

Atom Transfer Radical Polymerization of Styrenesulfonic Acid Sodium Salts (SSNa) in Aqueous Phase

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Summary

Aqueous ATRP of SSNa has been investigated in the presence of initiator, 2-bromo-2-methylpropionate (1), mediated with Cu(I)Br/bpy. When using water only as a polymerization solvent, some deviations from the living behaviors were observed, including a bimodal molecular weight distribution. It was found that the competitive coordination effect of water could be suppressed by using Cu(II)Br or variation of polymerization solvent. The addition of Cu(II)Br with the ratio of Cu(I)/Cu(II)= 1 was found to give the optimum results with 92% conversion achieved in approximately 60 min, leading to a polymer with a molecular weight close to the theoretical with a polydispersity index=1.20. Using mixture of water and methanol with the ratio of water/methanol=30/20 wt% also suppressed the formation of the high molecular weight fraction and more than 95 % conversion was achieved in 80 min. SEC of the resulting polymer was monodisperse with a polydispersity index =1.21.

Introduction

Poly(styrenesulfonic acid)(PSSA) and its salt are synthetic water-soluble polymers of great applications such as flocculants, antistatics, emulsifiers, catalysts for various reactions, ion-exchange resins and membranes, and are also convenient model compound for the investigation of the properties of biopolymers [1]. Especially PSSA have been used in the aqueous stabilization of insoluble poly(3,4-ethylenedioxythiophene) which has gained importance in highly transparent conducting materials[2-3].

Recent advance in polymer synthesis techniques have given rise to the importance of “living” free radical polymerization such as stable free radical polymerization (SFRP) [4], reversible addition-fragmentation chain transfer polymerization (RAFT) [5] and atom transfer radical polymerization (ATRP) [6-7]. In 1995, Keoshkerian et al. reported the SFRP of styrenesulfonic acid sodium salt (SSNa) in aqueous ethylene glycol(80%)[8]. In their study, TEMP(2,2,6,6-tetramethyl-1-piperidinyloxy) and potassium persulfate were used as radical scavenger and initiator, respectively. However the SPRP of SSNa was slow and the high reaction temperature was required. In 2001, McCormick et al. synthesized poly-SSNa (PSSNa) by RAFT. Polymerization of SSNa by RAFT was achieved in quantitative conversion within 1-2 hours and the resulting polymer was near monodisperse, with a narrow polydispersity index in the range of 1.12-1.25 [9]. Recently, Armes et al. reported the ATRP of a number of

hydrophilic monomers such as poly(ethylene glycol) methacrylate, sodium 4-vinylbenzoate and sulfonate methacrylate, and showed that those could be rapidly polymerized in water [10-12]. More recently, Liu et al, reported that the ATRP of SSNa in dimethylformamide at 130 °C gave PSSNa with somewhat broad molecular weight distribution of 2.1 [13]. We have attempted ATRP of SSNa, and found some deviation behaviors from livingness control under condition of Cu(I)Br/bipyridine (bpy) which is a standard condition of ATRP. This insufficient livingness may be due to the competitive coordination of water and ligand on the copper species.

In this article, the improving of livingness on the ATRP process for the synthesis of PSSNa has been studied. It was found that the competitive coordination effect of water could be suppressed by using a radical scavenger (Cu(II)Br) or variation of polymerization solvent. Here, it was reported that Cu(II)Br or methanol as a polymerization cosolvent could be effective on the living characters, and optimum conditions to give good livingness control for ATRP of SSNa were also provided.

Experimental

Materials

Cu(I)Br (Aldrich, 99.999%) and Cu(II)Br (Aldrich, 99.0%) were used as received. Initiator, 2-bromo-2-methylpropionate ester (1) of poly(ethylene glycol monomethyl ether) (MW=550), was synthesized by previous reported method [14]. Monomer, styrenesulfonic acid sodium salt (SSNa) (Aldrich, $\text{CH}_2=\text{CHC}_6\text{H}_4\text{SO}_3\text{Na}\cdot x\text{H}_2\text{O}$), and ligand, 2,2'-dipyridyl (bpy) (Aldrich, 99+%), were used as received. All other reagents and solvents were obtained from Aldrich and used without further purification.

Typical polymerization procedure for PSSNa via ATRP

The monomer (SSNa, 48.5 mmol) was dissolved in 50 g of solvent (water or mixture of water and methanol) and the solution was degassed by flushing argon gas for 1 hours. The reaction solution was bubbled by argon gas, and the catalyst (copper (I) bromide (0.8 mmol) or mixture of copper(I) and copper(II) bromides (0.8 mmol of total copper) and bpy (1.6 mmol) was added. The reaction solution was changed to brown and thermostatted by water bath at 25 °C. The initiator, 0.8 mmol of 2-bromo-2-methylpropionate (1), was added via a degassed syringe to start the polymerization. The reaction solution was became dark brown and exotherms of 4-6 °C were observed in the case of water only as a solvent.

Aqueous size exclusion chromatography (ASEC)

The molecular weights of the PSSNa were estimated by aqueous size exclusion chromatography, using two Waters Ultrahydrogel (250 and linear) columns that connected to a M930 solvent delivery module and a RI 750F refractive-index (RI) detector (Younglin Instrument Co., Korea). The mobile phase was used HPLC grade water at flow rate of 0.8 ml/min and included 0.1 M NaNO_3 for prevention of ionic polymer aggregation. Calibration was with near-monodisperse PSSNa standards

purchased from Polyscience Inc. Molecular weight averages and polydispersity indices were calculated using software from Younglin Instrument Co. SEC samples were taken at regular to assess the extent of polymerization. The dark brown solution turned blue by bubbling of oxygen gas and the catalyst, Cu(II)Br, was removed by passing silica column.

Results and discussion

ATRP of SSNa in water

Polymerization of SSNa was firstly carried out using a typical ATRP condition, Cu(I)Br/bpy ligand, in a ratio 1/2 as catalyst and 2-bromo-2-methylpropionate (1) as initiator, as shown in scheme Figure 1.

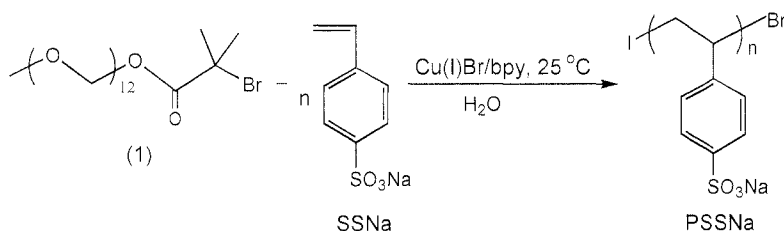


Figure 1. ATRP of SSNa using 2-bromo-2-methylpropionate (1), as a water-soluble initiator, mediated with Cu(I)Br/bpy.

Polymer molecular weight, polydispersity and yields were summarized in Table 1. When using a ratio SSNa/(1)/Cu(I)Br/bpy=60/1/1/2, in 16.7 wt% H₂O, 95% conversions were achieved in less than 30 min (Table 1, entry 1).

Table 1. Effects of the reaction conditions on ATRP of SSNa^a

Entry	Solvent	Time (min)	Conversion ^b (%)	Mn (SEC)	Mw/Mn (SEC)
1	H ₂ O	30	>95	22000	1.56
2 ^c	H ₂ O	60	92	14500	1.20
3	H ₂ O/MeOH(38/12)	40	98	14900	1.33
4	H ₂ O/MeOH(30/20)	80	>95	13800	1.21
5	H ₂ O/MeOH(27/23)	360	50	6300	1.16
6	H ₂ O/MeOH(25/25)	360	19	2500	1.18

^a Reaction conditions : SSNa/(1)/Cu(I)Br/bpy=48.5/0.8/0.8/1.6 mmol in 50 ml of water or the mixture of water and methanol.

^b Conversions were determined by precipitation into a methanol/acetone solution followed by filtration.

^c Catalyst was used a mixture Cu(I)Br (0.4 mmol) and Cu(II)Br (0.4 mmol).

As expected from such a rapid polymerization, the ranges of 1.45 to 1.60 in polydisperties were gained over the final product properties. Moreover, SEC analysis showed an initial bimodal polydisperties and the signal decrease of high molecular weight fraction with the degree of polymerization as shown in Figure 2. This bimodal polydispersity presumably indicates that the polymerization reactions proceeded with a side reaction of propagating species. The high molecular weight fraction may be caused by a side reaction such as coupling reactions of growing radicals at initial stage, and the low molecular weight fraction with narrow polydispersity may be resulted from the formation of the active species which is correspondent to the controlled polymerization, when the equilibrium between Cu(I) and Cu(II) is stabilized after a few minutes.

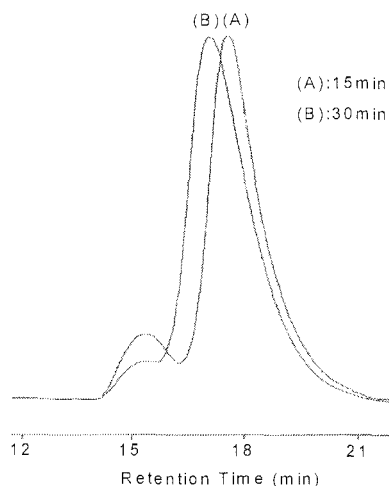


Figure 2. SEC curves of ATRP of SSNa at SSNa/(1)/Cu(I)Br/bpy=60/1/1/2, in 16.7 wt% H₂O

ATRP of SSNa using Cu(II)Br as a radical scavenger

Figure 3 shows the mechanism of ATRP based on the repetitive addition of a monomer to growing radicals, generated from dormant alkyl halides by reversible redox process. Several side reactions presumably take place in the aqueous ATRP. The competitive coordination of H₂O molecules with the ligand influences on the living character of ATRP [15]. It has already been reported that in the case of the polymerization of acrylates or methacrylates, polar solvents such as water can act as a competitive ligand on copper [16-18]. In ATRP of SSNa, the insufficient living character of previous section can be explained by a competitive coordination of water toward ligand in the initial stage. Because water is a bad ligand for Cu(I)Br but a good ligand for Cu(II)Br, this would shift the equilibrium towards the right-hand side of the reaction shown in Figure 3, thereby increasing of the overall rate of polymerization, and explaining the faster kinetics observed in aqueous copper mediated radical polymerization. In addition, the equilibrium shift to the right resulted in high

concentration of radical species $[R^*]$, which caused the coupling reaction of growing radical at initial stage.

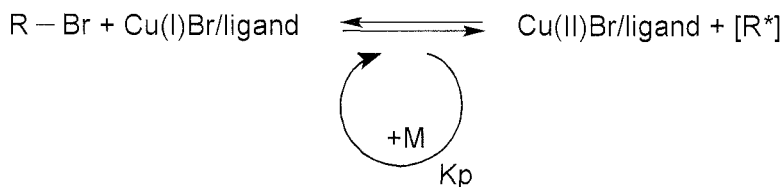


Figure 3. Schematic representation for the mechanism of ATRP

From the radical scavenger effect of Cu(II) species, it is deduced that the introduction of Cu(II)Br at the very beginning of the reaction shifts the equilibrium toward left to suppress the concentration of growing radicals $[R^*]$ which cause the uncontrolled formation of high molecular weight fraction. In this study, It was found that the addition of Cu(II)Br could avoid the uncontrolled reactions. Cu(I)Br/Cu(II)Br= 1, keeping the overall quantity of Cu(X)Br=0.8 mmol, was found to give the optimum results with 92% conversion achieved in approximately 60 min, leading to a product with a molecular weight close to the theoretical with a polydispersity index=1.20 (Table 1, entry 2).

Effects of methanol as a polymerization cosolvent

The ATRP of SSNa by Cu(I)Br/bpy was also carried out using water alone and a solvent mixture of water and methanol. These experiments will show the effects of methanol, as a polymerization cosolvent, on the living character. As shown in Figure 4, the rate of polymerization was decreased according to the amount of methanol.

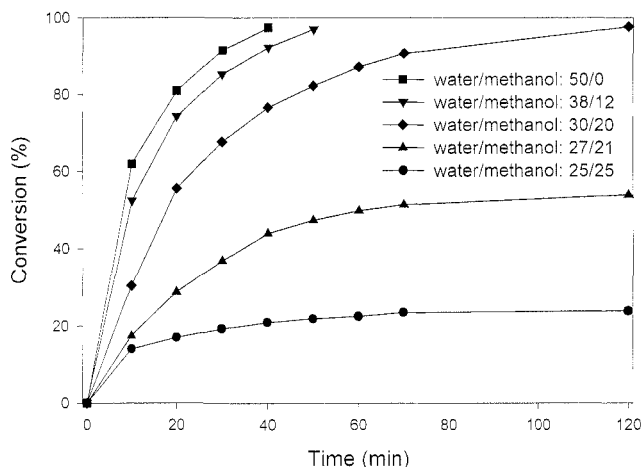


Figure 4. Conversions versus polymerization time with the variation of ratio of water/methanol.

Figure 5 shows the calibrated SEC curves of the PSSNa obtained in water (figure 5 (a)), solvent mixture (figure 5 (b) and figure 5 (c)). The increase of methanol content,

resulted in the decrease of high molecular weight fraction and narrower polydispersities ($M_w/M_n=1.56 \rightarrow 1.16$). However, when one used water only as a solvent, the molecular weight distribution was bimodal. The high molecular weight fraction and the molecular weight distribution were simultaneously increased with the amount of water. All these facts indicate that the use of methanol, as a lower coordination solvent to Cu(II) species than that of water, apparently suppressed the formation of the growing radicals in the same way of the above Cu(II)Br at the initial stage of ATRP of SSNa. This suppressed concentration of growing radicals may results in the slow polymerization and keeping away from the formation of high molecular weight fraction in bimodal polydispersities. At 30/20 ratio of water/methanol, 95 % conversion was achieved in 80 min (Figure 4) and M_n values with the narrow polydispersity were linearly proportional to monomer conversion (Table 1, entry 4 and Figure 5 (c)).

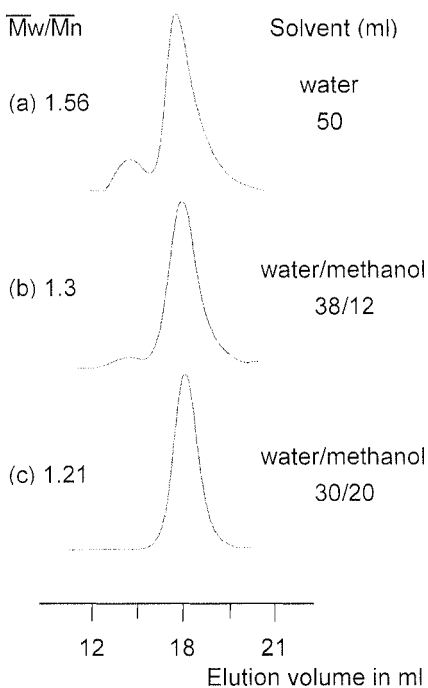


Figure 5. SEC curves and polydispersities of PSSNa obtained by ATRP 2-bromo-2-methylpropionate (1) / Cu(I)Br/bpy in various solvents at 25 °C.

Conclusions

This study has been demonstrated that initiator, 2-bromo-2-methylpropionate (1), mediated with Cu(I)Br/bpy leads to the ATRP of SSNa and the livingness in this system is largely improved by the solvent variation or the radical scavenger. This polymerization system showed that the competitive coordination effect of water could be suppressed by using Cu(II)Br or by using the mixture of water and methanol. The addition of Cu(II)Br, as a radical scavenger, with ratio of Cu(I)/Cu(II)= 1 was found to give the optimum results with 92% conversion achieved in approximately 60 min, leading to a product with a molecular weight close to the theoretical value with a low

polydispersity. Using the mixture of water and methanol with (30/20 wt%) suppressed the formation of the high molecular weight fraction and gave the well-controlled PSSNa.

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