3120 *Macromolecules* **2004,** *37,* 3120−3127

Polystyrene with Designed Molecular Weight Distribution by Atom Transfer Radical Coupling

Traian Sarbu, Koon-Yee Lin, John Ell, Daniel J. Siegwart, James Spanswick, and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received December 13, 2003; Revised Manuscript Received February 29, 2004

ABSTRACT: Copper-mediated atom transfer radical coupling (ATRC) was studied for monobrominated and dibrominated polystyrenes as well as their mixtures. In the ATRC process macroradicals, generated in situ by an atom transfer radical equilibrium, participate in coupling reactions in the presence of a reducing agent, such as nanosize copper, zerovalent iron, tin octanoate ($SnOct_2$), and ascorbic acid. ^1H NMR analyses performed on the coupling product of monobrominated polystyrene (PStBr) showed the disappearance of the signal attributed to the methine proton located in the α-position to the bromine. ATRC is influenced by the nature of ligand as well as the amounts of ligand and zerovalent metal used in the process. The molecular weight of the coupling product is a function of the extent of coupling, which is defined by the proportion of polymeric chains participated in the reaction. Thus, molecular weights of the ATRC products of monobrominated polystyrene were approximately twice higher than those of PStBr precursors, while the polydispersities were low. The coupling of α,*ω*-dibrominated homologues gave high molecular weight products with higher polydispersities.

1. Introduction

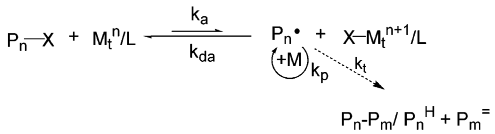
Atom transfer radical polymerization (ATRP) is one of the most robust methods developed for the synthesis of polymers with predetermined molecular weights and narrow molecular weight distributions (MWD).[1−7] Thus, polymers with novel functionalities, architectures, and compositions were prepared starting from a large variety of monomers.[8−12] The key of the ATRP process is the equilibrium between active ($P_n^\bullet$) and dormant species (P_nX) via a reversible redox reaction between a transition-metal compound complexed by a ligand (M_t^n/L). Dormant species form a radical ($P_n^\bullet$) and the metal halide in a higher oxidation state (XM_t^{n+1}/L) (k_a) (Scheme 1). The propagating radical reacts reversibly with the metal halide to regenerate the lower oxidation state transition metal and an oligomer with halogen end group (k_{da}). This process can then repeat itself, resulting in the formation of a well-defined polymer. Because the concentration of radicals is low, the contribution of the termination (k_t) can often be neglected.

The molecular weight control is achieved by a rapid and reversible deactivation of the propagating radicals, which results in a very low concentration of radicals, thus suppressing bimolecular termination. This is accomplished by the persistent radical effect,[13] with the formation of deactivator in the reaction medium in the form of higher oxidation state metal complex.[6] The role of the deactivator is to control the polymerization by reducing the reaction rate and the polydispersity of the polymer. The importance of deactivator for narrowing molecular weight distribution can be understood from eq 1:

$$\frac{M_w}{M_n} = 1 + \left(\frac{2}{p} - 1\right)\frac{k_p[RX]_0}{k_{da}[XCu^{II}]} \qquad (1)$$

where p is conversion, $[RX]_0$ is the initial concentration of the consumed initiator, $[XCu^{II}]$ is the concentration of copper complex in higher oxidation state, and k_p and k_{da} are the rate constants of propagation and deactivation, respectively.

Scheme 1. Equilibrium between Active and Dormant Species in ATRP



Thus, an increase in the concentration of deactivator leads to polymers with lower polydispersity. However, when too much deactivator is present in the system, the ATRP rate, R_p, decreases (eq 2).

$$R_p = k_p[M][P^*] = k_p\frac{k_a}{k_{da}}[M][RX]_0\frac{[Cu^I]}{[XCu^{II}]} \qquad (2)$$

It was previously shown that zerovalent metals, such as Cu^0 or Fe^0, can be used to enhance the rate of polymerization in ATRP reactions by reducing the amount of deactivator (Cu^{II} or Fe^{III}).[14,15] The addition of the zerovalent metal reduced excess deactivator by a simple electron-transfer process (Scheme 2). Removal of small amounts of Cu^{II} or Fe^{III} enhanced the rate, yet there was still a sufficient concentration of deactivator to maintain control of the polymerization.

Polymers synthesized from ATRP processes preserve the halogen end functionality, which can be further substituted in postpolymerization modification reactions.[9,16]

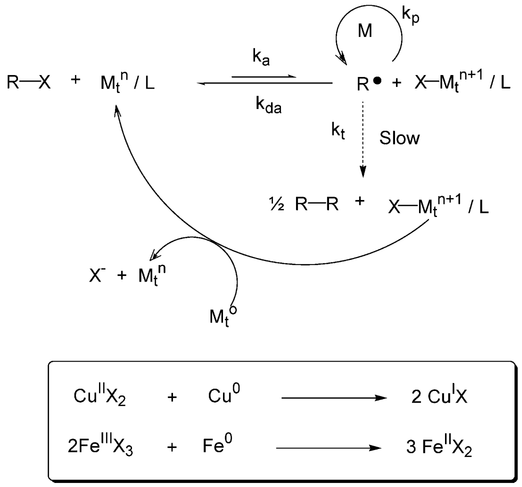
Recently, Fukuda[17] reported a study of recombination reaction of polystyrene radicals formed in the absence of monomer and presence of Cu^IBr/ligand and Cu^0. A high efficiency of coupling was obtained when elevated concentrations of model adduct were employed, which

---

* To whom the correspondence should be addressed.

10.1021/ma035901h CCC: $27.50

Scheme 2. Equilibrium in ATRP and the Reduction of Higher Oxidation State Metal Halide by Reaction with Zerovalent Metal



led to formation of higher concentrations of radicals. However, a certain amount of chains was formed by disproportionation. For the dibrominated adduct, the coupling reaction led to the formation of polymers with different chain lengths, whose distribution followed the theory of random coupling. Coupling reactions of bromine-terminated PSt in the presence of reducing agents, such as Cu^0 and ascorbic acid, were previously reported.[18] A similar approach was used to convert alkyl halides to alkoxyamines in the presence of Cu^0 species.[19]

Very recently, Yagci et al.[20] reported the atom transfer radical coupling (ATRC) of telechelic polystyrene using CuBr/tris[2-(dimethylamino)ethyl]amine (Me$_6$-TREN). In ATRC macroradicals are generated in situ by an atom transfer radical process. However, in contrast to ATRP, their concentration is not moderated to control polymerization but rather maximized to accelerate coupling.

This paper presents synthesis of polymers with unimodal and multimodal MWDs by copper-mediated ATRC of mono- and dibrominated polystyrene (PSt) using highly efficient nanosize copper as well as other reducing agents. The influence of different factors on the coupling reaction is discussed.

2. Experimental Part

Materials. Styrene (Acros, 99%) was dried over CaH$_2$ and then distilled under reduced pressure (65 °C/35 mmHg). CuBr (Acros, 98%) was purified by washing with glacial acetic acid, followed by 2-propanol, and then dried under vacuum. Toluene (Fisher, 99.8%) was distilled and stored under nitrogen. Immediately before use both monomer and solvent were purged with N$_2$ for at least 30 min. The initiator, ethyl 2-bromoisobutyrate (EBiB, Aldrich, 98%), was distilled prior to use. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) and 1,4,8,11-tetraazacyclotetradecane (Cy) (Cyclam, Lancaster) were used as received. 4,4′-Di(5-nonyl)-2,2′-bipyridine (dNbpy) was synthesized using a procedure described elsewhere.[21] Nanosize copper (d ~100 nm, Aldrich, 99.9+%) was used as received for coupling experiments. Unless specified, all other reagents were purchased from commercial sources and used without further purification.

Polymerization Procedure. In a typical experiment, CuBr (0.125 g, 0.87 mmol) and CuBr$_2$ (97 mg, 0.044 mmol) were added to a Schlenk flask, equipped with a stir bar, which was previously flamed, evacuated, cooled, and flushed with nitrogen. After sealing it with a rubber septum, the flask was degassed and backfilled with nitrogen three times and then left under nitrogen. Subsequently, styrene (10 mL, 0.087 mol) and toluene (0.5 mL), as a GC standard, were added. The complexing agent, PMDETA (190 μL, 0.92 mmol), was added, and the solution was stirred until the Cu complex had formed. The mixture was then frozen with liquid nitrogen and degassed by three freeze−pump−thaw cycles. Ethyl 2-bromoisobutyrate (128 μL, 0.87 mmol) as an initiator was introduced, and the vial was placed in an oil bath and stirred at 80 °C for 2 h. Then, the flask was removed from the thermostated oil bath, and the reaction was stopped by exposing to air after dilution with THF. The solution was filtered through a column filled with alumina, and the polymer (19.1% conversion) was recovered by precipitation in methanol and dried in a vacuum at 60 °C to constant weight. M_n = 1780 g/mol; M_w/M_n = 1.06. The same procedure was used for the synthesis of dibrominated polystyrene, using as initiator 190 μL (0.87 mmol) of dimethyl 2,6-dibromoheptanedioate (DMDBHD, 97%, Aldrich). Conversion 27.2% after 5 h; M_n = 2670 g/mol; M_w/M_n = 1.11.

Coupling Reactions. A Schlenk flask was charged with monobrominated polystyrene (PStBr with M_n = 1780 g/mol; 0.46 g; 0.26 mmol), synthesized as previously described, and CuBr (38 mg; 0.26 mmol). After it was evacuated and backfilled with nitrogen, 5 mL of toluene was added. When the polymer was completely dissolved, PMDETA (55 μL; 0.26 mmol) was introduced, and three freeze−pump−thaw cycles were performed. Then nanosize copper (17 mg; 0.26 mmol) was added to the reaction, and the flask was then placed in an oil bath and stirred at 70 °C. Samples were periodically withdrawn from the reaction mixture (and then diluted with THF) in order to follow the evolution of molecular weights. After 2 h the flask was removed from the thermostated oil bath, the solution (diluted with THF) was filtered through a column filled with alumina, and the polymer was recovered by precipitation in methanol and dried in a vacuum at 60 °C to constant weight. M_n = 3030 g/mol; M_w/M_n = 1.24. A similar procedure was used when dibrominated polystyrene (BrPStBr) was employed. In some experiments the molar ratios between reagents were varied in order to study their influence on the reaction.

Analyses. Conversions were determined on a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector and using a capillary column (CEC-Wax, 30 m × 0.53 mm × 1.0 μm, Chrom Expert Co.). The initial temperature was 40 °C (3 min hold), and the final temperature of 200 °C (5 min hold) was reached at a heating rate of 40 °C/min. Toluene, which was added initially to the mixture, was used as an internal standard for these measurements. Molecular weights were measured on a GPC system consisting of a Waters 515 pump, a Waters 717plus autoinjector, Polymer Standards Service 10^5, 10^3, 10^2 Å columns, and a Waters 410 RI detector against polystyrene standards. THF was used as eluent with a flow rate of 1 mL/min (30 °C). GPC-MALLS (multiangle laser light scattering) was performed in THF (flow rate of 1 mL/min; 30 °C) using a Waters 510 pump, three Styragel columns (Polymer Standards Service, pore sizes 10^5, 10^3, and 10^2 Å), and a Wyatt Technology DAWN EOS MALLS detector fitted with a 30 mW linearly polarized GaAs (gallium arsenide) laser tuned to 690 nm emission. The scattering cell was made from K5 glass with a refractive index of 1.518 76 (at 690 nm). The position of the 18 detectors relative to the incident laser beam covers a range from 22.5° to 147°. A value of 0.195 mL/g was used for dn/dc of PSt.[22] Data collection and processing were performed with ASTRA software (Wyatt Technology). NMR spectra were recorded on a 600 MHz Bruker spectrometer, using CDCl$_3$ as a lock solvent and TMS as a standard.

3. Results and Discussion

When the bromine-terminated polymer is reacted with copper(I) halide/ligand, the ATRP equilibrium is established, as presented in Scheme 1. In contrast with polymerization process, in ATRC the monomer is absent, and therefore the only possible reactions are the

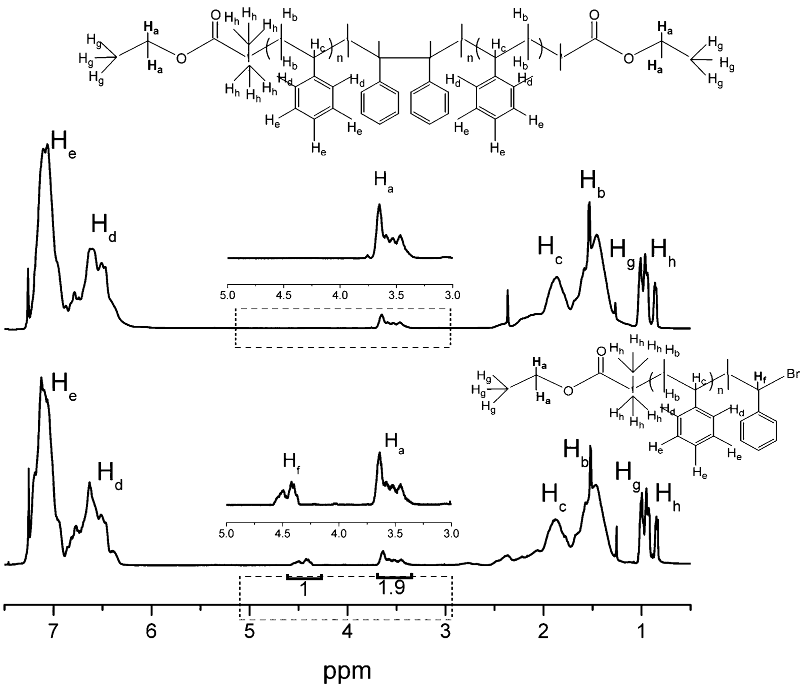


Figure 1. 600 MHz ^{1}H NMR spectra of PStBr ($M_n = 1040$; $M_w/M_n = 1.16$) and its coupling product.

activation–deactivation cycles and eventually termination. By addition of a sufficient amount of zerovalent metal, the deactivator—formed reversibly in activation step and irreversibly in termination—is reduced to metal halide in lower oxidation state (activator). In this way, the ATRP equilibrium can be affected by suppressing the deactivation, resulting in higher concentration of macroradicals in the system and thus favoring the bimolecular termination.

For the purpose of this study preservation of high chain end functionality is crucial because only the bromine-terminated chains can generate macroradicals via an atom transfer process. As was previously reported,[23] the contribution of termination, thermal self-initiation, and elimination of HBr, which all decrease the chain end functionality, may be minimized through adjusting the experimental parameters. Highly functional polymers may be prepared by stopping the reaction at low conversion. Dilution of reaction mixture with solvent may also reduce functionality. Therefore, the bulk polymerization technique was employed for the synthesis of functional polystyrene precursors, and the reactions were stopped at low conversion.

The chain end functionality was estimated from high-resolution ^{1}H NMR spectra. Figure 1 presents the ^{1}H NMR spectra recorded for polystyrene prepared using ATRP under the conditions described in the experimental part and the resulting ATRC product. Using 600 MHz ^{1}H NMR, signals due to both chain ends (R and X functionality) are visible and measurable. The signal from 3.46 to 3.63 ppm is characteristic for methyleneoxy protons (H_a) from the initiating ethyl 2-bromoisobutyrate moiety (R functionality). The asymmetric shape of this signal may be explained by the restricted motion of the ethyl group and some conformational effects. The signal from 4.35 to 4.46 ppm is attributed to the proton (H_f) located in the α-position of the bromine chain end (X functionality); it is relatively broad due to tacticity. The ratio between the ^{1}H NMR peak for the proton next to bromine chain end and the peak for the methyleneoxy protons was 1/1.9, thus indicating 95% chain end functionality of this polymeric precursor. The degree of polymerization (DP_n) was calculated from the ratio of the integrals of the H_a protons and the integrals of aromatic region (H_d and H_e at 6.3 to 7.4 ppm) as well as the aliphatic region (H_b and H_c at 1.2–2.1 ppm). The molecular weight estimated from ^{1}H NMR ($DP_n = 8$) agreed well with GPC data, indicating that polymer chains were predominantly initiated by the alkyl halide, while the contributions of thermal self-initiation and transfer reactions were negligible. The peaks at 0.8–1.1 ppm correspond to H_h and H_g methyl protons from the initiating group.

The spectrum of the coupling product shows the signals corresponding to H_a protons from the initiating group, while the signal of the proton (H_f) located in the α position of the bromine end functionality is absent, indicating a high degree of coupling.

3.1. Coupling of PStBr. The coupling process was monitored by GPC. When monobrominated polystyrene is employed in ATRC, the molecular weight of the polymer after coupling is related to initial molecular weight, $M_{n,0}$, and the extent of coupling x_c, which ranges between 0 and 1 and designates the fraction of polymeric chains that participated in the reaction.

The number-average molecular weight of the initial polymer is given by eq 3

$$M_{n,0} = \frac{\sum_i n_i M_i}{\sum_i n_i} \tag{3}$$

where M_i is the molecular weight and n_i the number of molecules of molecular weight M_i.

During the coupling process, in the reaction medium two populations of polymeric chains will coexist: (i) a fraction of macromolecules resulting from coupling of x_c initial chains, which consequently have molecular weight $2M_{n,0}$; the number of these chains is $(n_i x_c)/2$; (ii) a fraction $n_i(1 - x_c)$ of unreacted or unfunctionalized chains (also resulting from disproportionation), with molecular weight $M_{n,0}$.

The number of polymeric chains continuously decreases as the coupling advances. Therefore, the overall molecular weight of polymer M_n is given by eq 4[24]

$$M_n = \frac{\sum_i \left[x_c \frac{n_i}{2}(2M_i) + (1 - x_c)n_i M_i \right]}{\sum_i \left[x_c \frac{n_i}{2} + (1 - x_c)n_i \right]} \qquad (4)$$

or the corresponding form (eq 5).

$$M_n = \frac{2\sum_i n_i M_i}{(2 - x_c)\sum_i n_i} \qquad (5)$$

From eqs 5 and 3, the expression for the overall molecular weight of the resulting polymer is obtained (eq 6).

$$M_n = \frac{2}{2 - x_c} M_{n,0} \qquad (6)$$

The extent of coupling can be estimated using eq 7.

$$x_c = 2\left(1 - \frac{M_{n,0}}{M_n}\right) \qquad (7)$$

The principle of ATRC is to force the recombination of macroradicals formed from the activation reaction by drastically decreasing the deactivator concentration in the system. Macroradicals can recombine or disproportionate, but the recombination dominates in free radical polymerization of styrene and may approach 95%.[25,26] In ATRP it is possible that side reaction such as elimination can be enhanced at higher temperature.[23,27] Therefore, throughout this study the reaction temperature was kept between 60 and 70 °C.

3.1.1. Effect of Cu^0/RX. As discussed earlier, the zerovalent metal reacts with the metal halide in higher oxidation state, regenerating the activator. Because Cu^0 is not soluble in the reaction medium, the efficiency of this electron-transfer process should depend on its amount and surface area. Consequently, highly reactive nanosize copper was used throughout this study.

The extent of coupling reaction, when monobrominated PStBr is employed, can also be estimated by analyzing the number distribution of polymer chains (RI signal divided by molecular weight).[15,28] As shown in Figure 2, a monomodal distribution was observed after 2 h, indicating a nearly complete coupling. However, by analyzing the number distribution, one can find a small amount of the starting precursor that did not participate in the coupling process. This can be due to either incomplete functionality of starting PStBr or the disproportionation reaction or other side reactions. The coupling extent was estimated as ratio between coupled and initial number of chains, using the Gaussian fit of the curve. The two resolved peaks (dotted lines in Figure 2b) correspond to the starting PStBr precursor and the product of coupling. The obtained value, $x_c = 0.95$, is close to the coupling extent calculated from eq 7 ($x_c =$ 0.97). When calculating the extent of coupling using number distribution, we should take into account that the number of coupled chains is half of the number of reacted chains.

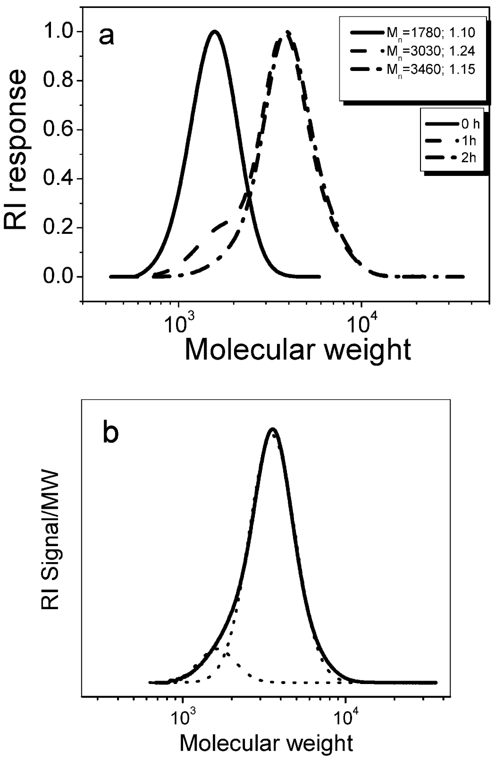


Figure 2. GPC traces (a) and number distribution plot (b) for coupling reaction of PStBr after 2 h. $[PStBr]_0$:$[CuBr]_0$:$[PMDETA]_0$:$[Cu^0]_0$ = 1:1:1:4; $[PStBr]_0 = 53$ mmol L^{-1}; solvent = toluene; temperature = 70 °C.

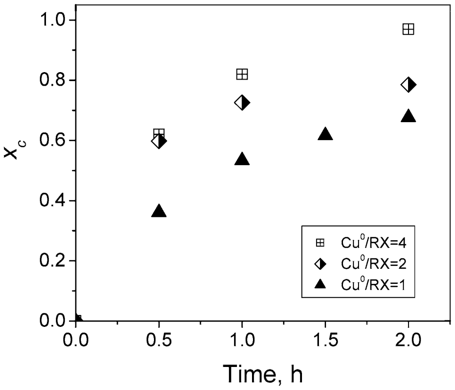


Figure 3. Dependence of coupling efficiency on ratio $[Cu^0]$/[RX] for the ATRC of PStBr. $[PStBr]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 1:1:1; $[PStBr]_0 = 53$ mmol L^{-1}; $M_{n,0} = 1780$; solvent = toluene; temperature = 70 °C; x_c was calculated according to eq 7.

Experiments run under similar conditions, but at different levels of Cu^0, showed that the coupling extent (calculated according to eq 7) increased with the amount of zerovalent metal employed in the reaction (Figure 3). The coupling reactions were rapid; more than 50% of the chains reacted in less than 1 h.

3.1.2. Effect of Ligand. The nature of ligand should also influence the ATRC; ligands that increase the activation rate in the ATRP equilibrium should accelerate coupling. Also, homogeneous systems should act faster than heterogeneous ones. Our studies showed that high coupling efficiencies were obtained with PMDETA and 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) as

Table 1. Influence of Ligand on ATRC of PStBr[a]

expt	ligand ([L]$_0$:[CuBr]$_0$)	[Cu^0]/[RX]$_0$	M_n	x_c[b]	x_c[c]	x_c[d]
1	PMDETA (1:1)	1	3030	0.83	0.73	0.81
2	PMDETA (1:1)	2	3220	0.89	0.81	0.84
3[e]	Cy (1:1)	1	2070	0.28	0.22	0.30
4[f]	Cy (2:1)	2	3460	0.97	0.95	0.98
5	dNbpy (2:1)	2	3380	0.95	0.92	0.95
6	bpy (2:1)	2	1980	0.20	0.21	0.18

[a] [PStBr]$_0$:[CuBr]$_0$ = 1:1; [PStBr]$_0$ = 53 mmol L^{-1}; $M_{n,0}$ = 1780 g/mol; solvent = toluene; temperature = 70 °C; reaction time = 2 h. [b] Calculated according to eq 7. [c] Estimated from number distribution. [d] Estimated from molecular weight distribution. [e] Experiment run at 60 °C. [f] [PStBr]$_0$ = 83 mmol L^{-1}.

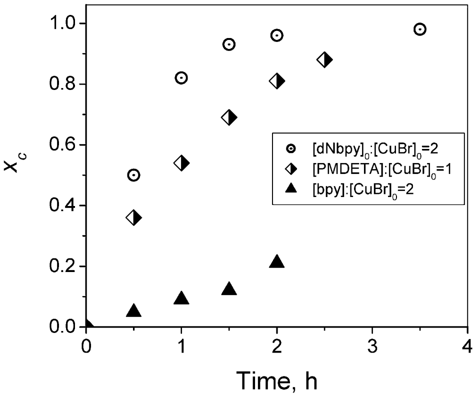


Figure 4. Variation of coupling efficiency in time for ATRC using different ligands [PStBr]$_0$:[CuBr]$_0$:[Cu^0]$_0$ = 1:1:2; [PStBr]$_0$ = 53 mmol L^{-1}; $M_{n,0}$ = 1780 g/mol; solvent = toluene; temperature = 70 °C; x_c was calculated according to eq 7.

Table 2. Influence of Cu^0/Ligand Ratio on ATRC of PStBr Using PMDETA as Ligand[a]

expt	[PStBr]$_0$	[CuBr]$_0$	[L]$_0$	[Cu^0]$_0$	M_n	x_c[b]	x_c[c]	x_c[d]
1	1	1	1	4	3100	0.85	0.84	0.87
2	1	1	2	4	3440	0.97	0.91	0.94
3	1	1	5	4	3500	0.98	0.95	0.99

[a] [PStBr]$_0$:[CuBr]$_0$:[Cu^0]$_0$ = 1:1:4; [PStBr]$_0$ = 53 mmol*l^{-1}; $M_{n,0}$ = 1780 g/mol; Ligand: PMDETA; solvent: toluene; Temperature: 70 °C; reaction time: 2 h; [b] Calculated according to eq 7. [c] Estimated from number distribution. [d] Estimated from molecular weight distribution.

ligands, but bipyridine (bpy) gave slower and even incomplete coupling under the same conditions (Table 1). The use of dNbpy as ligand allowed a fast reaction; about half of the polymeric chains reacted in 30 min (Figure 4). Comparatively, the ATRC in the presence of PMDETA was slower, but the coupling efficiency increased with time. A slower rate with PMDETA than with dNbpy can be assigned to a heterogeneity of the mixture, since PMDETA should form a more active catalyst than dNbpy.[29,30] The coupling in the presence of Cy had a higher efficiency at higher levels of ligand and zerovalent metal (runs 3 and 4 in Table 1). As can be seen from Table 1, the estimates of coupling extent from either eq 7 or molecular weight and number distributions were in relatively good agreement.

3.1.3. Effect of Cu^0/Ligand. The influence of concentration of ligand on ATRC was studied using 4-fold excess of Cu^0 over RX (Table 2). The reactions were fast; more than 95% of chains reacted in 2 h.

The x_c values became progressively higher when more ligand was used in the reaction. This indicates that excess PMDETA does not induce side reactions for styrene system, in contrast to acrylates.[31,32]

3.2. Coupling of BrPStBr. In contrast to coupling of monobrominated polymer, which yields dimers, the ATRC of α,ω-dibrominated polymers should lead to high molecular weight polymers via a step-growth process. The extent of coupling should be expressed by Carothers equation (eq 8).

$$x_c = 1 - \frac{M_{n,0}}{M_n} \qquad (8)$$

For the estimation of the coupling extent from GPC data, the number distribution cannot be used since the number of chains changes with the progress of ATRC. However, a good estimation of the coupling reaction can be obtained by resolving the multipeak plots of molecular weight.[33]

Since PMDETA is an inexpensive, commercially available ligand and allows an efficient coupling process, we studied the influence of several reaction conditions on ATRC using this ligand. The experimental data are presented in Table 3. Similar to ATRC of monobrominated PStBr, reaction rate was slow at room temperature. When reaction temperature was increased up to 90 °C, the coupling extent after 4 h was similar to that obtained after 24 h at room temperature (run 2 vs run 1 in Table 3). The extent of coupling increased when larger excess of Cu^0 was employed; thus, run 3 in Table 3 showed $x_c = 0.89$ after 27 h at room temperature, and polymer with high molecular weight was obtained. However, an additional increase of the Cu^0 levels did not result in significant changes to the coupling extent (runs 5 and 6 in Table 3).

The influence of ligand on the coupling of BrPStBr was similar to that observed for monobrominated polystyrene precursors (Table 4). The higher x_c values were obtained when dNbpy and PMDETA were used as ligands, similar to ATRC of PStBr (Figure 5). The extent of coupling in the presence of bpy was low, but high molecular weight polymers were obtained after 16 h (M_n = 16 970; PDI = 3.57). The reaction in the presence of PMDETA was slower than in the presence of dNbpy, but the polydispersity index of the resulting polymer was lower (1.80 and 3.77, respectively).

An evolution of molecular weight distribution for longer times in the presence of dNbpy is presented in Figure 6. After 30 min only dimers and uncoupled polymer were present. However, as the reaction advanced, molecular weight increased, and after 2 h 80% of BrPStBr was nearly completely consumed, yielding a product with M_n = 21 420. At this stage, no further consumption of the precursor was observed; however, the molecular weight increased, and the molecular weight distribution significantly broadened, yielding a significant fraction of very high molecular weight polymer ($M_n > 10^6$). This behavior does not follow a step-growth mechanism of coupling and must be due to some other reactions. We presume that in the presence of dNbpy some dehydrobromination may occur, leading to unsaturated chain ends. They can be considered as macromonomers, allowing to incorporate these chains as side chains by grafting through. In the case of double unsaturated chain ends, light cross-linking is possible. The resulting polymers may have structure similar to hyperbranched polymers with high polydispersities (Scheme 3).

To verify this hypothesis, we analyzed polymers by GPC coupled with a MALLS detector. While GPC

Table 3. ATRC of BrPStBr Using PMDETA as Ligand[a]

expt	$[\mathrm{BrPStBr}]_0$	$[\mathrm{CuBr}]_0$	$[\mathrm{L}]_0$	$[\mathrm{Cu}^0]_0$	T, °C	time, h	$M_{n,0}$	M_n	x_c[b]	x_c[c]
1	1	1	1	1	RT	24	2900	5 650	0.49	0.59
2	1	1	1	1	90	4	2900	5 550	0.48	0.56
3	1	1	1	4	RT	27	2900	26 160	0.89	0.98
4[d]	1	4	6	4	70	2	2670	39 800	0.93	0.99
5[d]	1	2	10	8	70	2	2670	42 170	0.94	0.96
6[d]	1	4	12	8	70	2	2670	37 500	0.92	0.98

[a] $[\mathrm{BrPStBr}]_0 = 20$ mmol L^{-1}; ligand = PMDETA; solvent = toluene. [b] Calculated according to eq 8. [c] Estimated from molecular weight distribution. [d] $[\mathrm{BrPStBr}]_0 = 40$ mmol L^{-1}.

Table 4. Influence of Ligand Nature on ATRC of BrPStBr[a]

expt	$[\mathrm{BrPStBr}]_0$	$[\mathrm{CuBr}]_0$	$[\mathrm{L}]_0$	$[\mathrm{Cu}^0]_0$	M_n	x_c[b]	x_c[c]
1	1	2	PMDETA (2)	2	9070	0.52	0.78
2	1	2	Cy (2)	2	5840	0.25	0.33
3	1	2	bpy (4)	2	5560	0.22	0.36
4	1	2	dNbpy (4)	2	11710	0.63	0.83
5	1	2	dNbpy (4)	4	21420	0.80	0.94

[a] $[\mathrm{BrPStBr}]_0 = 21$ mmol L^{-1}; $M_{n,0} = 4400$ g/mol; solvent = toluene; temperature = 60 °C; reaction time = 2 h. [b] Calculated according to eq 8. [c] Estimated from molecular weight distribution.

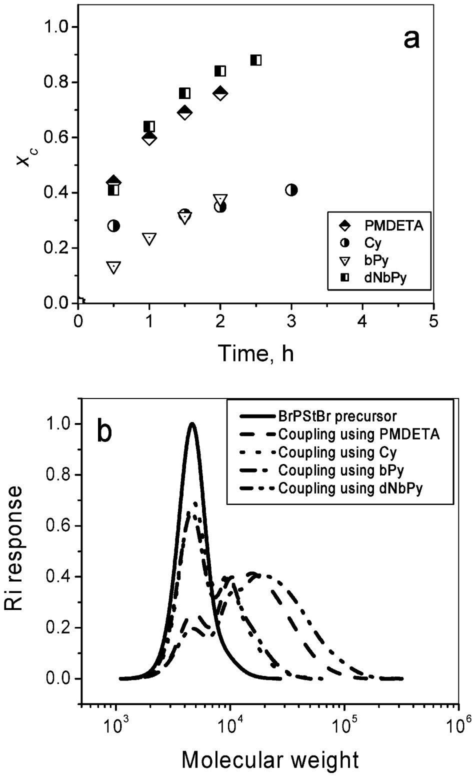


Figure 5. Dependence of coupling efficiency upon time (a) and GPC traces after 2 h (b) for coupling reactions of BrPStBr using different ligands (runs 1−4 in Table 4).

separates polymers in accordance to their hydrodynamic volume, MALLS detector allows the evaluation of molecular weights and root-mean-square (rms) radii for the eluted fractions. Analyses performed by GPC coupled with light scattering detector showed an abnormal behavior for the product of ATRC in the presence of dNbpy as ligand. As can be seen from Figure 7a, high molecular weight fractions elute at both small and high elution volumes. Similar behavior was previously reported for highly branched[34,35] and star polymer,[22] dendrimers,[36] and brushes.[37] As a consequence of entrapment of branched macromolecules in the column packing, they could elute later, together with lower molecular weight fractions.[35] Since at high elution volumes both low molecular weight polymer and

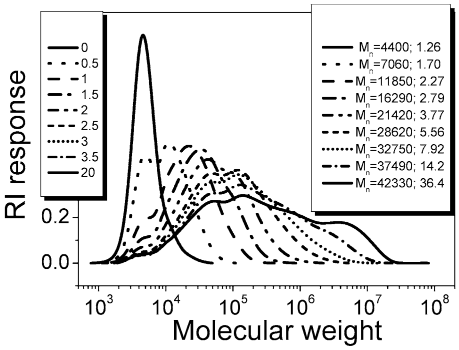
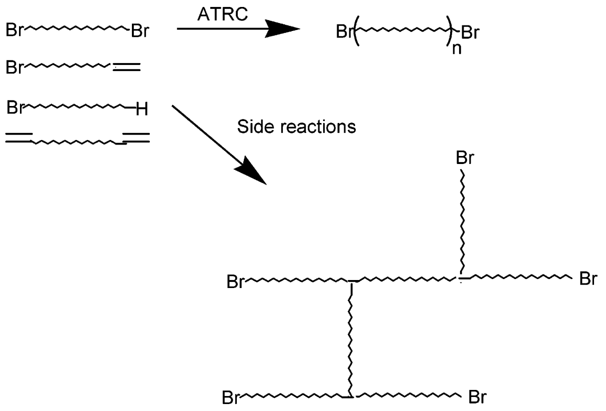


Figure 6. Variation of molecular weight distribution upon time for the coupling reaction in the presence of dNbpy (run 5 in Table 4). $[\mathrm{PStBr}]_0:[\mathrm{CuBr}]_0:[\mathrm{dNbpy}]_0:[\mathrm{Cu}^0]_0 = 1:2:4:4$; $[\mathrm{BrPStBr}]_0 = 21$ mmol L^{-1}; $M_{n,0} = 4400$ g/mol; solvent = toluene; temperature = 60 °C.

Scheme 3. Branched Structures in ATRC of Dibrominated Polymers



branched macromolecules are detected, the rms radius vs molecular weight plot exhibits a curvature in the region of low molecular weights (Figure 7b). This process can also happen for monobrominated polymers, yielding stars. Although proportion of stars is small, slightly higher values for x_c estimated from overall molecular weight (eq 7) than from number distribution graph of MW (cf. Table 1) can be explained this way.

3.3. Coupling of Mixtures of Mono- and Dibrominated Precursors. When mixtures of mono- and dibrominated PSt were employed in coupling reactions, the molecular weights of the resulting polymers were

Table 5. ATRC of Mixtures of $PStBr_{1430}$ and $BrPStBr_{3840}$[a]

expt	$[PStBr]_0/[BrPStBr]_0$	$[CuBr]_0$	$[L]_0$	$[Cu^0]_0$	$M_{n,0}$	M_n	x_c[b]	x_c[c]
1[d]	2/1	4	PMDETA (4)	8	2650	7 900	0.89	0.94
2	1/3	7	PMDETA (7)	14	3280	34 350	0.91	0.98
3	1/3	7	dNbpy (14)	14	3280	33 170	0.90	0.99

[a] $[RX]_0 = 68$ mmol L^{-1}; reaction time = 3 h; temperature = 70 °C; solvent = toluene. [b] Calculated according to eq 8. [c] Estimated from molecular weight distribution. [d] $[RX]_0 = 31$ mmol L^{-1}; experiment run at 60 °C.

Table 6. ATRC of Bromine-Terminated Polystyrene Using Different Reducing Agents (RA)[a]

expt	$[RA]_0$	$[RA]_0/[Cu^0]_0$	solvent	time, h	$M_{n,0}$	M_n	x_c[b]	x_c[c]
1	Fe^0[d]	4	toluene	18	4380	6870	0.72	0.68
2	Fe^0[e]	4	toluene	32	4380	6790	0.71	0.65
3	$SnOct_2$	2	toluene	22	4380	6550	0.66	0.62
4	$SnOct_2$	4	toluene	19	4380	6630	0.68	0.67
5[f]	ascorbic acid	4	toluene/water (5/3 v/v)	5	1800	2780	0.7	0.67
6[g]	ascorbic acid	1	toluene/water (3/3 v/v)	4	4500	22250	0.8	0.82

[a] $[PStBr]_0:[CuBr]_0:[PMDETA]_0 = 1:1:1$; $[PStBr]_0 = 21$ mmol L^{-1}; temperature = 70 °C. [b] Calculated according to eq 7. [c] Estimated from GPC data. [d] Suspension of Fe^0/Fe_3O_4 (60/40) in toluene. [e] Suspension of Fe^0/Fe_3O_4 (60/40) in water. [f] [RX] = 52 mmol/L. [g] [RX] = 9 mmol/L; ATRC performed on dibrominated polystyrene at 90 °C.

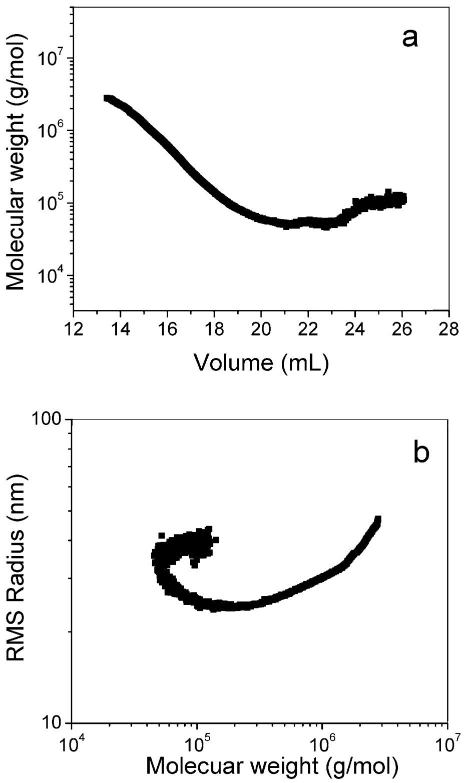


Figure 7. An illustration of the abnormal GPC elution for a coupling product of BrPStBr. Dependence of molecular weights on elution volume (a) and of the radius of gyration on molecular weight (b). $[PStBr]_0:[CuBr]_0:[dNbpy]_0:[Cu^0]_0 = 1:2:4:4$; $[BrPStBr]_0 = 21$ mmol L^{-1}; $M_{n,0} = 4400$ g/mol; solvent = toluene; temperature = 60 °C.

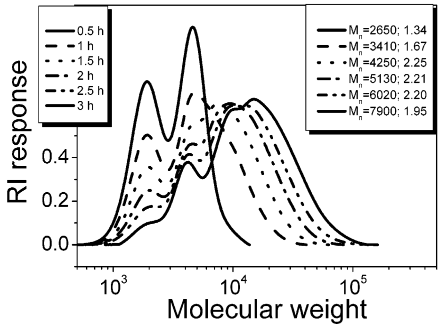


Figure 8. GPC traces for ATRC of mixtures of mono- and dibrominated polystyrene (ratio 2:1). $[PStBr_{1430}]_0:[BrPStBr_{3840}]_0:[CuBr]_0:[PMDETA]_0:[Cu^0]_0 = 2:1:4:4:8$; $[RX]_0 = 31$ mmol L^{-1}; temperature = 60 °C; solvent = toluene.

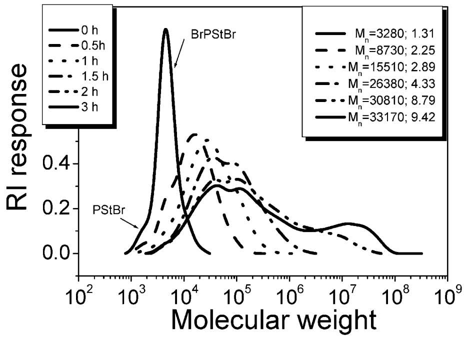


Figure 9. GPC traces for ATRC of mixtures of mono- and dibrominated polystyrene (ratio 1:3). $[PStBr_{1430}]_0:[BrPStBr_{3840}]_0:[CuBr]_0:[dNbpy]_0:[Cu^0]_0 = 1:1:7:14:14$; $[RX]_0 = 68$ mmol L^{-1}; temperature = 70 °C; solvent = toluene.

influenced by the ratio between these bromine-terminated polymers. This is the result of the number of successive couplings of the dibrominated polymer limited by the presence of monobrominated chains. Thus, when a mixture of $PStBr_{1430}$ and $BrPStBr_{3840}$ in the molar ratio 2/1 was used in coupling reaction, the molecular weight of the ATRC product was lowered due to the presence of the monobrominated PSt and the polydispersity index was 1.95 (Table 5).

The evolution of molecular weight distribution for this experiment is illustrated in Figure 8.

However, when the dibrominated PSt was predominant in the feed mixture ($PStBr_{1430}:BrPStBr_{3840} = 1:3$), the coupling products had higher molecular weights, and the polydispersity index was much larger (runs 2 and 3 in Table 5). Large fractions with ultrahigh molecular weights were observed, similar to coupling reactions of BrPStBr presented above (Figure 9). Nevertheless, a significant decrease in polydispersity index, compared with ATRC of BrPStBr, was observed.

3.4. ATRC of Bromine-Terminated Polystyrene Using Different Reducing Agents (RA). Not only Cu^0 can be employed in ATRC, but also other reducing agents. Previously, we reported the use of ascorbic acid for coupling of mono- and dibrominated polystyrene.[18] Table 6 presents the influence of different reducing agents on the ATRC of polystyrene. Thus, when zerovalent iron (reactive nanoscale iron particles (RNIP) from Toda Kogyo Corp., size <100 nm,) was used in coupling of PStBr, the reaction rate was slower compared to that of experiments performed with Cu^0, and the extent of coupling was limited to about 0.7 (runs 1 and 2 in Table 6). This behavior is explained by the fact that the highly active nanosized Fe^0 is "covered" by Fe_3O_4, which encumbers the reduction of the deactivator in the ATRC. The extent of coupling was practically the same when using nanosized Fe^0 as a suspension in either toluene or water.

Another good reducing agent is tin octanoate ($SnOct_2$), which enhances the rate of the ATRP by reducing the amount of deactivator in the reaction. The ATRC in the presence of tin octanoate showed a coupling extent similar to the process carried out with zerovalent iron (runs 3 and 4 in Table 6).

A higher reaction rate was observed when ascorbic acid was used in the ATRC of mono- and dibrominated polystyrene (runs 5 and 6 in Table 6). The extent of coupling depends on the amount of ascorbic acid used in the reaction.[18,38]

4. Conclusions

Copper-mediated atom transfer radical coupling was studied for mono- and dibrominated polystyrene as well as their mixtures. ATRC is influenced by the nature of ligand used in the process as well as the amounts of ligand and zerovalent metal. PMDETA and dNbpy are efficient ligands for this process, leading to high coupling efficiencies in short reaction time. The molecular weight of the coupling product is dependent on the bromine functionality of the polymeric precursor and the extent of coupling. Thus, molecular weights of the ATRC products of monobrominated polystyrene were approximately twice higher than those of PStBr precursors, while the polydispersities were low. The coupling of α,ω-dibrominated homologues gave high molecular weight products with higher polydispersities. When mixtures of PStBr and BrPStBr were used in ATRC, the molecular weights of the coupling products were influenced by the ratio between polymeric precursors.

ATRC can be also performed using other reducing agents, such as Fe^0, $Sn(Oct)_2$, or ascorbic acid.

Acknowledgment. The financial support from the ATRP/CRP Consortia at CMU and DOE (DE-FG07-02ER63507) is greatly appreciated. K.-Y.L. and J.E. acknowledge SURG and Howard Hughes, respectively, for their sponsorship. Virgil Simplaceanu and Dr. Roberto R. Gil are acknowledged for their help with NMR experiments and Dr. Mihaela Corina Iovu and Dr. Brent Sumerlin for useful discussions and GPC-MALLS.

References and Notes

(1) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.
(2) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901−7910.
(3) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866−868.
(4) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895−903.
(5) Matyjaszewski, K. *Chem.—Eur. J.* **1999**, *5*, 3095−3102.
(6) Matyjaszewski, K.; Xia, J. *Chem. Rev. (Washington, D.C.)* **2001**, *101*, 2921−2990.
(7) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev. (Washington, D.C.)* **2001**, *101*, 3689−3745.
(8) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901−915.
(9) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337−377.
(10) Pyun, J.; Matyjaszewski, K. *Chem. Mater.* **2001**, *13*, 3436−3448.
(11) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083−2134.
(12) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 2−166.
(13) Fischer, H. *Macromolecules* **1997**, *30*, 5666−5672.
(14) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348−7350.
(15) Sarbu, T.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2001**, *202*, 3379−3391.
(16) Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 9009−9014.
(17) Yoshikawa, C.; Goto, A.; Fukuda, T. *e-Polym.* **2002**, 13.
(18) (a) Sarbu, T.; Ell, J.; Matyjaszewski, K. *ACS Polym. Prepr.* **2002**, *43*, 213−214. (b) Otazaghine, B.; David, G.; Boutevin, B.; Robin, J. J.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2004**, *205*, 154−164.
(19) Matyjaszewski, K.; Woodworth, B. E.; Zhang, X.; Gaynor, S. G.; Metzner, Z. *Macromolecules* **1998**, *31*, 5955−5957.
(20) Yurteri, S.; Cianga, I.; Yagci, Y. *Macromol. Chem. Phys.* **2003**, *204*, 1771−1783.
(21) Kramer, R.; Lehn, J. M.; De Cian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 703−706.
(22) Frater, D. J.; Mays, J. W.; Jackson, C. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 141−151.
(23) Lutz, J.-F.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2002**, *203*, 1385−1395.
(24) One reviewer suggested a simplified form of this equation. Thus, before coupling $M_{n,0} = \sum_i n_i M_i / \sum_i n_i = m/n$, where m is the weight of polymer in a given sample and n the number of polymer chains in a sample. During coupling, the same weight of polymer, m, is considered, while n' is the new number of polymer chains. $n' = (x_c/2)n + (1 - x_c)n = (1 - x_c/2)n$. Hence, $M_n = m/n' = m/n(1 - x_c/2) = M_{n,0}/(1 - x_c/2)$ (eq 5).
(25) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991.
(26) Zammit, M. D.; Davis, T. P.; Haddleton, D. M.; Suddaby, K. G. *Macromolecules* **1997**, *30*, 1915−1920.
(27) Matyjaszewski, K.; Davis, K.; Patten, T. E.; Wei, M. *Tetrahedron* **1997**, *53*, 15321−15329.
(28) Matyjaszewski, K.; Shipp, D. A.; McMurtry, G. P.; Gaynor, S. G.; Pakula, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2023−2031.
(29) Qiu, J.; Matyjaszewski, K.; Thouin, L.; Amatore, C. *Macromol. Chem. Phys.* **2000**, *201*, 1625−1631.
(30) Pintauer, T.; McKenzie, B.; Matyjaszewski, K. *ACS Symp. Ser.* **2003** *854*, 130−147.
(31) Bednarek, M.; Biedron, T.; Kubisa, P. *Macromol. Chem. Phys.* **2000**, *201*, 58−66.
(32) Roos, S. G.; Muller, A. H. E. *Macromol. Rapid Commun.* **2000**, *21*, 864−867.
(33) We prepared mixtures of polymers with different molecular weights, but close enough to obtain bimodal distribution, which were analyzed by GPC; the ratios between fractions obtained by resolving the multipeak plots were in good agreement with proportions of mixed polymers.
(34) Cheng, G.; Simon, P. F. W.; Hartenstein, M.; Muller, A. H. E. *Macromol. Rapid Commun.* **2000**, *21*, 846−852.
(35) Podzimek, S.; Vlcek, T.; Johann, C. *J. Appl. Polym. Sci.* **2001**, *81*, 1588−1594.
(36) Percec, V.; Ahn, C.-H.; Cho, W.-D.; Jamieson, A. M.; Kim, J.; Leman, T.; Schmidt, M.; Gerle, M.; Moller, M.; Prokhorova, S. A.; Sheiko, S. S.; Cheng, S. Z. D.; Zhang, A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 8619−8631.
(37) Gerle, M.; Fischer, K.; Roos, S.; Muller, A. H. E.; Schmidt, M.; Sheiko, S. S.; Prokhorova, S.; Moller, M. *Macromolecules* **1999**, *32*, 2629−2637.
(38) Sarbu, T.; Lin, K.-Y.; Ell, J.; Spanswick, J.; Matyjaszewski, K. Manuscript in preparation.

MA035901H