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Synthesis of Hydroxy-Telechelic Poly(methyl acrylate) and Polystyrene by Atom Transfer Radical Coupling

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ABSTRACT: Hydroxy-terminated poly(methyl acrylate) (HO-PMABr) and polystyrene (HO-PStBr) were synthesized by atom transfer radical polymerization (ATRP) using a HO-functionalized initiator. These HO-functional polymers were further employed in an atom transfer radical coupling (ATRC) reaction in the presence of a zerovalent metal forming hydroxy-telechelic poly(methyl acrylate) (HO-PMA-OH) and polystyrene (HO-PSt-OH). In ATRC process macroradicals, generated in situ by an atom transfer radical equilibrium, take part in bimolecular termination reactions in the presence of a reducing agent, such as nanosize copper. The coupling of hydroxy-terminated PSt was fast; after 3 h more than 95% of polymeric chains being reacted. Under similar ATRC conditions, the coupling of poly(methyl acrylate) was slow since the ATRP equilibrium constant, and consequently radical concentration, is much smaller than those of polystyrene. This difficulty was overcome by introducing small amounts of St in the ATRC of polyacrylate. The acrylate radicals—generated during the activation step in the presence of cuprous halide complex—react with styrene producing styrene-terminated acrylate macroradicals that combine in a similar manner and at rates similar to polystyrene chains. Equimolar amounts of St vs polyacrylate chain end provided hydroxy-telechelic polymers with high coupling efficiency after a short reaction time. NMR analyses performed on the coupling product of hydroxy-terminated poly(methyl acrylate) showed the incorporation of catalytic amounts of St during ATRC.

Introduction

Atom transfer radical polymerization (ATRP) is perhaps the most versatile process among several controlled/living radical polymerization (CRP) processes developed in the past decade.[1−7] The essential feature of this method is the equilibrium between a low concentration of active propagating species and a large number of dormant chains via an electron transfer process promoted by a transition metal complex. As the contribution of bimolecular termination decreases, the characteristics of radical polymerization more closely resemble that of a living system, and thus polymers with controlled molecular weights and targeted architectures can be synthesized starting from a large variety of monomers.

ATRP has been used for the synthesis of new macromolecules with various compositions (homopolymers, random, periodic, block, graft, and gradient copolymers) and novel topologies (linear, star, comb, branched, hyperbranched, networks, etc.).[4,5,8−13] An important advantage of ATRP is its tolerance to many functionalities, and thus a variety of functional polymers have been synthesized from a wide range of monomers, such as substituted styrenes, (meth)acrylates, and acrylamides.[9,14−21] Furthermore, monofunctional polymers were readily obtained through ATRP of styrene (St) and acrylates by using various initiators containing functional groups, such as hydroxyl, amine, esters, thiol, allyl halides, oxazoline, or carboxylic acids.[19,20,22−32]

The radically transferable atom or group, most frequently a terminal halogen, present on the active terminus of the growing polymer chain, can undergo further transformations, such as nucleophilic substitution or radical addition, to allow the synthesis of telechelic polymers, which are valuable building blocks for the synthesis of composite materials or block copolymers. [33−39] However, end group transformation generally requires a large excess of reagent, and sometimes the resulting degree of functionalization is low.

Hydroxy-telechelic polymers, which are valuable intermediates for the preparation of polyurethanes or polyesters, can be synthesized by ATRP followed by end group transformation. Using this approach, hydroxy-telechelic poly(methyl methacrylate) (PMMA) was synthesized via ATRP using hydroxy-functionalized initiator and then end-capping with allyl alcohol.[40] Also, hydroxy-functionalized poly(methyl methacrylate) was obtained using 2-hydroxyethyl 2-bromoisobutyrate as the initiator and CuBr/*N*-(*n*-hexyl)-2-pyridylmethaneimine as a catalyst. After chain extension reaction with *n*-butyl acrylate, the diblock was reacted with aminopentanol in DMSO at 25 °C.[41] However, the two hydroxyl groups may react at different rates in subsequent reactions since they are attached to differently substituted C atoms. Therefore, there is an interest in preparing telechelic polymers with the same functional end group on each chain end.

A new approach for the preparation of telechelic polymers that avoids this hetero-telechelicity problem is atom transfer radical coupling (ATRC) of end-functionalized chains. In the ATRC process macroradicals, generated in situ by an atom transfer radical equilibrium, participate in termination reactions by coupling in the presence of a reducing agent, such as nanosize copper, zerovalent iron, tin octanoate ($SnOct_2$), and ascorbic acid.[42−44] However, currently only telechelic polystyrene has been synthesized via ATRC.[45,46] ATRC of polyacrylate chains has been so far unsuccessful due

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to much lower concentration of radicals formed in the ATRP equilibrium of acrylates than styrene.

In this article we introduce a new strategy for coupling of polyacrylate chains and report the synthesis of hydroxy-telechelic polystyrene and poly(methyl acrylate) obtained through ATRC of HO-precursors.

Experimental Section

Materials. Styrene (Acros, 99%) was dried over CaH_2 and then distilled under reduced pressure (65 °C/35 mmHg). Methyl acrylate (MA, Acros, 99%) was stirred over CaH_2 overnight and distilled under argon before use. CuBr (Acros, 98%) was purified according to a procedure previously described.[44] Toluene (Fisher, 99.8%) and acetone (Fisher, 99.7%) were distilled and stored under nitrogen. Immediately before use both monomers and solvents were purged with N_2 for at least 30 min. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) and 1,4,8,11-tetraazacyclotetradecane (Cy) (Cyclam, Lancaster) were used as received. Tris(2-dimethylaminoethyl)amine (Me_6-TREN) was prepared as previously described.[47] 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.

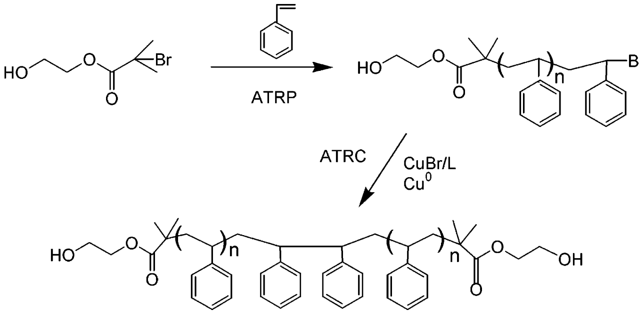
Synthesis of Hydroxy-Functionalized Initiator. A 500 mL round-bottom flask equipped with a magnetic stirrer was charged with 18.6 g (0.3 mol) of ethylene glycol (Aldrich, 99.8%), 41.28 g (0.2 mol) of *N,N′*-dicyclohexylcarbodiimide (DCC, Acros, 99%), 33.4 g (0.2 mol) of 2-bromo-2-methylpropionic acid (Aldrich, 98%), and 200 mL of methylene chloride. The solution was cooled in an ice−water bath, and 4-(dimethylamino)pyridine (248 mg, 2 mmol) was added under stirring. The reaction mixture was kept in the cooling bath for 5 min and then allowed to warm to room temperature and stirred overnight. Precipitated dicyclohexylurea was filtered off and washed twice with 25 mL of methylene chloride on the filter. The solvent was removed by rotary evaporation. The crude initiator, 2-hydroxyethyl 2-bromoisobutyrate (HO-BriBu), was purified by gradient column chromatography, using 4/1 to 2/3 v/v mixtures of hexane/ethyl ether. The 500 MHz ^{1}H NMR spectrum showed a clean product, free of difunctional initiator. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.92 (s, 6H, $C(CH_3)_2$), 2.39 (s, OH), 3.82 (t, 2H, $-CH_2OH$), 4.28 (t, 2H, OCH_2-).

Polymerization Procedure for the Synthesis of Hydroxy-Functionalized Polystyrene (HO-PStBr) and Poly(methyl acrylate) (HO-PMABr). In a typical experiment, CuBr (0.252 g, 1.75 mmol) and $CuBr_2$ (20 mg, 0.087 mmol) were added to a dried Schlenk flask, equipped with a stir bar. 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, 87 mmol) and toluene (0.5 mL), as a GC standard, were added. The complexing agent, PMDETA (0.38 mL, 1.83 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. 2-Hydroxyethyl 2-bromoisobutyrate (368 mg, 1.75 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 and diluted with THF. The solution was filtered through a column filled with alumina, and the polymer (35% conversion) was recovered by precipitation in methanol and dried in a vacuum at 60 °C to constant weight. $M_n = 2550$ g/mol; $M_w/M_n = 1.08$.

The same procedure was used for the synthesis of HO-PMABr at 50 °C, using 7.9 mL (0.087 mol) of methyl acrylate and 5 mL of acetone as a solvent. After passing the solution through a column filled with alumina, the residual solvent was removed under vacuum, at 60 °C, in a rotary evaporator. Conversion after 2 h was 37%, and $M_n = 1880$ g/mol and PDI = 1.05.

Coupling Reactions. To couple the hydroxy-functionalized polystyrene, HO-PStBr ($M_n = 2500$ g/mol) (0.9 g, 0.36 mmol), synthesized as previously described, and CuBr (56 mg, 0.36 mmol) were charged to a Schlenk flask. The flask was evacuated and backfilled with nitrogen, then 10 mL of toluene was added. When the polymer was completely dissolved, PMDETA (150 μL, 0.73 mmol) was introduced, and three freeze−pump−thaw cycles were performed. Nanosize copper (92 mg, 1.46 mmol) was then 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 4 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. The resulting polymer had $M_n = 4910$ g/mol and $M_w/M_n = 1.21$. The efficiency of coupling, $x_c = 0.98$, was estimated from molecular weight of the polymeric precursor and the coupling product, using an equation previously described for ATRC.[44]

Scheme 1. Synthesis of Hydroxy-Telechelic Polystyrene by ATRC



The procedure for coupling of hydroxy-functionalized poly(methyl acrylate) was similar to that of HO-PStBr. In a typical experiment, 1.8 g (0.96 mmol) of HO-PMABr ($M_n = 1880$ g/mol), 150 mg (0.96 mmol) of CuBr, 10 mL of toluene, 110 μL (0.96 mmol) of styrene, 0.4 mL (1.92 mmol) of PMDETA, and 243 mg (3.83 mmol) of nanosize copper were reacted at 70 °C for 5 h. In some experiments the molar ratios between reagents were varied in order to study their influence on the reaction.

Analyses. Monomer conversion was 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.). 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, and 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). NMR spectra were recorded on a 500 MHz Bruker spectrometer, using $CDCl_3$ as a lock solvent and TMS as a standard.

Results and Discussion

ATRC of Hydroxy-Functionalized Polystyrene. In the ATRC process, the equilibrium between active and dormant species is affected by suppressing the deactivation reaction through the addition of a sufficient amount of reducing agent, e.g., zerovalent metal. As a result, the formed macroradicals are not efficiently deactivated, thus favoring the bimolecular termination.[44] The synthesis of hydroxy-telechelic polystyrene through ATRP followed by coupling of HO-PStBr chains in the presence of Cu^0 is illustrated in Scheme 1.

Since only bromine-terminated chains can generate macroradicals via an atom transfer process, preservation of high chain end functionality is essential when forming polymers suitable for the coupling process. Therefore, during the syntheses of the hydroxyl-

Table 1. Synthesis of Telechelic HO-PSt-OH by ATRC

expt	$[\text{HO-PStBr}]_0$	$[\text{CuBr}]_0$	$[\text{ligand}]_0$	$[\text{Cu}^0]_0$	time (h)	$M_{n,0}$	$M_{n,c}$	$x_c{}^a$
1	1	1	2	1	3	4660	6640	0.60
2	1	1	2	2	2	3200	5080	0.74
3	1	1	2	2	3	4660	8100	0.85
4	1	1	2	4	2	3200	5880	0.91
5	1	1	2	4	3	4660	9030	0.97
6	1	1	2	4	3	1870	3630	0.97
7	1	1	2	4	3	1870	3640	0.97
8	1	1	2	4	3	2500	4910	0.98

[a] $[\text{HO-PStBr}]_0 = 22.6$ mmol L^{-1}; ligand: PMDETA; solvent: toluene; temperature: 70 °C.

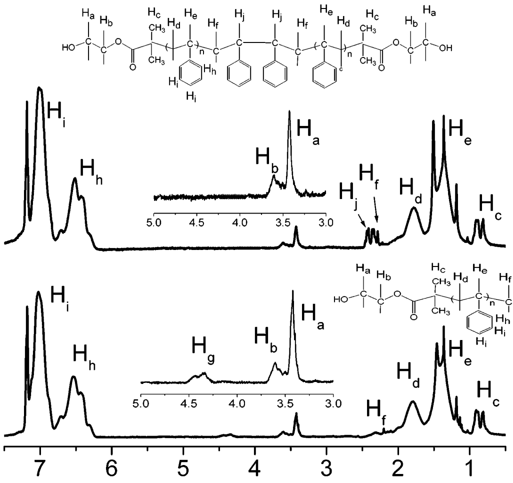


Figure 1. 500 MHz ^{1}H NMR spectra of HO-PStBr ($M_n = 2500$, $M_w/M_n = 1.08$) and its telechelic coupling product. $[\text{HO-PStBr}]_0$:$[\text{CuBr}]_0$:$[\text{PMDETA}]_0$:$[\text{Cu}^0]_0$ = 1:1:2:4; $[\text{HO-PStBr}]_0 = 22.6$ mmol L^{-1}; solvent: toluene; temperature: 70 °C; 3 h.

functional polystyrene and poly(methyl acrylate) precursors the reactions were stopped at low conversion to preserve the halogen chain end.

The chain end functionality was estimated from 500 MHz ^{1}H NMR spectra, since signals due to both chain ends (R and X functionality) are detectable. Figure 1 presents the ^{1}H NMR spectra of hydroxy-functionalized polystyrene prepared by ATRP and the resulting telechelic product. The signals at 3.42 and 3.61 ppm are characteristic for methylene-oxy protons (H_a and H_b) from the initiating 2-hydroxyethyl 2-bromoisobutyrate group (R functionality). As can be observed, the signal for protons H_b is shifted upfield due to shielding of those protons by aromatic rings in the chain. The signal from 4.34 to 4.46 ppm is attributed to the proton (H_g) 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 located α-position of bromine chain end and the peaks for the methylene-oxy protons from hydroxyethyl group was 1/4.12, thus indicating 97% 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 and H_b protons and the integrals of aromatic region (H_h and H_i at 6.2−7.3 ppm) as well as aliphatic region (H_e and H_d at 1.1−2.1 ppm). Molecular weight estimated from ^{1}H NMR ($DP_n = 21$) agreed well with GPC data, indicating that polymer chains were predominantly initiated by the alkyl halide, while the contribution of thermal self-initiation and transfer reactions was negligible. The peak at 0.81−0.92 ppm corresponds to H_c methyl protons from the initiating group.

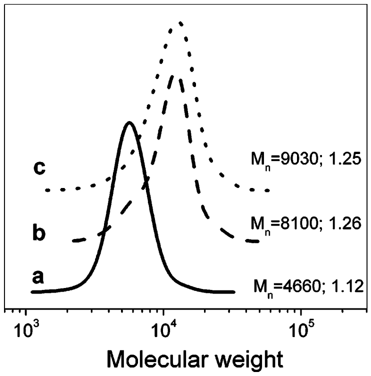


Figure 2. GPC traces for HO-PSt-Br precursor (a) and its coupling products. $[\text{HO-PStBr}]_0$:$[\text{CuBr}]_0$:$[\text{PMDETA}]_0$:$[\text{Cu}^0]_0$ = 1:1:2:2 (b) and $[\text{HO-PStBr}]_0$:$[\text{CuBr}]_0$:$[\text{PMDETA}]_0$:$[\text{Cu}^0]_0$ = 1:1:2:4 (c). $[\text{HO-PStBr}]_0 = 22.6$ mmol L^{-1}; solvent: toluene; temperature: 70 °C; 3 h.

In the ^{1}H NMR spectrum of the hydroxy-telechelic coupling product the signals corresponding to H_a and H_b protons from the initiating group are still detectable, while the signal of the proton (H_g) located in the α-position of the bromine end functionality was absent, suggesting a high degree of coupling. Instead, a new signal was observed at 2.36 ppm, corresponding to H_j protons, as was confirmed from HSQC (heteronuclear single quantum correlation) experiments that correlate the chemical shift of proton with the chemical shift of the directly bonded carbon as well as from ^{1}H−^{1}H COSY NMR.

The efficiency of the ATRC process (60−98%) was estimated from the extent of coupling (x_c), which correlates the molecular weights of the product ($M_{n,c}$) and precursor ($M_{n,0}$): $x_c = 2(1 - M_{n,0}/M_{n,c})$.[44]

The synthesis of hydroxy-telechelic polystyrene by ATRC was performed using highly efficient nanosize Cu^0 in the presence of CuBr as metal halide and PMDETA as a ligand. It was observed that coupling extent increased when the amount of zerovalent metal was increased from 2 to 4 molar ratio compared to precursor (runs 1 vs 3 and 5 and runs 2 vs 4 in Table 1 and Figure 2). This behavior, which was previously observed for coupling of monobrominated PSt, is a consequence of the heterogeneity of the system; i.e., the zerovalent metal Cu^0 is not soluble in the reaction medium. Therefore, the efficiency of this electron transfer process should depend not only on the specific surface but also on the total area of the nanosize Cu^0.

In reactions conducted with the same amount of reducing agent, changes in molecular weight of the precursor did not affect the coupling efficiency (experiments 6−8 in Table 1). The ATRC process is fast, with ~50% chains being reacted within 1 h (Figure 3).

ATRC of Hydroxy-Functionalized Poly(methyl acrylate). Previously, only ATRC of polysty-

Table 2. ATRC of HO-PMABr

expt	$[\text{HO-PMABr}]_0$	$[\text{CuBr}]_0$	$[\text{ligand}]_0$	$[\text{Cu}^0]_0$	$[\text{St}]_0$	time (h)	$M_{n,0}$	$M_{n,c}$	x_a[a]
1	1	1	1	4	0	61	1630	1750	0.14
2[a]	1	1	2	4	0	24	1630	1880	0.27
3[b]	1	1	2	4	0	42	1630	2230	0.54
4[b]	1	1	2	4	5	3	1630	3250	>0.99
5	1	1	2	4	5	3	1630	3250	>0.99
6	1	1	2	4	2	3	1630	3230	>0.99
7	1	1	2	4	1	2	4340	8600	0.86
8	1	1	2	4	1	3	4060	7420	0.90
9	1	1	2	4	1	4	3120	5750	0.92
10	1	1	2	4	1	5	1880	3560	0.94
11	1	1	2	4	0.5	20	4340	6240	0.6

[a] Me6TREN was used as ligand. [b] Cy as ligand; $[\text{HO-PMABr}]_0 = 60$ mmol L^{-1}; ligand: PMDETA; solvent: toluene; temperature: 70 °C.

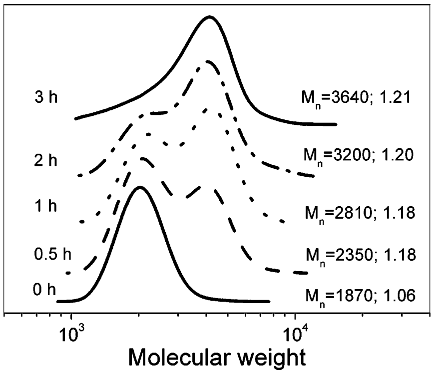


Figure 3. Dependence of molecular weight distribution upon time for ATRC of HO-StBr $[\text{HO-PStBr}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0:[\text{Cu}^0]_0 = 1:1:2:4$; $[\text{HO-PStBr}]_0 = 22.6$ mmol L^{-1}; solvent: toluene; temperature: 70 °C.

rene has been reported. The coupling of poly(methyl acrylate) chains is unattainable in a reasonable time because its ATRP equilibrium constant of a halo-terminated polyacrylates is approximately 10−100 times lower than that of the same halo group on a polystyrene.[14,48−50] Since termination is a bimolecular process, the coupling of poly(methyl acrylate) radicals is over 2 orders of magnitude slower than for polystyrene homologues. Attempts to couple HO-PMABr showed an extent of coupling $x_c = 0.14$ after 61 h when PMDETA was used as a ligand (run 1 in Table 2).

When either Me_6TREN or Cy was employed as the ligand, both of which give more active copper-based catalysts, the extent of coupling was increased, but the process was still very slow (runs 2 and 3 in Table 2).

However, when the ATRC process is conducted in the presence of a small amount of styrene, this monomer will react with acrylate radicals—produced from the activation step in the presence of copper halide—and thus will form styrene-terminated macroradicals. The newly formed species can combine in a manner similar to polystyrene chains. The product of the coupling reaction remains preponderantly a polyacrylate in nature, and consequently this linking monomer unit does not alter its properties (Scheme 2).

When an excess of styrene was added to the ATRC mixture, the coupling was fast with both Cy and PMDETA as ligand (runs 4 and 5 in Table 2). The broadening of molecular weight distribution observed upon coupling is probably due to secondary reactions, which were previously reported for ATRC of monobrominated polystyrene.[44] Similar results were obtained when the ratio $[\text{HO-PMABr}]_0/[\text{St}]_0$ was reduced to 2 (run 6 in Table 2 and Figure 4).

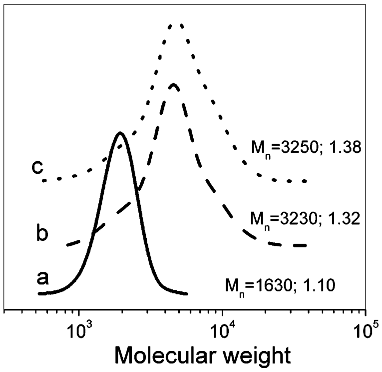
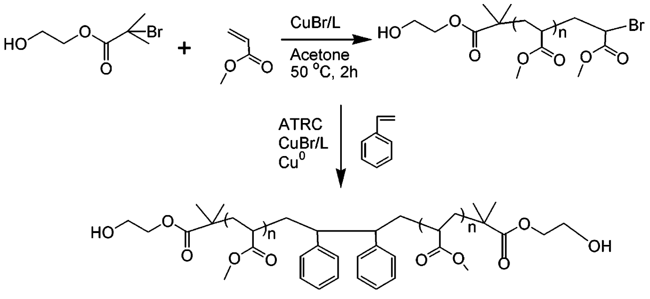


Figure 4. GPC traces for HO-PMABr precursor (a) and the products of ATRC in the presence of excess of styrene $[\text{HO-PMABr}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0:[\text{Cu}^0]_0:[\text{St}]_0 = 1:1:2:4:2$ (b) and $[\text{HO-PMABr}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0:[\text{Cu}^0]_0:[\text{St}]_0 = 1:1:2:4:5$ (c). $[\text{HO-PMABr}]_0 = 60$ mmol L^{-1}; solvent: toluene; temperature: 70 °C.

Scheme 2. Synthesis of Hydroxyl-Telechelic Poly(methyl acrylate) by ATRP Followed by ATRC



When equimolar amounts of styrene vs polyacrylate precursor were used in the ATRC, the extent of coupling was sufficiently high, over 85% of chains being reacted in 2 h (run 7 in Table 2). The extent of coupling improved up to 0.94 by increasing the reaction time to 3, 4, and 5 h (runs 8−10 in Table 2). However, decreasing the amount of styrene below equimolar leads to an incomplete coupling, even for long reaction time (run 11 in Table 2). Figure 5 comparatively presents GPC traces for ATRC of HO-PMABr in the presence of low amounts of styrene.

It seems that not only PMA*−PMA* coupling but also PMA*−PMASt* coupling is slow in comparison with PMASt*−PMASt* coupling. Fortunately, polystyrene propagation (PSt* + St) is much slower than cross-propagation (PMA* + St), and therefore 1 equiv of St is sufficient.

The NMR spectroscopy was used to study the coupling of poly(methyl acrylate) in the presence of styrene. Figure 6 presents the ^{1}H NMR spectra of the precursor

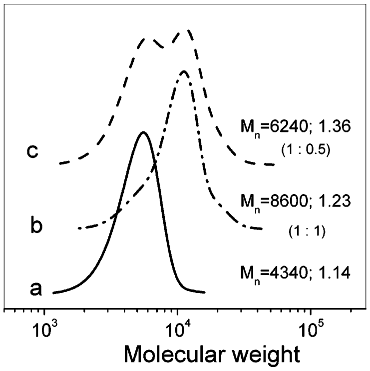


Figure 5. GPC traces for HO-PMABr precursor (a) and the products of ATRC in the presence of styrene in low concentrations $[\text{HO-PMABr}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0:[\text{Cu}^0]_0:[\text{St}]_0$ = 1:1:2:4:1 (b) and $[\text{HO-PMABr}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0:[\text{Cu}^0]_0:[\text{St}]_0$ = 1:1:2:4:0.5 (c). $[\text{HO-PMABr}]_0$ = 60 mmol L^{-1}; solvent: toluene; temperature: 70 °C.

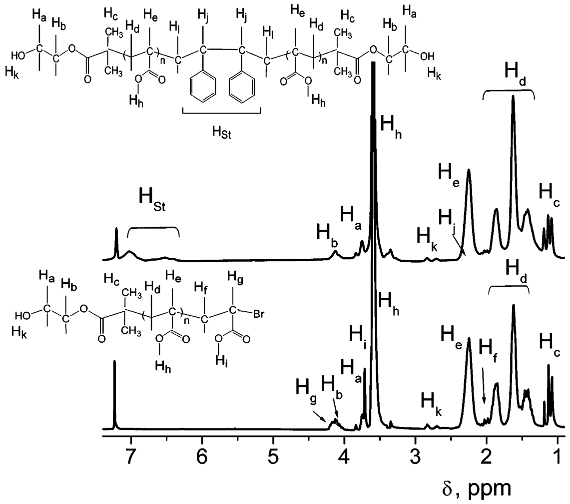


Figure 6. 500 MHz ^{1}H NMR spectra of HO-PMABr (M_n = 1880, M_w/M_n = 1.05) and its telechelic coupling product. $[\text{HO-PMABr}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0:[\text{Cu}^0]_0:[\text{St}]_0$ = 1:1:2:4:1; $[\text{HO-PMABr}]_0$ = 60 mmol L^{-1}; solvent: toluene; temperature: 70 °C; 5 h.

hydroxy-functionalized poly(methyl acrylate) and the resulting hydroxy-telechelic product after coupling in the presence of St. The signals at 3.78 and 4.14 ppm correspond to methylene-oxy protons (H_a and H_b) from the initiating 2-hydroxyethyl 2-bromoisobutyrate group, while the signal at 4.25 ppm—partially overlapped with signal H_b—is attributed to the proton (H_g) located in the α-position of the bromine chain end. ^{1}H−^{1}H COSY NMR evidenced two types of protons in the region from 4 to 4.3 ppm. Proton H_g, at 4.25 ppm, showed internal connectivity with two nonequivalent H_f protons. Protons at 4.15 ppm were coupled with protons at 3.78 ppm; they are methylene-oxy protons (H_b and H_a) from the initiating group (Figure 7a). Protons H_a showed also connectivity with proton H_k from the HO group. The degree of polymerization (DP_n) was calculated from the ratio of the integrals of methyl protons from the initiating group (H_c at 1.03−1.13 ppm) and the integrals of aliphatic region (H_d and H_e at 1.4−2.04 ppm) as well as methyl protons from ester groups (H_h at 3.6 ppm). Molecular weight estimated from ^{1}H NMR (DP_n = 18) agreed well with GPC data, indicating that polymer chains were predominantly initiated by the alkyl halide.

The ^{1}H NMR spectrum of the coupling product of poly(methyl acrylate) in the presence of equimolar amount of styrene and polymer showed the signals corresponding to methylene-oxy protons (H_a and H_b) from the initiating group, while no signal assignable to the proton located α-position of bromine chain end was detectable (Figure 6). The incorporation of styrene was evidenced by signals corresponding to aromatic protons H_{St} in the region 6.3−7.2 ppm. The ratio of the integrals of aromatic protons and the integrals of the signals corresponding to methylene-oxy protons (H_a and H_b) from the initiating 2-hydroxyethyl 2-bromoisobutyrate group (5.15:2), as well as H_c methyl protons from the initiating group (5.15:6.02), indicated the equimolar incorporation of styrene in the coupling product. ^{1}H−^{1}H COSY NMR of the coupling product illustrates only the presence of H_a and H_b protons and absence of correlation between H_g and H_f protons, indicating a high extent of coupling (Figure 7b).

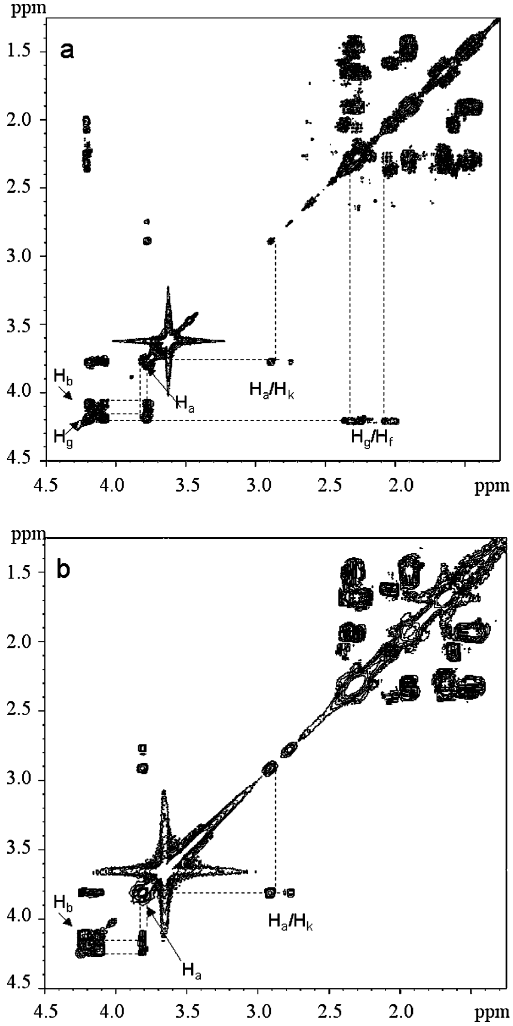
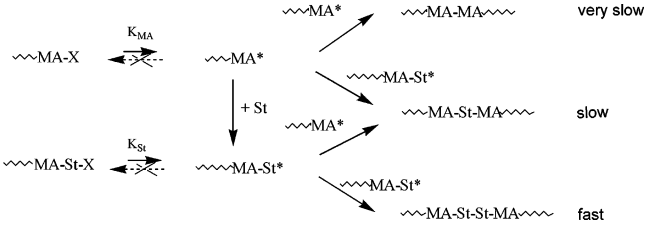


Figure 7. ^{1}H−^{1}H COSY NMR spectra (region 1.3−4.5 ppm) of HO-PMABr precursor (a) and the coupling product (b).

The rationale for the observed behavior of poly(methyl acrylate) coupling in the presence of styrene is illustrated in Scheme 3. Polyacrylate radicals produced in the activation step react fast with styrene, forming polystyrene-type species. Indeed, polyacrylate radicals react with styrene ~400 time faster than polystyrene homologues, as was estimated from their reactivity ratios.[51−53] When less than equimolar amount of styrene is used in ATRC of polyacrylate, both PSt* and PMA* radicals coexist in the system. The ATRP equilibrium constant for methyl acrylate is ~100 times smaller than

Scheme 3. Principle of ATRC of Polyacrylate in the Presence of Styrene



for styrene, and consequently concentration of PMA* radicals is also much smaller than PSt* radicals. Thus, PSt*−PSt* coupling is fast and PMA*−PMA* very slow, but PMA*−PSt* is also slow. Therefore, when $^1/_2$ equiv of St is used, there is fast PMASt*−PMASt* coupling, but half of PMA* chains are left unreacted. This explains the incomplete coupling observed for experiment performed with 0.5 molar ratio styrene/polymer. The most favorable conditions for ATRC of acrylates include an equimolar amount of St against polymer.

Conclusion

ATRP is capable of producing well-defined polymers with high end group functionality. Exploiting this feature, hydroxy-telechelic polystyrene and poly(methyl acrylate) were synthesized by ATRC using monohydroxy macromolecules obtained through ATRP. By adding a sufficient amount of an appropriate reducing agent, such as Cu^0, the equilibrium between active and dormant species was affected, thereby reducing the rate of the deactivation reaction and allowing radical−radical termination reactions, predominately coupling for styrene-based radicals, to occur. The 500 MHz ^{1}H NMR spectra revealed high chain end functionality for both polystyrene and poly(methyl acrylate) hydroxy-functionalized precursors, this being a requirement for an efficient coupling. The effectiveness of the electron transfer coupling process was mediated by the surface area and molar amount of the nanosize zerovalent metal. Although ATRC of polystyrene is a fast process, the coupling of polyacrylate is not viable because its ATRP equilibrium constant is approximately 100 times lower than that of PSt. Since termination is a bimolecular process, the coupling of PMA radicals is about 4 orders of magnitude lower than that of polystyrene. This was demonstrated by the observation that the efficiency of PMA coupling was low, even when ligands forming highly active catalyst complexes were employed. This work provided an efficient approach to overcome this problem; a small amount of styrene was included in the ATRC reaction, producing styrene-terminated radicals that could undergo efficient coupling. When ATRC of PMA was carried out in the presence of styrene, the extent of coupling was high, with the most efficient results obtained using an equimolar amount of styrene to polyacrylate chain end. 1-D and 2-D NMR spectra were effective in estimating the extent of coupling as well as in demonstrating the equimolar incorporation of styrene into the polyacrylate chains during the ATRC process. The telechelic PMA synthesized in this way contains limited units of St, and therefore its nature remains essentially polyacrylate.

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