SHORT COMMUNICATIONS

Living Radical Polymerization of Sodium 4-Styrenesulfonate Mediated by New Water-Soluble Nitroxides

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The recent development of the living radical polymerization (LRP) opened a new and versatile route to polymers with controlled molecular weights and narrow polydispersities. Nitroxide-mediated radical polymerization (NMRP),¹ atom transfer radical polymerization,^{2,3} and reversible addition-fragmentation chain transfer⁴ are typical methods of LPR. Extension of this process to water-soluble monomers is of great interest because water-soluble polymers and copolymers undergo a conformational change, or phase transition in response from external stimuli. Sodium 4-styrenesulfonate (NaSS), a typical water-soluble monomer, was polymerized by the LRP method. Although ATRP did not give any good results (polydispersity index (PDI) > 2.0),⁵ NMRP⁶⁻¹⁰ and RAFT¹¹ yielded poly-(NaSS) with narrow polydispersities. The first NMRP of NaSS was carried out using the potassium persulfate/sodium bissulfite initiating system in the presence of 2,2,6,6-tetramethylpiperidinyl-N-oxyl (TEMPO) at 125 °C.6 Although this method was later adopted by some groups,⁷⁻⁹ a large quantity of organic solvent (3:1 ethylene glycol-H2O) was necessary to use due to the low water solubility of TEMPO. This makes purification process of the resultant polymers complex. To overcome this disadvantage, water-soluble trimethylammonium or sulfonate group-carrying nitroxides were used in the polymerization of NaSS using the K2S2O8/Na2S2O5 initiating system.¹⁰ However, the polymerizations were quite slow. For example, upon the polymerization for 6 h at 130 °C, the conversions were only 0–41%. Furthermore, the $M_{\rm n}$ s of the resultant polymers were always below $1.0 \times 10^4 \text{ g mol}^{-1}$. In this communication we report the polymerization of NaSS initiated with water-soluble azo compounds in the presence of new water-soluble nitroxides 1 and 2.



The reaction of 2,2,4,6,6-pentamethyl-1,2,5,6-tetrahydropyrimidine¹² with an excess of 4-hydroxycyclohexanone at 60 °C in the presence of NH₄Cl gave 7-aza-4,12-dihydroxy-15-oxodispiro[5.1.5.3]hexadecane (**3**) in 19% yield after column chromatography.¹³ Oxidation of **3** with *m*-chloroperoxybenzoic acid in EtOH at room temperature gave **1** in 54% yield, and reduction of **1** with NaBH₄ in EtOH gave **2** in 94% yield.

The polymerizations of NaSS were carried out at 120 °C in the presence of **1** or **2** using D₂O as the solvent. The initiators used were water-soluble V-50 and VA-044. The half-life times of V-50 and VA-04 are less than 1 min in water at 120 °C. The conversions were determined by a comparison of the relative intensity of the peaks due to the vinylic protons (2H) of NaSS at $\delta = 5.13$ and 5.63 ppm with that of the peaks due to the aliphatic protons at $\delta = 1.3$ –2.5 ppm of poly(NaSS), and SEC measurements were carried out using poly(NaSS) standards (eluent 2:8 acetonitrile–water containing 0.05 mol L⁻¹ of NaNO₃ and 0.01 mol L⁻¹ of Na₂HPO₄). The results are summarized in Table I.

The ability of **1** to control the polymerization of NaSS was first evaluated, varying the **1**/V-50 ratios from 0.90 to 1.3. The mixtures of NaSS, V-50, and **1** in D₂O were heated at 120 °C for a given time in degassed sealed glass tubes. During the polymerization the mixtures were always homogeneous. In all polymerizations induction periods of 1–7 h were observed. The resulting polymers showed broad polydispersites (PDIs = 1.53-1.84) (run 1–3), indicating that that **1** did not satisfactorily control the polymerization of NaSS.

In the same manner, the polymerizations of NaSS were carried out in the presence of **2**. When the ratio of **2** to the azo compound was 1.3 (run 4 and 5), a long induction period (*ca.* 5 h) was observed, but the PDI of the resulting polymers was 1.16, demonstrating that the polymerization of NaSS proceeded in the satisfactory living fashion. When the nitroxide/V-50 ratio was 1.1 (run 6 and 7), the induction period was drastically shortened to 1 h and, after 2 h poly(NaSS) with $M_n = 3.46 \times$ 10^4 g mol^{-1} and PDI = 1.22 was obtained in 84% yield. This is the first rapid and well-controlled NMRP polymerization of NaSS in water. In contrast, when the ratio was reduced to 0.90 (run 8 and 9), the induction period was very short but the resulting poly(NaSS) showed a broad polydispersity of 1.59, indicating that the polymerization was insufficiently controlled.

The structural difference between 1 and 2 is small. However, only 2 showed an excellent ability to control the polymerization of NaSS. Unfortunately, the poor ability of 1 to control the polymerization is unclear. A plausible explanation may be a

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Run	NaSS (mmol)	Initiator ^b	Nnitoxide (mmol)	Time (h)	Conversion ^c (%)	$\frac{M_{\rm n}}{({\rm g}{\rm mol}^{-1})}$	PDI	$M_{n,\text{theor}}^{d}$ (g mol ⁻¹)
1	2.43	V-50	$1 (1.30 \times 10^{-2})$	13	88	47700	1.53	33800
2	2.43	V-50	$1 (1.10 \times 10^{-2})$	4	78	84500	1.84	35500
3	2.43	V-50	$1 (9.0 \times 10^{-3})$	3	96	60300	1.75	53300
4	2.43	V-50	2 (1.30×10^{-2})	5	8.8	e	e	3380
5	2.43	V-50	$2 (1.30 \times 10^{-2})$	7	73	32500	1.16	28100
6	2.43	V-50	$2 (1.10 \times 10^{-2})$	1	5.9	e	e	2680
7	2.43	V-50	$2 (1.10 \times 10^{-2})$	2	84	34600	1.22	38200
8	2.43	V-50	2 (9.0×10^{-3})	1	3.3	e	e	1830
9	2.43	V-50	2 (9.0×10^{-3})	2	75	41900	1.59	41700
10	2.43	VA-044	$2 (1.10 \times 10^{-2})$	2	61	26600	1.11	27700
11	4.85	VA-044	$2(1.10 \times 10^{-2})$	4	81	73800	1.17	73600
12	9.71	VA-044	$2 (1.10 \times 10^{-2})$	3	69	106000	1.32	125000

Table I. Polymerization of NaSS initiated with V-50 or VA-044 in D_2O at 120 °C in the presence of 2^a

^aD₂O 2.0 mL. ^bInitiator 1.00×10^{-2} mmol. ^cDetermined by ¹H NMR. ^d $M_{n,theor}$ is calculated using the equation $M_{n,theor} = ([monomer]/[nitroxide]) \cdot conversion \cdot MW_{NaSS}$. ^eNot measured.

gradual decomposition of 1 during the polymerization.

When VA-044 was used as the initiator, the polymerization rates were somewhat slower than the polymerization initiated with V-50, but the resulting polymers showed lower a PDI of 1.11 (run 10).

To obtain high molecular poly(NaSS)s the amount of the monomer was increased from 2.43 to 4.85 and 9.71 mmol without changing the amounts of initiator, nitroxide, and solvent. The results are summarized in Table I (run 11 and 12). Although the polymerization systems became very viscous at high conversions, the polymerization proceeded to 69–81% conversions and the resulting poly(NaSS)s showed large $M_{\rm n}$ s of 7.38 × 10⁴–1.06 × 10⁵ g mol⁻¹ and low PDIs of 1.17–1.32. The above results demonstrate that high molecular weight poly(NaSS)s can be obtained by using the present polymerization system.

In order to confirm the polymer structure some poly(NaSS)s were isolated by precipitation of the reaction mixtures into MeOH/acetone (2:1 in vol., 10-fold excess) according to the literature.¹⁰ The ¹H NMR spectra of the polymers obtained showed a complete agreement with that of the authentic sample prepared radically.

Finally, repolymerization of NaSS from the isolated poly(NaSS) was carried out to confirm the livingness. A mixture of NaSS (0.50 g), poly(NaSS) ($M_{\rm n} = 2.66 \times 10^4 \, {\rm g \, mol^{-1}}$, PDI = 1.11) (0.10 g) in H₂O (2.0 mL) was heated at 120 °C for 10h, and the chain extended polymer (65% yield) was obtained by pouring the mixture into a large amount of MeOH/ acetone. The SEC measurements of the poly(NaSS) showed $M_{\rm n} = 1.00 \times 10^5 \,\mathrm{g \, mol^{-1}}$ and PDI = 1.28, indicating the polymerization of NaSS from the macroinitiator proceeded in a living fashion. Figure 1 shows the SEC traces of the macroinitiator and the resulting chain extended poly(NaSS). The SEC trace of the chain extended poly(NaSS) is shifted to a higher molecular weight region and no peak is observed in the region corresponding to the molecular weight of the macroinitiator. This SEC result indicates a near quantitative attachment of the alkoxyamine moiety to one end of the macroinitiator polymer chain.

CONCLUSIONS

Water-soluble nitroxides 1 and 2 were prepared and used as a mediator in the polymerization of NaSS. Although 1 showed a poor control for the polymerization of NaSS, 2 demonstrated



Figure 1. SEC traces of (a) macroinitiator ($M_n = 2.66 \times 10^4 \text{ g mol}^{-1}$, PDI = 1.11) and (b) the chain extended poly(NaSS).

an excellent ability to control the polymerization of NaSS to give poly(NaSS)s with narrow polydispersities in high yields in a short polymerization time (2 h).

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