Studies on the Preparation of α,ω-Telechelic Polymers by the Combination of Reverse Atom Transfer Radical Polymerization and Atom Transfer Radical Coupling Processes

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Monofunctional polystyrenes with cyano, carboxylic acid, and hydroxyl terminal groups were synthesized by reverse atom transfer radical polymerization (RATRP) using corresponding azo initiators in conjunction with copper and iron complexes. These functional polymers were further used in the atom transfer radical coupling (ATRC) reaction in the presence of Cu(I) and Cu(0) in order to obtain telechelic polystyrenes. In the iron-mediated system, while RATRP experiments gave satisfactory results, the corresponding ATRC process yielded polymers with low functionality. The copper-mediated system, however, gave contrary results. In the RATRP step, initiation efficiency was rather low and polymers with relatively higher polydispersity were obtained. ATRC reactions of these polymers were efficient in obtaining telechelics and a maximum extent of coupling $q_{max} = 0.99$ can be attained under appropriate conditions.

Key Words: Reverse atom transfer radical polymerization (RATRP), atom transfer radical coupling (ATRC), azo-initiator, telechelics.

Introduction

Telechelic polymers are important building blocks for the construction of various polymer materials.[1−3] Telechelic polymers having a variety of functional groups are prepared by a wide range of polymerization methods, namely anionic,[4] cationic,[5] ring opening,[6] group transfer,[7,8] free radical,[9] metathesis,[10−17] step growth[1] polymerization, and chain scission[1] processes. Among them, living ionic polymerization methods are usually preferred since they allow the preparation of well-defined telechelics with better control of functionality, molecular weight, and polydispersity. On the other hand, ionic techniques have serious limitations because of the requirement of high purity monomers and solvents, and monomer selectivity.

Telechelics can also be prepared under classical free radical polymerization conditions by using a large amount of functional initiator or performing the polymerization in the presence of a functional transfer

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agent. Free radical copolymerization of olefinic monomers with suitable heterocyclic monomers also yields telechelics: however, non-functionalized end group formation is unavoidable due to the mutual side reactions of the free radical process. Therefore, the overall structure of telechelics was not controlled or well defined. Controlled radical polymerization has recently become an established method for obtaining various polymer architectures, such as block, graft, and star, and gradient/statistical copolymers, hyperbranched polymers, and inorganic/hybrids.[18,19] Atom transfer radical polymerization (ATRP),[19−22] nitroxide-mediated polymerization (or stable radical mediated polymerization (NMP),[23,24] and reversible addition fragmentation transfer (RAFT)[25,26] processes are well-known techniques in this field. Among them, ATRP seemed to be the most versatile method because of its simplicity and applicability to a wide range of monomers. ATRP involves reversible homolytic cleavage of a carbon-halogen bond by a redox reaction between an organic halide (R-X) and a transition metal, such as copper(I) salts. It can also be performed by using conventional azo or peroxy initiators via reverse atom transfer radical polymerization (RATRP).[27]

ATRP provides monofunctional polymers by using functionalized halogenated initiators. The second functional group could be incorporated by transformation of the halogen end group. Such transformation may be realized by means of standard organic procedures, like nucleophilic substitutions or radical additions of allylic compounds; however, these reactions often do not proceed quantitatively and some side reactions, such as elimination, may also occur concomitantly.

We have recently proposed an alternative route for directly obtaining α,ω-telechelics via the combination of ATRP and atom transfer radical coupling (ATRC) processes.[28] The ATRP initiator having aldehyde, tertiary amine, phenolic, and carboxyl groups was used for the styrene polymerization to yield a polymer with the desired chain end at the α-end, and couplings of ω-halide ends were then carried out using the ATRC process (Scheme 1).

= CO, OH, COOH, N(CH$_3$)$_2$, X = Halide, L = Ligand

= polystyrene
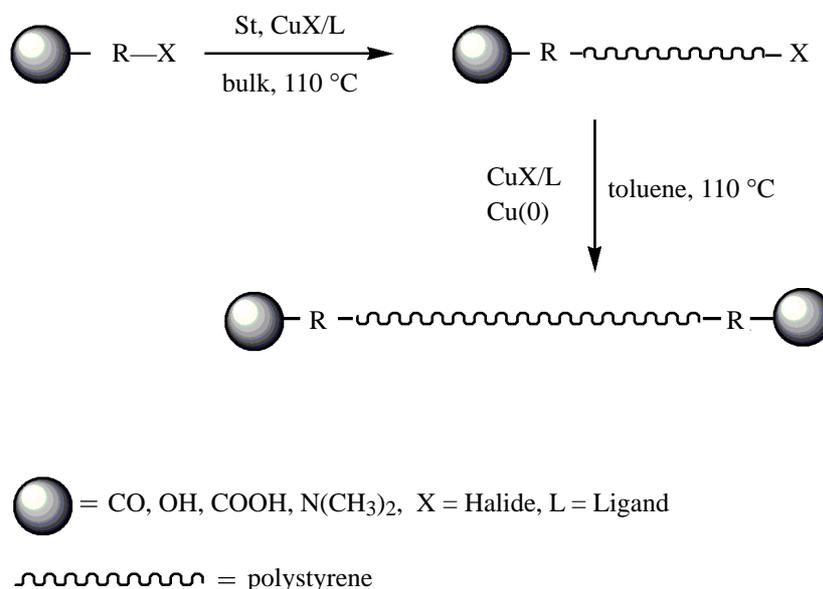
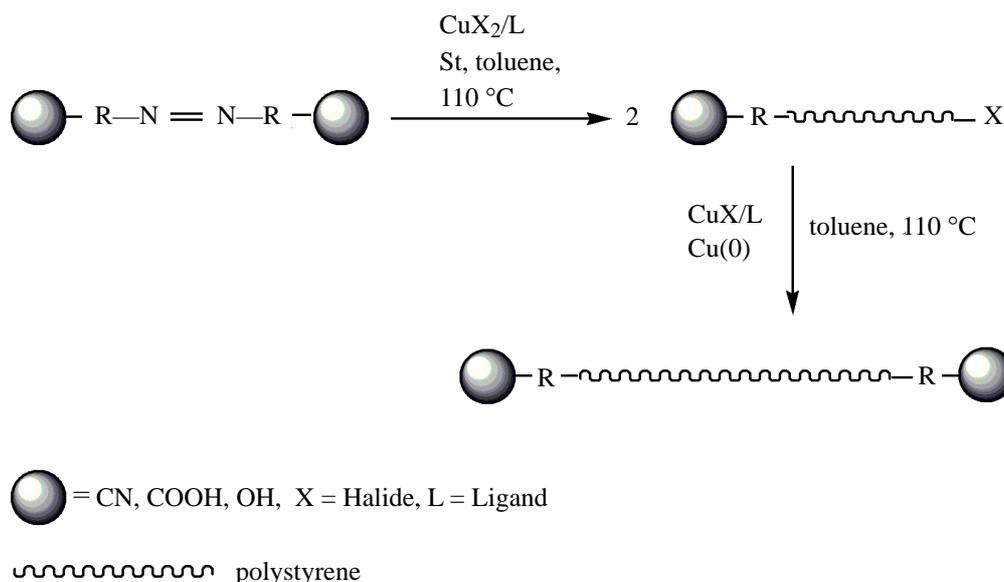**Scheme 1.** Synthesis of α,ω-telechelics via the combination of ATRP and ATRC processes.

Several other successful studies concerning ATRC reactions of different halide terminated polymers have also been reported;[28−33] however, in all these studies the process requires separate synthesis of functional

ATRP initiators via organic reactions, usually involving several steps. In the RATRP process, however, it is not necessary to use alkyl halides. These initiating halides are directly generated from the deactivation of the radicals produced from the conventional initiators by Cu(II) and Fe(III).

It seemed, therefore, appropriate to use functional azo initiators in RATRP to yield monofunctional polymers, directly. This way, alkyl halide is formed by homolytic cleavage of a functional azo initiator. The process proceeds further according to the classical ATRP. The obtained polymers are used in ATRC according to the procedure described in the previous work. The overall process presented in this paper is outlined in Scheme 2.

Scheme 2. Synthesis of α,ω-telechelics via the combination of RATRP and ATRC processes.

Experimental

Materials

Styrene (Merck) was purified by the usual methods, and distilled in vacuum from CaH_2 just before use. Toluene was distilled and dried over Na wire. N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) (Aldrich) was distilled before use. The initiators, namely 2,2′-azobisisobutyronitrile (AIBN) (Aldrich), 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (AMHP) (Wako), 1,1′-azobis(cyclohexane-1-carbonitrile) (ACCN) (Wako), 4,4′-azobis(4-cyanopentanoic acid) (ACPA) (Wako), 2,2-bipyridine (bpy) (Aldrich), and triphenylphosphine (PPh_3) (Fluka), were used without further purification. CuBr (Aldrich), $CuBr_2$ (Aldrich), CuCl (Aldrich), $CuCl_2$ (Aldrich), and $FeCl_3$ (Acros) were used as received.

General Procedure for Reverse Atom Transfer Radical Polymerization (RATRP)

A round-bottom flask equipped with a magnetic stirrer and a lateral neck with a tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Catalyst ($CuBr_2$, $CuCl_2$, $FeCl_3$ or $FeBr_3$), ligand (bpy, PPh_3 or PMDETA), initiator (AIBN, AMHP, ACCN or ACPA, Scheme 3.1), and styrene were introduced under inert atmosphere. The flask was placed in an oil bath warmed to 110 °C or 130

°C, according to the chosen metal/ligand system, and stirred at that temperature for a given time, after which the reaction was stopped and the mixture was diluted with THF, and then finally poured into 10-fold methanol. The solid was collected after filtration and dried in an oven at 40 °C at reduced pressure overnight. The polymers were purified by passing through a silica gel column using THF as eluent and reprecipitated in methanol.

General Procedure for Atom Transfer Radical Coupling (ATRC)

A round-bottom flask equipped with a magnetic stirrer and a lateral neck with a tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Monotelechelic PS obtained by RATRP, catalyst (CuBr or CuCl), ligand (Me$_6$TREN or PMDETA), Cu^0, and toluene (solvent) were introduced into the flask under nitrogen. The flask was placed in an oil bath warmed to 110 °C and stirred at that temperature. After a given time, the system was opened, the solution was concentrated by passing a flow of nitrogen, and the polymer was precipitated in methanol. The solid was collected after filtration and drying at 40 °C in vacuum overnight. Further purification was achieved by passing the polymer through a silica gel column using THF as solvent and reprecipitation in methanol.

Characterization

^{1}H NMR spectra of the samples were recorded on a Bruker 250 MHz spectrometer using tetramethylsilane as the internal standard. FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer. Molecular weights were determined 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 the flow rate was 0.3 mL·min^{-1}; a Waters 410 differential refractometer was used as the detector.

Results and Discussion

RATRP of St

The criterion of a controlled radical polymerization is to maintain the fast equilibrium between the growing radicals and dormant species. In ATRP or RATRP, such equilibrium is achieved with a metal complex that changes between n and $n + 1$ oxidation states. RATRP has already been established for both copper and iron complexes. Here, the initiators of the following structure (Chart), namely ACPA (for acid functionality), AIBN (for cyano functionality), ACCN (for cyano functionality), and AMHP (for hydroxyl functionality), were used as radical sources.[34]

A transition-metal complex (CuCl$_2$/PMDETA, CuBr$_2$/PMDETA, or FeCl$_3$/PPh$_3$) was employed in its higher oxidation state. At higher temperatures and in the presence of the monomer, the initiator system became a conventional ATRP initiating system by decomposition of the radical initiator, forming radicals, which then reacted with the higher transition-state metal to form the polymeric halide, and the complex of the transition metal in its lower oxidation state (Scheme 2).

The polymerizations were performed in bulk, at 110 °C and 130 °C, depending on the transition metal complex used in the reaction. The theoretical molecular weights ($M_{n,th}$) were calculated using the following equation (1).

$$M_{n,th} = \frac{[M_0]}{2[I_0]}(M_w)(\text{conversion}) + M_I \tag{1}$$

M_0 and I_0 are the initial molar concentrations of the monomer and initiator, and M_w and M_I are the molecular weights of the monomer and initiator, respectively.
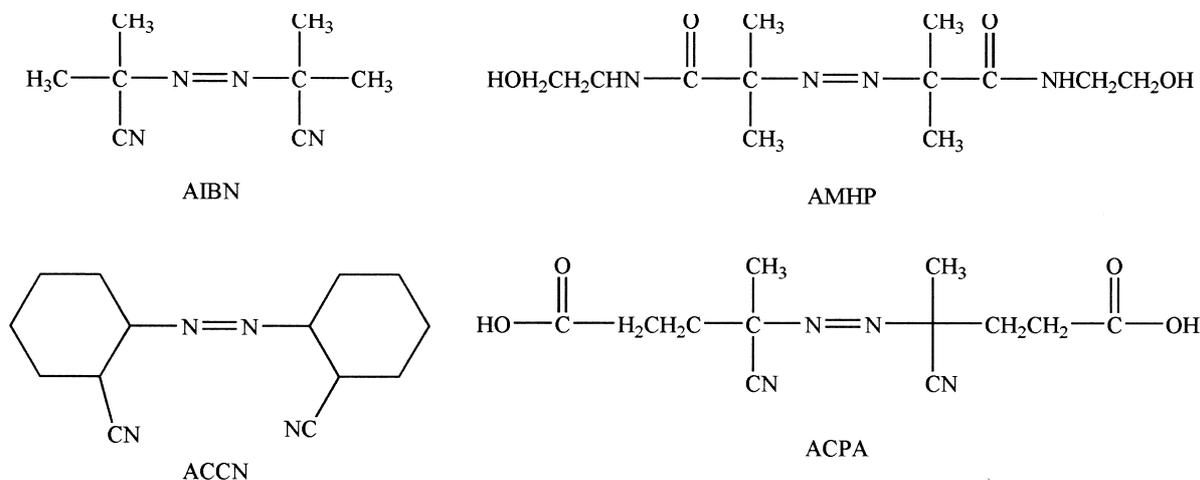
Chart. Structures of the initiators used in RATRP.

$M_{n,NMR}$ were calculated using the values of the integrals of characteristic end peaks for each polymer in comparison with the integrals of aromatic protons of PSt.

Polymerizations were carried out by using 2 different transition metal complexes, $FeCl_3/PPh_3$ and $CuBr_2/PMDETA$. The results for bulk polymerization of St are compiled in Tables 1 and 2.

Table 1. Conditions and results of RATRP of styrene using azo initiators with different functional groups in the presence of the $FeCl_3/PPh_3$ complex.

Initiator	Functional Group	Time (min)	Conversion (%)	$M_{n,NMR}$	$M_{n,GPC}$	M_w/M_n	Polymer
ACPA	COOH	60	11.2	2330	2370	1.74	**R1**
AMHP	OH	90	13.8	2190	2220	1.47	**R2**
AIBN	CN	90	26.8	2940	3180	1.62	**R3**

Temperature: 130 °C; $[St]_0 = 8.75$ mol L^{-1}; $[M]_0:[I]_0:[FeCl_3]_0:[PPh_3]_0 = 200:1:4:12$

Table 2. Conditions[a] and results of RATRP of styrene using azo initiators with different functional groups in the presence of the $CuBr_2/PMDETA$ complex.

Initiator	Functional Group	Time (min)	Conversion %	$M_{n,NMR}$	$M_{n,GPC}$	M_w/M_n	Polymer
ACPA	COOH	30	38.2	8400	8670	1.33	**R4**
ACCN[b]	CN	30	10.8	2950	2670	1.45	**R5**
AMHP	OH	30	82.0	11850	12400	2.26	**R6**

[a] Temperature: 110 °C; $[St]_0 = 8.75$ mol L^{-1}; $[M]_0:[I]_0:[CuBr_2]_0$ $[L]_0 = 50:1:2:2$

[b] Metal halide = $CuCl_2$

As seen from these results, all the azo compounds readily initiated RATRP of styrene. The polymerizations using the $CuBr_2/PMDETA$ ligand system gave higher conversions in shorter reaction times. Although similar polydispersity was attained in both systems, the observed molecular weights were higher when $CuBr_2/PMDETA$ was used.

ATRC of Mono-functional PSt

The RATRP process, regardless of the ligand system utilized, is expected to yield polymers having the functional group coming from the initiator at one end and the bromo function at the other end. The resulting polymers were used in ATRC for the synthesis of α,ω-difunctional polystyrenes (Table 3).

Table 3. Conditions[a] and results of ATRC reactions of polymers with different functional groups.

Monofunctional Polymer	Time (min)	Metal Halide	$M_{n,NMR}$	$M_{n,GPC}$	M_w/M_n	f^b	Coupling Product
R1	4320	CuCl	2980	2820	1.73	0.59	**C1**
R2	4320	CuCl	3330	3030	1.72	0.68	**C2**
R3	2760	CuCl	$-^c$	3660	1.65	0.58	**C3**
R4	2760	CuCl	16430	12780	1.26	0.74	**C4**
R5	1440	CuCl	3930	4190	1.48	0.78	**C5**
R6	4320	CuBr	$-^c$	24750	1.75	0.99	**C6**

[a] Temperature: 110 °C; solvent = toluene; [monofunctional polymer]:[CuCl]:[Ligand]:[Cu^0] = 1:1:2:5 concentration of monofunctional polymer = [monofunctional polymer] = 15×10^{-3} mol L^{-1}

[b] Coupling efficiency = $f = M_{n,GPC}$ (bifunctional polymer)/2 $M_{n,GPC}$ (monofunctional polymer)

[c] Not determined.

Interestingly, the coupling reactions with monofunctional polymers (R1-R3) prepared using FeCl$_3$ resulted in limited efficiency. The ferric salt used in the RATRP step could not be completely removed, even after rigorous filtration and purification processes. The observed low efficiency, up to 60%, may have been due to the participation of these residual Fe species in the redox reactions during the ATRC process. Notably, the coupling reactions with the corresponding copper-derived polymers were more successful and virtually quantitative coupling (C6) could be achieved under appropriate conditions, i.e. by using the CuBr ligand and prolonged reaction times. It should be indicated that the coupling efficiencies were estimated by comparing the molecular weights of the polymer before and after the ATRC process. A typical example for the polymer obtained using C5 is presented in Figure 1.
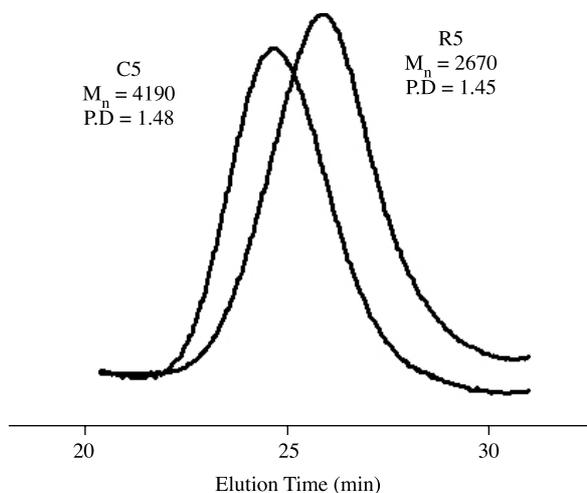

Figure 1. GPC traces of monofunctional PSt R5 and corresponding telechelic PSt C5.

As can be seen, the molecular weight shifted to a higher elution volume indicating successful coupling. The successful coupling was also evidenced by ^{1}H NMR analysis. As can be seen from Figures 2-4, where the spectra were recorded with the initial polymers and the coupling products, the proton located in the α-position of the bromine end group disappeared after coupling in each case. The initiator fragments were also identified; however, the carboxylic acid and hydroxyl protons were not detectable in the ^{1}H NMR spectra, probably due to associations with the traces of water present in the solvent and high molecular weights of the polymers. Similar behavior was observed in the spectra of the commercially available starting initiator and corresponding functionalized polymers.
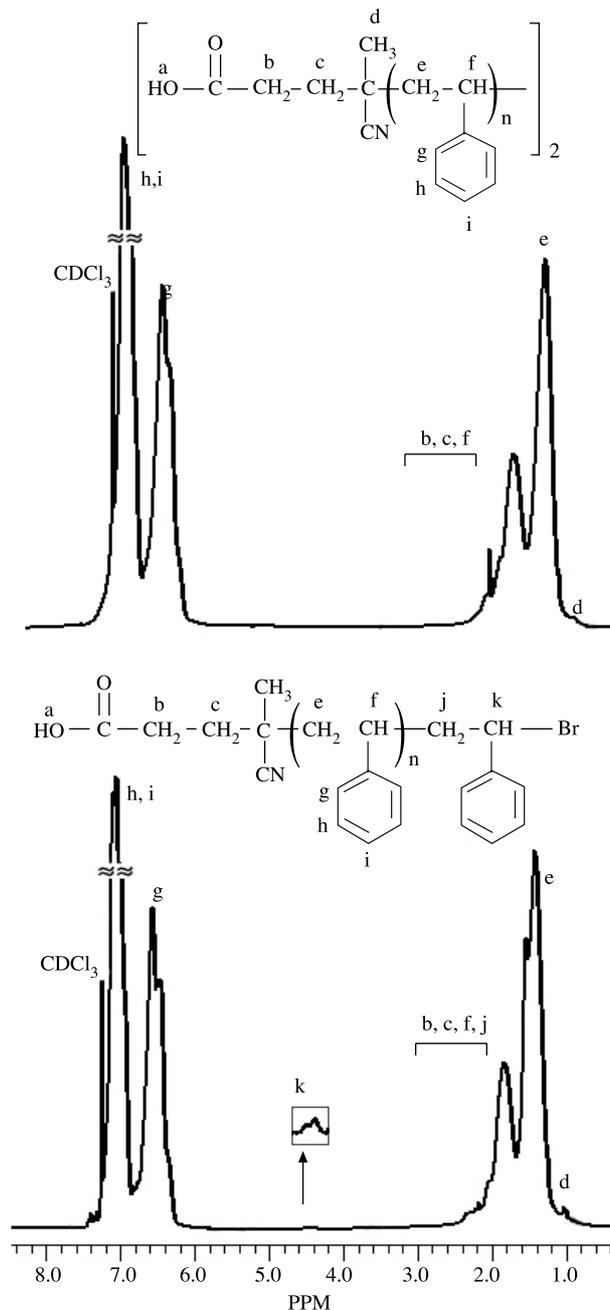
Figure 2. ^{1}H NMR spectra of monofunctional PSt R4 with COOH functionality (CDCl$_3$) and telechelic PSt C4 (CDCl$_3$).
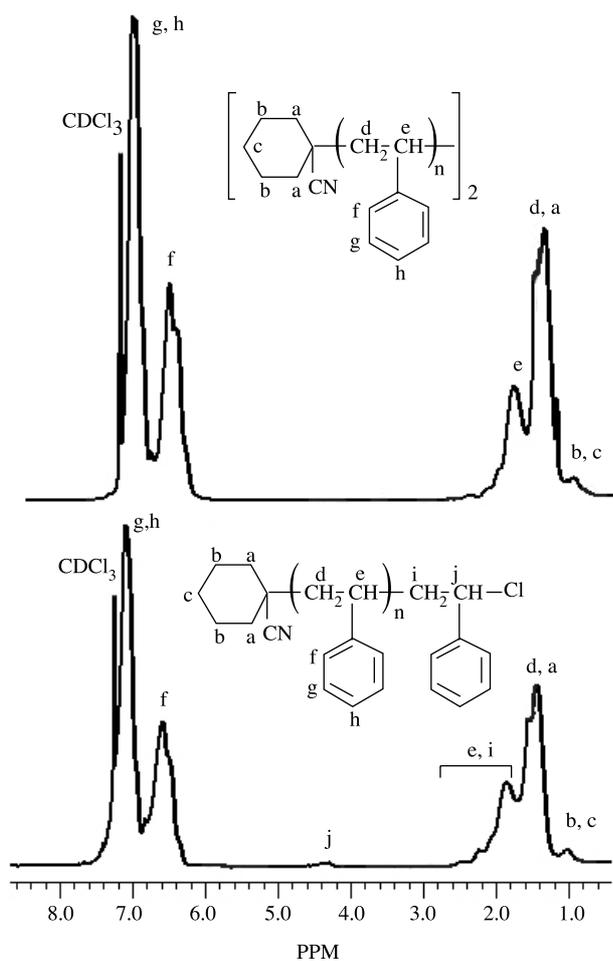
Figure 3. ^{1}H NMR spectra of monofunctional PSt R5 with COOH functionality (CDCl$_3$) and telechelic PSt C5 (CDCl$_3$).
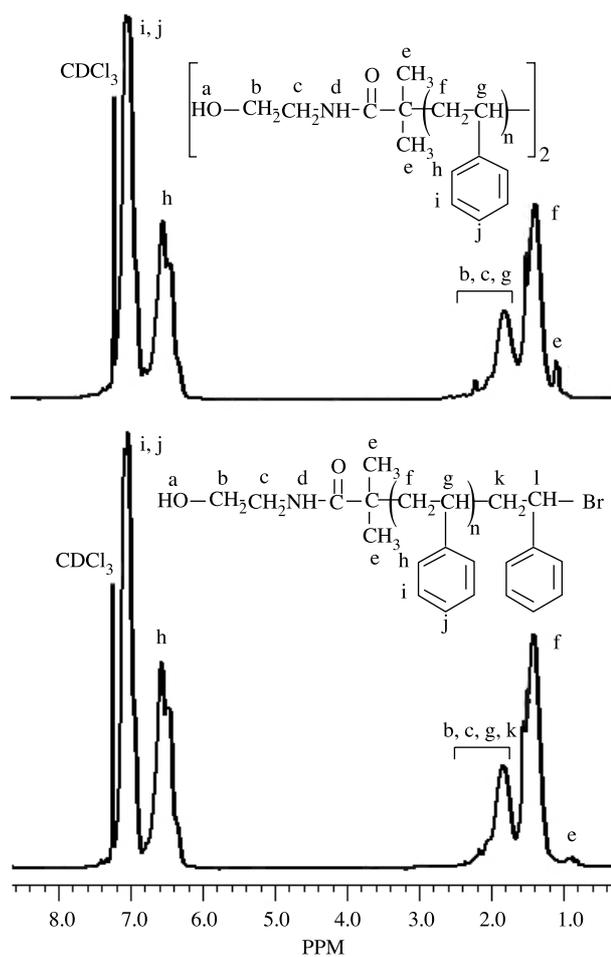
Figure 4. ^{1}H NMR spectra of monofunctional PSt R6 with COOH functionality (CDCl$_3$) and telechelic PSt C6 (CDCl$_3$).

Conclusion

In this work we studied the preparation of α, ω-telechelic polymers of styrene by the combination of RATRP and ATRC processes. Two different initiating systems were applied in conjunction with several functional azo initiators in RATRP for the preparation of monofunctional polystyrenes. Low efficiency was observed with iron-derived polymers in the redox reactions during the ATRC process due to the participation of the residual Fe species, which could not be removed by conventional purification processes. Notably, the coupling reactions with the corresponding copper-derived polymers were more successful and virtually quantitative coupling could be achieved under appropriate conditions, i.e. by using the CuBr ligand and prolonged reaction times, 99% functionalization could be obtained.

Acknowledgment

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