Stable Free Radical Polymerization of Styrene: Controlling the Process with Low Levels of Nitroxide

Paula J. MacLeod,* Richard P. N. Veregin,
Peter G. Odell, and Michael K. Georges

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

Received October 11, 1996
Revised Manuscript Received January 21, 1997

Introduction. In recent years there has been a heightened interest in "living" radical polymerizations. "Living" radical polymerizations may not meet the exacting definition of living found in ionic polymerization, but they do show a linear increase in M_n as a function of conversion, give polydispersities in the 1.1−1.3 range, and can form block copolymers.[1] One class of living radical polymerizations is stable free radical polymerizations (SFRP), where a stable free radical, such as a nitroxide, is used to control the polymerization. In 1993, Georges *et al.* demonstrated that high conversion, narrow polydisperse polystyrene resins could be prepared by the SFRP process.[2]

The narrow polydispersities and controlled molecular weights from SFRP reactions are the result of two key steps. First, the reactions are done at temperatures where initiation is rapid and all of the chains are formed at about the same time. Second, and most important, the initiated polymer chains, $P_n^\bullet$, are reversibly capped by a stable free radical,[3] such as the nitroxide TEMPO (2,2′,6,6′-tetramethylpiperidinyl-1-oxy), $T^\bullet$, to give a dormant living polymer chain, L_n. This equilibrium is denoted by eq 1.[4,5] Capping of the initiated chains by nitroxide has been coined germination, as it is the required step to produce a living chain.[5] While this capped polymer chain is dormant at temperatures less than 100 °C for TEMPO, at sufficiently high temperatures, above 115 °C, homolysis of the NO−C bond gives a growing polymer chain radical, $P_n^\bullet$, and the nitroxide radical. Complete details of the mechanism of the formation of the living chains have been discussed elsewhere.[5]

$$P_n^\bullet + T^\bullet \rightleftarrows L_n \qquad (1)$$

The efficiency of chain capping, germination efficiency, depends on the initial level of nitroxide. During initiation, an excess of nitroxide is present to increase the germination efficiency. The ratio of initiator to nitroxide used depends on the initiator and germination efficiencies. Typically, initiator:nitroxide ratios of 1.3:1 to 1.1:1 are used for the styrene/TEMPO/benzoyl peroxide (BPO) system. These ratios are a result of a BPO initiator efficiency of 50−60% and high germination efficiencies at 135 °C.

Excess nitroxide facilitates the capping reaction, but it also slows propagation by pushing the equilibrium, eq 1, to the capped form which does not propagate. However, the overall rates of polymerization are less sensitive to the initial TEMPO:BPO ratio for styrene polymerization than might be expected. For example, when the TEMPO:BPO ratio is increased, for instance from 1.1:1 to 1.3:1, the additional TEMPO does not all become free nitroxide. Rather, the increased amount of nitroxide is largely consumed in capping more radicals and this feedback loop buffers the nitroxide concentration. A recent publication discusses the pivotal role of the nitroxide in these reactions.[5]

As stated in this publication: "The concept of germination efficiency can only be properly applied to systems with the correct stoichiometry of nitroxide to initiator to provide a practical living system." This paper explores what happens to the rates of reaction and the livingness when the stoichiometry of initiator to nitroxide is much lower than the ratios typically used.

Results and Discussion. A series of styrene polymerizations were performed varying the TEMPO:BPO ratio from 1.35:1 to 0.50:1 and the results are given in Table 1. The concentration of BPO (400 mg in 40 g of styrene) has been kept constant, while the concentration of TEMPO is varied. The general polymerization and characterization (molecular weights, conversion, and nitroxide level) details have been described previously.[5] There have been thorough studies done on the stable free radical polymerization of styrene using ratios in the 1.1:1 to 1.3:1 range.[5] These experiments are repeated here for comparison only.

Polymerization of styrene using TEMPO:BPO ratios in the 1.1:1 to 1.3:1 range give polydispersities <1.3 and conversions between 30−70% after 5 h at 135 °C. Plots of M_n as a function of conversion and semilogarithmic plots of conversion as a function of polymerization time (corrected for the nitroxide concentration) have been shown to be linear for TEMPO:BPO ratios in the 1.3:1 to 1.1:1 range, suggesting the system is living under these conditions.[5] As the ratio is lowered from 1:1 down to as low as 0.6:1 the polydispersities do broaden somewhat but remain close to 1.4. Even at a ratio of 0.48:1 the polydispersity, 1.6, is only slightly above the theoretical minimum polydispersity of 1.5, where termination is primarily controlled by combination of two polymer radicals.

The molecular weight distributions and conversions were monitored for a reaction with a TEMPO:BPO ratio of 0.5:1. An overlay of the corresponding GPC molecular weight distributions is shown in Figure 1. At 7 min of reaction at 135 °C the M_n is 7500 with a conversion of 31%. The molecular weight increases to M_n 11 200 after 0.5 h, is 14 000 at 1 h, and after 2 h is 17 600 at a conversion of 75%. Using a TEMPO:BPO ratio of 0.5:1 might not be typical conditions to provide a practical living system, however, Figure 1 shows the molecular weights start low and the molecular weight distribution moves to higher molecular weights over time. Examination of conversion vs time behavior shows a rapid initial polymerization to about 31% conversion in the first 7 min, as shown in Figure 2. After this time the conversion increases much more slowly. During initiation the number of moles of initiating radicals far exceeds the moles of nitroxide present and termination consumes a large portion of the excess free radical, [P•], allowing the nitroxide level to return to that expected for a SFRP reaction.

The decomposition of the BPO is dependent on the internal temperature of the polymerization; therefore, in a separate experiment the internal temperature of the polymerization using a 0.5:1 TEMPO:BPO ratio was closely monitored. Within the first 7 min the reaction temperature reached about 120 °C, and then there was an exotherm that raised the temperature to 146 °C over the course of 40 s. This exotherm is not observed when the stoichiometry of nitroxide and initiator are more closely matched. The data of Barrett[6] was used to calculate the decomposition rate of the benzoyl peroxide

Table 1. Polydispersity and Conversion Data (after 5 h at 135 °C) for the Stable Free Radical Polymerization of Styrene as a Function of the TEMPO:BPO Ratio

TEMPO:BPO	M_n	polydispersity	% polymer
1.35:1	6 576	1.21	33
1.22:1	12 817	1.20	60
1.10:1	15 163	1.29	75
1.06:1	15 764	1.36	77
1.00:1	16 537	1.35	74
0.90:1	18 444	1.38	81
0.81:1	19 209	1.38	79
0.70:1	20 127	1.45	80
0.61:1	22 695	1.41	94[a]
0.48:1	20 965	1.60	83[b]

[a] TGA analysis after 4 h of reaction. [b] TGA analysis after 2.5 h of reaction.

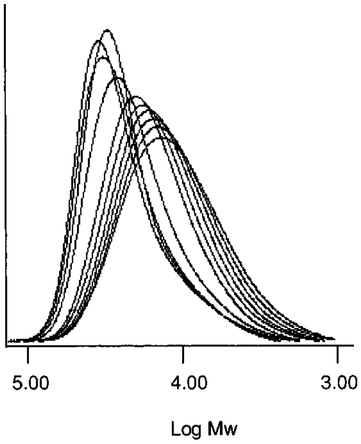

Figure 1. GPC distributions of polystyrene samples showing the incremental increase of molecular weight with time. The molecular weight increases from right to left. Starting at the far right the samples were taken at 4, 7, 11, 17, 24, 32, 60, 90, 120, and 150 min respectively.

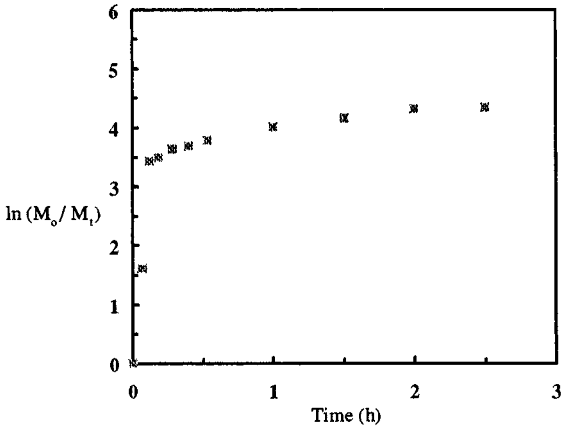

Figure 2. Semilogarithmic plot of conversion vs time for bulk polymerization of styrene with 0.5:1 TEMPO:BPO ratio, [BPO] = 0.038 M, at 135 °C.

as the temperature changes. During the exotherm and the subsequent 20 s, the remaining 85% of the initiator is consumed and the supply is exhausted. The samples at 4 and 7 min appear to bracket this pulse of initiation during which a large population of initiator fragments are produced. During this burst of initiation the amount of TEMPO is insufficient to rigorously control all of the chains initiated and termination dominates producing a population of low molecular weight dead material. However, there is also a population of living chains which gives the linear increase in M_n with conversion shown on the graph.

The use of small amounts of nitroxide relative to initiator in the styrene system does not result in a perfectly living polymerization; however, the deviation from livingness only occurs during initiation. During initiation the nitroxide controls the growth of the chains that terminate, resulting in dead polymer with a low molecular weight, as opposed to the high molecular weight dead chains produced in a conventional radical polymerization. The remaining chains, capped with nitroxide, continue to grow in a living fashion.

As a control, an autopolymerization of styrene, in the absence of nitroxide and initiator, was performed. After 3 h the autopolymerization reaction had gone to 43% conversion with a M_w of 315 000 and a polydispersity of 1.78. In contrast, in 2.5 h an SFRP reaction using ≈400 mg of BPO and a TEMPO:BPO ratio of 0.5:1.0 goes to 73% conversion with a M_w of 27,500 and a polydispersity of 1.50. When styrene and BPO are heated at 135 °C in the absence of nitroxide the reaction mixture becomes very viscous in less then 30 min. A polymer sample taken after 30 min had a M_w of 65 K with a polydispersity of 3.45. These controls show that even a small amount of nitroxide (in the 0.5:1 TEMPO: BPO polymerization) has a significant moderating effect.

We are currently studying the SFRP process using low nitroxide:initiator ratios by ESR and will report our findings in a future publication.

Conclusions: The polydispersity and conversion in the stable free radical polymerization of styrene can be tuned by varying the TEMPO:BPO ratio from 1.3:1 to 0.5:1. There is a self-correcting mechanism in the stable free radical polymerization of styrene that adjusts the number of growing chains and regardless of the initial initiator/nitroxide level the system moves toward an equilibrium concentration of free nitroxide. Polymerizations using low ratios, *i.e.* 0.5:1, result in rapid irreversible termination that produces a low molecular weight dead polymer and reversible termination by nitroxide to produce a population of living chains.

Acknowledgment. P.J.M thanks the NSERC for an Industrial Research Fellowship.

References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *ACS Polym. Div., Polym. Prepr.* **1994,** *35(2),* 582. b) Listigovers, N. A.; Georges, M. K.; Odell. P. G.; Keoshkerian, B. *Macromolecules* **1996**, *29,* 8992.
(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26,* 2987.
(3) Solomon, D. M.; Rizzardo, E.; Cacioli, P. US Patent 4,581,429. Rizzardo, E. *Chem. Aust.* **1987**, *54,* 32.
(4) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26,* 5316.
(5) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29,* 2746.
(6) Barrett, K. E. J. *J. Appl. Polym. Sci.* **1967,** *11,* 1617.

MA961510+