

(Cu(OTf)₂, Aldrich, 98%); 4,4'-di-*tert*-butyl-2,2'-dipyridyl (dTbpy, Aldrich, 98%); tetrahydrofuran (THF, Burdick and Jackson HPLC/UV grade); and chloroform-*d* (CDCl₃, Acros, 99.8 atom%) were used without further purification. Styrene (Aldrich, 99%) and anisole (Aldrich, 99.7%) were distilled from calcium hydride under vacuum and stored in a sealed glass ampoule under argon at -15 °C.

2.2. Synthesis of 9-(2,2,6,6-tetramethyl-4-hydroxypiperidinyl-4-hydroxypiperidinyl)fluorene (Scheme 2, 1)

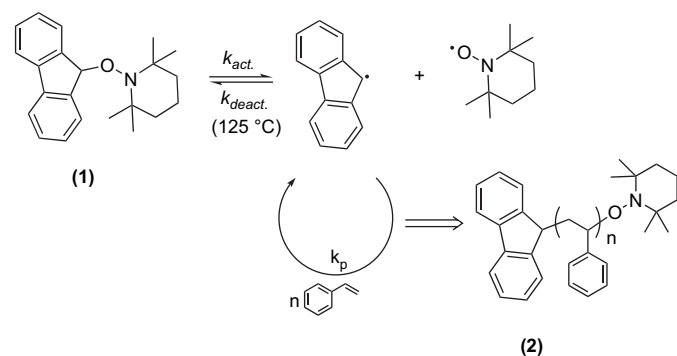
The initiator, 9-(2,2,6,6-tetramethyl-4-hydroxypiperidinyl-4-hydroxypiperidinyl)fluorene, was prepared from 9-bromofluorene using a method adopted from literature [17]. 9-Bromofluorene (0.907 g, 3.7 mmol), Cu(OTf)₂ (0.013 g, 0.037 mmol), TEMPO (0.69 g, 3.8 mmol), and dTbpy (0.040 g, 0.15 mmol) were dissolved in benzene (5.0 mL). The solution was degassed under vacuum by four freeze-thaw cycles, sealed from the vacuum line, and placed in an oil bath at 75 °C with stirring for 24 h. Excess TEMPO was removed by eluting the product solution through an alumina column in hexanes. Removal of the solvent yielded the product as a nearly colorless oil (60–75% yield), which was found to solidify when cooled in a freezer. The resulting crystals were found to have a melting point of 67–69 °C. The structure of the product was verified by ¹H NMR: δ 7.9 (d, Ar-H), 7.7 (m, Ar-H), 7.4 (m, Ar-H), 7.3 (m, Ar-H), 5.9 (s, R₂CH(OR')), 1.6 (m, CR₂H₂), 1.2 (s, TEMPO methyls), 1.0 (s, TEMPO methyls).

2.3. NMP of styrene (100:1 monomer-to-initiator ratio)

In a typical nitroxide-mediated polymerization, styrene (4.0 mL, 34.9 mmol) and 9-(2,2,6,6-tetramethyl-4-hydroxypiperidinyl-4-hydroxypiperidinyl)fluorene (0.112 g, 0.349 mmol), synthesized as described above, were added with a stir bar to a flamed reaction vessel and attached to a vacuum line. If used, anisole (0.25 mL) was also added at this time. The solution was degassed by four freeze-thaw cycles and then placed in a 125 °C oil bath. These conditions were maintained for the duration of the reaction, after which the mixture was typically sufficiently viscous to prevent rotation of the stir bar. The product was then dissolved in THF and precipitated in cold methanol as a bright white polymer. Reactions were typically allowed to proceed to approximately 50% conversions. The polymers were purified by redissolution in THF followed by reprecipitation in cold methanol; this was found to effectively remove low molecular weight, UV-absorbing impurities (Fig. 1).

2.4. Characterization

The number average molecular weights (*M_n*s) and polydispersity indices (PDIs) were measured by gel permeation chromatography. The system consisted of a Waters 1515 isocratic pump, a Waters 717



Scheme 2. Reaction scheme for the NMP of styrene using 9-(2,2,6,6-tetramethyl-4-hydroxypiperidinyl-4-hydroxypiperidinyl)fluorene (1) as the unimolecular initiator, leading to a fluorene end-labeled polystyrene (2).

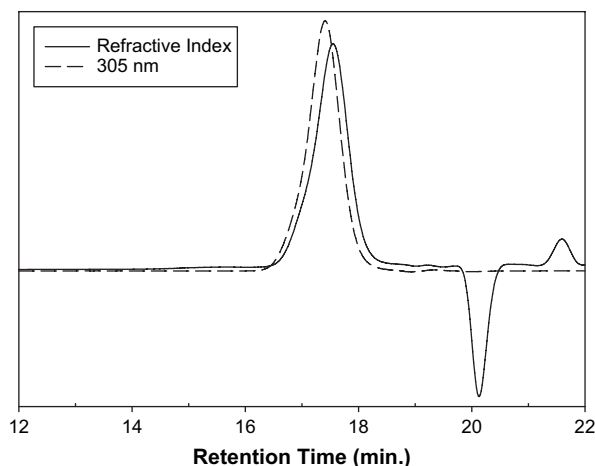


Fig. 1. GPC traces of polystyrene formed by NMP using 1 as the initiator (Table 1, entry 2). Solid line: normalized RI trace; dashed line: normalized UV trace (305 nm).

autosampler, two Pl-gel 5 mm Mixed C columns (Polymer Labs), a Waters 2487 dual wavelength detector, and a Waters 2414 refractive index (RI) with THF as the mobile phase. The instrument was interfaced with a personal computer running the Waters Breeze software. A 10-point calibration using polystyrene standards (Polymer Laboratories, *M_p* range: 5.0 × 10²–3.05 × 10⁶ Da) was used to obtain molecular weights and polydispersities.

To determine the degree of fluorene labeling, polystyrene, synthesized and washed as above and then collected by vacuum filtration, was dried to a constant mass using a vacuum oven. The number average molecular weight was determined by GPC and used to prepare solutions with concentrations of 0.15 mM in THF. Absorbance spectra were acquired on Gentech TU-1901 dual-beam UV-Vis spectrometer, and fluorescence spectra were obtained using a system consisting of a Horiba Jobin Yvon Fluorolog controlled by a SpectraCQ computer and interfaced with a personal computer running Datamax 2.2 software. Samples were excited at 305 nm, and THF was again used as the solvent.

In cases where the reaction progress was monitored, 250 μL aliquots were removed from the reaction mixture at various time intervals and added to 0.75 mL portions of chloroform-*d*. ¹H NMR spectra were obtained on a Varian 400 MHz NMR (25 °C, 16 scans per sample) and processed using the VNMRJ software. Monomer conversion was determined by comparing the area of the vinylic β-protons at 5.4 ppm and 5.9 ppm (solely due to monomeric styrene) to the entire aromatic region (due to both monomeric and polymeric styrene). The aromatic region contains phenylic monomeric protons and vinylic α-protons from the monomeric styrene (the vinylic α-protons are included in the integration of the aromatic region because as the polymerization proceeds, these protons overlap with the aromatic region of polystyrene). The area of the aromatic region due to the monomeric protons (both vinylic and phenylic) was calculated based on the average area of the vinylic β-protons (at 5.0 ppm and 5.7 ppm), and was expressed as a percentage of the overall aromatic region. At each reaction time, this calculation was repeated and compared to the initial percentage at monomer conversion = 0%, allowing for calculation of monomer conversion at each reaction time. From these conversion values, [M]_t could be calculated, taking into account the decrease in reaction volume for each calculation as styrene is converted into polymer.

3. Results and discussion

As mechanistically illustrated in Scheme 2, a series of NMP reactions of styrene employing the fluorene-based alkoxyamine,

Table 1
Results of the NMP of styrene using **1** as the unimolecular initiator under various conditions

Entry	M: ^a	M_n^b	PDI	% Labeling ^c
1	100:1	6320	1.20	65
2	42:1	1623	1.17	70
3	100:1	3190	1.14	70
4 ^d	100:1	4570	1.15	75
5 ^d	100:1	1800	1.16	90
6	100:1	4010	1.15	75
7	100:1	1460	1.14	80
8	192:1	2570	1.18	80
9 ^e	100:1	–	–	NA

Reactions were run in bulk styrene at 125 °C for approximately 48 h, unless indicated differently.

^a Initial ratio of styrene to 9-(2,2,6,6-tetramethyl-4-hydroxypiperidinyloxy)-fluorene.

^b Apparent number average molecular weight compared to PS standards, as determined by GPC.

^c Percent of polymer chains labeled with fluorene, as determined by UV–vis spectroscopy.

^d Reactions were run using anisole (12.5% total volume).

^e Reaction was run at 100 °C, and no polymer was formed.

9-(2,2,6,6-tetramethyl-4-hydroxypiperidinyloxy)fluorene (**1**) were performed. Homolysis of the C–O bond on **1** is expected to generate initiating fluorene radicals, which, after propagation, will lead to fluorene-labeled polystyrene (**2**). When carried out in bulk styrene or with added anisole (12.5% by volume) at 125 °C, the polystyrene produced was found to possess low PDI values (typically less than 1.20) and M_n values close to those expected based on monomer-to-initiator ratios and yields (Table 1, entries 1–7). The consistently low PDI values (ranging from 1.13 to 1.20) are indicative of a controlled radical polymerization. Typical GPC traces (both RI and UV at 305 nm, an absorbance maximum for fluorene) of the polymers are shown in Fig. 1, with the GPC–UV trace indicating that the polymeric species at least qualitatively contains the fluorene chromophore (Scheme 2, **2**); this trace also indicates that after washing, the polymer contains no detectable UV-absorbing impurities.

In order to further verify the controlled nature of the polymerization, M_n values, PDI values (both determined by GPC), and monomer conversions (calculated from ¹H NMR spectra) were monitored over the course of a typical polymerization. As Fig. 2 indicates, the molecular weight values were found to increase linearly ($R^2 > 0.99$) with percent monomer conversion, while PDI values remained low (<1.20) throughout the course of the reaction, exhibiting a slightly decreasing trend. The experimentally

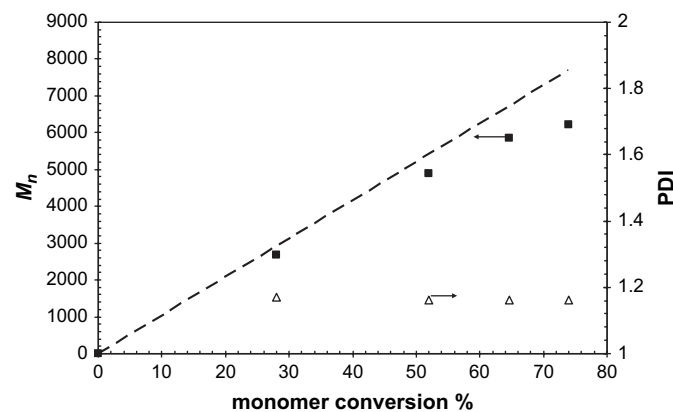


Fig. 2. Number average molecular weight (M_n) and PDI (M_w/M_n) vs. % monomer conversion for the NMP of styrene using **1** as the initiator at 125 °C. M_n and PDI values were determined by GPC; % monomer conversions are calculated from ¹H NMR. Dotted line represents theoretical M_n values based on monomer-to-initiator ratio. [M]:[I] = 100:1; [M] = 8.72 M; [I] = 8.75×10^{-2} M.

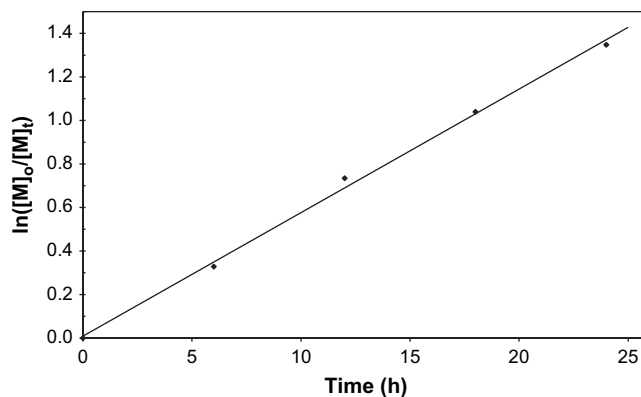


Fig. 3. First order kinetic plot for the NMP of styrene using **1** as the initiator at 125 °C. [M]:[I] = 100. [M] = 8.72 M; [I] = 8.75×10^{-2} M.

determined M_n values (■), were found to match closely with the theoretical values (dashed line), calculated by monomer-to-initiator ratios at various conversions. A kinetic plot (Fig. 3), displaying $\ln([M]_0/[M]_t)$ as a function of reaction time, indicates that the NMP of styrene proceeded with first order with respect to monomer concentration ($R^2 > 0.99$). The lack of an observed induction period implies rapid establishment of the k_{act}/k_{deact} equilibrium (Scheme 2).

GPC–UV detection at 305 nm is consistent with the polymeric product containing the fluorene chromophore, as polystyrene itself does not absorb at this wavelength [35]. To quantify the extent of fluorene labeling, UV–vis spectra were obtained for THF solutions of the isolated, purified polymer. As shown in Fig. 4 (solid line), the absorbance trace for the polymer (Scheme 2, **2**) displays a maximum near 305 nm, which is consistent with fluorene-labeled polystyrene [1]. Using the Beer–Lambert law and approximating the extinction coefficient of the polymer-bound fluorene to be equal to that of fluorene itself [36], the percentage of polymer chains containing the fluorene chromophore can be accurately calculated (Table 1). High but not quantitative labeling was consistently observed in each case (labeling ranged from approximately 70% to 90%).

Also shown in Fig. 4 (dashed line) is the UV–vis trace of the fluorene-based initiator (**1**), which shows an absorbance shoulder near 305 nm, approximately the same wavelength as the local maxima of the fluorene-labeled polystyrene. To unambiguously verify that the polymeric product contains the fluorene species

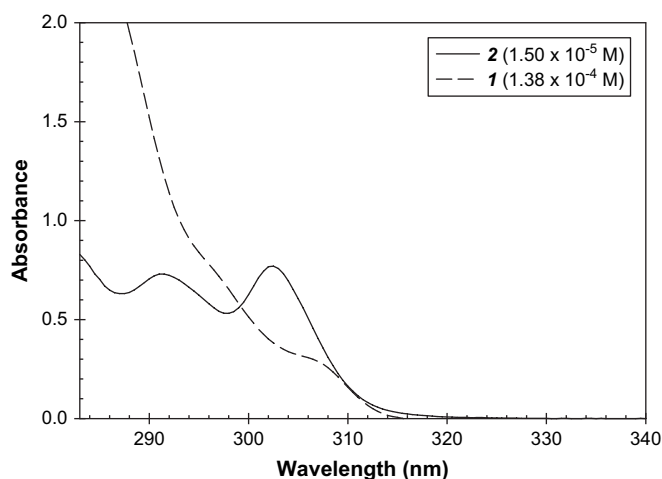


Fig. 4. UV–vis absorbance spectra of **1** (1.38×10^{-4} M) and fluorene-labeled polymer (1.50×10^{-5} M; Table 1, entry 1).

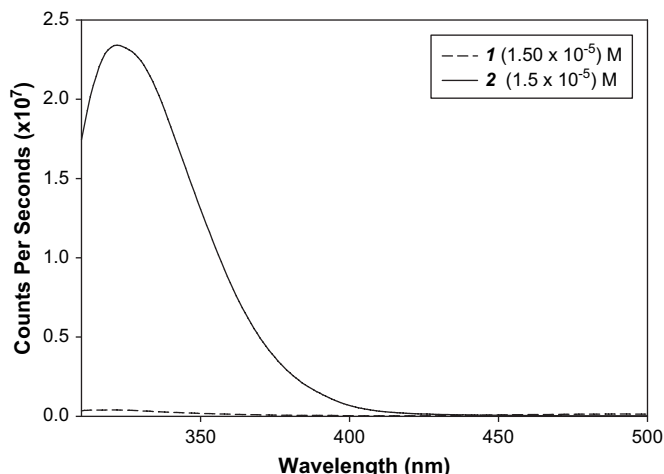


Fig. 5. Fluorescence spectra of **1** (1.38×10^{-4} M) and fluorene-labeled polymer (1.50×10^{-4} M; Table 1, entry 1).

(Scheme 2, **2**) rather than simply being unlabeled polystyrene with embedded initiator (**1**), fluorescence spectra were obtained for both the polymer product and the unimolecular initiator, **1** (Fig. 5). When irradiated at 305 nm, THF solutions of the polymer **2** (prepared and purified as previously described) and THF solutions of the free initiator **1** produced drastically different fluorescence spectra. This is most likely due to differences in substitution at the 9-position of the fluorene, providing strong evidence that the fluorene species is indeed covalently bound to the polystyrene.

Because a portion of polymer chains was not labeled with the fluorene chromophore, an initiating pathway in addition to that shown in Scheme 2 must be occurring. This is likely due to thermal initiation of styrene during the reaction, leading to polystyrene chains lacking the fluorene end group. The presence of TEMPO in the reaction mixture mediates the growth of propagating polystyrene radicals regardless of the initiating mechanism, thus the overall growth of the polymer chains proceeds in a controlled fashion. Attempts to eliminate or reduce chains originating from thermal initiation by lowering reaction temperatures were unsuccessful (Table 1, entry 9), as the reduced temperatures were insufficient to maintain the essential equilibrium between dormant and active radicals, and polymer was not produced.

4. Conclusion

High amounts of fluorene end-labeled polystyrene (~80% labeling) were prepared by NMP using a fluorene-based alkoxyamine (**1**) as a unimolecular initiator. The resulting polymers possessed low PDI values, while monitored reactions showed M_n values to be linearly related to percent monomer conversion while

also being near theoretical values. The rate of the reaction was found to be of first order with respect to monomer conversion, consistent with a controlled polymerization. Due to the high reaction temperatures used, thermal initiation of styrene was speculated to be responsible for the less-than-quantitative fluorene labeling.

Acknowledgements

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- [36] $\epsilon = 7800 \text{ cm}^{-1} \text{ M}^{-1}$ for fluorene in THF solution at the absorbance maximum near 305 nm. The extinction coefficient of polymer-bound fluorene is approximated to be identical to this value.