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Notes

Electron Spin Resonance Studies of the Stable Free-Radical Polymerization of Styrene

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

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Introduction

Styrene has been shown to polymerize readily via nitroxide-mediated stable free-radical polymerization (SFRP) and mechanistic details have been published elsewhere.[1−4] For styrene polymerizations, nitroxide: initiator ratios of 1.3:1 to 1.1:1 are typically used when the nitroxide is 2,2′,6,6′-tetramethylpiperidinyl-1-oxy (TEMPO) and the initiator is benzoyl peroxide (BPO). Recently, we have gone back to examine the role of the initiator to nitroxide ratio in these polymerization reactions.[5] Our study included a range of TEMPO−BPO ratios from 1.3:1 down to as low as 0.5:1. At ratios in the 0.5:1 range there was some rapid irreversible termination during the brief initiation period, as well as reversible termination by nitroxide. The reversible termination gave a population of capped chains that continued to grow in a living fashion, and the irreversible termination gave a lower molecular weight dead chain component that was observed as tailing in the molecular weight distributions (GPC) of the living population.

The role of free nitroxide in the SFRP process is pivotal and has been studied in detail for polymerizations where the TEMPO−BPO ratio is in the 1.1:1 to 1.3:1 range.[1−4] Scaiano and co-workers[6] have studied the use of stoichiometric initiators for controlled styrene polymerizations and have reported that chain termination occurs until sufficient TEMPO is liberated to support the capping reaction. Our data on chain extensions and unimer reactions also support this idea.[7] If a polymerization is initiated using a TEMPO-terminated polymer or a unimer, and monitored by electron spin resonance (ESR), free nitroxide is detected. The level is similar to what one would observe if the polymerization had been initiated using peroxide or azo initiators and an excess of nitroxide. In the SFRP of styrene there is an equilibrium level of free nitroxide that the system strives to attain.

The free nitroxide concentration during initiation and propagation is also of interest when the polymerization is initiated with a deficiency of nitroxide. This paper discusses the ESR studies of the SFRP process when a large excess of initiator is used relative to nitroxide, i.e., where the TEMPO−BPO ratio is 0.5:1.

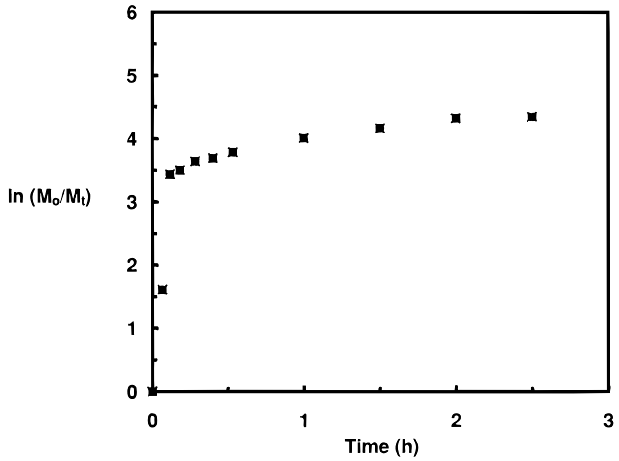

Figure 1. Rate of polymerization of styrene at 135 °C using a 0.5:1 molar ratio of TEMPO−BPO.

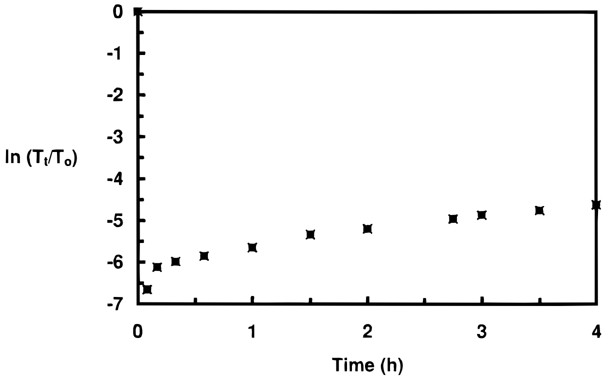

Figure 2. Semilog plot of TEMPO concentration versus polymerization time for bulk polymerization of styrene with a TEMPO−BPO ratio of 0.5:1, $[BPO]_0 = 0.038$ M, 135 °C.

Results and Discussion

The free nitroxide level for a styrene polymerization performed at 135 °C with a TEMPO−BPO ratio of 0.5:1 was monitored by ESR spectroscopy. The ESR studies were done in a manner identical with those previously reported.[4] The plot of ln (M_0/M_t) vs time is shown in Figure 1 and the plot of $\ln(T_t/T_0)$ vs time is shown in Figure 2 (M_0 is the initial monomer concentration and M_t is the concentration after time t; T_0 and T_t are the initial concentration of TEMPO, [TEMPO], and the [TEMPO] after time t, respectively). In the first few minutes of the reaction the nitroxide level drops dramatically, reaching a minimum and then gradually rising. The value at the minimum represents 0.002% of the original nitroxide concentration. The amount of free nitroxide, ln T_t/T_0, in the −6 to −5 range, is the same as when ratios of 1.1:1 to 1.3:1 are used.[4] There

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* Author to whom correspondence is addressed. Telephone: 905-823-7091. E-mail: paula_macleod@xn.xerox.com.

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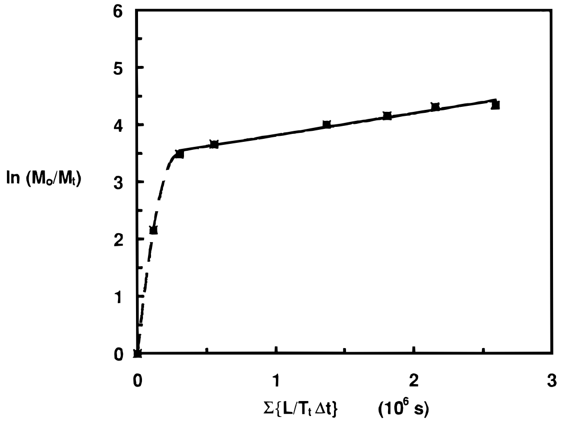

Figure 3. Rate of polymerization, at 135 °C with a TEMPO−BPO ratio of 0.5:1, corrected for the total number of chains and for the nitroxide concentration, *T*, as described in ref 4. The linear fit to the last six data points has $r = 0.9857$. The curve between the first three data points is shown as a guide to the eye only. *L* is the number of living chains. See ref 4 for more details.

is a gradual increase in the nitroxide concentration over time that is also observed for TEMPO−BPO ratios of 1.3:1 and 1.1:1 at 135 °C.[4] The increase in [TEMPO] has been attributed to chain termination.

Figure 3 shows the polymerization rate when the TEMPO−BPO ratio is 0.5:1 (taken from Figure 1), where the plot has been corrected to account for the nitroxide concentration and the number of living chains, as discussed in ref 4. A plot of $\ln(M_0/M_t)$ vs the corrected free nitroxide level for a living polymerization should be linear, indicating that the number of living chains is constant. The plot in Figure 3 has two distinct regions. The first region of the plot represents the first 7 min of the reaction where the polymerization is very fast because the nitroxide level is too low to control the polymerization and $\ln(M_0/M_t)$ increases rapidly. In the second region, $\ln(M_0/M_t)$ increases linearly at a much slower rate with a slope, $k_{obs} = k_p/K$ (where k_p is the propagation rate constant and K is the equilibrium constant for the capping reaction), of $3.9 \pm 0.9 \times 10^{-7}$ s^{-1}. To obtain the value for the slope, it was assumed that the number of living chains is equal to the initial amount of TEMPO added.[8] In other words, termination of the conventional chains has removed them from consideration, and it is assumed that essentially all of the TEMPO is consumed to cap chain ends and that all of these capped chains are living and grow by a nitroxide-mediated process.[4] This value of k_{obs} is the same as the value of $3.6 \pm 0.5 \times 10^{-7}$ s^{-1} measured previously at 135 °C (all error limits are at the 95% confidence level), where the TEMPO−BPO ratio was 1.1:1 to 1.3:1.[4] The similarity of the k_{obs} values supports the interpretation that the second region of the curve in Figure 3 represents a living polymerization. Extrapolating this portion of the curve to zero suggests that approximately 30% of the conversion is due to conventional polymerization. A conventional polymerization occurs in the first few minutes of the polymerization, while the polymer conversion after the first 7 min arises from a living polymerization.

Conclusions

ESR studies have shown that after initiation, the level of free nitroxide, when low ratios of TEMPO−BPO are used, i.e., 0.5:1, is the same as that when higher ratios such as 1.3:1 are used. In the stable free-radical polymerization of styrene the number of growing chains is adjusted, regardless of the initial initiator/nitroxide level, to move the system toward an equilibrium concentration of free nitroxide. Polymerizations at the low ratios are characterized by an initial fast and predominantly conventional polymerization, which adjusts the nitroxide to radical chain end ratio to a level sufficient to result in a subsequent living free-radical polymerization.

References and Notes

(1) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 582. (b) Listigovers, N. A.; Georges, M. K.; Odell, P. G.; Keoshkerian, B. *Macromolecules* **1996**, *29*, 8992.
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(7) Unpublished results, manuscript in preparation.
(8) This is an oversimplification because TEMPO could be consumed through the promoted dissociation of BPO, although this should not be an important process under these conditions.[4] As well, the contribution of styrene thermal polymerization has not been considered.

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