Living Free-Radical Aqueous Polymerization

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Introduction. It has recently been reported that narrow polydisperse (PD) resins can be synthesized by a stable free-radical polymerization (SFRP) process by using nitroxide stable free radicals to react reversibly with the propagating polymer chains.[1-3] Due to the interest in environmentally friendly polymers, which generally are water soluble, it was thought that extension of this process to water-soluble polymers could be beneficial, especially since narrow polydisperse water-soluble polymers cannot be prepared directly by conventional living polymerization systems. Functional groups, which impart water solubility to monomers and polymers, are not compatible with ionic polymerization systems, requiring these groups to be protected prior to polymerization and deprotected thereafter. In this paper we report the extension of the SFRP process to the synthesis of poly(styrenesulfonic acid, sodium salt), providing a novel, direct route to a water-soluble narrow-polydispersity resin. Many of the materials prepared had narrower polydispersities than the poly(styrenesulfonic acid, sodium salt) standards available to calibrate the gel permeation chromatograph.

Solution polymerizations with styrenesulfonic acid, sodium salt (SSNa) were performed, in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, free radical) in aqueous ethylene glycol (80%) at 125 °C. While a number of different initiating systems were tried, the best one, to date, is potassium persulfate/sodium bisulfite. Typically, polymerizations were performed over 6 h at monomer to initiator ratios of 20/1 and nitroxide to initiator ratios of 2. Molecular weights were determined by gel permeation chromatography (GPC) using Shodex OH-pak KB-800 columns with molecular weight cutoffs of 4000, 100 000, 400 000, and 4 000 000. The columns were calibrated with poly(styrenesulfonate, sodium salt) standards obtained from Pressure Chemical Co. with a mobile phase of 0.1 M sodium nitrate at a flow rate of 0.8 mL/min. Molecular weight growth was studied with samples removed from the reaction mixture at various times during the polymerization. Samples were isolated by precipitation into a methanol/acetone solution followed by filtration. Percent conversions were calculated from the isolated weight of the polymer. Reagents were used as received from the supplier without any prior purification.

Results and Discussion. To demonstrate the flexibility of this process to prepare a wide range of molecular weight materials, a series of poly(styrenesulfonate, sodium salt)–TEMPO-terminated (PSS-T) resins were synthesized. As illustrated in Table 1, it was possible to vary the molecular weights from very low (8000) to very high (900 000), while maintaining narrow polydispersities. These polydispersities can be compared to a polydispersity of 2 obtained for a conventional free-radical polymerization of PSSNa.

Table 1. Molecular Weight Ranges

M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PD	convn
16.8	33	1.96	91[a]
7.2	8.0	1.12	49
30	36	1.21	97
46.5	62.2	1.33	85
162.6	216.7	1.33	87
356.4	467	1.31	60
762.7	900	1.18	25[b]

[a] Control experiment with no TEMPO (i.e., conventional polymerization). [b] Low conversion due to the high viscosity of the reaction medium.

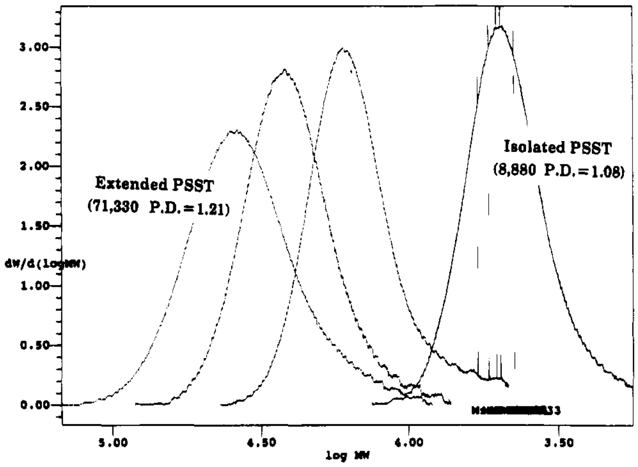

Figure 1. Molecular weight growth by chain extension.

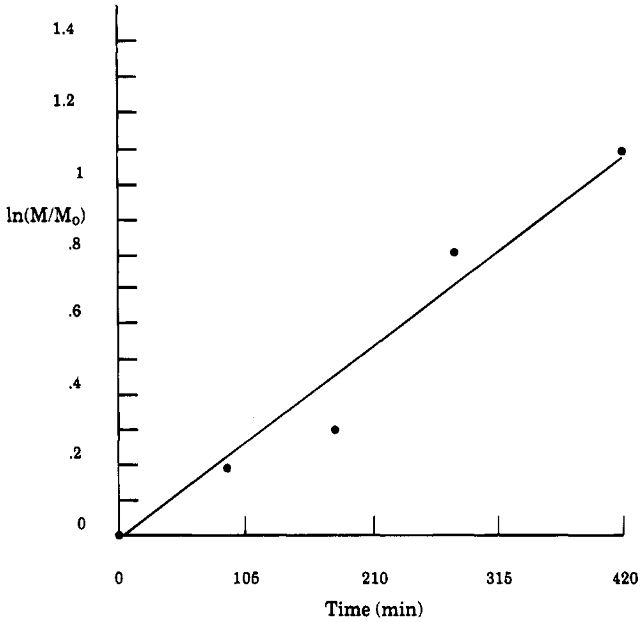

Figure 2. Conversion vs time.

As is the case for other polymers prepared by the SFRP process,[1-3] the water-soluble PSS-T resins can be isolated and reacted further under the appropriate conditions by heating them in the presence of a monomer. Reaction with the original monomer results in chain extension. To illustrate this, a PSS-T resin (8800 and a PD of 1.08) was prepared under standard conditions. The resin was isolated by precipitation in a methanol/acetone solution, filtered, and dried under vacuum at 50 °C overnight. A portion of the resulting solid resin was redissolved in an aqueous ethylene glycol solution containing SSNa and heated at 125 °C for 3 h. The polymeric product was isolated as described above for the starting polymer. The weight-average molecular weight of the product, as determined by GPC, was 71 330 and the PD was 1.21. A comparison GPC plot of the starting polymer and final polymer (Figure 1) shows a shifting of the GPC peak of the starting material to higher molecular weight. No new peak or shoulder is evident in the GPC plot which suggests that no new chain formation due to autopolymerization occurs, indicating that the new product is derived from the starting polymer and that a living polymerization mechanism is at work. The higher molecular weight materials (>100 000) presented in Table 1 were prepared by chain extension reactions.

The more conventional test of livingness is shown in Figure 2 where a plot of conversion $[-\ln(M/M_0)]$ versus time is illustrated. The curve goes through the origin and is a straight line.

Finally, the marked difference in polydispersity between a PSST resin prepared by the SFRP process and a conventional free-radical polymerization process resin can be seen in Figure 3.

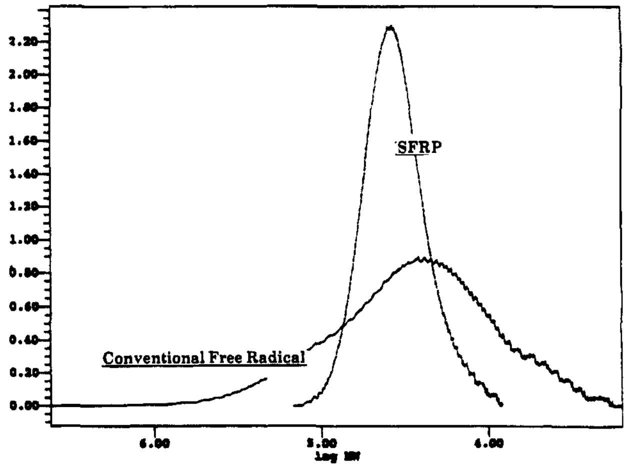

Figure 3. SFRP vs conventional free-radical polymerization.

In summary, we have developed an SFRP process that allows for a novel, direct route to narrow-polydispersity water-soluble poly(styrenesulfonate, sodium salt). The molecular weight of the polymer can be varied from very low to very high while maintaining narrow polydispersities. A key feature of these piperidinyloxy-terminated resins is that they can be isolated, stored at room temperature, and then subsequently used for further reaction, as, for example, in chain extensions to prepare higher molecular weight polymers. The extension of this work to other water-soluble monomers and block copolymers is ongoing and will be reported on in the future.

References and Notes

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CORRECTIONS

Karim Mazeau, William T. Winter, and Henri Chanzy*: Molecular and Crystal Structure of a High-Temperature Polymorph of Chitosan from Electron Diffraction Data. Volume 27, Number 26, December 19, 1994, pp 7606–7612.

The received dates given in this article were incorrect. The correct dates are as follows: Received August 10, 1994; Revised Manuscript Received September 21, 1994.

This article treats the same topic as the preceding paper. Toshifumi Yui,* Kiyohisa Imada, Kenji Okuyama, Yutaka Obata, Katsumi Suzuki, and Kozo Ogawa: Molecular and Crystal Structure of the Anhydrous Form of Chitosan. Volume 27, Number 26, December 19, 1994, pp 7601–7605 (Received June 17, 1994; Revised Manuscript Received August 19, 1994).

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