Molecular Weight Control by a "Living" Free-Radical Polymerization Process

Craig J. Hawker

*IBM Almaden Research Center, 650 Harry Road
San Jose, California 95120-6099*

The ability to accurately control macromolecular architecture is becoming an increasingly important aspect of polymer chemistry. Typically well-defined macromolecular architectures are prepared by stepwise,[1] transition-metal-catalyzed,[2] or anionic processes.[3] However, a long-term goal of synthetic polymer chemists has been the development of a radical polymerization process which possesses many of the desired characteristics of these more challenging methods and leads to well-defined materials. Specifically, these characteristics are molecular weight control, end group control, ability to form block copolymers, and a "living" nature. Recently, Georges et al.[4] have reported that low polydispersity (PD) polymers can be prepared by free-radical chemistry using a system that can be considered to be a living polymerization. This seminal report was based on the use of stable nitroxide free radicals, such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), as thermally labile "capping" agents for the growing polymer chain, which in turn leads to control of the polymerization. Previously, TEMPO had been used to trap the initiating species in a variety of free-radical polymerizations[5] and to reversibly terminate a growing polymer chain, producing low molecular weight oligomers.[6] We report herein the use of a modified TEMPO-based initiator that allows accurate molecular weight control and block copolymer formation and gives rise to well-defined end groups.

The modified free-radical initiator was prepared by heating a mixture of benzoyl peroxide and TEMPO with an excess of styrene at 80 °C under argon. This gave a large number of products, from which the desired monoadduct, 1, could be separated by flash chromatography and obtained in 42% yield. Structural identification of 1 was by ^1H and ^{13}C NMR spectra coupled with microanalysis and mass and infrared spectroscopy (Scheme 1). The isolation of 1 as a major product relies on the extremely low rates of reaction of nitroxides with oxygen-centered radicals, such as the benzoyloxy radical, and their near-diffusion-controlled rates with carbon-centered radicals, such as those derived from the addition of a benzoyloxy radical to styrene. Prolonged exposure of 1 to air, light, and moisture resulted in no detectable decomposition and demonstrates the stable nature of the aminoxy group. At elevated temperatures (>100 °C), however, these molecules have been shown to be thermally unstable and dissociate in an equilibrium process to give TEMPO and a radical, 2.[7] In the presence of excess monomer, 2 would initiate a *single* growing polymer chain, and the presence of the TEMPO "counter" radical would suppress deactivation reactions (Scheme 2). Therefore, in analogy with anionic polymerizations, accurate control of molecular weight may be achieved by the use of preformed TEMPO-based initiators such as 1 and the calculated molar excess of monomer.
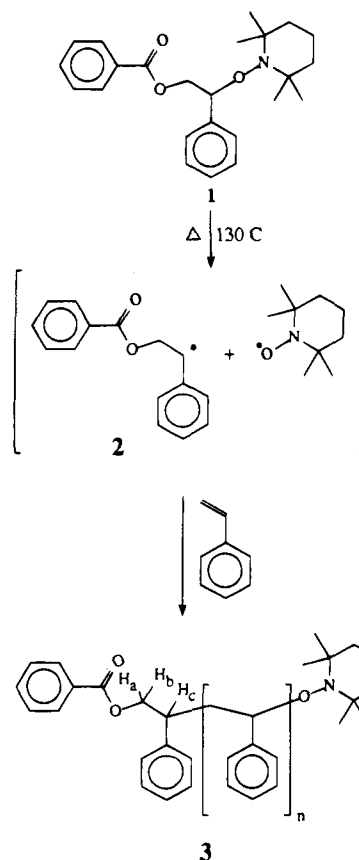
Scheme 1

1
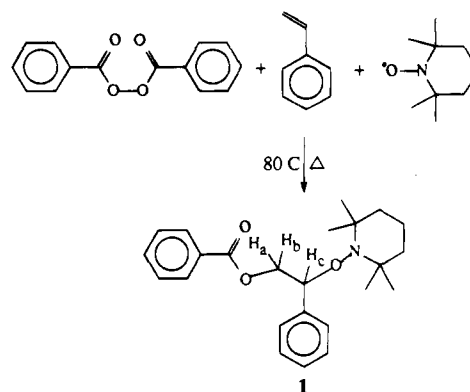
Scheme 2

Table 1 shows the results of heating a neat mixture of 1 with a calculated amount of styrene at 130 °C under argon for 72 h.[8] Remarkably, the experimental molecular weights of the derived polymers are close to the theoretical values calculated from the feed ratio of styrene to 1. At molecular weights below 30 000, the agreement between experimental[9] and calculated M_n values is excellent, and as the molecular weight increases, this difference increases only slightly. Even at molecular weights of over 100 000, the experimental value is still within 10% of the calculated value. In agreement with the results of George et al.,[4] the polydispersities of all the polymers obtained were low and well below the theoretical limiting polydispersity of 1.5 for a conventional free-radical process. Monitoring of a

(1) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(2) Gorman, C. B.; Ginsburg, E. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 1397.
(3) Quirk, R. P.; Lynch, T. *Macromolecules* **1993**, *26*, 1206.
(4) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(5) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982**, *15*, 1188. Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909.
(6) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4,581,429, March 27, 1985. Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32.
(7) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316.

(8) The isolated yields of all polymers were approximately 90%, indicating that conversion was very high. This agrees with the finding of Georges,[4] who found 90% conversion after 69 h at 123 °C.
(9) M_n values were determined experimentally by gel permeation chromatography using commercially available narrow molecular polystyrene samples as standards.

11186   *J. Am. Chem. Soc., Vol. 116, No. 24, 1994*

Communications to the Editor

Table 1. Comparison of GPC Molecular Weights with Calculated Molecular Weights for Polystyrenes, **3**

M_n (exptl)	M_n (calcd)	PD^a	M_n (exptl)	M_n (calcd)	PD^a
3 450	3 330	1.15	54 500	59 500	1.29
4 900	5 200	1.14	82 000	90 500	1.36
13 000	13 500	1.10	110 000	123 000	1.41
25 500	28 000	1.20			

^{a} Polydispersity.
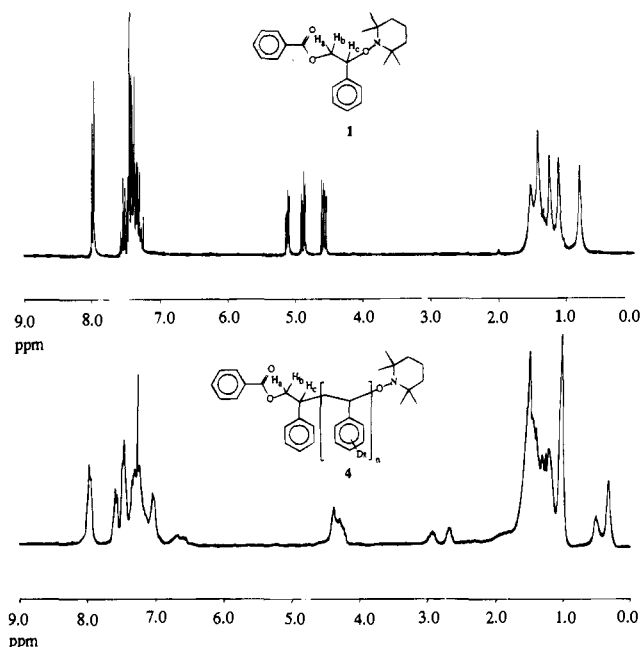
Figure 1. Comparison of the 300 MHz ^{1}H NMR spectra of modified initiator, **1**, and polymer obtained after reaction with styrene-d_8, **4**.

single polymerization by size exclusion chromatography at regular intervals also supported the earlier work of George.[4] The molecular weight of the polymer was found to gradually increase with time and maintained a very narrow molecular weight distribution.

The nature of the chain ends for polymers derived from **1** as the initiator was probed by polymerizing deuterated styrene under the same conditions as above and observing the ^{1}H NMR spectrum of the resultant polymer, **4** (M_n = 3000). Comparison of the ^{1}H NMR spectrum of **1** with that of the polymer **4** shows a number of interesting features (Figure 1). The protons H$_a$, H$_b$, and H$_c$ derived from the styrene unit in **1** appear as three AB quartets at 4.50–5.20 ppm; however, on reaction with styrene-d_8, the resonances for H$_a$ and H$_b$ shift slightly upfield and appear as a broad multiplet at 4.35 ppm, while H$_c$ suffers an even more dramatic upfield shift and appears as a broad doublet at 2.80–3.05 ppm. This behavior is fully consistent with the anticipated structure of **4**, where the electron-withdrawing TEMPO unit is replaced by a deuterated polystyrene chain, and the effect would be most pronounced for H$_c$ rather than H$_a$ and H$_b$. Other points of note are the doublet at 8.00 ppm for the benzoyl group in the spectra of both **1** and **4** and the set of resonances between 0.40 and 1.70 ppm for the TEMPO unit in both spectra. Comparison of the integration values for the various resonances in the spectrum shows that the 1:1 ratio of TEMPO and (benzyloxy)styrene units is maintained. Analysis of the ^{1}H NMR spectra of the low molecular weight nondeuterated polystyrene samples revealed similar features, and comparison of the integration values for the end groups with the main polystyrene chain gave molecular weights similar to those obtained from the GPC measurements, indicating no loss of chain ends. From these results it can be concluded that the polymers prepared using **1** have a single benzoyloxy end group and a single TEMPO end group. Analysis of **4** also showed that the end groups were stable to prolonged exposure to light,
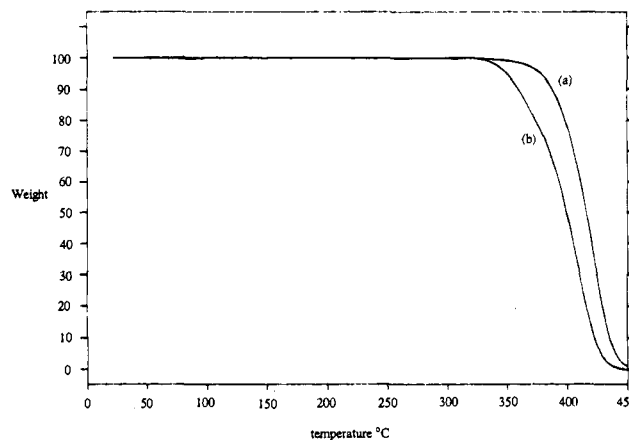
Figure 2. Comparison of the TGA curves (N$_2$, 10 °C min^{-1}) for polystyrenes of comparable molecular weights: (a) standard free-radical polystyrene and (b) TEMPO polystyrene.

air, and moisture. The thermal lability of the TEMPO chain end did have a small effect on the thermal stability of the polymers produced. As can be seen in Figure 2, "standard" polystyrene shows 10% weight loss at 385 °C, while the polystyrene produced by the above TEMPO process shows a 10% weight loss at 360 °C. The temperature of initial decomposition is also depressed by ca. 25 °C in the TEMPO case; this slight lowering of the thermal stability is in agreement with the thermal lability of the TEMPO chain end.

Since the end groups of the polymers (e.g., **3**) obtained from the above polymerizations are essentially the same as those of the initiator **1**, it might be expected that the stability and reactivity of **3** and **1** would be similar. Therefore, thermolysis of such a polymer in the presence of a dissimilar unsaturated monomer units would lead to reactivation of the active chain ends and formation of a block copolymer. To demonstrate block copolymer formation, consider a mixture of **3** (DP ≈ 50) and 100 mol equiv of *p*-acetoxymethylstyrene at 130 °C under argon for 72 h. After purification, the polymer obtained was shown by ^{1}H NMR to have a ca. 1:1 molar ratio of styrene to *p*-acetoxymethylstyrene units. This, coupled with the molecular weight increase from M_n = 4900 (PD = 1.13) to 9500 (PD = 1.42), demonstrates that block copolymer formation can be achieved using polymers having a TEMPO chain end and that relatively narrow polydispersities and defined block lengths can be obtained. While this work was in progress, Endo et al.[10] reported the use of anionically produced polystyrenes having an aminoxy end group to prepare block copolymers, while Georges[4] reported the copolymerization of styrene and butadiene with BPO and TEMPO.

In conclusion, a free-radical polymerization procedure based on a modified TEMPO-based initiator, **1**, has been developed which has many of the features of living anionic polymerizations. Molecular weights can be accurately controlled, end groups are well defined, and block copolymer formation is possible. Benefits of this procedure are that the initiating system is extremely stable and the reaction conditions require no solvent or rigorous experimental and purification techniques.

Supplementary Material Available: Preparation and characterization data for **1** and description of the polymerization of styrene using **1** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(10) Yoshida, E.; Ishizone, T.; Hirao, A.; Nakahama, S.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 1993.