Investigation on Chain Transfer Reaction of Benzene Sulfonyl Chloride in Styrene Radical Polymerization

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Abstract: The free radical polymerization of styrene was initiated with azobis(isobutyronitrile) in the presence of benzene sulfonyl chloride. Analysis of the terminal structures of the obtained polystyrene with ^{1}H NMR spectroscopy revealed the presence of a phenylsulfonyl group at the α-end and a chlorine atom at the ω-end of each polystyrene chain. The terminal chlorine atom in the polystyrene chains was further confirmed through atom transfer radical polymerization (ATRP) of styrene and methyl acrylate using the obtained polystyrenes as macroinitiators and CuCl/2,2'-bipyridine as the catalyst system. GPC traces of the products obtained in ATRP at different reaction times were clearly shifted to higher molecular weight direction, indicating that nearly all the macroinitiator chains initiated ATRP of the second monomers. In addition, the number-average molecular weights of the polystyrenes increased directly proportional to the monomer conversions, and agreed well with the theoretical ones.

Keywords: chain-transfer reactions, benzene sulfonyl chloride, atom transfer radical polymerization (ATRP), block copolymers, telomerization.

Introduction

Free radical additions of sulfonyl halides to olefins catalyzed by transition metals or in the presence of traces of initiators have been studied extensively.[1-13] Recently, sulfonyl chlorides have been used as efficient initiators for transition metal catalyzed atom transfer radical polymerization (ATRP).[14-28] However, as far as we know, there is only one paper in the literature dealing with the chain-transfer reaction of sulfonyl chlorides in the free radical polymerization. Matsuda *et al.*[29] determined chain-transfer constants (C_{tr}) of arene- and alkanesulfonyl chlorides at 60 °C in styrene and methyl methacrylate polymerization using the conventional P_n (degree of polymerization)-C_{tr} relationship. Large C_{tr} values for the polystyrene radical were obtained with the sulfonyl chlorides (0.1-2.6) compared to that with CCl$_4$ (0.007-0.015). They proposed a simple chain-transfer reaction mechanism as shown in eq. (1).

$$\sim\text{P·(polymer radical)}+\text{RSO}_2\text{Cl} \rightarrow \sim\text{PCl}+\text{R SO}_2\text{·} \qquad (1)$$
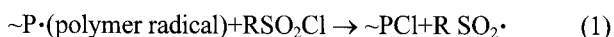
This mechanism is very similar with that of telomerization,[30] which is a convenient method for the preparation of polymers with controlled molecular weights and predetermined functionalities. Several groups used trichloromethyl-

end-grouped poly(vinyl acetate), which was prepared via telomerization of vinyl acetate with CCl$_4$ as a telogen, as a macroinitiator of ATRP for the synthesis of block copolymers.[31-34] In this study, the chain-transfer reaction mechanism of benzene sulfonyl chloride (BSC) in styrene polymerization initiated by azobis(isobutyronitrile) (AIBN) was investigated by analyzing the terminal structures of the obtained polystyrenes with ^{1}H NMR spectroscopy. The polystyrene chain ends were further confirmed through ATRP of styrene and methyl acrylate (MA) using the obtained polystyrenes as macroinitiators.

Experimental

Materials. Styrene (Polymerization grade, Yanshan Petrochemical Co.) and MA (Polymerization grade, Beijing Dongfang Chemical Factory) were dried over CaH$_2$ overnight, distilled under reduced pressure, and stored at -15 °C. BSC (Shanghai Tingxin Chemical Reagent Co.) was distilled under reduced pressure before use. CuCl (Shanghai Reagent Factory) was stirred in glacial acetic acid, washed with ethanol, and then dried in a vacuum oven at 70 °C. Benzene and xylene were dried over anhydrous MgSO$_4$. 2,2'-Bipyridine (bpy, Beijing Shiying Chemical Factory) and all other reagents were used without any further purification.

Polymerization of Styrene in the Presence of Benzene Sulfonyl Chloride. The polymerization of styrene was car-

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ried out in the presence of benzene sulfonyl chloride in benzene at 60 °C using AIBN (1.2×10^{-2} M) as the initiator. In a typical experiment, the mixture of AIBN (0.14 g, 0.854 mmol), styrene (31.2 g, 300 mmol), benzene sulfonyl chloride (1.615 g, 9.148 mmol) and benzene (34 mL) was added to a 100 mL dry round-bottom flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, it was degassed and purged with argon three times and then kept under argon. After the mixture was allowed to stir at ambient temperature for 5 min, the flask was placed in an oil bath thermostated at 60 °C. The polymerization was stopped by pouring the reaction mixture into a large amount of cold methanol.

ATRP with Polystyrenes Obtained Above as Macroinitiators. In a typical experiment, the polystyrenes obtained above (2.518 g, $M_{n, GPC}$ = 9,050, M_w/M_n=1.37), CuCl (0.0297 g, 0.3 mmol) and bpy (0.0936 g, 0.6 mmol) were added to a 50 mL two-necked round-bottom flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, it was degassed and purged with argon three times and then kept under argon. A mixture of deoxygenated styrene (4.264 g, 41 mmol) and xylene (4.7 mL) was added to dissolve the macroinitiators. After the macroinitiator had been dissolved, the flask was immersed in an oil bath thermostated at 110 °C. At definite time intervals, portions of the sample were withdrawn from the flask using an argon-filled gas-tight syringe to determine monomer conversions and molecular weights.

Characterization. Monomer conversion was determined gravimetrically. The number-average molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC) equipped with Waters Microstyragel columns (HR3, HT3, and HT4) and Waters 515 High Performance Liquid Chromatography (HPLC) with a 410 refractive index detector. Measurements were conducted in distilled tetrahydrofuran (THF) at a flow rate of 1 mL/min at 30 °C. Polystyrene standards were used to generate the calibration curve. ^{1}H NMR spectra were recorded on a Bruker AV600-MHz spectrometer with CDCl$_3$ as the solvent and tetramethylsilane as an internal standard.

Results and Discussion

The polymerization of styrene was carried out in the presence of BSC in benzene at 60 °C using AIBN as initiator and stopped at a low conversion (<15%). Chain-transfer constant of BSC, C_{tr}, was determined using the following equation:

$$1/P_n = 1/P_{n0} + C_{tr}[BSC]_0/[St]_0 \qquad (2)$$

where P_n and P_{n0} are the degrees of polymerization in the presence and the absence of BSC, and $[BSC]_0$ and $[St]_0$ are the initial concentrations of BSC and styrene, respectively. Figure 1 shows the relationship between $1/P_n$ and $[BSC]_0$/
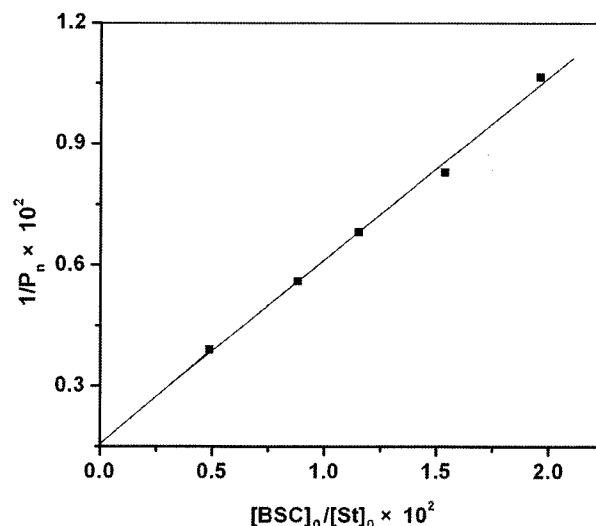

Figure 1. Plot of $1/P_n$ vs. $[BSC]_0/[St]_0$ for styrene radical polymerization in benzene at 60 °C initiated with AIBN.

$[St]_0$. It can be seen that the plot of $1/P_n$ vs $[BSC]_0/[St]_0$ was a straight line. C_{tr} was then equal to the slope of this straight line, which was 0.451. This value was very close to that (0.443) reported by Matsuda[29] in the styrene bulk polymerization system and was much bigger than those of CCl$_4$ (0.007-0.015 at 60 °C) and C$_6$H$_5$CCl$_3$ (0.00575 at 60 °C),[35] showing that benzene sulfonyl was benefit for the transfer of chlorine atom.

The terminal structures of the obtained polystyrenes were analyzed by ^{1}H NMR spectroscopy. Three polystyrene samples with relatively low molecular weights were investigated, which were obtained at higher BSC concentrations (see Table I). In order to remove all the impurities including residual BSC and AIBN, the polystyrene samples were precipitated in excess methanol from THF solution and dried under vacuum at room temperature. Figure 2 shows the ^{1}H NMR spectra of the polystyrenes. The signals at 6.30-7.20 and 1.29-2.20 ppm are the characteristic signals of polystyrene segments. The peaks **b** at 3.09-3.30 ppm and **c** at 4.28-4.56 ppm correspond to the signals of the methylene protons next to the sulfonyl group and the end-standing methine proton next to the chlorine atom, respectively. The signal **a** at 7.28-7.47 ppm is ascribed to the five aromatic

Table I. The Comparison of Number-average Molecular Weight Determined by GPC with Those by ^{1}H NMR

Sample No.	$[BSC]_0/[St]_0^*$	I_b/I_c	$M_{n, GPC}$ (g/mol)	$M_{n, NMR}$ (g/mol)
A	0.10	2.19	3,680	4,100
B	0.05	2.00	6,170	6,670
C	0.03	1.99	9,050	9,390

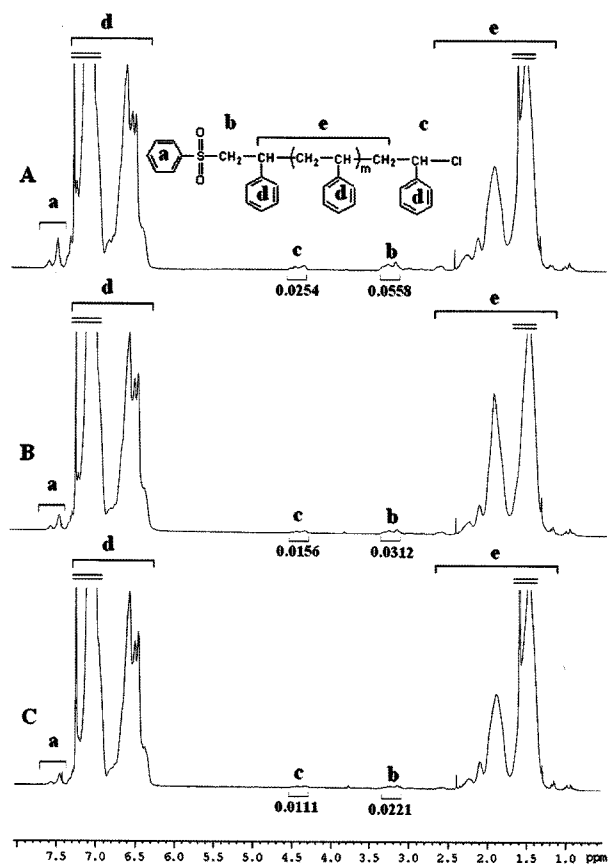*Reaction conditions: $[AIBN]_0$=1.2×10^{-2} M, $[St]_0$=4.196 M, in benzene at 60 °C.

Figure 2. ^{1}H NMR spectra of three polystyrenes obtained in the presence of different amount of BSC. For reaction conditions, see Table I.

Figure 3. GPC traces of polystyrene macroinitiators and the products obtained via ATRP of styrene in xylene at 110 °C. Reaction conditions: $[St]_0$=4.35 M. (A) $[St]_0$:[Macroinitiator $A]_0$:$[CuCl]_0$:$[bpy]_0$=185:1:1:2; (B) $[St]_0$:[Macroinitiator $B]_0$: $[CuCl]_0$:$[bpy]_0$= 105:1:1:2; (C) $[St]_0$:[Macroinitiator $C]_0$:$[CuCl]_0$: $[bpy]_0$=145:1:1:2. For the molecular weights of macroinitiator A, B and C, see Table I.

protons of BSC.

By comparing the integral value of methine proton next to the chlorine atom (c) with that of aromatic protons of polystyrene segments (d), the number-average molecular weights of the polymers could be calculated. The results are listed in Table I. It can be seen that M_n determined by ^{1}H NMR was very close to that by GPC, indicating that there was a chlorine atom per polystyrene chain and no bimolecular coupling termination reaction existed, at least at low monomer conversion. Furthermore, the ratios of I_b/I_c were all about 2.0 (Table I), where I_b and I_c are the integral values of methylene protons next to the sulfonyl group (signal b) and that of methine proton adjacent to the chlorine atom (signal c), implying the incorporation of phenylsulfonyl group ($C_6H_5SO_2$-) and chlorine atom at each end of polystyrene chain.

In order to further confirm that there was one chlorine atom at the ω-end of each polystyrene chain obtained in the presence of BSC as a chain-transfer agent, the polystyrenes thus obtained were used as macroinitiators for ATRP. ATRP was first reported by two groups of Sawamoto and Matyjaszewski independently in 1995.[36,37] It involves the use of an alkyl halide initiator in conjunction with a transition metal complex. The principle of ATRP[38,39] is that the complex, for
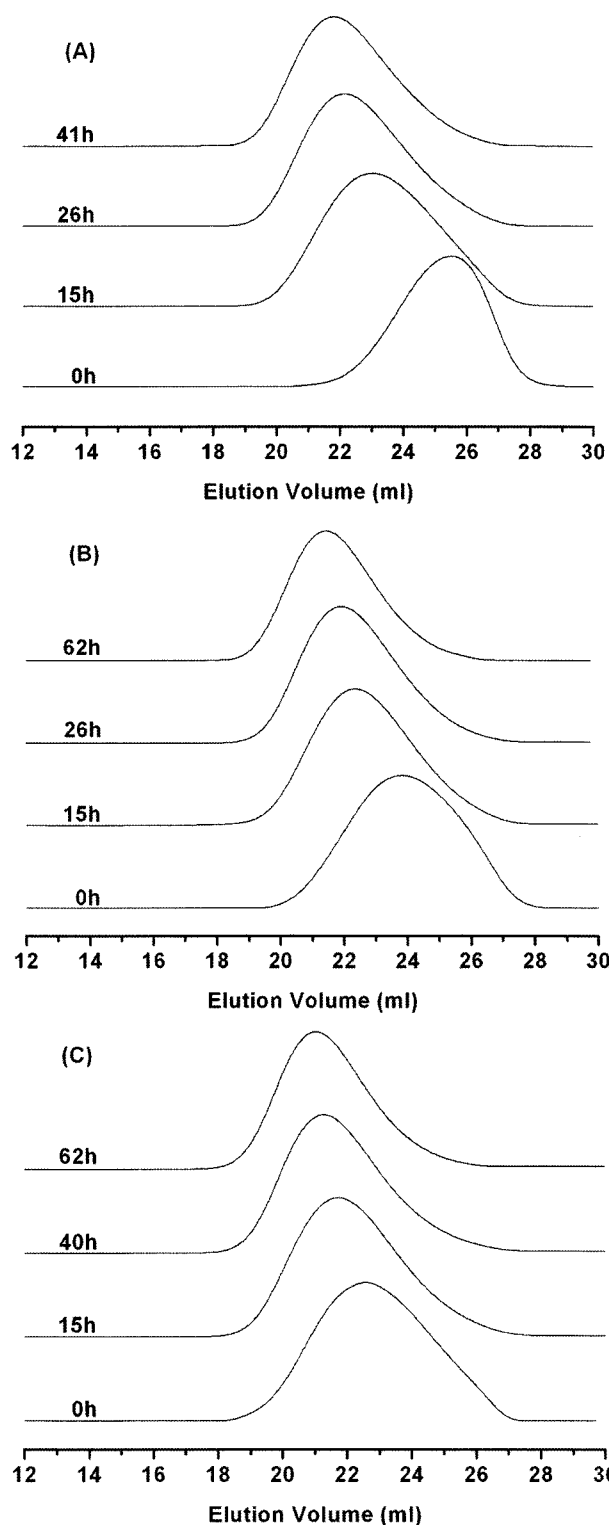
example copper (I) chloride with bipyridine, maintains an equilibrium between active polymeric radicals and dormant polymer chains. This ensures a low concentration of active radicals, minimizing termination reactions. This allows "living" conditions to be maintained during a radical polymerization so that polymers with controlled molecular weights and low polydispersities can be obtained.

The ATRP of styrene was carried out in xylene at 110 °C with three polystyrenes having different molecular weights prepared in the presence of BSC as the macroinitiators and CuCl/bpy complex as the catalyst. The GPC traces of the products obtained at different reaction times are shown in
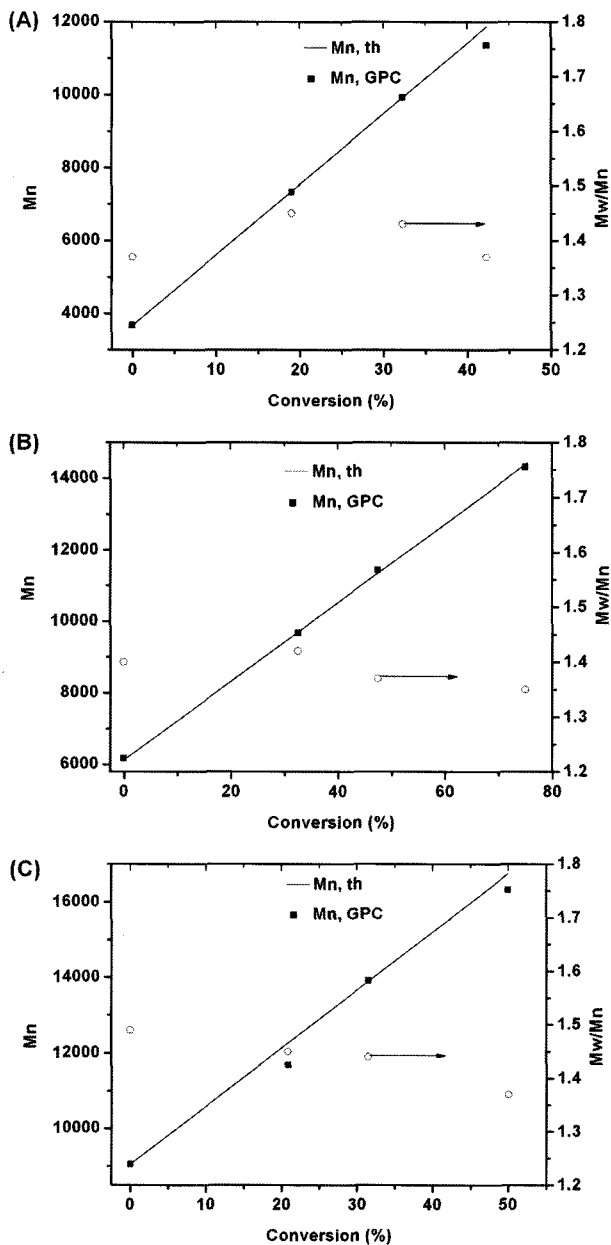
Figure 3. It can be seen that the molecular weights shifted to higher molecular weight direction without any trace of the polystyrene macroinitiators, indicating that all the macroinitiator chains initiated ATRP of styrene. In addition, as shown in Figure 4, the polydispersities were relatively low throughout the polymerization process, and the number-average molecular weights of polystyrenes increased in directly proportional to monomer conversions, and agreed well with the theoretical ones, $M_{n,th}$, which were calculated from the amount of the consumed monomer (Δ[M]), the amount of the macroinitiator ([I]), and the molecular weights of styrene (104 g/mol) and the macroinitiator using the following equation:

$$M_{n,th} = \Delta[M]/[I] \times 104 + M_{n, macroinitiator}$$

(3)

The thermal bulk free radical polymerization of styrene without the use of AIBN and in the presence of BSC was also carried out. The molar ratio of BSC to styrene was 1:14.
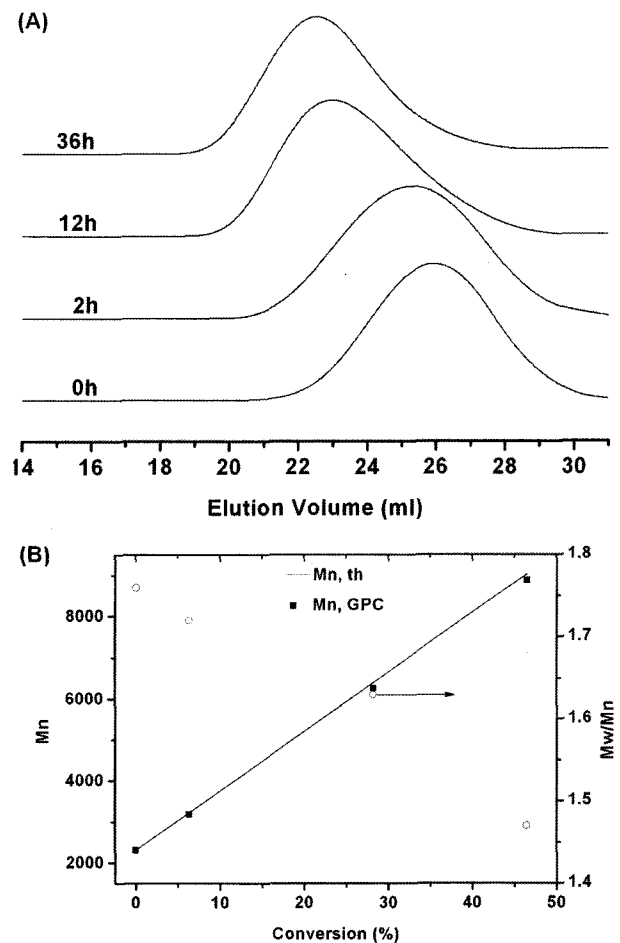

Figure 4. Conversion dependence of number-average molecular weight and M_w/M_n. For reaction conditions, see Figure 3.

Figure 5. GPC traces of the obtained polymers and conversion dependence of number-average molecular weight and M_w/M_n for ATRP of styrene in xylene at 110 °C with thermally polymerized polystyrene as a macroinitiator. Reaction conditions: [St]$_0$=4.35 M. [St]$_0$:[Macroinitiator ($M_{n, GPC}$= 2,310 g/mol)]$_0$:[CuCl]$_0$:[bpy]$_0$= 139:1:1:2.

After reaction for 25 h, the polymerization was stopped by pouring the reaction mixture into a large amount of cold methanol. The monomer conversion was 85 %, and the number-average molecular weight of the obtained polymer determined by GPC was 2,310 g/mol. This polymer was also used as macroinitiator for ATRP of styrene with CuCl/ bpy as a catalyst. The results are shown in Figure 5.

A halogen telechelic polymer can be used as the macroinitiator for the ATRP of a second monomer. In this respect, styrene-acrylate block copolymers prepared by ATRP with chlorine-ended polystyrene as macroinitiator were reported as early as 1995.[37,40] Therefore, ATRP of methyl acrylate initiated by polystyrene chain obtained with BSC as a chain-transfer agent was also carried out to further verify that there was one chlorine atom at the ω-end of polystyrene chain.

Figure 6 shows the GPC traces of the polymerization products and polystyrene macroinitiator. It can be seen that the molecular weights shifted to higher molecular weight direction obviously, indicating that most of the macroinitiator chains initiated ATRP of methyl acrylate and styrene-methyl acrylate block copolymers were obtained successfully.

The ^{1}H NMR spectrum of one styrene-methyl acrylate block copolymer is shown in Figure 7. The peaks for the five aromatic protons (**a**) of BSC and the methylene protons (**b**) next to the sulfonyl group still existed, and the characteristic signal **f** at 3.66 ppm for methyl protons of poly (methyl acrylate) appeared. The triplet peaks **h** at about 4.34 ppm were attributed to the signal of the end-standing methine proton next to the chlorine atom. By comparing the integral value of peak **h** with that of methoxyl protons **f**, the number-average molecular weight of the block copolymer could be calculated to be 5,680, which was about equal to that deter-
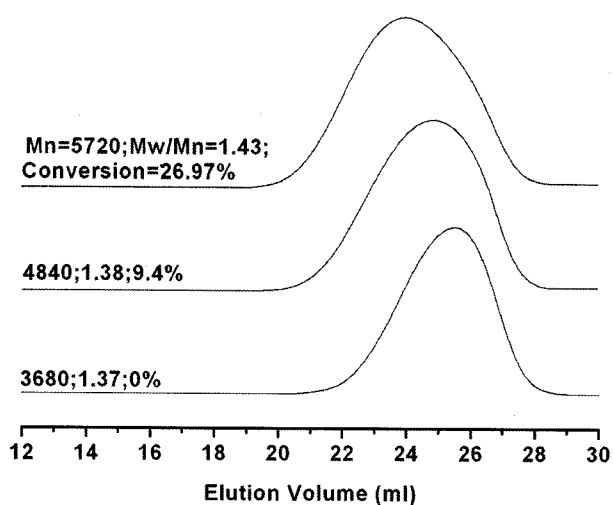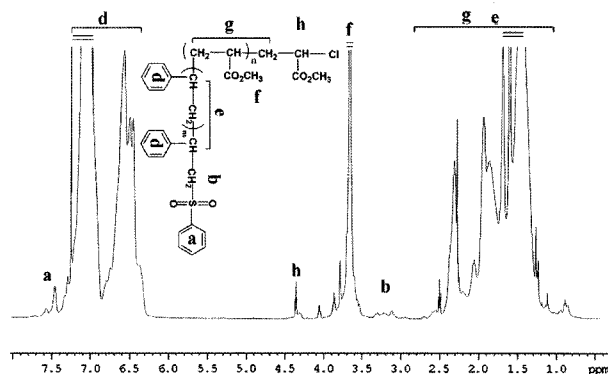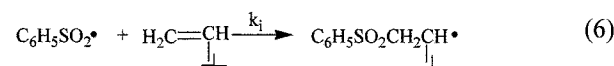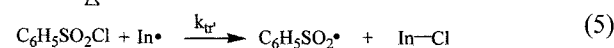

Figure 7. ^{1}H NMR spectrum of styrene-methyl acrylate block copolymer.

mined by GPC (5720). The above results confirmed that well-defined styrene-methyl acrylate block copolymers were obtained.
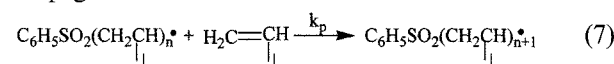
Conclusions

According to the above results, the following mechanism for styrene radical polymerization in the presence of BSC was proposed:
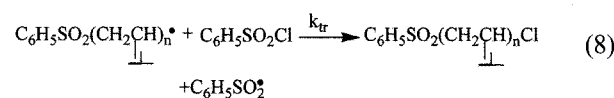
Initiation

$$AIBN \xrightarrow[\Delta]{k_d} In\bullet \tag{4}$$

$$C_6H_5SO_2Cl + In\bullet \xrightarrow{k_{tr'}} C_6H_5SO_2\bullet + In\!-\!Cl \tag{5}$$

$$C_6H_5SO_2\bullet + H_2C\!=\!CH \xrightarrow{k_i} C_6H_5SO_2CH_2CH\bullet \tag{6}$$

Propagation

$$C_6H_5SO_2(CH_2CH)_n^\bullet + H_2C\!=\!CH \xrightarrow{k_p} C_6H_5SO_2(CH_2CH)_{n+1}^\bullet \tag{7}$$

Chain transfer

$$C_6H_5SO_2(CH_2CH)_n^\bullet + C_6H_5SO_2Cl \xrightarrow{k_{tr}} C_6H_5SO_2(CH_2CH)_nCl \tag{8}$$
$$+C_6H_5SO_2^\bullet$$

Eq. (4) to (6) are initiation steps, where In· represents an initiator radical. The phenylsulfonyl radical is generated by abstracting chlorine atoms from BSC to initiator radical (eq. (5)), then it adds irreversibly to styrene monomer, generating styrene radical (eq. (6)), which subsequently initiates the polymerization of styrene (eq. (7)). The propagating polystyrene radical abstracts the chlorine atom from BSC too, forming dead polystyrene chain having a chlorine atom at the ω-end, and at the same time a new phenylsulfonyl radical is generated (eq. (8)). It should be emphasized that the termination reaction between polymeric radicals can be neglected, at least at higher BSC concentrations.

References

Figure 6. GPC traces of styrene-methyl acrylate block copolymers obtained at different monomer conversions for ATRP of methyl acrylate in toluene at 90 °C with polystyrene A ($M_{n, GPC}$= 3,680 g/mol) as macroinitiator. Reaction conditions: [MA]$_0$= 5.21 M; [MA]$_0$:[Macroinitiator]$_0$:[CuCl]$_0$: [bpy]$_0$=205:1:1:3.

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