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Studies on the Preparation of Telechelic Polymers by Atom Transfer Radical Polymerization and Cross Coupling Processes

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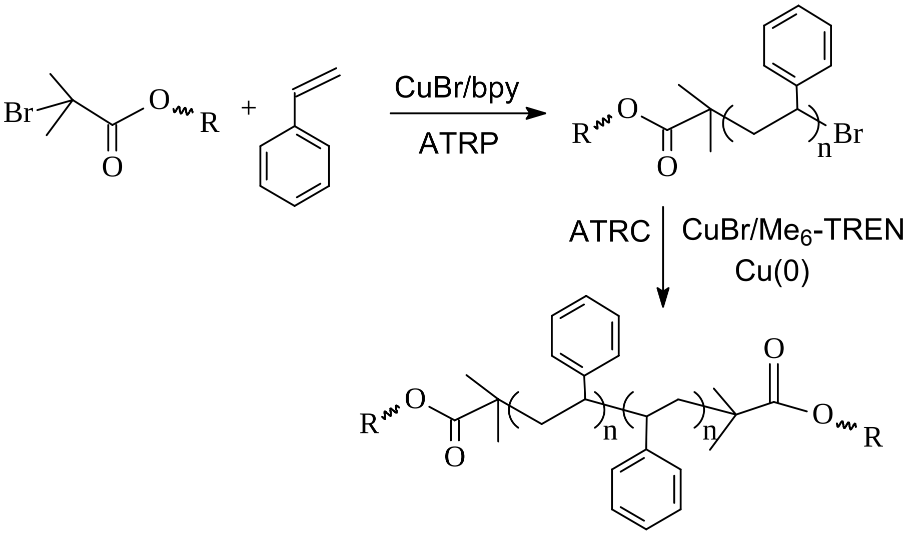
Abstract: Combination of Atom Transfer Radical Polymerization (ATRP) and Atom Transfer Radical Cross Coupling (ATRCC) processes as a route to prepare telechelic polymers was described. The concept is based on the activation of the dormant species at the chain ends of polystyrene (Br-PS-Br or PS-Br) prepared by ATRP and functional ATRP initiator (F-R-Br) in the absence of a monomer. Depending on the type of polystyrene used in the system, cross coupling of these active species gives α,ω-polystyrene and ω-polystyrene telechelics. Detailed investigations using a model system revealed that the efficiency of functionalization was not very high because of the self-coupling of the species derived from the polymer and functional initiator. However, the highest functionalization (X_f=0.85) was achieved by introducing a small amount of styrene in the ATRCC.

Introduction

Telechelic polymers are defined as macromolecules that contain two reactive end groups [1]. Telechelic polymers, having variety of functional groups, are prepared by a wide range of polymerization methods namely, anionic [2], cationic [3], ring opening [4], group transfer [5,6], free radical [7], and step-growth [1] polymerization, and chain scission [1] processes. Recent developments in controlled/living radical polymerization provide possibility to synthesize well-defined telechelic polymers also with radical routes. Among the various controlled radical polymerization routes, Atom Transfer Radical Polymerization (ATRP) seemed to be the most versatile because of its simplicity and applicability to many vinyl monomers. Quite a number of functional initiators were successfully used in ATRP to prepare functional styrene and acrylate type polymers. Obviously, ATRP leads to the formation of monofunctional telechelics since the other chain always contains halogen due to the fast deactivation process. Therefore, α,ω-telechelics can only be prepared by transformation of the halide end group either by nucleophilic substitution, or free radical reaction or electrophilic addition catalyzed by Lewis acids. We have recently proposed an alternative route for obtaining directly α,ω-telechelics via combination of ATRP and Atom Transfer Radical Coupling (ATRC) processes [8]. The ATRP initiator having aldehyde, tertiary amine, phenolic and carboxyl groups were used for the styrene polymerization to yield a polymer with the desired chain end at the α-end and couplings of ω-halide ends then carried out using ATRC process (Scheme 1).



R = -COOH, -CHO, -Ph-OH, -N(CH$_3$)$_2$

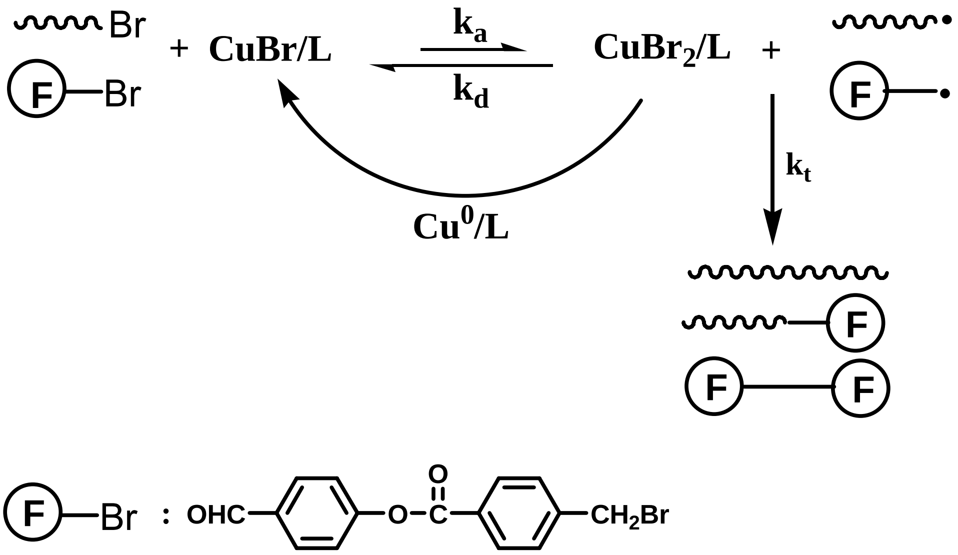
Scheme 1. Synthesis of telechelic polymers by ATRP and ATRC processes.

This approach was further extended for the preparation of telechelics of polyacrylates [9] and polyfluoroacrylates [10]. Keul and co-workers applied ATRC to produce multiblock copolymers [11]. While poly(phenylene oxide)-*b*-polystyrene (PPO-*b*-PS) and PS-*b*-PPO-*b*-PS were successfully transformed into tri- and multi-block copolymers by using ATRC, similar attempts for the corresponding polycarbonate based block copolymers were failed because of the chain degradation of the polycarbonate segment during ATRC process.

The ATRC approach for the preparation of telechelics has some drawbacks. First, the corresponding initiators with desired functionality have to be synthesized and then used in ATRP to yield α-functional polymers. Secondly, some macroradicals, generated from the ω-halide ends at ATRC conditions, undergo termination by disportionation rather than combination. Obviously, the ratio of combination to disproportionation depends on the type of radicals. Moreover, the radical concentration has to be sufficiently high at the equilibrium. Therefore, polystyrene seemed to be the most suitable precursor in the ATRC application because of the termination mode and high concentration of the radicals in the ATRP equilibrium. Additionally, even if the coupling efficiency is quantitative and polymers contain two functionalities per chain, the molecular weights of the ATRC products are approximately doubled than those of the precursors. This would certainly limit the further uses of the telechelics in various applications, such as polycondesation. Therefore, it will be appropriate to verify the applicability of Atom Transfer Cross Coupling (ATRCC) reaction of dibrominated polymers with the functional bromoinitiators, for the preparation of α,ω-telechelics without significant change in molecular weight. Thus, model ATRCC reactions between monobrominated polystyrene (PS-Br) and low molecular weight bromo functional compound, (***F***-R-Br), having aldehyde functionality, have been described. Here, bromo end groups of the polymer and ATRP initiator serve as the active sites for the radical generation. The influence of different factors on coupling reactions has also been discussed.

Results and Discussion

As stated in the introduction section, we deliberately selected PS-Br as a model polymer in our experiments for the simplicity. Obviously, the use of Br-PS-Br would have led to a more complex situation as more coupling products are expected to be formed and much high molecular weight polymers would be obtained because of the possible polymer-polymer coupling reactions at both ends. In ATRCC system, macroradicals and low molar mass radicals are generated *in situ* from PS-Br and ***F***-R-Br, respectively in the same way as shown in Scheme 2. Termination reaction occurs by coupling of these two radicals, and formation of monofunctional polymer in the presence of a reducing agent such as zerovalent copper. However, at least in principle, not only the desired mono aldehyde functional polymer but also various side products may be formed due to the self coupling reactions of macroradicals generated from PS-Br, and low –molecular weight radicals from ***F***-R-Br. The possible reactions of our model system are depicted in Scheme 2.



Scheme 2. General reactions of ATRCC process.

The chain end functionality was investigated by ^{1}H NMR analysis. Figure 1 represents the ^{1}H NMR spectra recorded for PS-Br prepared by ATRP and its coupling product in the presence of ***F***-R-Br. The signal at 4.38 ppm was attributed for -C*H*(Ph)Br (Figure 1a). When the spectrum of the coupling product was investigated (Figure 1b), the characteristic chemical shift for aldehyde proton was detected at 10.01 ppm. The aromatic protons of the initiator near the carbonyl groups appeared at 7.94 ppm. The other aromatic protons of the initiator were noted at around 7.34 ppm. It should be pointed out that the signal of the proton (r) located in the α-position of the bromine end functionality disappeared after the reaction, confirming the efficient coupling reaction of PS-Br chains. However, the number of the styrene repeating units of the coupling product, which was estimated from the peak area integration of aromatic region (6.58 ppm), showed not only functional polymer formation but also coupling of the macroradicals occured during ATRCC reaction. Protons originating from the self coupling reaction of PS-Br (-CH-CH-) were located in 2–2.5 ppm region and overlapped with the other CH_2 and CH protons of the polystyrene chains.

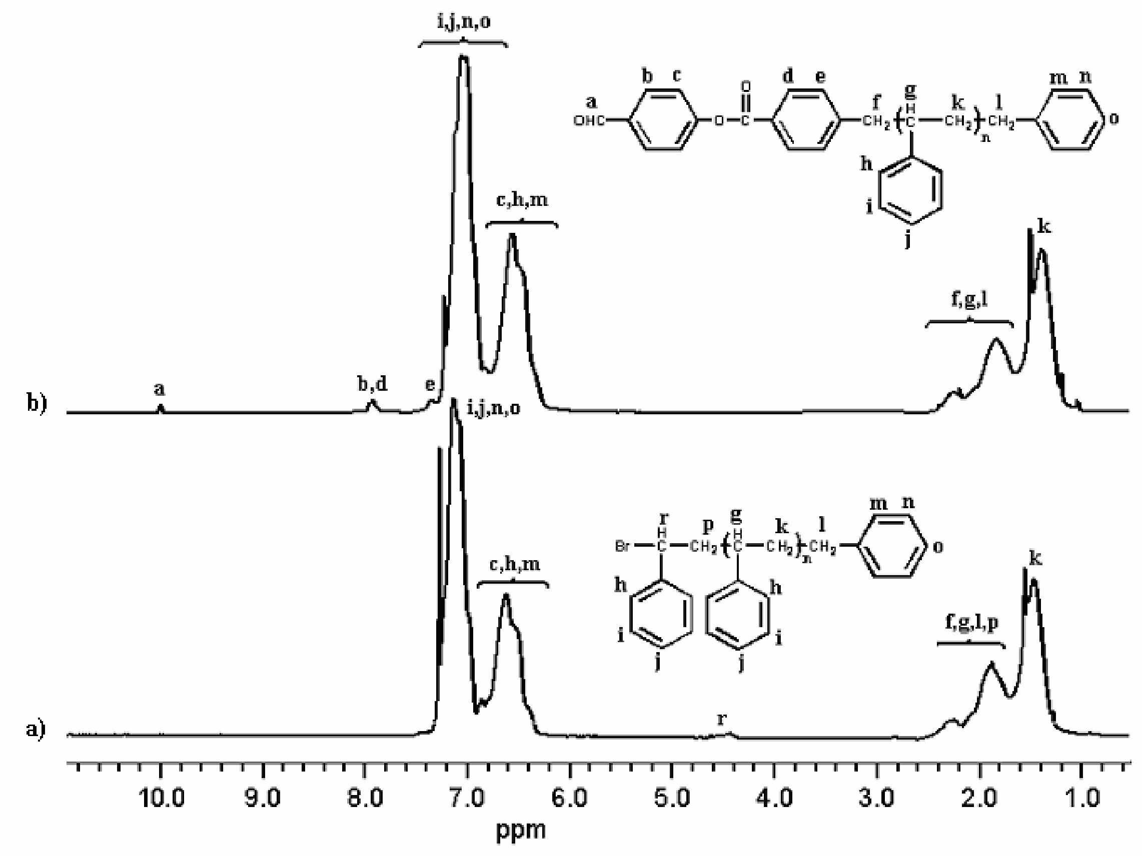


Fig. 1. ^{1}H NMR spectra of PS-Br ($M_n = 2132, M_w / M_n = 1.2$) (a) and its coupling product (b).

Calculation of Functionalization

The chain end functionality was estimated from ^{1}H NMR and compared with those from GPC measurements. During the coupling process, in the reaction medium, three type of polymers were expected to be formed; (i) from coupling reaction between PS-Br and F-R-Br (PS-R-F), having molecular weight $M_{n,o} + Mw_{F\text{-}R\text{-}Br}$ (ii) from coupling reaction of the initial chain (PS-PS) having molecular weight $2M_{n,o}$ (iii) from unreacted PS-Br having molecular weight $M_{n,o}$. We have assumed that in the final mixture the PS-R-F, PS-PS and PS-Br are presented in x:y:z. Also, the amount of unfunctionalized chain resulting from disproportionation was negligible.

The degree of functionalization (x_f) and polymer-polymer coupling (x_c) can be estimated by using following equations.

$$x_f = x\,(PS\text{-}R\text{-}F) \,/\, [\, x\,(PS\text{-}R\text{-}F) + 2y\,(PS\text{-}PS) + z\,(PS\text{-}Br)\,] \qquad (1)$$

$$x_c = 2y\,(PS\text{-}PS) \,/\, [\,(\, x\,(PS\text{-}R\text{-}F) + 2y\,(PS\text{-}PS) + z\,(PS\text{-}Br))] \qquad (2)$$

When no signal was noticed in the ^{1}H-NMR spectra of the products at 4.38 ppm, z was assumed as 0 (absence of unreacted chains). In other cases the relation between x and z is:

$$x / z = I_{\text{-CHO}} / I_{\text{-CH(Ph)Br}} \qquad (3)$$

where $I_{\text{-CHO}}$ and $I_{\text{-CH(Ph)Br}}$ are the intensities of the signals corresponding to the aldehyde functionality and -CH(Ph)Br, respectively.

Tab. 1. Effect of $[Cu^o]_o$ / $[CuBr]_o$ / $[L]_o$ ratio on ATRCC.

Run	$[RX]_o$[a] ([PS-Br]/[***F***-R-Br])	$[CuBr]_o$	$[Cu^o]_o$	$[L]_o$	$M_{n,o}$[b]	M_n[b]	x_f[c]	x_c[d]	x_c[e]	$x_{PS\text{-}Br}$[c]
1	1	6.2	31.2	45	1918	3677	0.00	1	1	<0.01
2	1	3.7	18.7	27	1918	3855	0.20	0.80	0.99	<0.01
3	1	3.1	15.6	22.5	2132	3051	0.56	0.44	0.62	<0.01
4	1	1.5	7.8	11.2	1918	2949	0.17	0.83	0.70	<0.01
5	1	0.6	3.1	4.5	1918	2453	0.20	0.51	0.44	0.28
6	1	1	4	2	1918	2295	0.00	0.30	0.34	0.69
7	1	1	2	2	1918	2020	0.00	0.29	0.12	0.71

a) $[RX]_o$=$[PS\text{-}Br]_o$/[***F***-R-Br]$_o$:1/15, $[PS\text{-}Br]_o$:1.37 mM, reaction time: 4h, ligand:PMDETA, temperature:110 °C. b) Calculated from GPC based on polystyrene standards. c) Calculated from ^{1}H NMR spectrum by using eq 1. d) Calculated from ^{1}H NMR spectrum by using eq 2. e) Calculated from GPC by using $x_c = 2(1 - M_{n,o} / M_n)$ [13].

We have investigated the effect of various parameters such as catalyst concentration, [PS-Br]/[***F***-R-Br] ratio, PS-Br concentration, molecular structure of the bromo end groups and time dependence on the ATRCC system. Table 1 shows the effect of change of composition of catalytic system on the product formation, namely [RX] / $[Cu^o]_o$ / $[CuBr]_o$ / $[L]_o$. It is known that the zerovalent metal (Cu^o) reacts with the metal halide in higher oxidation state, enhancing the rate of polymerization in ATRP reactions by reducing the amount of deactivator (Cu^{II}). Similarly, the increase of the amount of Cu^o and the PMDETA leads to the increase of formation of PS-R-***F*** (experiments 3-5 in Table 1). The Cu^o is not soluble in the reaction medium and therefore, excess amount of Cu^o provides more surface area for the efficient electron-transfer process. It was reported that the excess PMDETA, does not induce side reactions for styrene system [13]. It was observed that when catalyst concentration is significantly low, the reaction is suppressed, and yields unreacted polymer with little but some PS-PS coupling product. As expected, with the increase of catalyst concentration the PS-R-***F*** formation increases. But at very high catalyst concentration self-coupling reactions are dominant.

The effect of concentration of ***F***-R-Br with respect to PS-Br in the coupling process was also investigated (Tab. 2). The desired end group functionalization (PS-R-***F***) increases with the increase of ***F***-R-Br concentration up to a certain level (Runs 8-10) and then, decreases due to the possible self-coupling reactions of the functional initiator.

Another important parameter of coupling process is the PS-Br concentration. As it can be seen from Table 3, at relatively low PS-Br concentration, limited functionalization was attained because of the low radical concentration. Apparently, the highest value of functionalization obtained was 0.56, beyond this value, we were not able to achieve, by altering the reaction conditions.

Tab. 2. Effect of [PS-Br]/[***F***-R-Br] ratio on ATRCC.

Run	$[RX]_o^a$ ([PS-Br]/[***F***-R-Br])	$M_{n,o}^b$	M_n^b	x_f^c	x_c^d	x_c^e	$x_{PS\text{-}Br}^c$
8	1/5	1918	2872	0.08	0.92	0.68	<0.01
9	1/10	1918	4002	0.15	0.85	0.99	<0.01
10	1/15	2132	3051	0.56	0.44	0.62	<0.01
11	1/30	2132	3384	0.30	0.70	0.88	<0.01
12	1/50	2132	3264	0.35	0.65	0.82	<0.01

a) $[PS\text{-}Br]_o$: 1.37 mM, $[Cu^o]_o$ / $[CuBr]_o$ / $[L]_o$:15.6/3.1/22.5, reaction time: 4h, ligand: PMDETA, temperature: 110 °C b) Calculated from GPC based on polystyrene standards. c) Calculated from ^1H NMR spectrum by using eq 1. d) Calculated from ^1H NMR spectrum by using eq 2. e) Calculated from GPC by using $x_c = 2(1 - M_{n,o}/M_n)$ [13].

Tab. 3. Effect of [PS-Br] concentration on ATRCC.

Run	[PS-Br] mM	$M_{n,o}^b$	M_n^b	x_f^c	x_c^d	x_c^e	$x_{PS\text{-}Br}^c$
13	4.45	2132	3090	0.28	0.72	0.62	<0.01
14	2.74	2132	3443	0.32	0.68	0.76	<0.01
15	1.37	2132	3051	0.56	0.44	0.62	<0.01
16	0.91	2132	3151	0.34	0.66	0.64	<0.01

a) $[RX]_o = [PS\text{-}Br]_o$ / $[\boldsymbol{F}\text{-}R\text{-}Br]_o$:1/15, $[PS\text{-}Br]_o$: 1.37 mM, $[Cu^o]_o$ / $[CuBr]_o$ / $[L]_o$:15.6/3.1/22.5, reaction time: 4h, ligand: PMDETA, temperature: 110 °C. b) Calculated from GPC based on polystyrene standards. c) Calculated from ^1H NMR spectrum by using eq 1. d) Calculated from ^1H NMR spectrum by using eq 2. e) Calculated from GPC by using $x_c = 2(1 - M_{n,o}/M_n)$ [13].

It has also been observed that under the experimental conditions mentioned above the highest functionalization was achieved after 2h and then the composition of reaction mixture does not change significantly with time (Fig. 2).

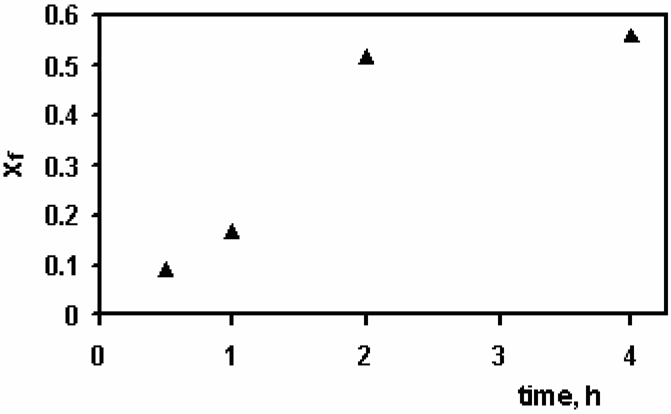


Fig. 2. Variation of coupling efficiency in time for ATRCC using PMDETA as a ligand. $[PS\text{-}Br]_o$ / $[\boldsymbol{F}\text{-}R\text{-}Br]_o$/ $[Cu^o]_o$ / $[CuBr]_o$ / $[L]_o$: 1/15/15.6/3.1/22.5, $[PS\text{-}Br]_o$: 1.37 mM.

Following Matyjaszewski's strategy [14], styrene monomer was added in the system. This was necessary for having the structurally similar chain ends. In the system investigated here, two different bromine terminated radical center with different ATRP equilibrium constant were present. The addition of a small amount of styrene would initiate polymerization via ATRP. As a result, styrene–terminated radicals are simultaneously formed from both this polymerization and initial PS-Br. This experiment was carried out in toluene at 110 °C with $[\text{PS-Br}]_o$ /[St] / [***F***-R-Br]$_o$/ $[\text{Cu}^o]_o$ / $[\text{CuBr}]_o$ /$[\text{L}]_o$ =1/10/15/15,6/3,1/22,5. Under these conditions the highest functionalization (x_f: 0.85) with $M_n = 3039$ with 1.33 polydispersity was achieved. The increase of molecular weight of the resulting telechelic from the initial value ($M_n = 2495$) is due to the addition of short styrene unit as well as functional initiator.

Conclusions

Preparation of telechelic polymers by the combination of ATRP and ATRCC processes was investigated on a model system using aldehyde functional ATRP initiator and monobrominated polystyrene. The influence of different factors on coupling reactions was discussed. It was concluded that the method is successful only when a small amount of styrene was used at the ATRCC step.

Experimental part

Materials

Styrene (Merck) was purified by usual methods, and distilled in vacuum from CaH_2 just before use. Toluene was distilled and dried over Na wire. Dichloromethane a product of Baker was dried with P_2O_5. Immediately before use the monomer and solvent were purged with N_2 for at least 30 min. N,N,N’,N’’,N’’-Penta methyldiethylenetriamine (PMDETA, Aldrich), was distilled before use. Benzylbromide (Fluka), ethyl-2-bromoisobutyl bromide (Aldrich), ethylene glycol (Aldrich), triethylamine (J.T. Baker), CuBr (Aldrich), Cu^o (Aldrich) were used as received.

*Synthesis of 4-formylphenyl-4-(bromomethyl)benzoate (**F**-R-Br)*

The synthesis of 4-formylphenyl-4-(bromomethyl)benzoate (***F***-R-Br) has been reported elsewhere [8].

Synthesis of 1,2-Bis(bromoisobutrylloxy)ethane

1,2-Bis(bromoisobutrylloxy)ethane, as difunctional initiator, was synthesized according the described procedure [12].

General Procedure of Atom Transfer Radical-Polymerization (ATRP)

-Preparation of Monobrominated Polystyrene (PS-Br)

A round bottom flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and back-filled with dry nitrogen several times. CuBr (0.062g, 0.43 mmol), PMDETA (89.7μL 0.43 mmol), benzylbromide as an initiator (51.6 μL, 0.43 mmol), and styrene (5 mL, 43 mmol) were introduced under N_2 atmosphere. The flask was heated at 110°C in an oil bath and stirred for 30 min. Then the mixture was diluted with THF, and passed through an alumina column to remove the complex salts. Precipitation of the polymer was performed in ten-fold volume of methanol. The solid was then collected after filtration and kept for drying at 40 °C in vacuum for overnight.

Preparation of Dibrominated Polystyrene (Br-PS-Br)

Dibrominated polystyrene (Br-PS-Br) was synthesized using the same methodology described above using 1,2-bis(bromoisobutrylloxy)ethane, as an initiator instead of benzylbromide, and toluene was used as solvent.

General Procedure of Atom Transfer Radical Coupling (ATRCC)

The coupling reaction between PS-Br and ***F***-R-Br was carried out in N_2 atmosphere using CuBr and Cu^o as catalyst, PMDETA as a ligand, and toluene as a solvent at 110 °C. To remove the complex salts, the polymer solution was diluted in THF and passed through an alumina column followed by precipitation in methanol after 4h. The solid was collected after filtration and drying at 40 °C in vacuum for overnight.

Characterization

^{1}H NMR spectra of the sample were recorded on a Bruker 250 MHz spectrometer using tetramethylsilane as the internal standard. Molecular weights were determined by using a gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) where THF was used as the eluent and flow rate of 0.3 mL min $^{-1}$ and a Waters 410 Differential Refractometer was used as detector.

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