles of polymethylene by adding a single $-CH_2-$ unit at a time by insertion between a carbon−boron bond.[4] While this method allows for the synthesis of macrocycles of controllable molecular weights and low polydispersity index (PDI) values (including cyclic polymers of high molecular weight values inaccessible by end-to-end coupling), it lacks versatility in that it is incompatible with vinyl polymers. Notably, ring-opening metathesis polymerization (ROMP) has recently been used to make polymer macrocycles without linear precursors by using a cyclic derivative of Grubbs' catalyst.[5] The polymers are eventually "pinched off" from the catalyst as macrocycles by intramolecular ring-closing metathesis during the course of reaction. This system does not allow for control over molecular weights and polydisperisities, and is again incompatible with common vinyl monomers.

In the traditional synthesis of macrocycles from linear presursors, α,ω-dilithiopolystyrene (LiPStLi) or α,ω-dipotassiopolystyrene (KPStK) are first produced by anionic methods and subsequently employed in two consecutive S_N2 reactions with a bifunctional electrophile, the second being intramolecular when performed under high dilution ($\sim 10^{-4}$ M).[6] The simplified reaction sequence is shown in Scheme 1, A. Such reactions are tedious to perform due to the high reactivity of polymer anions and thus rigorous purification is needed to keep them "living", with the degree of difficulty further increased by a cyclization reaction that requires simultaneous dilute addition of both the polymer dianion and bifunctional electrophile into a reaction mixture.[7] The development of controlled radical polymerization methods, especially atom transfer radical polymerization (ATRP) and nitroxide mediated polymerization (NMP), has opened the door to experimentally more lenient syntheses of well-defined telechelic linear precursors.[8] A major drawback remains the requirement of compatibly reactive α,ω end groups, which must be installed postpolymerization. For example, intramolecular click chemistry[9] (Scheme 2B) and intramolecular ring closing metathesis[10] have proven highly efficient in producing macrocycles, but rely on synthetic modification of polymer chains prior to employment in cyclization reactions. This general strategy may create multiple problems: polymer modification must be quantitative to produce high yields of cyclic products and the cyclic products will necessarily include new functionality as a consequence of these modifications, which may or may not be desirable. Lastly, modification of the polymer chain ends prior to coupling adds step(s) to the overall synthetic route to produce macrocycles.

In this contribution, a simple method for the production of high yields of macrocyclic polystyrene (PSt) is presented, relying on consecutive atom transfer reactions: (1) ATRP to produce dibrominated PSt (BrPStBr) precursors (Scheme 2A) and (2) atom transfer radical coupling (ATRC) (Scheme 2, parts B and C). The ATRC reaction can occur either intermolecularly, leading to "step" polymers (Scheme 2B), or, intramolecularly, leading to cyclic polymers (Scheme 2C). We demonstrate that high yields of cyclic polymer are formed by the addition of the BrPStBr into the reaction mixture under pseudo high dilution conditions

Experimental Section

Materials. CuBr (98%, Aldrich), $CuBr_2$ (99%, Aldrich), benzal bromide (97%, Aldrich), nanosized Cu(0) (99.8%,

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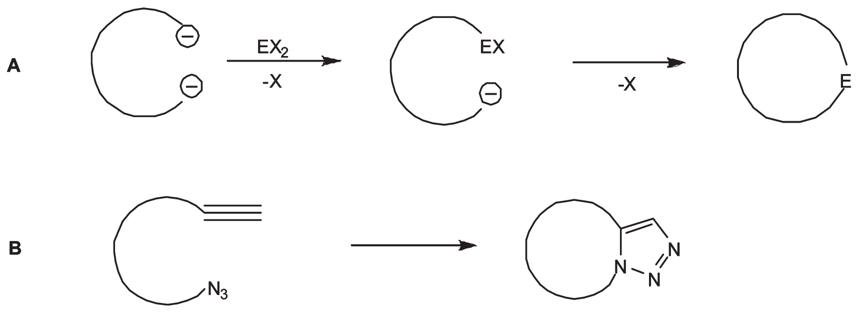
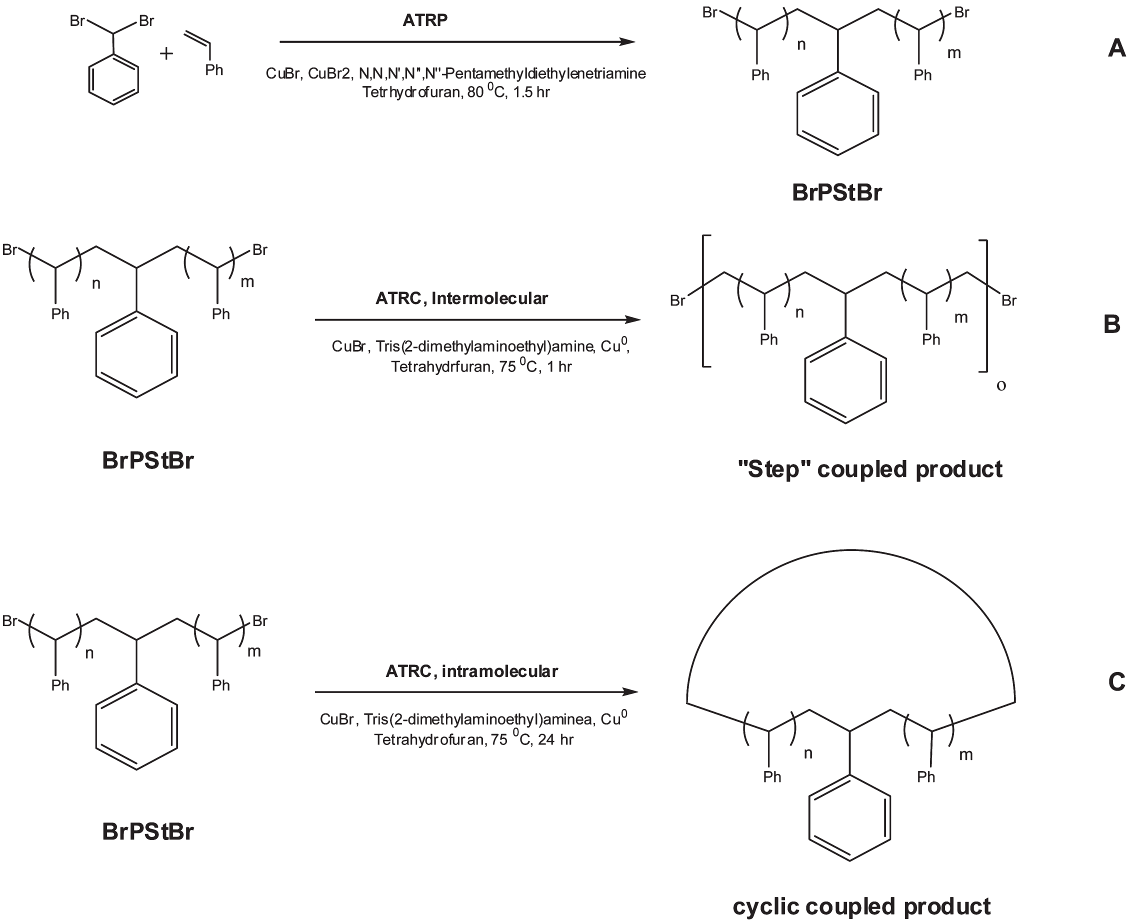
Scheme 1. General Strategies for Cyclization of Linear Precursors: (A) Consecutive S_N2 Reactions between a Polymer Dianion and a Bifunctional Electrophile, and (B) Click Chemistry between Azide and Alkyne End Groups



Scheme 2. (A) Atom Transfer Radical Polymerization (ATRP) of Styrene Using a Bifunctional Initiator To Generate Dibrominated Polystyrene Precursors (BrPStBr), (B) Intermolecular Atom Transfer Radical Coupling (ATRC) of the BrPStBr To Form a Coupled "Step" Polymer, and (C) Intramolecular ATRC of the BrPStBr To Form the Coupled Macrocyclic Polymer



Aldrich), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) (99%, Aldrich) and alumina (Aldrich) were used as received. Styrene (99%, Aldrich) was distilled from calcium hydride under reduced pressure and stored in a sealed glass ampule at −15 °C. Tetrahydrofuran (THF) was passed through a Grubbs-type purification column before use. Tris-[2-(dimethylamino)ethyl]amine (Me_6TREN) was generously synthesized and provided by Prof T. Pintaur according to a modified procedure.[11]

Synthesis of α,ω-Dibrominated Polystrene (BrPStBr) Using ATRP. For [monomer]/[initiator] = 125:1, CuBr (100 mg, 0.7 mmol) and $CuBr_2$ (80 mg, 0.36 mmol) were added to a flamed, 50 mL, 2-neck round-bottom flask, and the reaction flask was placed on a Schlenk line with a septum on the remaining neck. The flask was evacuated, after which styrene (4.0 mL, 35 mmol) and benzal bromide (47 μL, 0.28 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 70 °C and stirred for several minutes to allow the contents to reach the temperature of the bath, after which PMDETA (145 μL, 0.7 mmol) was added via an argon flushed syringe to commence the polymerization. After 90 min, the reaction mixture was diluted with THF, followed by purification by passing through an alumina column to remove the copper. The ultra white powder was characterized by gel permeation chromatography (GPC) (apparent number-average molecular weight (M_n), 2100; polydispersity index (PDI), 1.15; conversion, 35%).

Typical Procedure for the Intermolecular ATRC of Dibrominated Polystyrene ("Step" Polymerization). In a typical experiment, dibrominated polystyrene (BrPStBr with M_n = 1330 g/mol, PDI = 1.16; 100 mg, 0.07 mmol), CuBr (50 mg, 0.35 mmol), and nanosize copper (22 mg, 0.35 mmol) were added to a 50 mL round-bottom flask that was previously flamed, evacuated, and cooled. After the flask was sealed with a rubber septum, 2 mL of THF were introduced into the flask via argon-flushed syringe. Three freeze−pump−thaw cycles were performed, and the flask was placed in an oil bath and stirred at 70 °C. The reaction was initiated by introducing Me_6TREN (94 μL, 0.035 mmol) via argon-flushed syringe. After 1 h, the flask was removed from the oil bath and the solution was diluted with THF. Coupled product was analyzed directly from the crude reaction mixture (M_n = 6272; PDI = 1.68; approximately 90% was found to have intermolecularly coupled, as estimated by the areas under the RI GPC traces).

Typical Procedure for the Intramolecular ATRC of Dibrominated Polystyrene (Synthesis of Macrocyclic PSt). A 500 mL Schlenk flask containing a 100 mL THF solution of CuBr (574 mg, 4.0 mmol, 40 mM) and nanosized copper (254 mg, 4.0 mmol, 40 mM) was sealed with a rubber septum, evacuated with 4 freeze−pump−thaw cycles, backfilled with N_2, and sealed from the Schlenk line. The flask was then placed in an oil bath and stirred at 75 °C. After allowing the metal solution to reach the temperature of the bath, Me_6TREN (1.07 mL, 4.0 mmol, 40 mM) was introduced via an argon-flushed syringe. A syringe pump held a 50 mL syringe containing an 18 mL THF solution of the BrPStBr (M_n = 4025 g/mol, 3.5 mg; 870 nmol; 48 μM solution), which had separately been subjected to three freeze−pump−thaw cycles and backfilled with N_2. The solution of BrPStBr was slowly dripped through a needle piercing the rubber septum into the stirring THF solution of the metal ligand, over approximately 24 h (approximate rate = 0.75 mL/h, 2 μmol/h). After the contents of the syringe had been added to the reaction mixture, the reaction mixture was stirred for an additional 1 h. The contents of the reaction flask were concentrated under reduced pressure, and the coupled polymer was analyzed directly without precipitation by GPC. Percent cyclic product was estimated by peak areas of the RI traces of the coupled product. The reacted polymer was passed through an alumina column and precipitated into cold methanol prior to analysis by NMR spectroscopy and matrix assisted laser desorption/ionization - time-of-flight (MALDI−TOF) mass spectrometry. (M_n, 3170; PDI, 1.06; ⟨G⟩, 0.80; yield of cyclic polymer, 90% based on RI GPC traces).

Characterization. The polymers were analyzed on a Waters 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 μm Mixed C columns (Polymer Laboratories) held at 25 °C with a flow rate of 1 mL/min capable of separating polymers of 200−1 000 000 Da; a Waters 2487 dual wavelength UV detector and a Waters 2414 RI detector. A 10 point calibration using polystyrene standards (Polymer Laboratories, M_p range = 5.0×10^2 to 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 600 MHz FT-NMR at room temperature. MALDI−TOF spectra were obtained with an Applied Biosystems 4700 Proteomics Analyzer using 10 mg/mL dithranol and 1 mg/mL silver trifluoroacetate, both in THF. The polymer samples were mixed 10:1:1 (matrix:Ag:sample). Samples were analyzed in reflector positive mode, 1000−5000 Da, with a total of 1250 shots collected.

Results and Discussion

Intermolecular "Step" ATRC. In order to optimize reaction conditions for the intramolecular ATRC reaction phase of the reaction (Scheme 2C), intermolecular ATRC (Scheme 2B) was first performed on BrPStBr precursors using varying amounts of ligand, copper bromide and copper (0). Activation of the chain ends by metal-catalyzed, homolytic C−Br cleavage creates carbon-based radicals that undergo radical−radical coupling reactions. As expected, when ATRC was performed at relatively high concentrations of both the BrPStBr precursor and varying molar excess amounts of copper bromide (CuBr), tris[2-(dimethylamino)-ethyl]amine (Me_6TREN), and Cu^0 in THF at 70 °C for 1 h, higher molecular weight step polymerization products were formed in high yields (Table 1). On the basis of these results, it was determined that the presence of Cu^0 was essential in achieving high levels of coupling as evidenced by the larger "step" polymers formed in its presence (trial 3 vs trials 1,2). Further increasing the equivalents of Cu^I and ligand showed no additional improvement in the extent of elongation (trial 4 vs trial 3). Gel permeation chromatography (GPC) traces of the ATRC intermolecular products demonstrated a near quantitative shift to higher molecular weights when Me_6 TREN (illustrated in Figure 1) was used as ligand, consistent with high amounts of activation of bromine end groups on the precursor and efficient radical−radical coupling in the intermolecular ATRC reaction. The intermolecular coupling reaction was less efficient when PMDETA was employed as the ligand compared to analogous Me_6TREN trials, as evidenced by less dramatic shifts to higher values in the M_n of the coupled product.

Table 1. Intermolecular ATRC of BrPStBr (M_n, 1330; PDI, 1.16): Formation of "Step" Polymers[a]

	ATRC product[b]		
trial	M_n	PDI	[BrPStBr]:[CuBr]:[L]:[Cu^0][c]
1	3250	2.01	1:5:5:0
2	1460	1.62	1:10:10:0
3	8125	1.68	1:5:5:5
4	5860	1.56	1:10:10:5

[a] Precursor is α,ω-dibrominated PSt (BrPStBr), formed by atom transfer radical polymerization using benzal bromide as the initiator. Precursors were purified by running through an alumina column prior to characterization and use in atom transfer radical coupling (ATRC) reactions. Apparent number-average molecular weight (M_n), and polydispersity index (PDI) values were obtained by gel permeation chromatography (GPC) based on polystyrene standards. [b] Coupling was performed at 70 °C for 1 h in tetrahydrofuran at [BrPStBr] ~ 350 mM. Coupled product was analyzed by GPC without any purification. [c] Initial molar ratios of components in ATRC reaction.

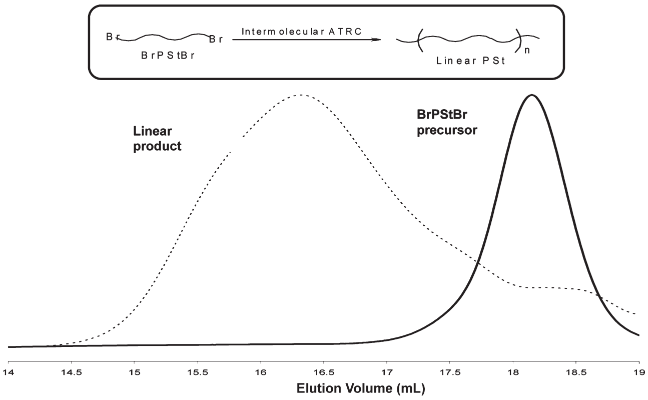


Figure 1. Gel permeation chromatography (GPC) traces of the dibrominated PSt precursor (BrPStBr) (solid line; M_n, 1330; PDI, 1.16) and the product of a step polymerization (dotted line; M_n, 8125; PDI, 1.68) preformed via atom transfer radical coupling with [BrPStBr]:[CuBr]:[tris[2-(dimethylamino)ethyl]amine]:[Cu] in varying ratios. BrPStBr was precipitated and purified by column chromatography prior to GPC analysis; "step" polymer was analyzed without any purification.

Table 2. Intramolecular ATRC of BrPStBr: Formation of Cyclic Polymers

	precursor[a]		ATRC product[d]			
trial	M_n[b]	PDI[c]	M_n	PDI	% cyclic[e]	⟨G⟩[f]
1	2110	1.21	2985	1.84	40[g]	
2	1390	1.17	1180	1.26	> 90[h]	0.82
3	2100	1.15	1830	1.43	95[h]	0.84
4	2945	1.10	2440	1.05	90[h]	0.80
5	4025	1.10	3170	1.06	90[h]	0.80

[a] Precursor is α,ω-dibrominated PSt (BrPStBr), synthesized and purified in an identical manner as described in Table 1. [b] Number-average molecular weight. [c] Polydispersity index. [d] Atom transfer radical coupling (ATRC) was performed by pseudo high dilution addition of BrPStBr solution (48 μM) into a refluxing tetrahydrofuran solution of [CuBr] = [L] = [Cu^0] = 40 mM . Cyclic polymers were characterized by gel permeation chromatography without any purification. [e] Percentage of cyclic polymer in ATRC product, as estimated by areas under the RI traces on the gel permeation chromatograms. [f] Ratio of M_p values of cyclic and BrPStBr precursor. [g] BrPStBr precursor was added dropwise over approximately 12 h. [h] BrPStBr precursor was added dropwise over approximately 24 h.

Intramolecular "Cyclic" ATRC. The preference toward intramolecular ATRC (Scheme 2, C) and the production of cyclic polymers are expected to be a function of the concentration of BrPStBr in the reaction solution. Thus, a THF solution of BrPStBr precursor was added dropwise at a fairly high rate (~4.2 mL/h), into a refluxing THF solution of CuBr, Me_6TREN, and Cu^0 and both inter- and intramolecular ATRC reaction were found to compete (Table 2, trail 1). GPC analysis showed the presence of cyclic material is clearly evident by the shift to longer elution volumes, consistent with reduced hydrodynamic radii of the cyclic product.[12] A broad portion of the trace at lower elution volumes, along with the higher PDI value of the ATRC, was consistent with a mixture of both cyclic polymer and higher molecular step polymer formed. When the BrPStBr precursor was added at a slower rate (~0.75 mL/h, Table 2, trials 2−5), the observed ATRC products were predominantly cyclic as evidenced by the ratio of the peak average molecular weight (M_p) of the coupled product relative to that of the BrPstBr precursor (given as ⟨G⟩ values). The ⟨G⟩ values found in our ATRC system, ranging from 0.80 to 0.84, were found to be consistent with literature values of cyclic polymers produced by anionic methods.[13] A typical GPC trace of the cyclic ATRC product along with that of the BrPStBr precursor is shown in Figure 2. On the basis of the relative areas of the GPC traces of the ATRC product, the amount of cyclic polymer formed in the reaction was estimated to be ≥90%. In all cases, characterization of the ATRC product by GPC was performed on the unprecipitated, crude polymeric product to avoid inadvertent fractionation and allow for a more accurate comparison to the BrPStBr precursor.

Mechanistic Account. To further investigate the coupling reaction leading to cyclic polymers, the ^1H NMR spectrum of the BrPStBr precursor was compared to that of the ATRC product. As expected, the C(H)−Br terminal methine protons were clearly evident in the precursor yet absent in the coupled product (Figure 3), indicating that the C−Br termini in the BrPStBr precursors were quantitatively activated in the atom transfer step of the ATRC. This is consistent with our results showing high amounts of "step" product formed in the intermolecular ATRC study (Table 1) and the high yield of cyclic polymers formed (Table 2). Once activated, the carbon-based radicals will react in one of three possible routes: head to head coupling (radical−radical coupling leading to cycles or step polymers), hydrogen abstraction from solvent or other external source (leading to "dead" chain ends), or disproportionation with another polymer radical (Scheme 3, pathways 1, 2, and 3, respectively). Of these possible termination pathways, we[14] and others[15] have shown that head-to-head coupling of PSt radicals is favored

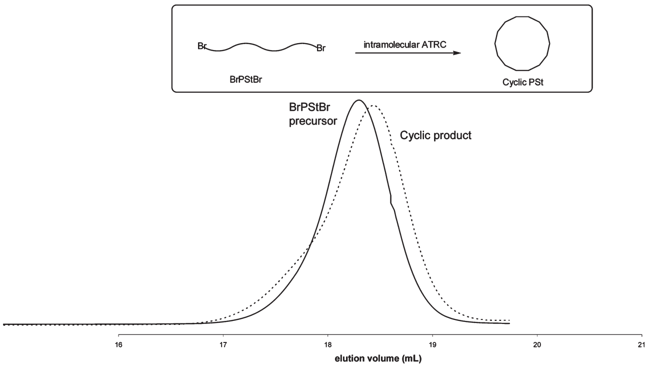


Figure 2. Gel permeation chromatography traces of the dibrominated precursor (solid line; number-average molecular weight (M_n) = 1395; polydispersity index (PDI) = 1.17) and the subsequent cyclic product formed by intramolecular atom transfer radical coupling (dotted line; M_n = 1180; PDI = 1.26).

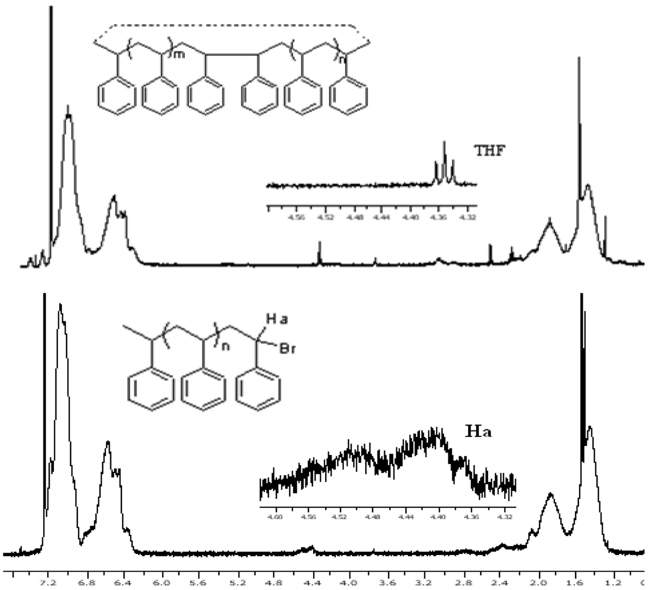
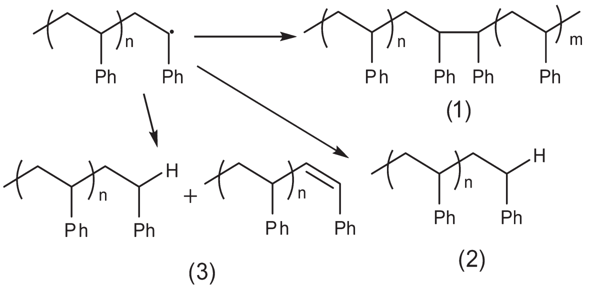
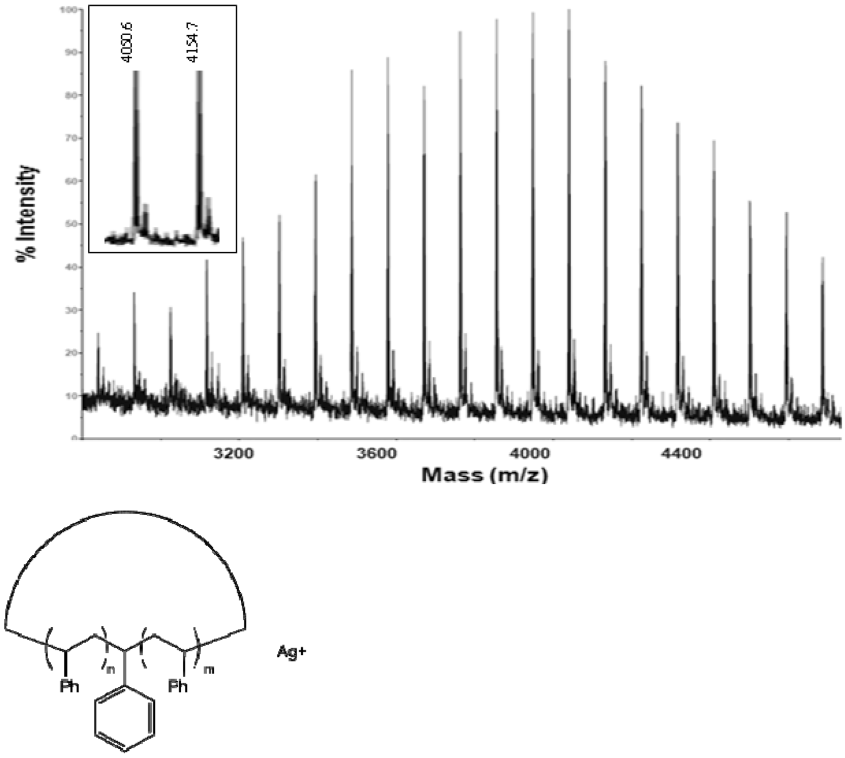


Figure 3. 600 MHz ^1H NMR spectra of dibrominated percursor (bottom, only one chain end shown in illustration) and the corresponding cylic polystyrene (top) generated by intramolecular atom transfer radical coupling. Inset shows the region of the terminal methine resonances.

Scheme 3. Possible Fates of Polystyrene Radicals Produced by the Homolytic Cleavage of the C−Br Bond[a]



[a] Key: (1) head-to-head radical coupling of two terminal radicals, (2) hydrogen abstraction, and (3) disproportionation.



Calculated m/z values	Experimental m/z values
3009.9 (n+m = 27)	3010.0
3114.1 (n+m = 28)	3113.1
3218.2 (n+m = 29)	3218.1
3322.4 (n+m = 30)	3322.4
3426.4 (n+m = 31)	3427.3
3530.7 (n+m = 32)	3530.4
3634.8 (n+m = 33)	3634.4
3739.0 (n+m = 34)	3738.4
3843.1 (n+m = 35)	3842.5
3947.3 (n+m = 36)	3946.6
4051.4 (n+m = 37)	4050.6
4155.6 (n+m = 38)	4154.7
4259.7 (n+m = 39)	4259.7
4363.9 (n+m = 40)	4363.8

Figure 4. Matrix assisted laser desorption/ionization - time-of-flight spectra of cyclic atom transfer radical coupling product (Table 1, run 5) along with cyclic structure consistent with the major series. Inset shows expanded region between two signals. Table shows comparison between calculated *m*/*z* values based on the expected cyclic structure and experimentally observed values.

in ATRC systems using monobrominated PSt as the precursor (simply by a quantitative shift to double the precursor M_n). Comparing bimolecular termination reactions of PSt radicals (disproportionation vs radical−radical coupling), it has been shown by others that $>95\%$ of the chain end radicals undergo termination via radical−radical coupling.[16] Thus, as expected, radical−radical coupling is the dominant pathway in the reaction systems reported here, leading to either "step" or cyclic product in high yields.

To further elucidate the fate of the polymer radical chain ends and conclusively verify the cyclic architecture of the ATRC products listed in Table 2, both the BrPStBr precursors and cyclic ATRC product were analyzed by MALDI−TOF mass spectroscopy. The major series of the

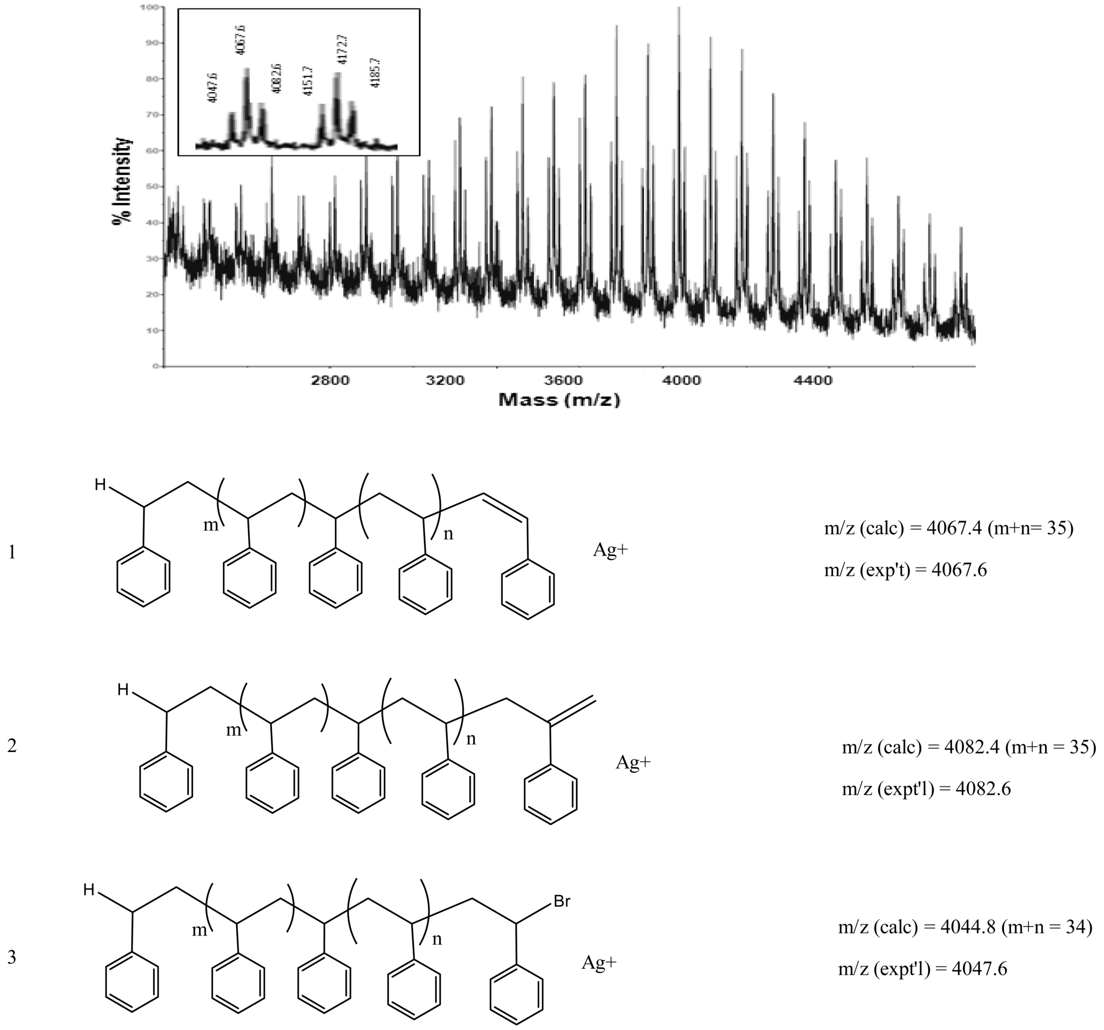


Figure 5. Matrix assisted laser desorption/ionization - time-of-flight spectrum of dibrominated precursor along with proposed structures of linear polymers responsible for the observed signals. Inset shows expanded region between two signals. (1) Is formed by disproportionation, (2) is formed by oxygenation followed by loss of benzylic group, and (3) is proposed to be formed by bromine remaining on one end. A single hydrogen atom is shown on the left-hand side as it is the atom abstracted by the radical formed during fragmentation.

MALDI−TOF spectrum of the intramolecular ATRC product (Figure 4) was determined to be consistent with the molecular weight of the expected macrocyclic polymer chains with an associated silver cation; the mass differences between the peaks being that of a single styrene unit. Also shown in Figure 4, along with structure of the cyclic polymer/ion, are both calculated *m*/*z* values and experimental *m*/*z* values obtained from MALDI−TOF spectrum. The agreement between this values (within 1 Da in every case), coupled with GPC data and NMR data, conclusively demonstrate the cyclic architecture of the intramolecular ATRC products.

Conversely, MALDI−TOF analysis of the BrPStBr precursor (Figure 5) generated a more complicated spectrum with three signals for each peak. Multiple *m*/*z* series for brominated PSt, due to cleavage of the labile C−Br chain end bond during anaylsis, is consistent with what others have reported.[16] While the exact fate of the chain ends after C−Br cleavage is not entirely known, previous MALDI−TOF analysis of ATRP products suggests that the molecular weight distributions observed are due to some combination of the dispropotionation and chain end degradation.[17] The major series in linear spectrum can be attributed to loss of bromine, followed by disproportionation (Figure 5, structure 1). The minor, higher molecular weight series is consistent with loss of bromine and oxidation, followed by loss of a benzylic group (structure 2). Both of these structures are consistent with reports by others.[17,18] It is not clear what the minor, lower molecular weight series corresponds to. It most closely matches the mass expected when one bromine group remains intact, while the other is cleaved and abstracts a hydrogen (structure 3).

Conclusion

To summarize, high yields (>90%) of cyclic PSt were produced by intramolecular ATRC by simply adding BrPStBr, produced by ATRP, slowly into a solution of CuBr, Me_6TREN, and copper. The cyclic structure of the products was confirmed with a combination of GPC, ^{1}H NMR and MALDI−TOF analyses.

Acknowledgment. The authors are grateful for financial support from a Henry Dreyfus Teacher Scholar Award and the Dr. Gebhardt Research Fellowship. They also thank Rebekah Woolsey of the Nevada Proteomics Center (supported by NIH Grant No. P20 RR-016464 from the INBRE Program of the National Center for Research Resources) for her assistance in obtaining MALDI−TOF spectra.

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