Accurate Control of Chain Ends by a Novel "Living" Free-Radical Polymerization Process

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Received November 1, 1994
Revised Manuscript Received February 8, 1995

Accurate control of polymerization processes to give well-defined telechelic and end-functionalized macromolecules is becoming an increasingly important aspect of polymer chemistry.[1] This interest is driven by the ability of end-functionalized polymers to form networks, undergo chain extension or produce various types of block copolymers on reaction with comonomers or coblocks, and form macromonomers.[2] Typically, accurate control of chain ends is accomplished using either anionic,[3] cationic,[4] or ring-opening polymerization techniques.[5] While these procedures are undoubtedly successful, they do suffer from rigorous synthetic requirements and incompatibility with a variety of functional groups. Free-radical polymerizations are synthetically less rigorous and in some cases offer an alternative route to chain end-functionalized macromolecules containing reagent-sensitive groups attached to the main chain and/or chain ends. However, the major drawback of free-radical processes is that they lead to polydisperse products without accurate control over the molecular weight and, more importantly, the number of chain ends. The latter is due to the competing combination and disproportionation termination steps and the inefficiency of the initiations step which leads to functionalities less than or greater than theoretically expected.[6] For example, Moad[7] has shown that for the benzoyl peroxide initiated polymerization of styrene the initiation step leads to at least six active species which in turn lead to a final macromolecule where the number of benzoyl chain ends per macromolecule varied from 1.4 to 2.3. This paper reports a novel free-radical polymerization process which allows control over both molecular weight and chain ends.

Recently, it has been shown that the use of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) based initiators,[8,9] or systems containing TEMPO,[10,11] for the bulk free-radical polymerization of vinyl monomers, such as styrene, results in a "living" process. Initially, researchers used a combination of TEMPO and a radical initiator to control the polymerization.[10,11] However, we have recently shown that the adduct, **1**, is a very efficient initiator of the polymerization of styrene at 130 °C and gives polystyrenes with accurately controlled molecular weights and low polydispersities (ca. 1.1–1.2).[8] This high level of control is due to each molecule of **1** initiating a single chain with significantly reduced, if any, termination reactions occurring. A consequence of this initiating system is that one chain end is derived from the initiator while the other is derived from the TEMPO "counter" radical, and this feature may permit the synthesis of chain end-functionalized polymers.

To investigate this question, two synthetic strategies were examined. The initial strategy relies on the synthesis of functionalized monoadducts of styrene and TEMPO and their subsequent use as polymerization initiators. These functionalized initiators were prepared by modifying the ester functionality, which is present in **1**, with the desired functional group. For example, **1** was hydrolyzed with potassium hydroxide to give the hydroxyl derivative, **2**, in 87% yield after purification. Polymerization of deuterated styrene (50 equiv) with **2** at 130 °C for 72 h gave the hydroxyl-terminated polystyrene **3** (M_n(SEC) = 4950, P.D. = 1.11) in 92% yield after purification (Scheme 1). Comparison of the ^{1}H NMR spectrum of the initiator, **2**, with that of the polymer, **3**, reveals that the protons H_a, H_b, and H_c derived from the styrene unit of **2** shift upfield on reaction with styrene-d_8, with the shift for H_c being the most dramatic (Figure 1). Comparison of the integration values for the various resonances in each spectra also shows that the 1:1 ratio of TEMPO and hydroxy-

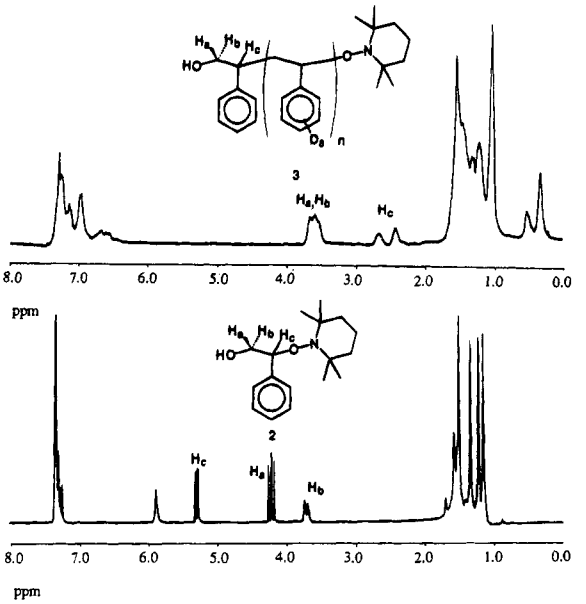
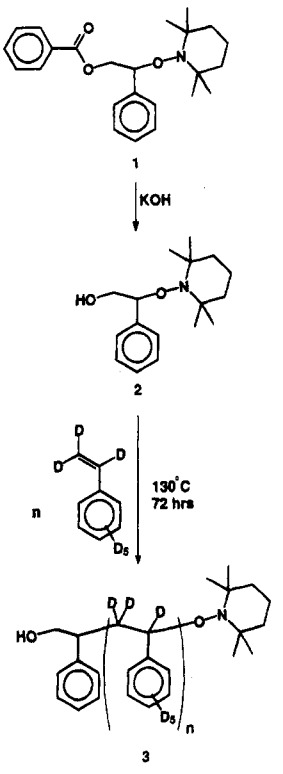


Figure 1. Comparison of the 300-MHz ^{1}H NMR spectra of initiator **2** and polymer obtained after reaction with styrene-d_8, **3**.

Scheme 1



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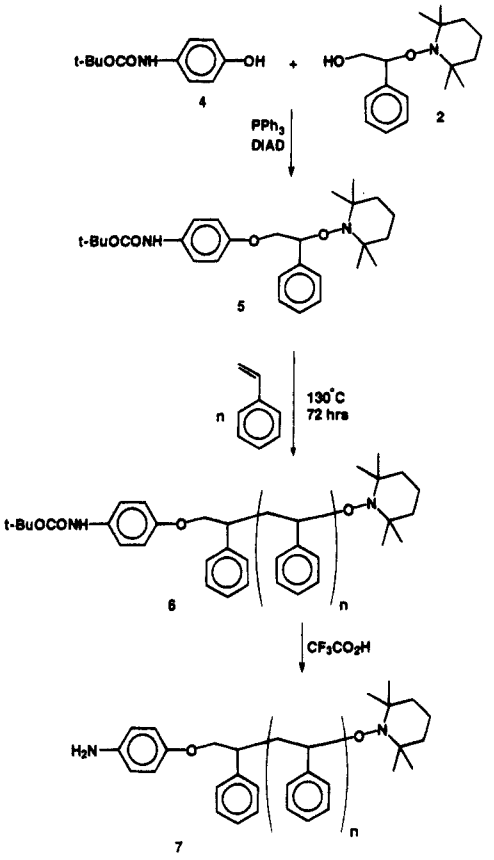
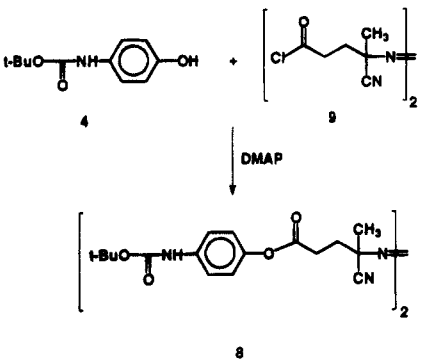
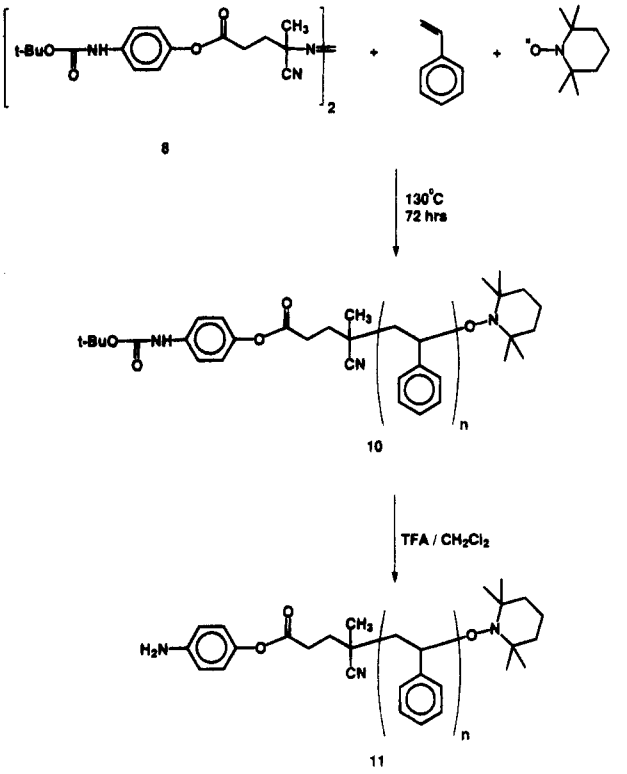
Scheme 2



Scheme 3



Scheme 4



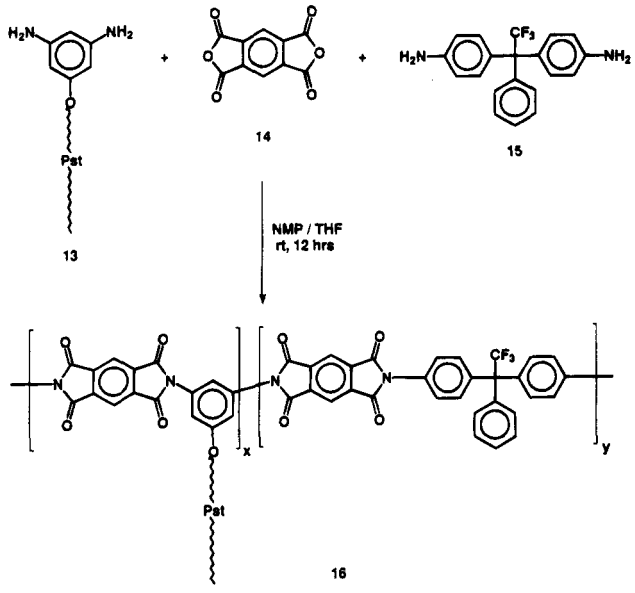
styrene units is maintained in the polymer **3**. These results are consistent with the polymer **3** having a single hydroxymethyl functional group as one chain end and a TEMPO group as the other chain end.

To further demonstrate the feasibility of this approach as a means of controlling chain ends, **2** was modified by reaction with *N*-(*tert*-butoxycarbonyl)-4-aminophenol (**4**) under standard Mitsunobu conditions.[12] The functionalized initiator, **5**, which contains a protected amino group was obtained in 63% yield after purification. Polymerization of styrene (140 equiv) with **5** at 130 °C for 72 h afforded the functionalized polystyrene **6**, which was shown to have a polydispersity of 1.16 and a number-average molecular weight of 13 500 (SEC).[13] This is in good agreement with the theoretically expected value for M_n of 14 500.[14] The t-Boc protected amino group of **6** could be deprotected with trifluoroacetic acid to give the monoamino-terminated polystyrene, **7**, (P.D. = 1.16, M_n = 13 500) (Scheme 2). Significantly, potentiometric titration of **7** yielded a number-average molecular weight of 13 000 which is in excellent agreement with the value determined by size-exclusion chromatography and demonstrates that living free-radical polymerizations using TEMPO-based initiators allow for accurate introduction of functional chain ends. The polymerization conditions associated with this novel process also allow a wide range of functional groups to be introduced.

An alternative procedure for the synthesis of chain end-functionalized polymers relies on the "in-situ" generation of active species which carry both the desired functional group and a TEMPO unit. These active species are formed by the reaction of functionalized initiators with styrene and TEMPO in the polymerization mixture and also lead to control of the chain ends. For example, the functionalized azobis(isobutyronitrile) (AIBN) derivative, **8**, was prepared in 66% yield by reaction of the bisacid chloride, **9**, with **4** (Scheme 3). Initiation of the polymerization of styrene (150 equiv) with **8** in the presence of 2 equiv of TEMPO at 130 °C was shown to be a living system by GPC analysis in a manner similar to that reported by Georges.[10] After 72 h, the isolated polymer, **10**, was found to have a M_n of 14 000 (SEC) and a polydispersity of 1.21 which is ca. 90% of the theoretical value (15 500). Deprotection of **10** afforded the monoamino-terminated polystyrene, **11**, which on potentiometric titration yielded a value for M_n of 13 500 (Scheme 4). This is in excellent agreement with the value determined by size-exclusion chromatography and demonstrates the feasibility of this approach.

The use of the corresponding 3,5-diaminophenol derivative, *N*,*N*-bis(*tert*-butoxycarbonyl)-3,5-diaminophenol (**12**), in both of the above procedures was shown to produce essentially the same results, though potentiometric titrations yielded a value for M_n of approximately half that observed by SEC. However, this is fully consistent with the structure of **13** since, while only one chain end is functionalized, it is functionalized with a diamino-substituted phenyl ring.

Scheme 5



The utility of functionalized polystyrenes prepared by these methods was demonstrated by the synthesis of polystyrene/polyimide block copolymers. The diamino-terminated polystyrenes are ideally suited for the preparation of graft copolymers, and reaction of **13** with 1,2,4,5-benzenetetracarboxylic dianhydride (**14**), and 2,2-bis(4′-aminophenyl)-2-phenyl-1,1,1-trifluoroethane (**15**) was found to give a polystyrene/polyimide graft copolymer, **16**, containing 15% by weight polystyrene (Scheme 5). Size-exclusion chromatography demonstrated the absence of polystyrene homopolymer, while DSC, DMA, and TEM all revealed features consistent with graft copolymer formation and microphase separation. The corresponding polymerization reaction with monoamino-terminated polymers, such as **11**, was shown to produce ABA triblock copolymers.

In conclusion, we have demonstrated that accurate control of chain ends can be realized in TEMPO-based living free-radical polymerizations. Functionalized polystyrenes of controlled molecular weight and low polydispersity can be prepared either by a modified TEMPO-based initiator or by the use of a functionalized initiator in the presence of TEMPO. The presence of a single end group bearing either one or two functional groups was further confirmed by the synthesis of triblock and graft polystyrene/polyimide copolymers.

Acknowledgment. We thank NIST for financial support through ATP Contract No. 70 NANB-3H-365.

Supplementary Material Available: Experimental procedures of **1**, **2**, **4**, **5**, **8**, and various other compounds used in this study (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(2) Percec, V.; Pugh, C.; Nuyken, O.; Pask, S. D. In *Comprehensive Polymer Chemistry*; Allen, G., Bevington, J. C., Eds.; Pergamon: Oxford, U.K., 1989; Vol. 6, p 281. Goethals, E. J. *Telechelic Polymers: Synthesis and Applications*; CRC Press: Boca Raton, FL, 1989.
(3) Hirao, A.; Hattori, I.; Sasagawa, T.; Yamaguchi, K.; Nakahara, S.; Yamazaki, N. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 59.
(4) Keszler, B.; Chang, V. S. C.; Kennedy, J. P. *J. Macromol. Sci., Chem.* **1984**, *A21*, 307.
(5) Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1985**, *68/69*, 39.
(6) Eastmond, G. C. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F., Eds.; Elsevier: Amsterdam, The Netherlands, 1976; Vol. 14a, p 65.
(7) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982**, *15*, 1188.
(8) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11314.
(9) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2* (2), 66.
(10) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(11) Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32. Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4,581,429, March 27, 1985.
(12) Hughes, D. L. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley and Sons: New York, 1992; Vol. 42, Chapter 2.
(13) M_n values were determined experimentally by size-exclusion chromatography using commercially available narrow molecular weight polystyrene samples as standards.
(14) Theoretical values are based on the relative molar ratio of initiator and monomer and the assumption that one molecule of initiator initiates a single chain with no termination.

MA946062P