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# Narrow Polydispersity Polystyrene by a Free-Radical Polymerization Process—Rate Enhancement

**Michael K. Georges,* Richard P. N. Veregin, Peter M. Kazmaier, Gordon K. Hamer, and Marko Saban**

*Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada L5K 2L1*

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We recently reported the synthesis of resins, by a free-radical polymerization process, with polydispersities (PDs) well below the theoretical limit of 1.5 calculated for a conventional free-radical polymerization process.[1-3] Polymerizations were carried out at temperatures such that the initiator half-life was less than 5 min, enabling simultaneous chain initiation. Nitroxide stable free radicals (SFRs) were used to reversibly terminate the propagating chains, reducing the ubiquitous irreversible chain termination of conventional free-radical polymerization processes. Molecular weights were observed to increase linearly with time and conversion, and resins were obtained with PDs between 1.15 and 1.3. However, long reaction times and low molecular weights limited the usefulness of this reaction for industrial applications. Initial bulk polymerizations, performed at 125 °C, required about 70 h to go to high conversions (>85%) and provided resins with molecular weights of about 10 000 or less.[1]

We originally thought that a low concentration of steady-state free-radical propagating chains in the reaction mixture at any given time reduced the probability of two chains irreversibly terminating by coupling, thereby enabling narrow polydispersity resins to be obtained. Increasing the rate of reaction, it was argued, would require an increase in the steady-state concentration of propagating chains and lead to an increase in coupling and polydispersity.

At the same time we were interested in increasing the rate of the nitroxide SFR-mediated polymerization, we were also concerned about autopolymerization of the monomer due to the elevated temperatures (>110 °C) that were necessary for the polymerization. It has been reported that strong organic acids, such as camphorsulfonic acid (CSA), could be used to reduce the autopolymerization of styrene.[4] We were, therefore, interested in studying the effect CSA would have on the polydispersity of styrene-based resins, assuming autopolymerization might result in some broadening of the polydispersity.

A series of styrene polymerizations were performed, according to the general procedure described in ref 1, in an oil bath maintained at 135 °C, using benzoyl peroxide (BPO) as the initiator and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) as the stable free radical, with varying amounts of CSA. Molecular weights were determined, on samples taken directly form the reaction mixture, by gel permeation chromatography using Ultrastyragel columns of pore sizes $10^4$, 2 × 500, and 100 Å and a Waters 410 differential refractometer. The columns were calibrated with polystyrene standards. PDs were taken as the ratio of $M_w$ to $M_n$. Percent conversions were obtained from residual monomer analysis by gas chromatography. The results are summarized in Table 1.

While Shero et al. observed no rate increase in the polymerization of styrene initiated by *tert*-butyl perbenzoate in the presence of CSA,[4] the rate of polymerization of a TEMPO-mediated polymerization was dramatically increased in its presence. For a given reaction time, in this case 5.5 h, both the molecular weight and percent conversion increase with increasing amounts of CSA. The polydispersity is approximately linear in CSA concentration, with increasing CSA concentration leading to higher polydispersities, as shown in Figure 1. CSA concentrations greater than about 0.02 M result in PDs higher than those obtained for the original reaction performed without CSA.[1] While it could be argued that the increase in PD is due to higher conversion, further experimentation suggested that this was not the case. Table 2 summarizes the molecular weight and PDs of resins prepared using 0.036 M CSA. In this example, relatively high polydispersities are obtained even at low conversions and stay relatively high throughout the course of the reaction although the PDs are still below the theoretical limiting value of 1.5 of a conventional free-radical polymerization process. On the other hand, repeating the reaction with a CSA concentration of 0.018 M gives narrow PD resins early in the reaction and the PD actually decreases with conversion (Table 3).

Higher molecular weight products are also obtained in the presence of CSA. In fact, polystyrene resins of

**Table 1. Effect of CSA on the Rate of TEMPO-Moderated Free-Radical Polymerization**[a]

| sample | CSA (M) | $M_n$ ($10^{-3}$) | $M_w$ ($10^{-3}$) | PD | convn (%) |
|---|---|---|---|---|---|
| I | 0 | 8.8 | 10.1 | 1.13 | 24 |
| II | 0.0045 | 13.1 | 15.2 | 1.16 | 51 |
| III | 0.009 | 16.0 | 19.0 | 1.18 | 59 |
| IV | 0.018 | 21.6 | 27.2 | 1.26 | 76 |
| V | 0.023 | 23.1 | 30.6 | 1.32 | 81 |
| VI | 0.027 | 24.8 | 34.2 | 1.38 | 92 |

[a] Oil bath temperature 130 °C; reaction time 5.5 h.

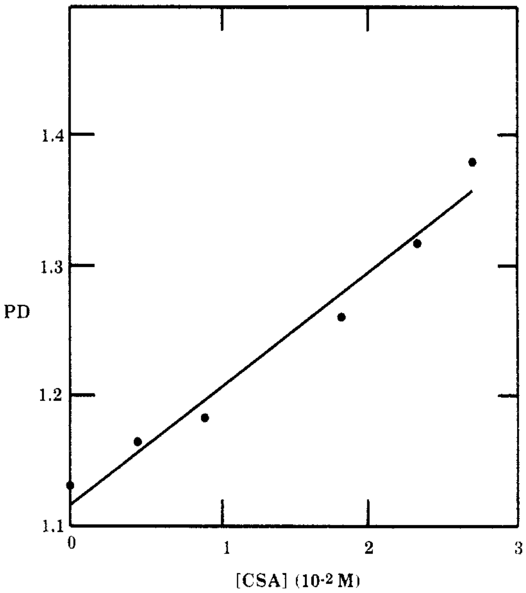

**Figure 1.** Plot of polystyrene polydispersity with CSA concentration. The data are taken from Table 1.

**Table 2. Effect of 0.036 M CSA on the Rate of a TEMPO-Moderated Free-Radical Polymerization**[a]

| sample | rxn time (h) | $M_n$ ($10^{-3}$) | $M_w$ ($10^{-3}$) | PD | convn (%) |
|---|---|---|---|---|---|
| I | 0.5 | 5.3 | 8.1 | 1.51 | 9 |
| II | 1.0 | 9.0 | 12.7 | 1.41 | 21 |
| III | 1.5 | 12.3 | 17.1 | 1.39 | 35 |
| IV | 2.0 | 15.2 | 21.0 | 1.38 | 52 |
| V | 3.5 | 21.6 | 29.7 | 1.37 | 75 |
| VI | 5.5 | 23.2 | 32.2 | 1.39 | 88 |

[a] Oil bath temperature 130 °C.

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**Table 3. Effect of 0.018 M CSA on the Rate of a TEMPO-Moderated Free-Radical Polymerization[a]**

| sample | rxn time (h) | $M_n$ ($10^{-3}$) | $M_w$ ($10^{-3}$) | PD | convn (%) |
|---|---|---|---|---|---|
| I | 0.5 | | | | 0 |
| II | 1.0 | 1.6 | 2.3 | 1.40 | 2 |
| III | 1.5 | 5.0 | 6.6 | 1.31 | 14 |
| IV | 2.0 | 8.4 | 10.6 | 1.26 | 23 |
| V | 3.5 | 15.9 | 19.1 | 1.20 | 54 |
| VI | 5.5 | 19.8 | 23.4 | 1.18 | 76 |

[a] Oil bath temperature 130 °C.

molecular weights greater than 100 000 with polydispersities less than 1.4 have been realized. Heating a solution of CSA (0.018 g), TEMPO (0.013 g), and BPO (0.015 g) in styrene (36 g) in an oil bath maintained at 127 °C for 3 h gives a resin with $M_n$ = 107 556, $M_w$ = 147 412, and PD = 1.37.[5]

Substituting the CSA with benzoic acid or diphenylacetic acid had no effect on the rate of reaction.[6]

In summary, it has been demonstrated that the rate of polymerization of nitroxide-mediated stable free-radical polymerization processes for styrene-based polymers and copolymers can be dramatically increased by the addition of camphorsulfonic acid. Very narrow polydispersity resins are obtained with CSA concentrations of 0.02 M or less, while larger amounts of CSA result in slight increases in polydispersity. The CSA concentration, thus, provides a means to increase the polydispersity, if desired, in a controlled fashion. In addition, higher molecular weight resins can be obtained in the presence of CSA compared to polymerizations performed in its absence.

## References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.

(2) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316.

(3) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2* (2), 66.

(4) Buzanowski, W. C.; Graham, J. D.; Priddy, D. B.; Shero, E. *Polymer* **1992**, *33* (14), 3055.

(5) Georges, M. K. Unpublished data.

(6) Benzoic acid, a byproduct of the dissociation of BPO, is not innocuous in the reaction; its effect will be reported in a future publication.