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# Communications to the Editor

## Convenient Synthesis and Application of a New Unimolecular Initiator

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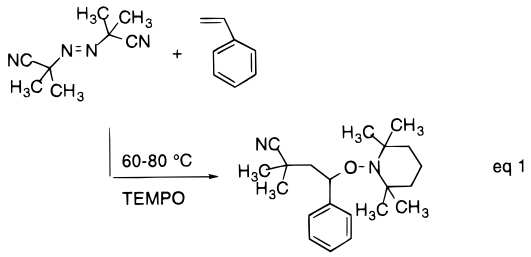
Living polymerization is one of the most convenient methods for the synthesis of polymers with controlled molecular weights and properties.[1] Recent development of living radical polymerization has further expanded the capability of the living polymerization methods, which allowed the facile preparation of a wide variety of polymers, copolymers, and functionalized polymers with predetermined structures and properties.[2] Living radical polymerization was accomplished by conducting the polymerizaton in the presence of reversible binding radicals or transition-metal complexes.[3] Recently, in-




eq 1

**2**

tensive research has been focused on developing unimolecular initiators.[4] The unimolecular initiators offer the advantages of fast reaction rates and allow the facile construction of block copolymers and graft copolymers and other complex macromolecular structures.[5] Several nitroxides-based unimolecular initiators have been reported. However, these initiators were usually synthesized in multiple steps, which often results in low yields and tedious separations. We report here a convenient synthesis of a new unimolecular initiator and the preliminary study on the application of this initiator for the synthesis of several narrowly dispersed polymers and block copolymers.

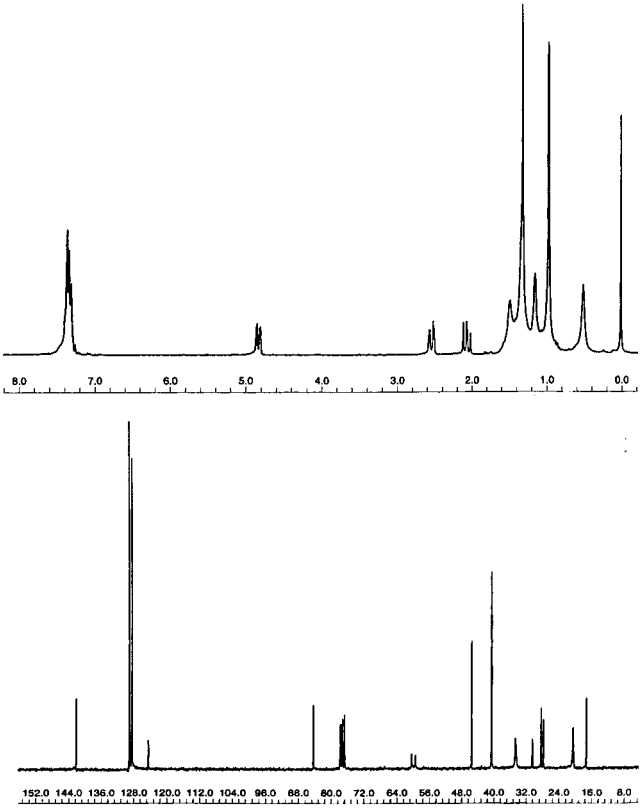


**Figure 1.** $^{1}H$ and $^{13}C$ NMR spectra of **2**.

We have recently disclosed the high-yield facile synthesis of active unimolecular living radical polymerization initiators by direct formation of TEMPO adducts of AIBN or benzyol peroxide.[4g] For example,

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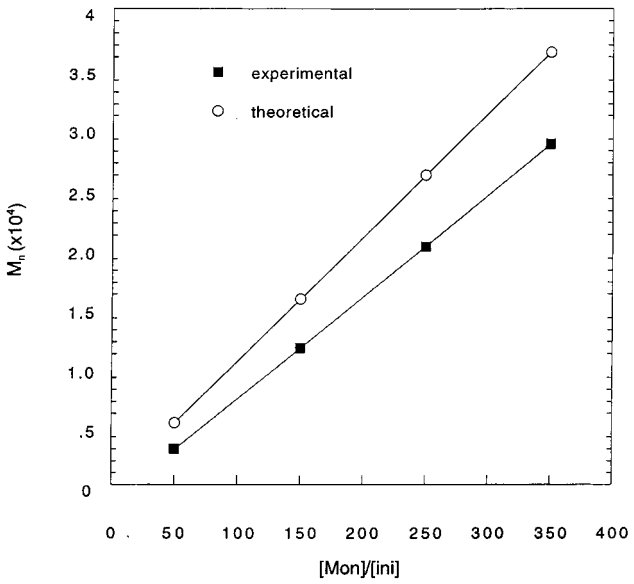
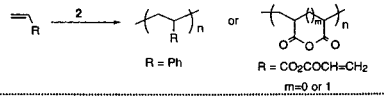



**Figure 2.** Dependence of molecular weights vs the ratio of monomer to initiator.

**Table 1. Synthesis of Narrowly Dispersed Polymers Using 2 as an Initiator**




| Entry | Monomer | Monomer/2 | T (°C)/t (h) | Yield(%)[a] | $M_n$[b] | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| 1 | $CH_2$=CHPh | 350:1 | 130/68 | 95 | 32,300 | 1.10 |
| 2[c] |  | 150:1 | 130/40 | 82 | 15,100 | 1.19 |

[a] Isolated yields. [b] Molecular weights were determined by gel permeation chromatography in THF using polystyrene as standards. [c] Polymerization was carried out in DMF or DMAc, and molecular weight was determined in DMAc solvent.

1-(2′-cyano-2′-propoxy)-2,2,6,6-tetramethyl-1-piperidine, **1**, was synthesized by direct treatment of AIBN with TEMPO. **1** is often the major isolated product even in the presence of excessive amount of other reactive molecules. However, in the presence of 1 equiv of styrene and 0.5 equiv of TEMPO, a new compound, 2,2-dimethyl-4-phenyl-4-(2′,2′,6′,6′-tetramethylpiperidinoxy)-butanenitrile, **2**, was isolated (eq 1) in 42% yield.[6] **2** was characterized by both $^1$H and $^{13}$C NMR spectroscopy (Figure 1) and elemental analysis.[6] The resonances at $\delta$ 4.84, 2.54, and 2.06 ppm are characteristic peaks for methine and methylene protons of the styrene moiety in **2**. The peaks between 0.2 and 1.75 ppm correspond to the resonances of the TEMPO unit in **2**. The reaction is quite sensitive to the concentration of TEMPO in solution. For example, increasing the amount of TEMPO results in the isolation of exclusively 1-(2′-cycano-2′-propoxy)-2,2,6,6-tetramethyl-1-piperidine.[4g] This is consistent with the observation that at higher TEMPO concentration, the trapping rate of the tertiary carbon radical by TEMPO is much faster than that of the radical reacting with styrene.

The polymerization of styrene was conducted using **2** as an initiator at a temperature range of 120−130 °C yielding polystyrene with narrow molecular weight distributions (entry 1, Table 1). The experimental molecular weights match well with the theoretically predicted values. The molecular weights also increase linearly with the percentage of monomer conversion, which indicates that the polymerization is living (Figure 2). The reactivity of the initiator **2** toward the styrene polymerization is similar to that of the benzoylperoxide−styrene−TEMPO adduct reported previously by other workers.[4a] The living polymerization was further demonstrated by the facile formation of block copolymers. For example, 30 equiv of 4-*tert*-butylstyrene was first polymerized in the presence of **2** to yield poly(*tert*-butylstyrene) ($M_n$ = 4300, PDI = 1.34). The polymer was isolated and purified by precipitation in methanol and dried in vacuo. The resulting polymer was redissolved in 30 equiv of styrene, and the solution was heated to 130 °C. As expected, the polymerization reinitiated to yield a diblock copolymer, which was isolated by precipitation in methanol ($M_n$ = 7000, PDI = 1.2).

The nature of the living polymer chain end was also probed by polymerizing a deuterated styrene-$d_8$ in the presence of **2**. The $^1$H NMR spectrum of the resulting polymer ($M_n$ = 1700) is shown in Figure 3. The spectrum reveals several interesting features of the polymer chain ends. Proton $H_a$ is observed as a broad doublet at 2.51−2.73 ppm due to the coupling with the adjacent protons and deuterium. TEMPO resonances are observed as multiplets between 0.2 and 2 ppm, similar to those of

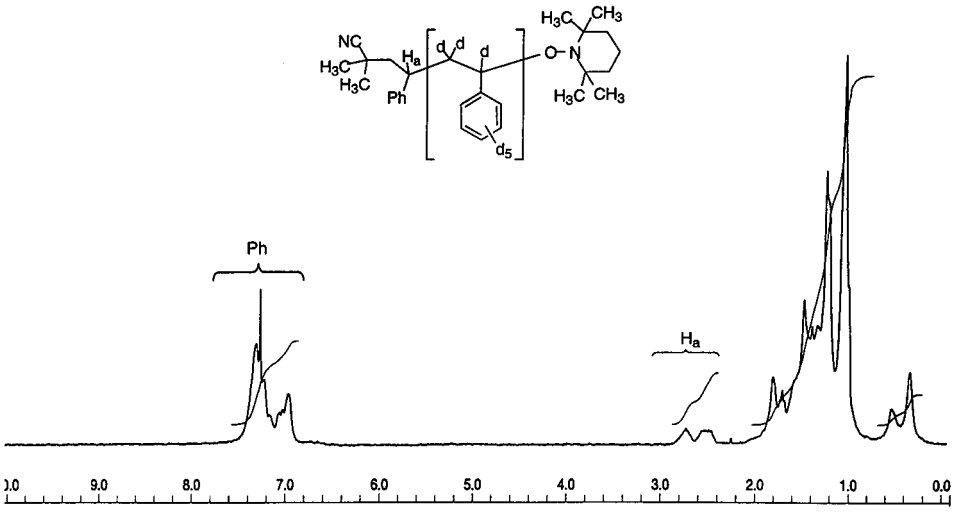



**Figure 3.** Incorporation of **2** into the polymer chain end in the polymerization of deuterated styrene-$d_8$.

the starting initiators. The signals of methylene end groups shift upfield and overlap with the TEMPO resonances. Comparison of the integrations of TEMPO, phenyl and methine resonances indicates that only one TEMPO and one (2-cyano-2-propyl)styrene unit incorporate into each polymer chain.

To further explore the application of **1**, the polymerization of acrylic anhydride (entry 2) was also examined. Poly(anhydride) is known as a biodegradable polymer. Poly(acrylic anhydride) also has the advantage of easy modification to other functionalized polymers. In the presence of AIBN, acrylic anhydride undergoes cyclopolymerization to yield poly(cyclic anhydride) with high molecular weights and a broad polydispersity index (PDI > 3). The polymerization is apparently uncontrollable, and the polymer produced is insoluble in common organic solvents. In the presence of **1**, acrylic anhydride undergoes smooth cyclopolymerization in polar solvents, such as DMF or dimethylacetamide, to yield soluble poly(cyclic anhydride) with a narrow molecular weight distribution. The narrow molecular weight distribution indicates that the polymerization might be a potential controllable radical process.[7] To our knowledge, the synthesis of narrowly dispersed poly(cyclic anhydride) has not been reported in the past. The polymers are sparsely soluble in common organic solvents at room temperature. The NMR spectra of the polymers exhibit broad resonances, which has prevented the accurate interpretation of the microstructures. To overcome this problem, polymers were readily hydrolyzed to the corresponding polyacids, which can be dissolved in methanol-$d_6$ to give clean spectra. Two carbonyl resonances were observed at 177.0 and 178.9 ppm in a 1:1 ratio, indicating the formation of equal amounts of five- and six-member ring structures in the polymer backbones.

In conclusion, we have demonstrated a convenient and simple synthesis of a new active living radical polymerization initiator. The initiator can be used to initiate the living radical polymerization of styrene as well as to synthesize narrowly dispersed poly(cyclic anhydride). The investigation of the polymerization of other monomers using this new initiator is being investigated.

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## References and Notes

(1) (a) Webster, O. W. *Science* **1991**, *251*, 887. (b) Webster, O. W. *Macromol. Eng.* **1995**, 1.

(2) (a) Gravert, D. J.; Datta, A.; Wentworth, P.; Janda, K. D. *J. Am. Chem. Soc.* **1998**, *120*, 9481. (b) Husseman, M.; Malmstroem, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424. (c) Georges, M. K.; Hamer, G. K.; Listigovers, N. A. *Macromolecules* **1998**, *31*, 9087. (d) Grubbs, R. B.; Hawker, C. J.; Dao, J.; Frechet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 270. (e) Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373.

(3) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (b) Georges, M. K. *Polym. Mater. Sci. Eng.* **1999**, *80* 283. (c) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (d) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (e) Matyjaszewski, K. *ACS Symp. Ser.* **1997**, *665*, 12. (f) Matyjaszewski, K.; Coessens, V.; Nakagawa, Y.; Xia, J.; Qiu, J.; Gaynor, S.; Coca, S.; Jasieczek, C. *ACS Symp. Ser.* **1998**, *704*, 16.

(4) (a) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185. (b) Hawker, C. J. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 1456. (c) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904. (d) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943. (e) Braslau, R.; Burrill, L. C., II; Siano, M.; Naik, N.; Howden, R. K.; Mahal, L. K. *Macromolecules* **1997**, *30*, 6445. (f) Hawker, C. J.; Hedrick, J. L.; Malmstrom, E. E.; Benoit, D.; Dao, J.; Barclay, G. G. *Polym. Prep.* **1998**, *39*, 626. (g) Wang, D. K.; Wu, Z. *Macromolecules* **1998**, 31, 6727. (h) Bergbreiter, D. E.; Walchuk, B. *Macromolecules* **1998**, *31*, 6380.

(5) Mecerreyes, D.; Atthoff, B.; Boduch, K. A.; Trollsaas, M.; Hedrick, J. L. *Macromolecules* **1999**, *32*, 5175. (b) Hawker, C. J.; Hedrick, J. L.; Malmstrom, E.; Trollsas, M.; Stehling, U. M.; Waymouth, R. M. *ACS Symp. Ser.* **1998**, *713*, 127—139.

(6) Typical procedure: A mixture of 2,2′-azobisisobutyronitrile (AIBN) (0.815 g, 4.96 mmol), styrene (0.542 g, 5.2 mmol), and TEMPO (0.382 g, 2.44 mmol) was degassed three times using a freeze—pump—thaw cycle and sealed under vacuum. The mixture was heated at 80 °C for 16 h to yield a pale yellow oil, which was purified by flash column chromatography on silica gel (EtAc:hexanes = 1:20) to afford (0.34 g, 42.5%) alkoxyamine **2** as a white solid (mp: 96—97 °C). $^1$H NMR ($CDCl_3$): $\delta$ 7.36—7.29 (m; 5 H), 4.82 (dd; 1H, $J$ = 11.0, 2.3 Hz), 2.54 (dd; 1 H, $J$ = 13.3, 3.8 Hz), 2.06 (dd; 1H, $J$ = 14.5, 12.0 Hz), 1.57—0.98 (m; 22 H), 0.51 (b; 2 H). $^{13}$C NMR ($CDCl_3$): $\delta$ 142.13, 129.01, 128.35, 124.39, 84.33, 60.34, 59.41, 45.48, 40.51, 34.65, 34.42, 30.46, 28.32, 27.82, 20.52, 17.30. IR (KBr, cm$^{-1}$): 3027 (m, Ar CH), 2976, 2943 (vs, alkyl CH), 2231 (m, CN), 1470, 1456 (S, Ar), 1371, 1358 (m), 1257, 1209, 1133, 983, 919, 761, 703. Anal. Calcd for $C_{21}H_{32}N_2O$ (328.5): C, 76.78; H, 9.82; N, 8.53. Found: C, 76.97; H, 10.08; N, 8.43.

(7) The polymerization of acrylic anhydride in the presence of **2** is not a living process as evidenced from the study of the dependence of molecular weights versus percent conversion although polymers obtained typically have relatively narrow polydispersity indices.

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