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# Facile Synthesis of New Unimolecular Initiators for Living Radical Polymerizations

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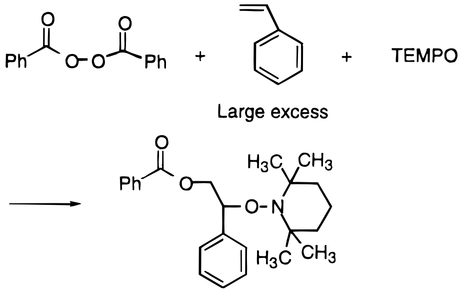
**Introduction.** Living polymerizations are powerful techniques for the synthesis of macromolecules with precisely controlled structures and properties.[1] Recent developments of living radical polymerizations have extended the scope and application of living polymerization methods, which results in the synthesis of a wide variety of new polymers and, in particular, functionalized polymers with predetermined molecular weights and properties.[2] The great advantage of the radical polymerization is that the reaction is tolerant to many functional groups and can be carried out in several different conditions.[3]

Living radical polymerization was achieved through the successful control of stability and concentrations of propagating radicals by addition of stable radicals to the polymerization systems, or via the reversible atom transfer reactions.[4] The generally used stable radicals are TEMPO and organometallic radicals. The polymerizations initiated with a two-component initiator-stable radical system usually exhibit much slower polymerization rates because of the presence of excess stable radicals. Recently, unimolecular initiators were developed for use in the initiation of living radical polymerizations (eq 1).[5d] These initiators have facilitated the construction of complex macromolecular architectures.[6] The synthesis of unimolecular initiator, such as **1** (eq 1), however, requires the use of large excess of styrene, prolonged reaction time at elevated temperatures in addition to tedious product isolation and purification processes. The low yield (≤40%) has also limited its practical uses for large scale synthesis. In this paper, we report an easy synthesis of new unimolecular initiators and their applications for living radical polymerizations.



(1)

**1**

**Experiment. Materials.** Benzoyl peroxide (BPO), azobisisobutyronitrile (AIBN) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were purchased from Aldrich and used as received. Monomers were purified by distillation under vacuum before the polymerization. Benzene was distilled from sodium benzolphenone ketyl.

**Instrument**. $^1$H NMR spectra were measured by a Brucker AM 250 (250 MHz) spectrometer. $^{13}$C NMR spectra were recorded at 62.9 MHz on a Brucker AM 250 spectrometer. Elementary analysis was performed by Microanalysis, Inc. Molecular weights were estimated from gel permeation chromatography equipped with a Waters 410-differential refractometer. A flow rate of 1.0 mL/min. was used, and samples were prepared in THF. Polystyrene standards were used for calibration. Polydispersity index (PDI) was determined by the ratio of weight average ($M_w$) to the number average molecular weight ($M_n$).

**Synthesis of 1-Benzoylperoxy-2,2,6,6-tetramethyl-1-piperidine (2).** To a solution of BPO (1.236 g, 5 mmol) in dry benzene (10 mL) was added dropwise a solution of TEMPO in benzene (10 mL, 1 M) (*Caution*! exothermic explosion could occur if BPO and TEMPO were mixed directly!). After addition, the reaction mixture was refluxed under nitrogen for 1 h. A pink solid was obtained after evaporation of solvent. The crude material was further purified by recrystallization from a mixture of ether/pentane, yield 2.268 g (97%) white solid. MP.: 98.0−99.5 °C. IR (Nujol mull, cm$^{-1}$): 3018, 2985, 2947, 1717, 1601, 1386. $^1$H NMR (CDCl$_3$, 250 MHz): $\delta$ (ppm) 8.08 (d, $J = 6.5$ Hz, 2H), 7.40 (m, 3H), 1.70−1.65 (m, 6H), 1.40 (s, 12H). $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) 174.22, 135.51, 131.42, 129.87, 127.99, 65.60, 37.39, 27.99, 20.54, 16.22. Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.02; H, 8.97; N, 5.06.

**Synthesis of 1-(2′-Cyano-2′-propoxy)-2,2,6,6-tetramethylpiperidine (3).** A solution of TEMPO (1.611 g, 97%, 10 mmol) and AIBN (0.8281 g, 5 mmol) in benzene (10 mL) was heated to 60 °C for 4 h. The solvent was evaporated, and the crude product was purified by flash chromatography on silica gel eluted with ethyl acetate/hexane (1:5). A pink oil (1.8 g, 82%) was obtained. $^1$H NMR (C$_6$D$_6$): $\delta$ (ppm) 1.40 (s, 6H), 1.31 (br., 6H), 1.16 (s, 6H), 1.06 ppm (s, 6H). $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) 113.97, 65.99, 51.22, 31.96, 25.92, 18.98, 18.36, 11.95, 8.43. IR (neat−KBr plate, cm$^{-1}$): 2990, 2985, 2200, 1495, 1450.

**General Procedure for the Polymerization Reactions.** All the reactions were performed in a nitrogen-filled Schlenk tube equipped with a Teflon valve. The initiator **2** or **3** was dissolved in the monomers. The reaction mixture was degassed three times using a freeze−pump−thaw cycle, and was heated in an oil bath to the desired temperatures. Polymers were isolated by precipitation in methanol and dried in vacuo. In a typical procedure: A solution of **2** (200 mg, 0.72 mmol) dissolved in styrene (7.10 g, 68.3 mmol) was degassed three times using a freeze−pump−thaw cycle. The tube was then filled with N$_2$ and heated to 130 °C under stirring. As the polymerization proceeded, the viscosity of the system increased gradually, and the reaction was stopped after 30 h. After the mixture was cooled to room temperature, methylene chloride (30 mL) was added to dissolve the polymer. The solution was precipitated into methanol (200 mL) to give a white powder (6.53 g, 92%). $^1$H NMR (CDCl$_3$): $\delta$ (ppm) 7.10 (b, 3H), 6.59 (m, 2H), 1.85 (b, 1H), 1.45 (b, 2H). $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) 145.52, 129.43, 127.93, 125.82, 124.65, 41.76, 39.74. GPC: $M_n = 18\,800$; $M_w = 22\,000$; PDI = 1.12.

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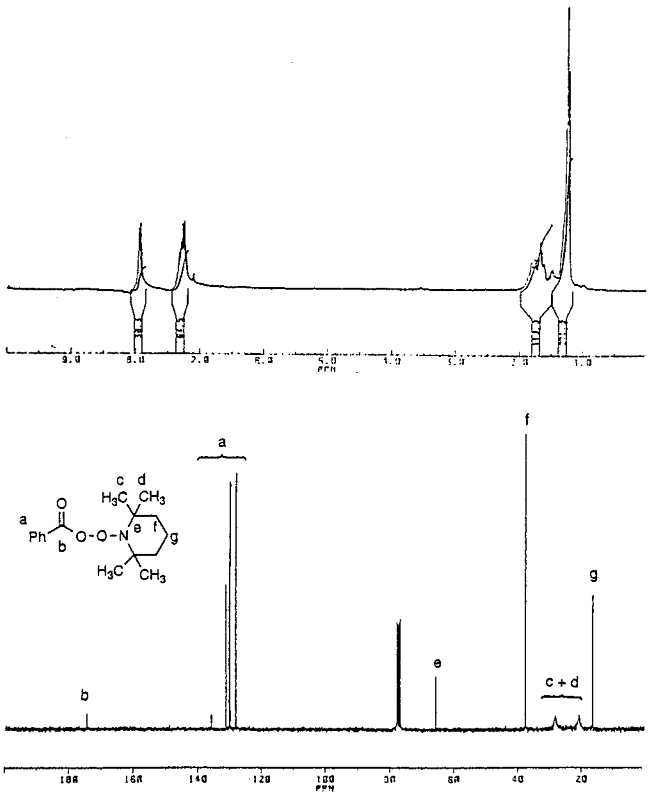
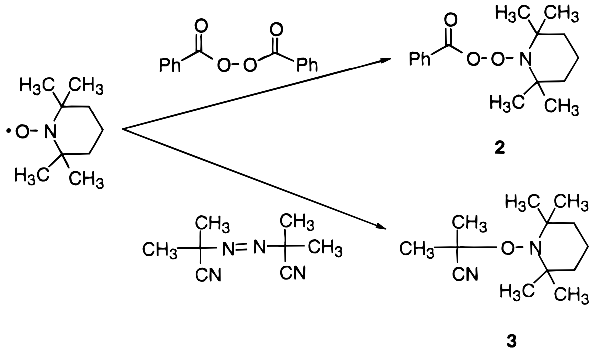


**Figure 1.** $^{1}H$ and $^{13}C$ NMR spectra of **2**.

**Scheme 1. Synthesis of Initiators**



**Synthesis of Block Copolymer**. To a freshly distillated *tert*-butylstyrene (200 mg) was added polystyrene (200 mg, $M_w$ = 10 400, $M_n$ = 9 400, PD = 1.12) prepared using **2** as an initiator. The homogeneous mixture was heated to 130 °C for 8 h, and the solution solidified. The polymer (281 mg, 70%) was isolated according to the general workup procedure. GPC: $M_w$ = 22 000, $M_n$ = 16 400; PDI = 1.34.

**Results and Discussion.** Initiators **2** and **3** can be easily synthesized in high yield from the direct reaction of BPO and AIBN with TEMPO, respectively (Scheme 1). For example, when BPO is treated with 2 equiv of TEMPO at room temperature in benzene, an exothermic reaction was observed. After the mixture was refluxed for 1 h, the product, 1-benzoylperoxy-2,2,6,6-tetramethyl-1-piperidine, **2**, was isolated as a white solid in 97% yield.[7] Compound **2** is characterized by both $^{1}H$ and $^{13}C$ NMR and by IR spectroscopy (Figure 1). In the $^{13}C$ NMR spectrum of **2**, peaks at 174.2, 65.6, 27.99, and 20.54 ppm correspond to the carbonyl group, quarternary carbon next to nitrogen and methyl group, respectively. The broadening of $CH_3$ resonances in the $^{13}C$ NMR indicates the presence of slow exchange process between the equatorial and axial $CH_3$ groups due to the ring-flip. The structure was further confirmed by elemental analysis. Compound **2** is stable at room temperature and generates benzoyloxy and TEMPO radicals upon heating. Similarly, refluxing a benzene solution of AIBN and TEMPO gives 1-(2′-cycano-2′-propoxy)-2,2,6,6-tetramethyl-1-piperidine **3** as a pink oil in near quantitative yield.[8] The oil can be further purified by flash column chromatography on silica gel. The product was characterized by both $^{1}H$ and $^{13}C$ NMR spectroscopy.

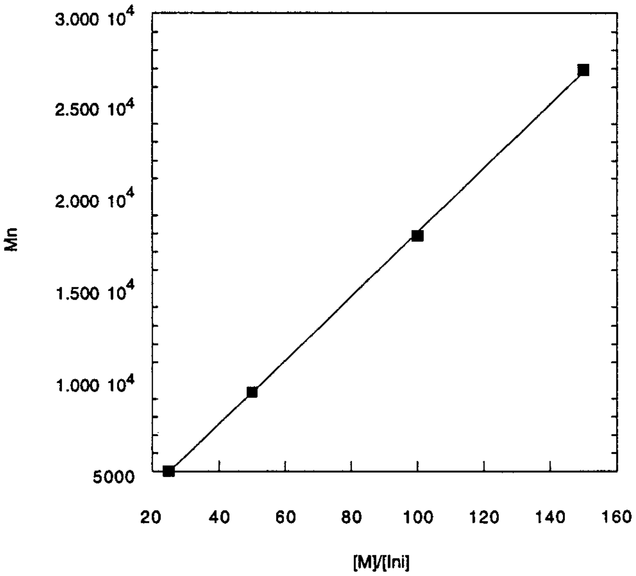
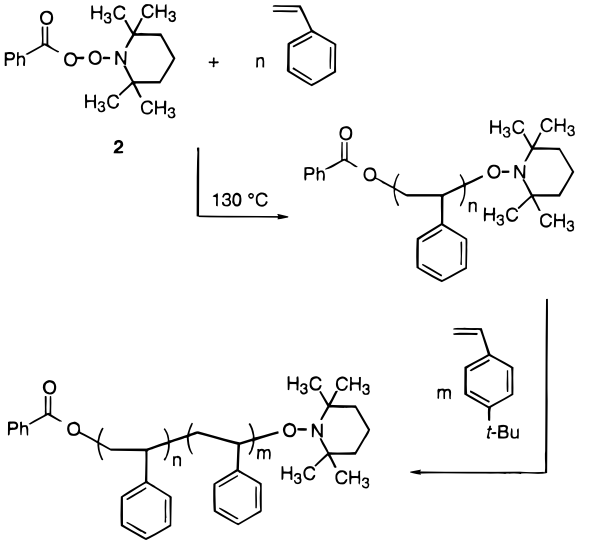


**Figure 2.** Plot of molecular weight ($M_n$) vs the ratio of $[M_n]$/[Ini].

The bulk polymerizations of styrene were conducted using **2** and **3** as initiators, respectively. The polymerization was generally carried out in a medium-wall glass tube sealed with a Teflon valve at 130 °C. When 100 equiv of styrene was polymerized using **2** or **3** as an initiator, the polymers obtained have molecular weights of 18 000 and 11 000 and molecular weight distributions of 1.11 and 1.19, respectively.[9] The molecular weight distribution is similar to that of the polymer obtained when **1** is used as an initiator. The narrow molecular weight distribution suggests that the polymerization is living. Up to 1000 equiv of styrene can be polymerized by **2** to give polystyrene with a relatively narrow polydispersity (1.30). When 25 equiv of styrene is polymerized using **2** as an initiator, the incorporation of benzoyl and TEMPO fragments to the polymer chain ends was observed as evidenced from the end-group resonances at 165.6, 36.26, 28.53, and 17.20 ppm in the $^{13}C$ NMR spectrum. To further investigate the living characters of the polymerization, we carried out the following studies. When the number average molecular weights were plotted versus the ratio of monomer vs catalyst, a straight line was obtained as shown in Figure 2. This strongly indicates that the polymerization is living. Further support for the living polymerization of styrene initiated by **2** and **3** was from the facile synthesis of block copolymers of styrene-*co*-*tert*-butylstyrene. For example, when 200 equiv of styrene was first polymerized using **2** as an initiator, the polymer was isolated by precipitation from MeOH and dried in vacuo. The collected polystyrene was redissolved in 200 equiv of *tert*-butylstyrene. When the temperature was

**Scheme 2. Formation of Block Copolymers**



increased, the polymerization reinitiated again. The reaction mixture was heated continuously at 130 °C for 8 h, and the polymer was isolated. Both NMR and GPC data indicate the formation of block copolymers (Scheme 2).

Polymerization of styrene using **2** as an initiator was also attempted at 100 °C; there was, however, no polymerization even after heating for 30 h. The polymer was isolated in 41% yield after reacting for 72 h at 110 °C. The polymer obtained has a slightly broad polydispersity index (PDI = 1.28). These observations suggest that the normal styrene polymerization temperature using **2** as an initiator is in the range of 120−130 °C, which is similar to that of using **1** as an initiator.

Under identical conditions, styrene polymerization initiated by **2** is also observed to proceed in an overall faster rate than that of the polymerization initiated by **1** or **3**.[10] For example, polymers can be isolated in 87% and 77% yields after reacting for 24 h using **2** and **1** as initiators, respectively.

**Conclusions.** We have demonstrated the facile synthesis of a new type of initiators. These initiators can initiate the living radical polymerization of styrenes. Due to the ease of synthesis, these initiators are expected to have broad practical applications in terms of generating polymers and telechelic polymers with controlled structures and properties. Using these initiators to synthesize other polymers with controlled structures and a detailed study of the polymerization rates are currently underway, which will be reported in due course.

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## References and Notes

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(9) We have observed that molecular weights of the polymers obtained using **2** as an initiator are usually higher than the theoretical values. This might be attributed to the difference in the rate of initiation vs the rate of the propagation when **2** is employed as an initiator. For a detailed discussion, see: Gold, L. *J. Chem. Phys.* **1958**, *28*, 91.
(10) For example, polymerizations initiated by **2** and **3** are completed in 30 and 48 h, respectively. However, the polymerization initiated by **1** was reported to be completed in 72 h; see ref 5a.

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