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Universal Chain-End Coupling Conditions for Brominated Polystyrenes, Polyacrylates, and Polymethacrylates

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Abstract: Atom transfer radical coupling (ATRC), performed with or without radical traps, has allowed for high extents of coupling (X_c) for a variety of brominated polymers, yet structurally different polymeric chain ends require unique reagents and reaction conditions. Inspired by a similar study that focused on universal conditions for the controlled polymerization of different monomers using atom transfer radical polymerization (ATRP), this work focuses on developing a single set of conditions (or conditions with as little variation as possible) that will achieve extents of coupling greater than 80% or end-brominated chains of polystyrene (PSBr), poly(methyl methacrylate) (PMMABr), and poly(methyl acrylate) (PMABr). The radical traps α -phenyl-tert-butyl nitron (PBN), 2-methyl-2-nitrosopropane (MNP), and nitrosobenzene (NBz) were chosen in this study, along with copper catalysts, reducing agents, and nitrogen-based ligands. Ultimately, a single set of effective reaction conditions was identified with the only difference being the radical trap used: MNP was effective for coupling PSBr and PMABr while NBz was necessary to achieve similarly high extents of coupling for PMMABr.



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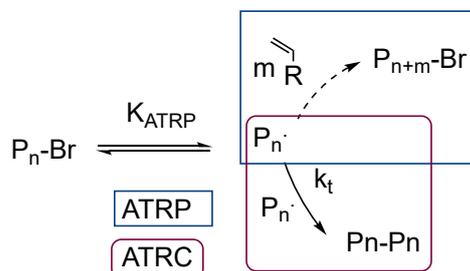
Keywords: atom transfer radical polymerization; atom transfer radical coupling; polyacrylates; polystyrenes

1. Introduction

Polymers formed using reversible deactivation radical polymerization (RDRP) techniques will have a labile end group [1–4], which can be exploited in post-polymerization reactions through the activation of polymer radicals [5–14]. These polymer radicals can then undergo coupling sequences to form dimers [6–9,12], deblocks [5,11,14], or macrocycles [10,13,14], depending on the nature of the polymer end group and the reaction conditions. In the case of polymers formed by atom transfer radical polymerization (ATRP), the result is typically a bromine-terminated polymer chain that can be activated into polymer radicals in a post-polymerization atom transfer step. These polymer radicals can then be induced to favor coupling in an atom transfer radical coupling (ATRC) sequence, which results in the joining of chain ends. These atom transfer radical reactions, polymerization versus coupling, are summarized in Scheme 1.

A group led by Hawker and Haddleton [15] astutely noted that unique ATRP conditions and components were required for each major monomer class (styrenes, acrylates, and methacrylates) in order to achieve the desired controlled polymerization with high chain-end fidelity. For example, differing rates of polymerization (k_p) and differing stabilities of the chain-end radical for each monomer class often meant specific ligands and catalysts were needed to appropriately adjust and maintain the essential K_{ATRP} [3,16,17]. Identifying the conditions necessary to effectively apply ATRP across different classes of polymers thus becomes a time-consuming task, often plagued by trial and error, for the experimenter. To this end, Hawker and Haddleton set about to discover a set of universal conditions for ATRP using reagents that were commercially available and inexpensive. Chain-end fidelity

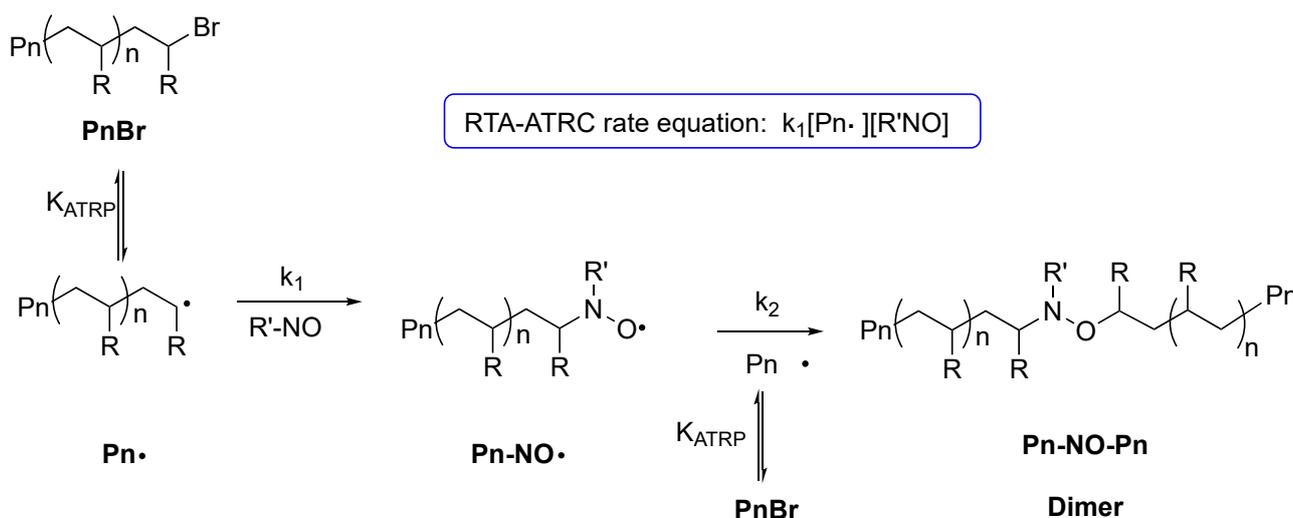
was verified by chain extension polymerization reactions on the end-brominated chains, creating either diblocks or homoblocks.



Scheme 1. Similarity of ATRP mechanism and ATRC mechanism, with the difference being the fate of the polymer radical ($P_n\cdot$).

Inspired by this work, our group explored the possibility of using a common set of conditions that can successfully lead to chain-end coupling across the major polymer classes using the following specific polymers: polystyrene (PS), poly(methyl acrylate) (PMA), and poly(methyl methacrylate) (PMMA). One difficulty involved is that two of the three polymers above resist coupling by radical-radical termination in traditional ATRC sequences; PMA and PMMA require intervention to induce chain-end coupling of their radicals. In the case of PMA, both styrene-assisted ATRC [18] or radical trap-assistance [19] have proven capable of leading to high extents of coupling. Similarly, the bulky PMMA radicals, which favor disproportionation, require radical trap-assistance to undergo substantial dimerization [12,19]. On the other hand, PS radicals can be successfully coupled into dimers [6,8,20–24] or macrocycles [10,20,25] under a wider range of ATRC-type conditions and are less sensitive to the presence [21,22] or structure of a radical trap [26]. Since applicability across all classes was a defined requirement, radical traps were used in all coupling reactions.

The ability to join polymer chain ends together in high yields is an important synthetic tool in manipulating traditional polymer chains into new shapes, sizes, and topologies for specific applications. The mechanism for radical trap-assisted atom transfer radical coupling (RTA-ATRC) is summarized in Scheme 2.



Scheme 2. Mechanism and kinetic expression of RTA-ATRC.

Shown in Figure 1 is a summary of the goal of this endeavor, which involves finding radical trap-assisted ATRC conditions that are transferable to all polymer classes as exemplified by PSBr, PMABr, and PMMABr. ATRC conditions were deemed “successful”

if there was 80% coupling or higher. The reaction parameters that were explored were inspired by conditions used in previously reported ATRC-type reactions, providing useful starting points for the coupling experiments detailed below.

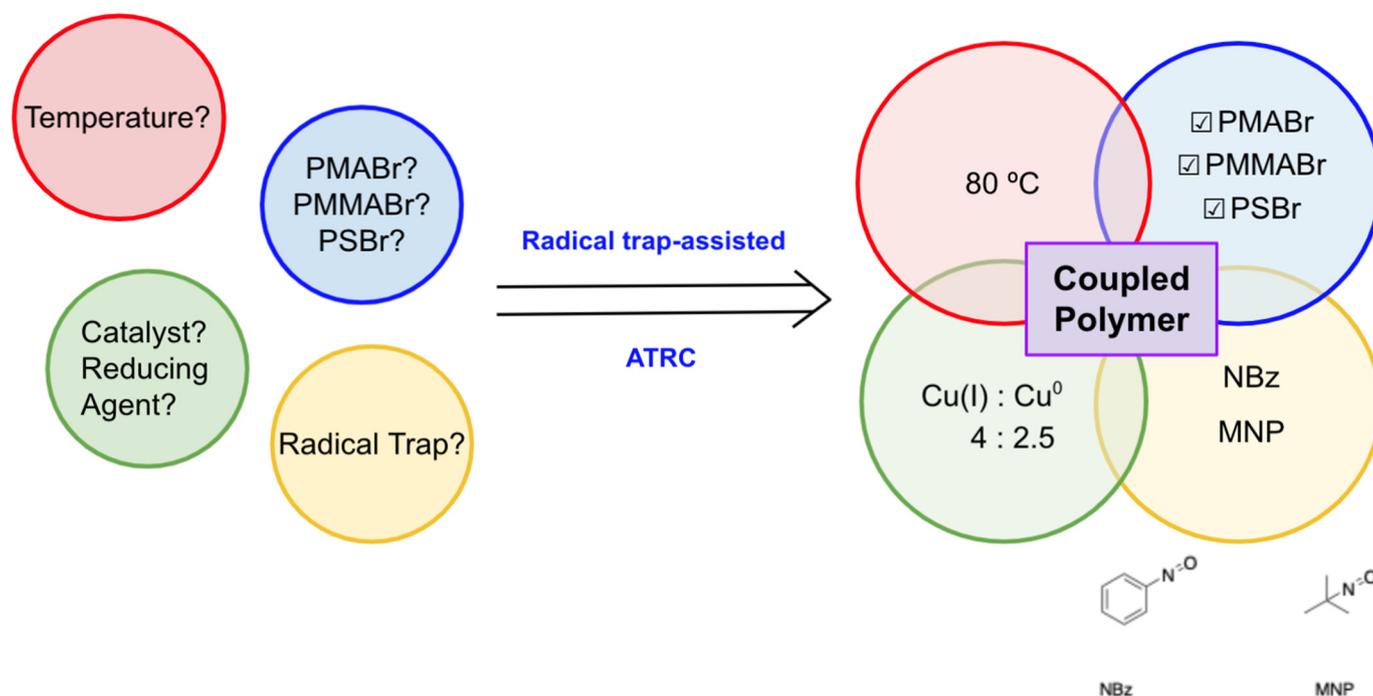


Figure 1. Summary of the challenge of finding common ATRC-type conditions across all three major classes of brominated polymers prepared by ATRP.

2. Materials and Methods

2.1. Materials

Copper(I) bromide (CuBr, 98%, Aldrich), copper metal (Cu⁰, –625 mesh APS 0.50–1.50, 99%, Alfa Aesar), and copper(II) bromide (CuBr₂, 99%, Aldrich) were used as received and stored in desiccators. The solvents tetrahydrofuran (THF, stabilized with BHT ≥99.8%, VWR), hexanes (≥98.5%, VWR), and methanol (≥99.8%, VWR) were used as received. Reagents styrene (S, ≥99%, Aldrich), methyl acrylate (MA, >99.0%, TCI), and methyl methacrylate (MMA, 99%, Aldrich), (1-bromoethyl)benzene (BEB, 97%, Aldrich), ethyl α-bromoisobutyrate (EBIB, 98%, Aldrich), N, N, N', N''-pentamethyldiethylenetriamine (PMDETA, >99.0, TCI), and tris[2-(dimethylamino)ethyl]amine (Me₆TREN, 97%, Aldrich) were stored in the refrigerator and used as received. The radical traps 2-methyl-2-nitrosopropane dimer (MNP, 99%, Aldrich), α-phenyl-tert-butyl nitron (PBN, ≥99.5, Aldrich), and nitrosobenzene (NBz, ≥97%, Aldrich) were used as received and stored in the freezer. Note that no reagents were purified prior to use in an attempt to simplify the entire polymerization-to-coupling sequence.

2.2. Typical Procedure for the Synthesis of Monobrominated Polystyrene (PSBr) Using ATRP

Styrene (4.0 mL, 34.9 mmol), CuBr (100 mg, 0.698 mmol), and (1-bromoethyl)benzene (BEB, 95 μL, 0.698 mmol) were added into a custom-made Schlenk flask, which was capped with a rubber septum and attached to the Schlenk line. The contents of the flask were exposed to three freeze-pump-thaw cycles before being placed on a heat plate with custom-fit block heaters and equipped with a digital contact thermoregulator (Chemglass CG-1994-V015) set to 80 °C and left to stir for 5 min. PMDETA (146 μL, 0.698 mmol) was then added to the reaction flask via syringe to begin polymerization. After 120 min, the reaction flask was removed from the heat and placed into an ice bath, followed by exposure to

the atmosphere, dilution with THF, and precipitation into a white powder using ice-cold methanol (Mn: 2290; Đ: 1.08).

The synthesis of monobrominated poly(methyl methacrylate) (PMMABr) via ATRP was performed in an analogous fashion but using ARGET ATRP, with methyl methacrylate (4.5 mL, 37 mmol), CuBr₂ (188 mg, 0.84 mmol), ethyl α-bromoisobutyrate (EBIB) (126 μL, 0.84 mmol), PMDETA (176 μL, 0.84 mmol), and precipitated with ice-cold cyclohexanes. The synthesis of monobrominated poly(methyl acrylate) (PMABr) via ATRP was performed in an analogous fashion with methyl acrylate (4.5 mL, 49.97 mmol), CuBr (142 mg, 0.999 mmol), EBIB (72 μL, 0.4997 mmol), PMDETA (208 μL, 0.999 mmol), and rotary evaporated instead of precipitated with methanol.

2.3. Typical Procedure for RTA-ATRC of PSBr

A representative RTA-ATRC reaction was performed as follows: molar ratio of [PSBr]:[MNP-CuBr]:[Cu⁰]:[PMDETA] = 1:1:4:2.5:8 in THF, monobrominated polystyrene (PSBr, 198 mg, 0.09 mmol, 2127 g/mol), methyl nitrosopropane (MNP, 9.6 mg, 0.09 mmol), CuBr (51.6 mg, 0.36 mmol), Cu⁰ (14.3 mg, 0.225 mmol), and THF (6 mL) were added into a custom-made Schlenk line round-bottom flask. Concentrations of PSBr were consistently kept at approximately 15 mM. The reaction flask, sealed with a rubber septum, was attached to the Schlenk line. The flask was exposed to three freeze-pump-thaw cycles before being placed onto a heat plate set to 80 °C. After 5 min of heating and stirring, PMDETA (150 μL, 0.72 mmol) was added into the reaction chamber via syringe. After 60 min, the reaction flask was removed from the heat and placed into an ice bath, filtered into a GPC vial, diluted with THF, and analyzed via GPC.

Reactions with other polymers, ligands, or radical traps were performed in an analogous fashion with differences in molar ratios and/or temperatures noted in the Tables. For PSBr and PMMABr, the reaction flask was removed from the heat and placed into an ice bath, followed by exposure to the atmosphere and precipitation into a white powder using ice-cold methanol. For RTA-ATRC reactions of PMABr, reaction components were rotary evaporated instead of precipitated with methanol.

2.4. Typical Procedure for Thermolysis of PSBr-RTA-ATRC

Approximately 100 mg of precipitated PSBr-RTA-ATRC product was dissolved in 3 mL DMF. The open container was placed on a 140 °C hotplate for one hour while stirring at 600 rpm. A small amount of the thermolysis solution was passed through a 0.45 micron filter and diluted with THF before analysis by GPC. All thermolysis reactions were performed in an analogous fashion, regardless of polymer class. The PMABr-RTA-ATRC reaction mixture was passed through a 0.45 micron filter and dried by rotary evaporation before dissolving in DMF to create a 100 mg/3 mL (w/v) thermolysis solution.

2.5. Characterization

All RTA-ATRC reaction samples were removed from the flask, filtered, and diluted with THF before characterization by gel permeation chromatography (GPC) without purification. GPC analysis was done on a system comprised of a Shimadzu CBM-20A communications module, a Shimadzu DGU-20A degassing unit, a Shimadzu SIL-20A auto sampler, a Shimadzu LC-20AD pump, and Wyatt T-rEX RI detector. The instrument was interfaced with a PC and was operated using PSS WinGPC Unichrom software. Separations were performed using a PSS SDV analytical 1000 angstrom and a 100,000 angstrom column in sequence, housed inside a Shimadzu CTO-2A column oven set to 40 °C. THF was used as an eluent at an optimized flow rate of 1.00 mL/min, and a 10-point calibration was performed using Agilent EasiCal PS standards. The data analysis was performed using the PSS WinGPC software.

3. Results

Brominated precursors for each polymer class were prepared using ATRP and subjected to a variety of coupling conditions. Success was gauged by the coupling (X_c) values of the raw ATRC reaction mixtures, preventing inadvertent fractionation and artificially high coupling values. X_c were rounded to the nearest 0.05 to allow for a more realistic assessment of the coupling conditions.

To this end, we first attempted several coupling reactions of brominated PMA, prepared by ATRP, under an array of conditions (Table 1) that were inspired by previous studies [13,24]. When using PBN or NBz as the radical trap (Trials 1–7), less than 65% coupling was consistently observed despite adjustments made to the temperature and the ratios of the catalyst, reducing agent, and radical trap relative to the polymer chain end. Particularly, the radical trap PBN gave extremely poor results and was not explored further for coupling PMA.

When using NBz (Trials 2–7) or MNP (Trials 8–11) as a radical trap, coupling reactions performed at 80 °C typically resulted in higher X_c values compared to analogous reactions performed at 40 °C (for example, Trial 3 versus Trial 6 for NBz; Trial 8 versus Trial 10 for MNP). This trend was more apparent for MNP compared to NBz as the radical trap. In fact, when the temperature was increased to 80 °C with a full equivalent of radical trap, reactions using MNP saw dramatic improvements in X_c values, reaching near quantitative levels (Trial 11). Shown in Figure 2 are GPC traces of the PMABr precursor and unpurified coupled product formed via RTA-ATRC using MNP as the radical trap (Table 1, Trial 11), with a clear shift to lower elution volumes for the coupled product.

Next, we tested an array of conditions for coupling brominated PMMA chains, formed by ARGET ATRP (Table 2). When coupling brominated PMMA chains, the radical trap-assist plays an essential role: PMMA radicals have greater steric bulk, and so, without a radical trap-assist, these radicals favor disproportionation as the bimolecular termination pathway [27,28]. However, as was with PMA radicals, the radical trap that is used is an important consideration. As shown in Table 2, when either PBN and MNP was used as the radical trap, relatively low extents of coupling with PMMA was observed (Trials 12 and 17). In the case of MNP as the trap, the bulky *t*-butyl group of the radical trap likely sterically hinders the joining of bulky PMMA chains, resulting in only ~20% coupling efficiency. However, when the less bulky NBz was used as the radical trap, the extent of coupling improved dramatically, up to around 90% (Trials 13–16).

Table 1. Characteristics of PMABr precursors and results of their RTA-ATRC reactions.

Trial	Radical Trap	T (°C)	Equivalents (Cu ⁰ :CuBr:PMDETA:Radical Trap) ^d	Precursor ^e Mn ^f	Precursor Đ ^g	Coupled Product ^h Mn	Extent of Coupling (X_c) ⁱ
1	PBN ^a	40	5:5:10:0.6	1570	1.08	1580	<0.1
2	NBz ^b	40	5:5:10:0.6	1570	1.08	1680	0.13
3	NBz	40	2.5:4:8:0.6	2060	1.08	2700	0.47
4	NBz	40	2.5:4:8:1	2900	1.1	4000	0.55
5	NBz	80	2.5:4:8:1	3520	1.06	4860	0.55
6	NBz	80	2.5:4:8:0.6	2900	1.1	4140	0.60
7	NBz	80	2.5:4:8:1	7740	1.07	11,400	0.64
8	MNP ^c	40	2.5:4:8:0.6	2050	1.17	2550	0.39
9	MNP	40	5:5:10:0.6	7670	1.19	9590	0.40
10	MNP	80	2.5:4:8:0.6	4710	1.07	7990	0.82
11	MNP	80	2.5:4:8:1	1420	1.06	2710	0.96

^a α -phenyl-tert-butyl nitron. ^b Nitrosobenzene. ^c 2-methyl-2-nitrosopropane. ^d All equivalents compared to 1 eq polymer. For further details on reaction conditions, see Experimental Section. ^e Precursors prepared by ATRP using ethyl α -bromoisobutyrate (EBIB) as initiator. See Experimental Section for details. ^f Number of average molecular weight, based on GPC-RI data calibrated using PS standards. ^g Dispersity = M_w/M_n , calculated from GPC-RI data. ^h All coupling reactions were run for 1 h at the temperature indicated, using the equivalents of reagents indicated. See Experimental Section for details. ⁱ Extent of coupling, as calculated by $2(1 - M_{n,precursor}/M_{n,coupled})$.

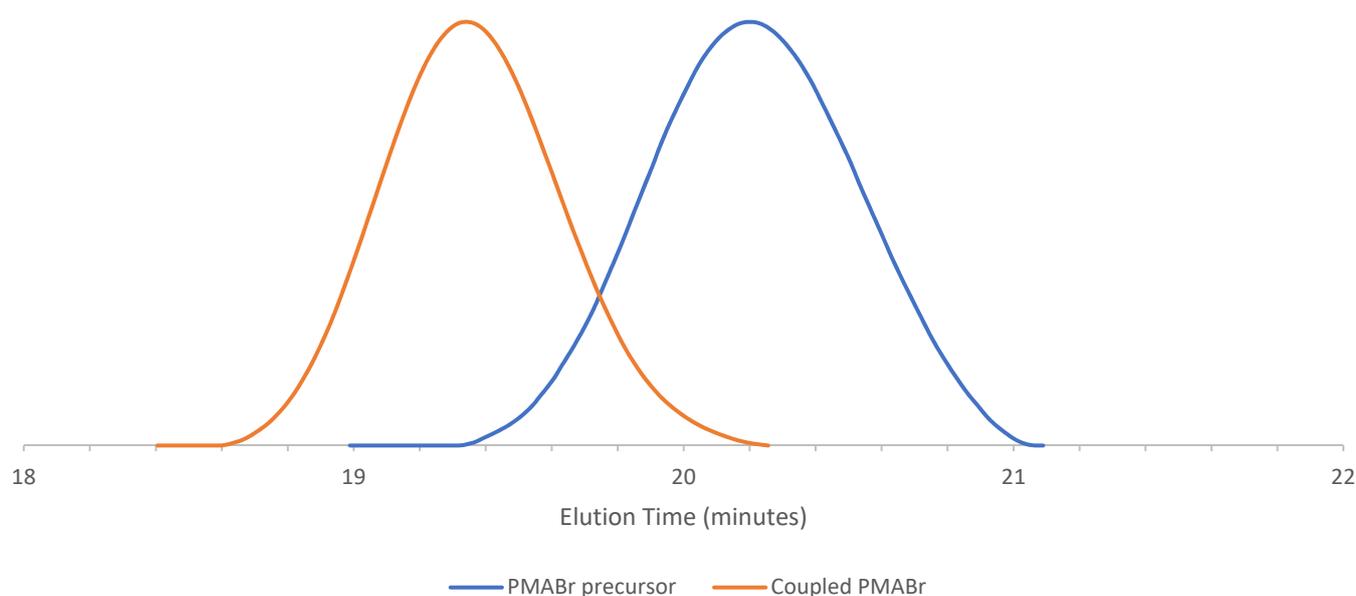


Figure 2. GPC traces of PMABr precursor (blue) and RTA-ATRC product (orange) under universal conditions using MNP as the radical trap-assist. Traces correspond to Table 1, Trial 11.

Table 2. Characteristics of PMMABr precursors and results of their RTA-ATRC reactions.

Trial	Radical Trap	T (°C)	Equivalents (Cu ⁰ :CuBr:PMDETA:Radical Trap) ^d	Precursor ^e Mn ^f	Precursor Đ ^g	Coupled Product ^h Mn	Extent of Coupling (Xc) ⁱ
12	PBN ^a	40	5:5:10:0.6	4370	1.18	5260	0.34
13	NBz ^b	40	2.5:4:8:0.6	4370	1.18	6920	0.74
14	NBz	40	5:5:10:0.6	4370	1.18	7030	0.76
15	NBz	80	2.5:4:8:0.6	2870	1.16	5360	0.93
16	NBz	80	2.5:4:8:1	2870	1.16	5070	0.87
17	MNP ^c	80	2.5:4:8:1	2870	1.16	3170	0.19

^a α -phenyl-tert-butyl nitron. ^b Nitrosobenzene. ^c 2-methyl-2-nitrosopropane. ^d All equivalents compared to 1 eq polymer. For further details on reaction conditions, see Experimental Section. ^e Precursors prepared by ATRP using ethyl α -bromoisobutyrate (EBIB) as initiator. See Experimental Section for details. ^f Number of average molecular weight, based on GPC-RI data calibrated using PS standards. ^g Dispersity = Mw/Mn, calculated from GPC-RI data. ^h All coupling reactions were run for 1 h at the temperature indicated, using the equivalents of reagents indicated. See Experimental Section for details. ⁱ Extent of coupling, as calculated by $2(1 - M_{n\text{precursor}}/M_{n\text{coupled}})$.

Similar to PMA, coupling of PMMA radicals generally increased when the reactions were performed at 80 °C rather than at 40 °C (Trial 13 versus Trial 15). While the reactions performed at lower temperatures (40 °C) produced reasonable extents of coupling (~75%, Trials 13 and 14), these results did not typically match the success of trials performed at higher temperatures (Trials 15 and 16). Changing the ratio of radical trap from 0.6 eq to 1 eq relative to PMMABr did not significantly impact the extent of coupling (Trials 15 and 16). Figure 3 shows a PMMABr precursor and its unpurified RTA-ATRC product formed with NBz as the radical trap (Table 2, Trial 16).

Finally, we focused on PSBr, chosen last because of its ability to be coupled under a wider assortment of ATRC-type reactions, including no radical trap at all [6,8,20–24]. Thus, we were able to simply retest conditions applied above using PMA and PMMA to join brominated PS chains (Table 3), also prepared using ATRP.

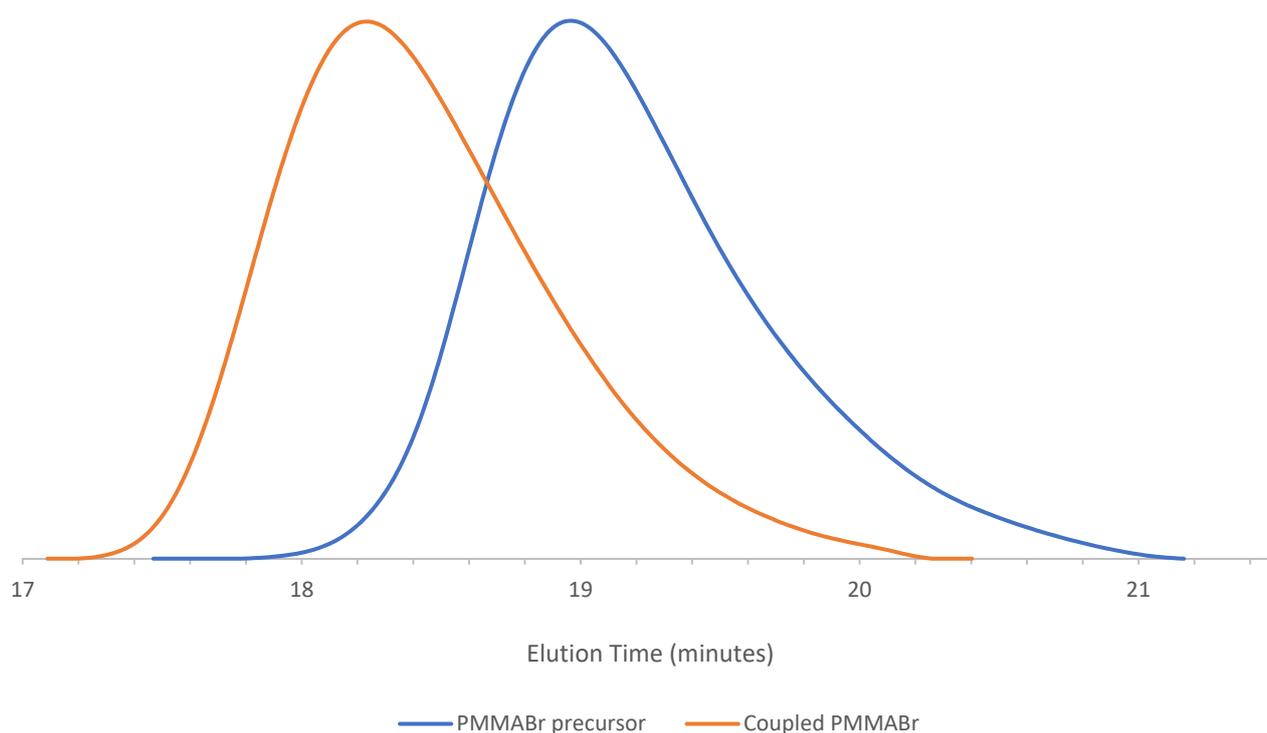


Figure 3. GPC traces of PMMABr precursor (blue) and RTA-ATRC product (orange) under universal conditions using nitrosobenzene as the radical trap-assist. Traces correspond to Table 2, Trial 16.

Table 3. Characteristics of PSBr precursors and results of their RTA-ATRC reactions.

Trial	Radical Trap	T (°C)	Equivalents (Cu ⁰ :CuBr:PMDETA:Radical Trap) ^d	Precursor ^e Mn ^f	Precursor Đ ^g	Coupled Product ^h Mn	Extent of Coupling (Xc) ⁱ
18	PBN ^a	40	5:5:10:0.6	2750	1.11	3000	0.17
19	NBz ^b	40	2.5:4:8:0.6	2710	1.09	4310	0.74
20	NBz	40	5:5:10:0.6	2750	1.11	4500	0.78
21	NBz	80	2.5:4:8:0.6	3000	1.01	4460	0.65
22	NBz	80	2.5:4:8:1	2170	1.08	3400	0.72
23	MNP ^c	40	2.5:4:8:0.6	2780	1.11	4730	0.82
24	MNP	40	5:5:10:0.6	2260	1.08	4080	0.90
25	MNP	80	2.5:4:8:1	3450	1.08	5950	0.84

^a α -phenyl-tert-butyl nitron. ^b Nitrosobenzene. ^c 2-methyl-2-nitrosopropane. ^d All equivalents compared to 1 eq polymer. For further details on reaction conditions, see Experimental Section. ^e Precursors prepared by ATRP using 1-bromoethylbenzene (BEB) as initiator. See Experimental Section for details. ^f Number of average molecular weight, based on GPC-RI data calibrated using PS standards. ^g Dispersity = Mw/Mn, calculated from GPC-RI data. ^h All coupling reactions were run for 1 h at the temperature indicated, using the equivalents of reagents indicated. See Experimental Section for details. ⁱ Extent of coupling, as calculated by $2(1 - M_{n\text{precursor}}/M_{n\text{coupled}})$.

Consistent with the scope of this work, we chose to concentrate on radical trap-assisted ATRC (RTA-ATRC) reactions with three radical traps: PBN, NBz, and MNP. As was the case for the other precursors, PBN was the least effective in assisting the coupling of PS radicals (Trial 18), confirming PBN to be a poor choice as a radical trap for all polymer classes. Next, using NBz as the radical trap, we were able to achieve a reasonable extent of coupling for PSBr at greater than 70%. No significant difference in coupling was observed when 0.6 eq of radical trap was used versus 1 eq (Trials 21 and 22), nor when the temperature was increased from 40 °C to 80 °C (Trials 19 and 21). Using MNP as the radical trap produced slightly greater extents of coupling reaching approximately 90%. For both NBz and MNP, an increase in coupling was only observed when the ratio of metals and ligands increased, which is consistent with previous studies [21,22] (Trial 19 versus Trial 20 and Trial 23 versus Trial 24). Figure 4 shows GPC traces of the PSBr precursor (blue) and the coupled product (orange), with a clear shift to shorter elution volumes and only a small

amount of unreacted precursor remaining (Table 3, Trial 25). Taken together, our findings show that PSBr can undergo successful coupling using either MNP or NBz as the radical trap, and at temperatures of either 40 °C or 80 °C.

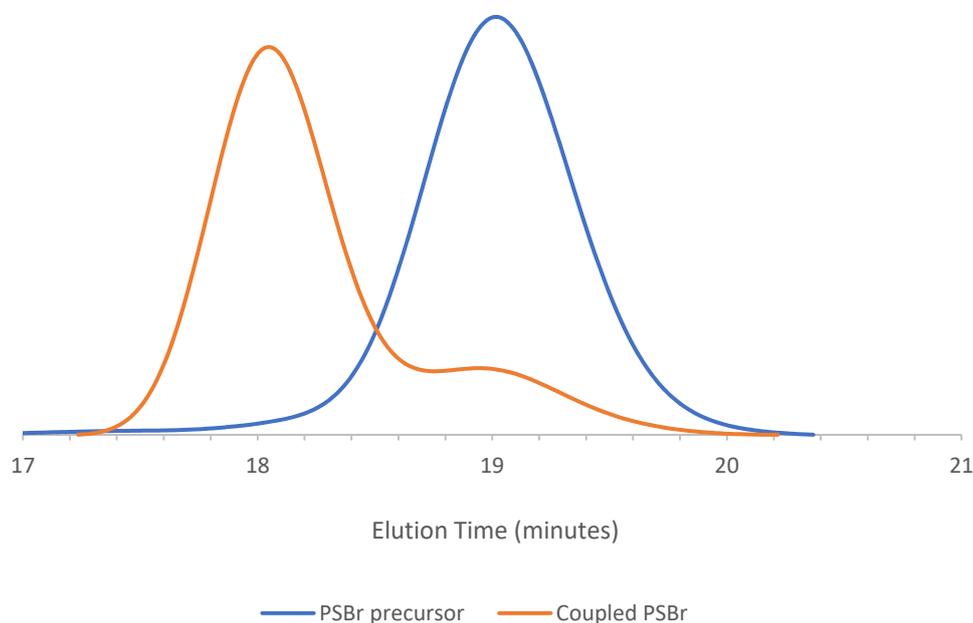


Figure 4. GPC traces of PSBr precursor (blue) and RTA-ATRC product (orange) under universal conditions using MNP as the radical trap-assist. Traces correspond to Table 3, Trial 25.

When a radical trap-assist is used, the polymers in our coupled product will be linked by an internal alkoxyamine that can be thermally cleaved at the C-O bond (Scheme 2). Shown in Figure 5 are purified products resulting from RTA-ATRC reactions (blue) prepared in using either NMP (for PSBr and PMMABr) or NBz (PMABr), along with the results of thermolysis (orange) in DMF at elevated temperatures (see Experimental Section). As can be seen in Figure 5, thermolysis results are consistent with an internal alkoxyamine installed in the coupled polymers.

Having tested all three polymer classes—poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), and polystyrene (PS)—we can single out the conditions that allowed for each of the three polymers to couple successfully (extent of coupling >80%). These conditions are detailed in Table 4 below. Note that the only difference in conditions is bolded: coupling PMMA radicals simply requires NBz as the radical trap, while both PS and PMA radicals are more effectively coupled using MNP as the radical trap.

Table 4. Characteristics of polymer precursors and results of their RTA-ATRC reactions. These correspond to Trials 11, 16, and 25 in earlier Tables.

Polymer	Radical Trap	T (°C)	Equivalents (Cu ⁰ :CuBr:PMDETA:Radical Trap) ^e	Precursor ^e Mn ^f	Precursor Đ ^g	Coupled Product ^h Mn	Extent of Coupling (Xc) ⁱ
PMABr ^c	MNP ^a	80	2.5:4:8:1	1420	1.06	2710	0.96
PMMABr ^c	NBz ^b	80	2.5:4:8:1	2870	1.16	5070	0.87
PSBr ^d	MNP	80	2.5:4:8:1	3450	1.08	5950	0.84

^a 2-methyl-2-nitrosopropane. ^b Nitrosobenzene. ^c Precursors prepared by ATRP using ethyl α -bromoisobutyrate (EBIB) as initiator. See Experimental Section for details. ^d Precursor prepared by ATRP using 1-bromoethylbenzene (BEB) as initiator. See Experimental Section for details. ^e All equivalents compared to 1 eq polymer. For further details on reaction conditions, see Experimental Section. ^f Number of average molecular weight, based on GPC-RI data calibrated using PS standards. ^g Dispersity = Mw/Mn, calculated from GPC-RI data. ^h All coupling reactions were run for 1 h at the temperature indicated, using the equivalents of reagents indicated. See Experimental Section for details. ⁱ Extent of coupling, as calculated by $2(1 - M_{n\text{precursor}}/M_{n\text{coupled}})$.

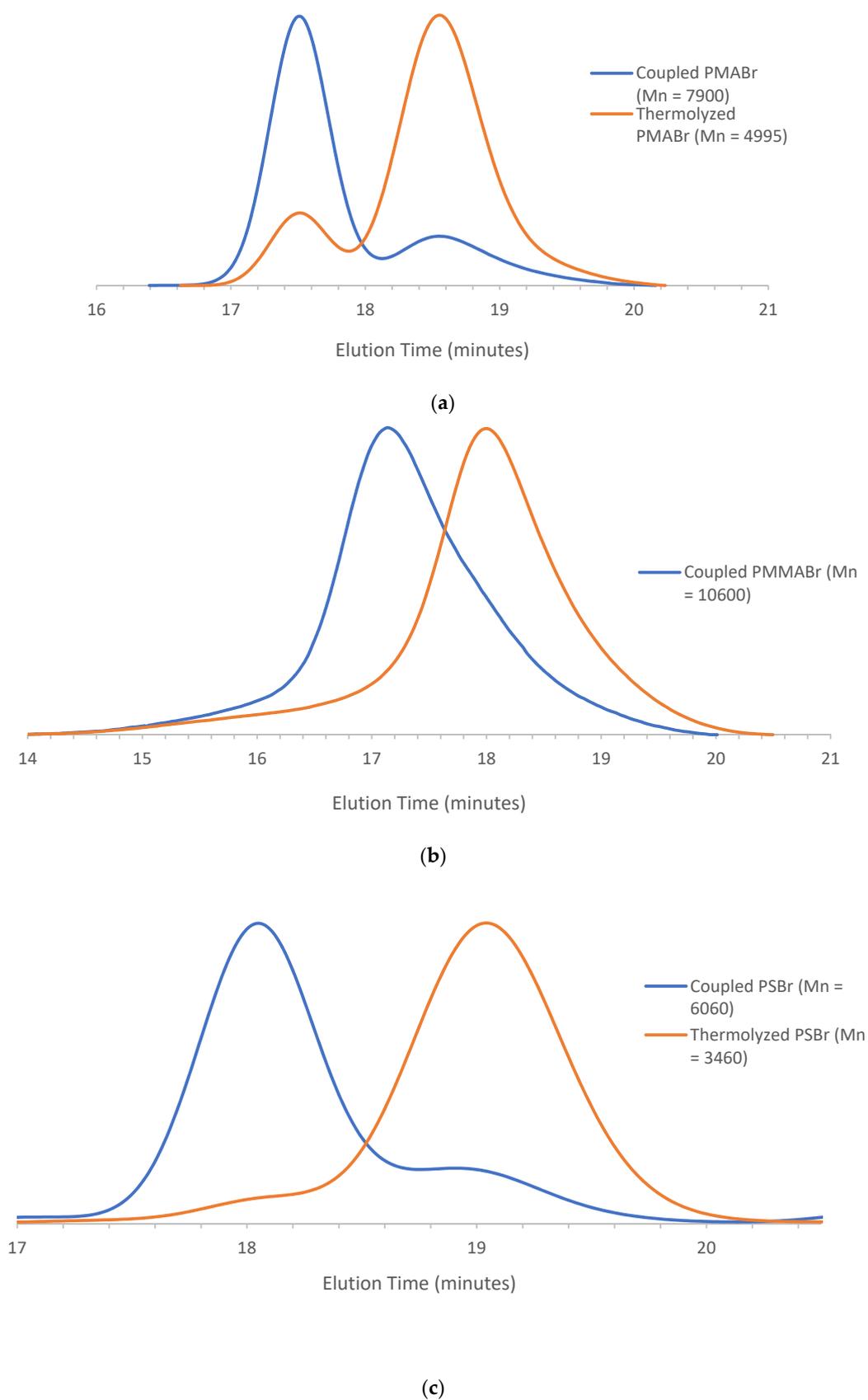


Figure 5. GPC traces of RTA-ATRC product pre- (blue) and post- (orange) thermolysis for (a) PMABr; (b) PMMABr and (c) PSBr. Note that the M_n values of the brominated precursor and thermolyzed product are given on each figure.

4. Conclusions

A near-common set of conditions has been found to successfully lead to chain-end coupling for all three major polymer classes: polystyrene (PS), poly(methyl acrylate) (PMA), and poly(methyl methacrylate) (PMMA). Using a ratio of 2.5:4:8:1 for Cu(0):CuBr:PMDETA:radical trap, respectively, at a temperature of 80 °C, we could consistently achieve greater than 80% coupling for PSBr, greater than 85% coupling for PMMA, and near quantitative yields for PMA. However, the choice of radical trap used for coupling is important. While MNP was the most effective radical trap for coupling PS and PMA, NBz was the most effective radical trap for coupling PMMA.

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