Chain End Functionalization in Nitroxide-Mediated “Living” Free Radical Polymerizations

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ABSTRACT: A novel method for the functionalization of vinyl polymers prepared by nitroxide-mediated living free radical procedures is reported. This strategy is based on the controlled monoaddition of maleic anhydride and maleimide derivatives to the alkoxyamine chain end followed by elimination of the mediating nitroxide radical. This allows the introduction of a wide variety of functional groups with high efficiency, while at the same time permitting the alkoxyamine functional group to be removed and the thermal stability of the polymer chain to be increased.

Introduction

The control of soft materials on the nanometer size scale is becoming an increasingly important aspect of polymer science as more research is directed toward the study of nanoscopic structures and materials.[1] The preparation of well-defined nanostructures requires molecular building blocks of defined structure; new synthetic methods for introducing functional groups at specific loci at either chain ends or along the backbone are emerging as powerful tools for the construction of these architectures.[2] While living anionic and cationic procedures have traditionally been employed for the synthesis of these well-defined structures, the limited functional group tolerance of these methods has stimulated the search for more general synthetic strategies.[3] Considerable effort has recently been devoted to the development of viable “living” free radical procedures for the synthesis of well-defined polymers with controlled incorporation of functional groups.[4]

The use of functionalized initiators gives polymer chains with a wide variety of functional groups using any of the three standard methods for “living” free radical polymerization: nitroxide-mediated,[5] ATRP,[6] and RAFT.[7] However, these approaches lead to an asymmetrically functionalized chain where one chain end is derived from the functional group of the initiator and the other chain end is derived from the mediating radical, an alkoxyamine in the case of nitroxide-mediated systems or a halide in the case of ATRP. While this dormant chain end is useful in the formation of block copolymers[8] or chain extension/cross-linking reactions, it can also be a liability due to facile “unzipping” of the chain if the processing or end-use conditions involve temperatures close to the ceiling temperature of the polymer. The development of new synthetic methods to specifically functionalize the dormant chain ends should enhance the thermal stability of these materials as well as provide access to telechelic polymers which are useful for the synthesis of triblock, multiblock, or multibranched architectures.[9]

While the dormant halide chain end has been successfully manipulated by a variety of authors for vinyl polymers prepared by ATRP,[10] little work has been carried out on developing methodologies for introducing specific functional groups at the ω-terminus of polymers produced by nitroxide-mediated free radical polymerizations.[11] This report details the facile reaction of both small molecule and polymeric alkoxyamines with maleic anhydride or maleimide derivatives, resulting in the introduction of reactive chain ends in a controlled and quantitative fashion.

Results and Discussion

The copolymerization of maleic anhydride with styrene is an effective strategy for the synthesis of a novel type of tapered block copolymer under living free radical conditions.[12] This strategy relies on the resistance of maleic anhydride to homopolymerization coupled with the living nature of the copolymerization process. These features can also be exploited for the selective end-functionalization of alkoxyamine chains. In this approach, the alkoxyamine-terminated polymer, **1**, is heated with an excess of maleic anhydride at elevated temperatures to append a single maleic anhydride unit at the chain end, **2** (Scheme 1). Since the addition of a second maleic anhydride unit is disfavored, the excess reagent can be used to drive the functionalization chemistry to completion, which is an important consideration for subsequent polymer modification reactions.

To test this hypothesis, the chemistry was initially examined with small molecule alkoxyamine derivatives[13] in an effort to model the polymeric chain end and to optimize the functionalization yield. This optimization is important since little, if any, purification of the polymer is possible after functionalization. The α-hydrido alkoxyamine, **3**, which polymerizes a wide variety of different monomer units,[14,15] was therefore chosen as the model. Reaction of **3** with 2.0 equiv of *N*-phenylmaleimide, **4**, in toluene was initially conducted at 100 °C and the course of the reaction followed by GC and TLC analysis.[14] The starting alkoxyamine disappears completely on heating, and a single product appeared at short reaction times. Prolonged heating led to the disappearance of this initial product and the formation of a second product. Isolation and characterization of

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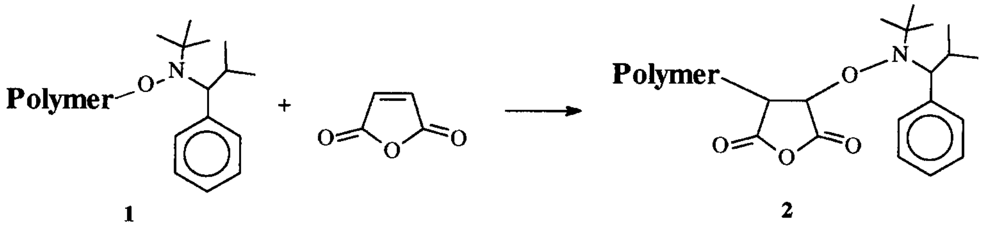
Scheme 1



Scheme 2

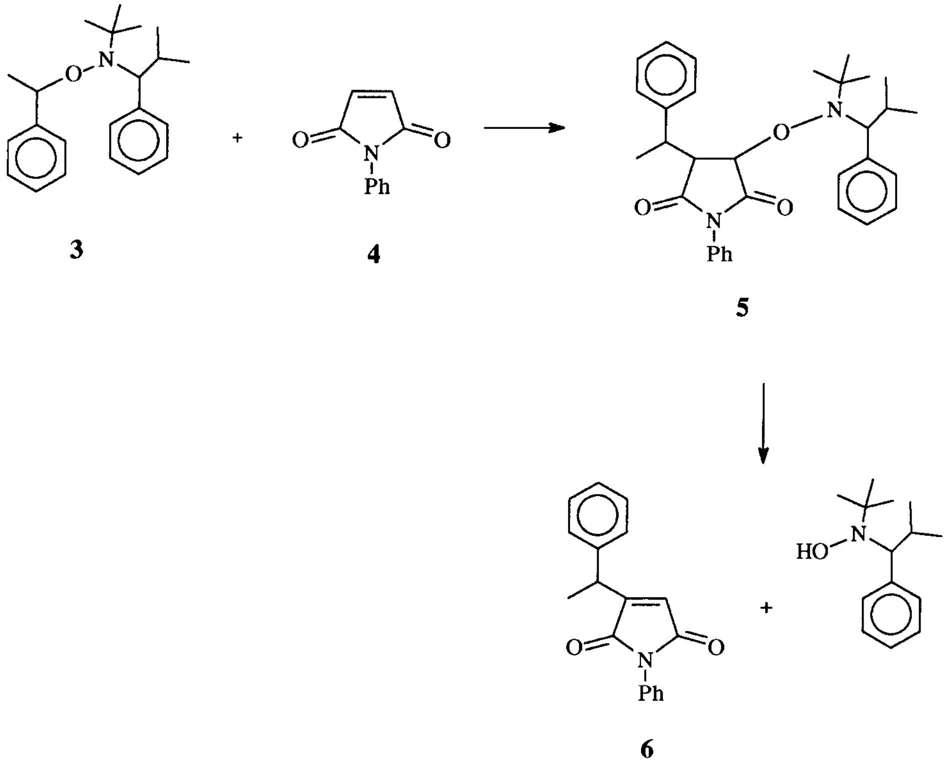


Table 1. Effect of Solvent and Reaction Conditions on the Yields of Nitroxide Adduct, 5, and the Eliminated Product, 6

				yield[a] (%)	
entry	solvent	time (h)	temp (°C)	**5**	**6**
1	toluene	1.1	116	56	23
2	xylene	3.0	125	3–4	80[b]
3	DMF	2.5	125	0	93

[a] Yield after purification by flash chromatography; remainder is starting material. [b] Only a trace of **5** (ca. 3–4%) was detected by TLC/HPLC analysis.

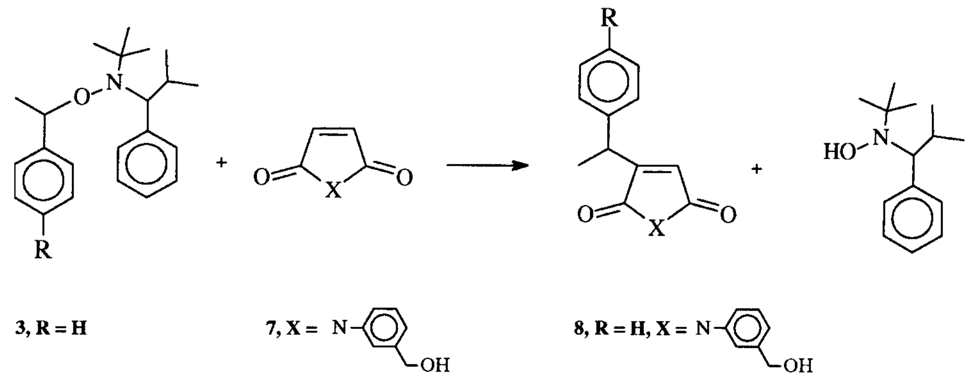
each of these products revealed that the initial product is the expected addition product, **5**, which upon heating eliminates the hydroxylamine to give the substituted maleimide derivative, **6** (Scheme 2).

The efficient production of **6,** with little if any observable side products, prompted an investigation into the effect of solvent and reaction time on the yields of **5** and **6**, respectively. As shown in Table 1, use of more polar solvents such as dimethylformamide and heating the reaction mixture at 125 °C for 2.5 h resulted in a significantly improved yield of the substituted maleimide derivative, **6**, which was obtained in 93% yield after purification. This optimized procedure was effective for the introduction of a range of substituted maleimide and maleic anhydride derivatives with little appreciable effect on the yield or efficiency of this reaction. For example, the reaction of **3** with the hydroxymethyl-substituted maleimide, **7**, at 125 °C in dimethylformamide for 2 h resulted in an 87% yield of purified hydroxy derivative, **8** (Scheme 3). Table 2 shows the range of functional groups introduced and the associated yields: maleic anhydride can be employed in the reaction to introduce a synthetically versatile anhydride group.

The efficiency of this reaction with small molecule models encouraged the extension of these studies to well-defined polystyrene derivatives. The alkoxyamine-terminated polystyrene, **12** (M_n = 4500; PDI = 1.09), was prepared from **3** under standard LFRP conditions[13] and heated with 4.0 equiv of *N*-phenylmaleimide, **4**, in DMF at 125 °C for 8 h to give the maleimide-terminated product, **13**, in essentially quantitative yield (Scheme 4). The crude product had the same molecular weight and polydispersity as the starting polymer, indicating that no chain coupling or degradation occurred during the reaction. Examination of the ^{1}H NMR spectrum revealed the characteristic disappearance of peaks due to the alkoxyamine unit at 0.40 and 0.80 ppm and in the case of deuterated polystyrene the appearance of the singlet for the maleimide proton at 6.27 ppm.

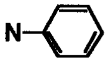
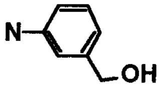
The degree of incorporation of the maleimide and the efficiency of alkoxyamine elimination were quantified by investigating maleimides and alkoxyamines labeled with a pyrene chromophore. Mitsunobu reaction of

Scheme 3

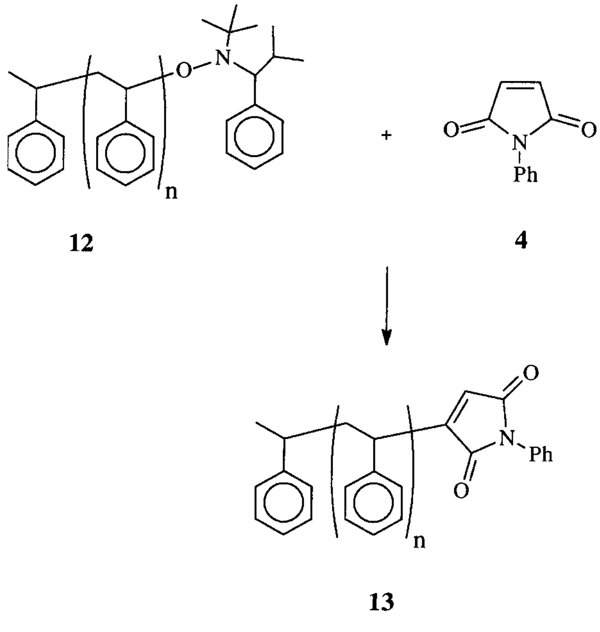


3, R = H   7, X = N–C$_6$H$_4$–CH$_2$OH   8, R = H, X = N–C$_6$H$_4$–CH$_2$OH

Table 2. Variation in the Yield of the Maleic Anhydride/ Maleimide Derivative, i.e. 6, with Changes in the Substituent, R, and the Maleic Substituent, X (See Scheme 3)

compd no.	R	X	yield (%)
6	H		93
8	H		87
9	H	N–Me	56
10	H	O	54
11	CH$_2$Cl		86

Scheme 4



12   **4**   **13**

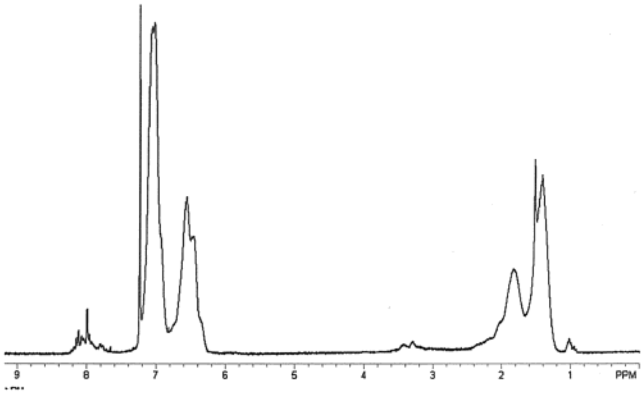


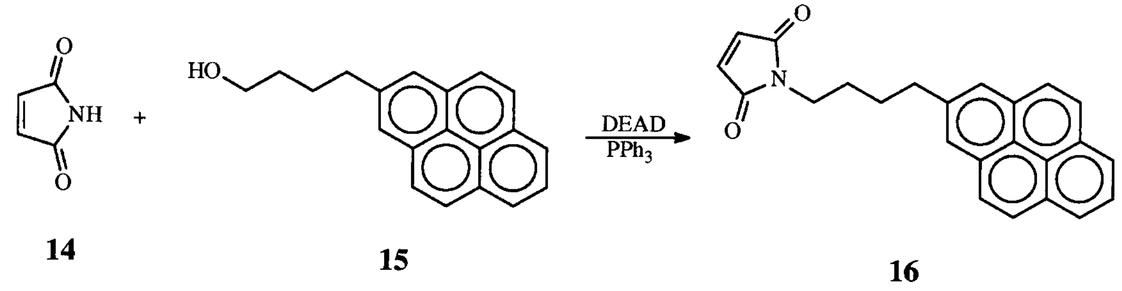
Figure 1. The 300 MHz ^{1}H NMR spectrum of the pyrene-labeled polystyrene, **17** (M_n = 4500; PDI = 1.07).

maleimide **14**, with 4-pyrenebutan-1-ol, **15**, afforded the pyrene-substituted maleimide, **16**, in 75% yield after purification (Scheme 5).[15] For a variety of alkoxyamine-terminated polystyrenes **12**, with molecular weights ranging from 2000 to 50 000, reaction with **16** gives pyrene-labeled polystyrene derivatives **17** (Scheme 6). The number of pyrene units introduced at the chain end was calculated by comparing the extinction coefficient of the labeled polymer with those for the small molecule derivatives **15** or **16**. Using this procedure, it was calculated that, for the range of molecular weights investigated, 0.98 ± 0.04 pyrene units were introduced.[16] These values were confirmed by ^{1}H NMR spectroscopy at lower molecular weights, where the peaks due to the pyrene group at 7.6–8.2 ppm could be integrated, compared with those for the polystyrene backbone at 6.4–7.2 ppm, and a molecular weight calculated (Figure 1). The close agreement of the NMR measurements with GPC molecular weights demonstrates conclusively that only one maleimide is added to the polymer chain under these reaction conditions.

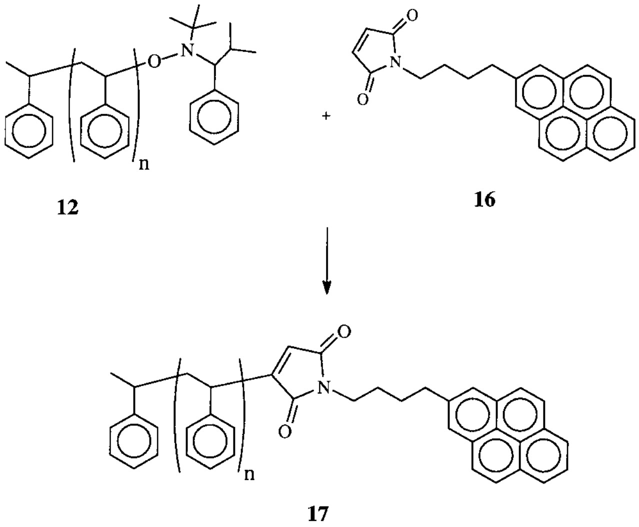
To demonstrate that the nitroxide unit was also eliminated from the chain end, a chromophore-labeled initiator **18** was used to prepare pyrene-terminated polystyrenes **19**, which were subjected to the same reaction conditions using *N*-phenylmaleimide, **4** (Scheme 7).[17] Significantly, the polystyrenes **13** obtained after reaction with **4** showed no absorbance due to a pyrene chain end, in direct contrast to the starting polymer **19**. These results demonstrate that elimination of the nitroxide via the hydroxylamine, e.g. **20**, is an efficient process for both small molecules and polymeric chain ends. Other polymers such as poly(*n*-butyl acrylate) and poly(isoprene) had similar reactivity, though in the case of poly(isoprene) reaction temperatures of 140 °C were required due to the reduced reaction rates for the isoprene chain ends.

Since the alkoxyamine chain end provides a facile means for generating a terminal radical, dormant chains containing alkoxyamines are prone to depolymerization at elevated temperatures. Removal of the alkoxyamine chain end should therefore enhance the thermal stability of these nitroxide-mediated living free radical polymers. To investigate the thermal stability of these materials, thermogravimetric analysis of a polystyrene with an alkoxyamine chain end **12** (M_n = 4400, PDI = 1.08) was compared with the product **17** (M_n = 4500, PDI = 1.07) obtained after exchange of the

Scheme 5



Scheme 6



nitroxide end group with 4-pyrenylbutylmaleimide, **16**. The molecular weight and polydispersity of the maleimide-terminated polymer **17** are essentially the same as those of **12**, indicating that the only difference in the two polymers is the nature of the end group. As can be seen in Figure 2, the alkoxyamine-terminated polystyrene **12** is less stable than **17** with thermal decomposition of **12** in a nitrogen atmosphere starting at ca. 250 °C, being complete by 410 °C. In contrast, the maleimide-terminated polystyrene **17** is significantly more stable, with decomposition beginning at 350 °C, being complete until 450 °C. We are currently exploring the use of this alkoxyamine/maleic exchange strategy for the preparation of specifically labeled macromolecules with complex architecture.

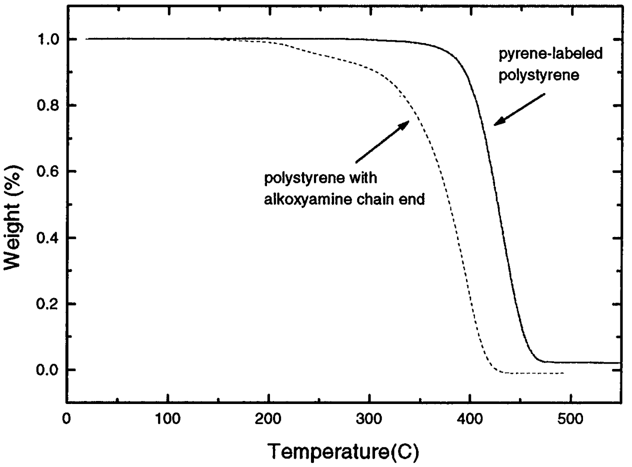


Figure 2. Comparison of TGA traces for chain end differentiated polystyrenes containing either an alkoxyamine chain end, **12** ($M_n = 4400$; PDI = 1.08), or a pyrene-substituted maleimide chain end, **17** ($M_n = 4500$; PDI = 1.07).

Conclusion

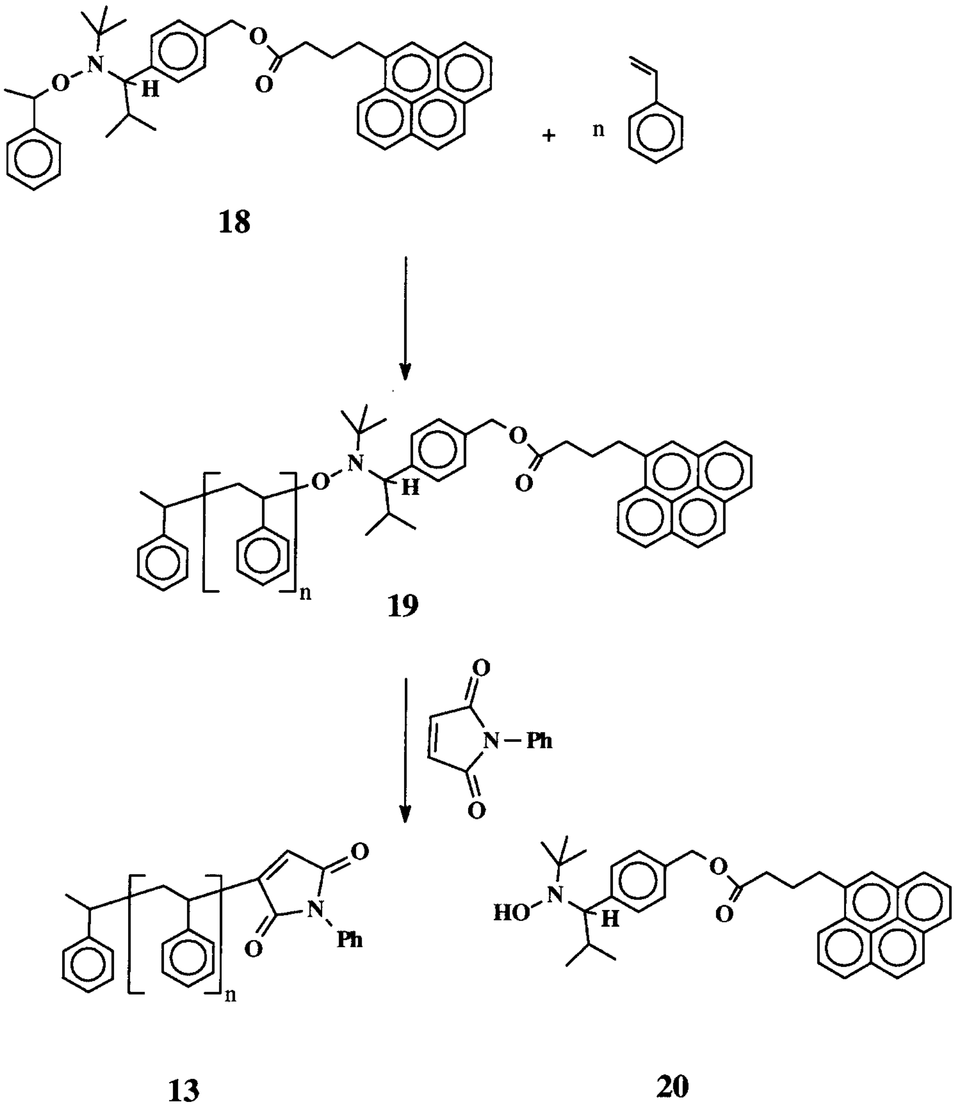
The chemistry of alkoxyamines is much richer than initially believed, being well-suited for the controlled functionalization of macromolecules. The reaction of alkoxyamines with maleic anhydride and maleimides leads to efficient introduction of a single unit in both small molecule and polymeric derivatives. The mild reaction conditions associated with this system allow for the introduction of a wide variety of functional groups that can be used in subsequent polymer modification reactions.

Experimental Section

All chemicals were purchased from Aldrich and used as received unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on Merck plates coated with silica gel 60 F_{254}. The silica gel for flash chromatography was Merck silica gel 60 (230−400 mesh ASTM). ^{1}H NMR and ^{13}C NMR spectra were recorded in chloroform-*d* solutions using a Bruker AM 250 spectrometer at 250 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Ultraviolet−visible (UV−vis) absorption spectroscopy was measured on a Hewlett-Packard 8452A diode array spectrophotometer. Gel permeation chromatography (GPC) was performed at 25 °C in THF (1 mL/min) on a Waters chromatograph equipped with four 5 μm Waters columns (300 × 7.7 mm), connected in series with increasing pore size (100, 1000, 100 000, and 1000 000 Å). Waters 410 differential refractometer and 996 photodiode array detectors were employed. The polystyrene molecular weights were calculated relative to linear polystyrene standards while the poly(*tert*-butyl acrylate) molecular weights were calculated relative to poly(*tert*-butyl acrylate) standards.

***N*-Phenyl-3-(2,2,5-trimethyl-4-phenyl-3-azaoxyhexyl)-4-(1′-phenylethyl)maleimide, 5.** The alkoxyamine **3** (325 mg, 1.0 mmol)[14] was dissolved in DMF (8 mL), and *N*-phenylmaleimide, **4** (346 mg, 2.0 mmol), added, and the solution was purged with argon for 5 min. The reaction mixture was then heated at 100 °C for 2 h with stirring and monitored by TLC until all the alkoxyamine had reacted. The DMF was then removed in vacuo, and the residue was purified by flash chromatography eluting with 3:1 hexanes/ethyl acetate. This gave the alkoxyamine−maleimide adduct, **5**, as a colorless oil (279 mg, 56%). ^{1}H NMR (100 MHz, $CDCl_3$): δ 7.47−7.00 (m, 14 H), 6.78 (d, 1 H, J = 7.2 Hz), 4.81 (d, 1H, minor, J = 5 Hz), 4.75 (d, 1 H, major, J = 6.5 Hz), 3.71−3.16 (m, 2 H), 2.56−2.53 (m, 1 H), 1.67 (m, 1H, J = 7.19 Hz), 1.49,1.37 (dd, 6H, J = 7.16 Hz, 37.45 Hz), 1.02, 0.90−0.88 (m, 9H), 0.46−0.39 (m, 3H). ^{13}C NMR: δ 176.40, 176.09, 175.60, 172.99, 172.82, 172.65, 141.41, 141.31, 141.26, 140.99, 140.84, 140.35, 131.64, 131.56, 131.49, 131.04, 130.43, 130.37, 129.72, 129.07, 129.02, 128.96, 128.89, 128.65, 128.57, 128.41, 128.12, 127.99, 127.76, 127.60, 127.46, 127.28, 127.20, 127.15, 126.68, 126.57, 126.50, 126.43, 126.32, 126.23, 102.14, 84.19, 82.61, 79.46, 79.08, 73.29, 72.98, 72.55, 72.42, 63.73, 61.20, 60.97, 60.73, 60.60, 54.77, 54.49, 54.36, 54.28, 53.64, 53.49, 41.84, 40.33, 40.25, 39.84, 32.25, 32.04, 31.01, 30.62, 30.52, 29.67,

Scheme 7



28.46, 28.30, 27.86, 27.67, 27.03, 26.90, 26.73, 22.41, 22.14, 21.46, 21.31, 21.11, 21.04, 19.35, 18.87, 18.76, 15.65, 15.35. HRMS exact mass calcd for $[M + 1]^+$ $C_{32}H_{38}N_2O_3$, 499.2961; found, 499.2954.

***N*-Phenyl-3-(1′-phenylethyl)maleimide, 6.** The alkoxyamine **3** (325 mg, 1.0 mmol) was dissolved in DMF (8 mL) and *N*-phenylmaleimide, **4** (346 mg, 2.0 mmol), added, and the solution was purged with argon for 5 min. The reaction mixture was then heated at 100 °C for 2 h with stirring, and then the temperature was raised to 125 °C and monitored by TLC until all the alkoxyamine had reacted and elimination of nitroxide was complete. This usually required heating for 2−4 h at 125 °C. The DMF was then removed in vacuo, and the residue was purified by flash chromatography eluting with 3:1 hexanes/ethyl acetate. This gave the maleimide derivative, **6**, as a colorless oil (258 mg, 93%). ^1H NMR (100 MHz, $CDCl_3$): δ 7.45−7.26 (m, 10 H), 6.39 (d, 1 H, $J = 1.6$ Hz), 4.11 (q, 1 H, $J = 6.72$ Hz), 1.64 (d, 3 H, $J = 7.23$ Hz). ^{13}C NMR: δ 169.67, 169.40, 153.42, 141.35, 134.21, 131.53, 128.02, 128.94, 127.65, 127.54, 127.35, 126.15, 125.86, 36.76, 19.88. HRMS exact mass calcd for $[M + 1]^+$ $C_{18}H_{15}NO_2$, 277.1102; found, 277.1103.

***N*-(3′-Hydroxymethylphenyl)maleimide, 7.** Maleic anhydride (5.88 g, 60.0 mmol) and 3-aminobenzyl alcohol (7.38 g, 60.0 mmol) were dissolved in 70 mL of 1,4-dioxane with stirring. Phosphorus pentoxide (12.0 g, 85.7 mmol) was added, and the reaction was heated to reflux for 3 h. The dark brown mixture was poured onto ice and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were then washed with brine, dried (magnesium sulfate), and evaporated to dryness. The crude product was purified by flash chromatography, eluting with 1:1 hexane/ethyl acetate. Yield: 18%. ^1H NMR (250 MHz, $CDCl_3$): δ 7.43−7.17 (m, 4 H), 6.76 (s, 2 H), 4.60 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.44, 143.26, 134.91, 131.95, 129.93, 127.11, 125.82, 125.18, 64.93. HRMS exact mass calcd for $[M + 1]^+$ $C_{11}H_9NO_3$, 203.0587; found, 203.0582.

***N*-(3′-Hydroxymethylphenyl)-3-(1′-phenylethyl)maleimide, 8.** The alkoxyamine **3** (325 mg, 1.0 mmol) was dissolved in DMF (8 mL) and *N*-(3′-hydroxymethylphenyl)maleimide, **7** (406 mg, 2.0 mmol), added, and the solution was purged with argon for 5 min. The reaction mixture was then heated at 100 °C for 2 h with stirring, and then the temperature was raised to 125 °C and monitored by TLC until all the alkoxyamine had reacted and elimination of nitroxide was complete. This usually required heating for 2−4 h at 125 °C. The DMF was then removed in vacuo, and the residue was purified by flash chromatography eluting with 3:1 hexanes/ethyl acetate followed by 1:1 hexanes/ethyl acetate. This gave the maleimide derivative, **8**, as a colorless oil (267 mg, 87%). ^1H NMR (100 MHz, $CDCl_3$): δ 7.44−7.23 (m, 9 H), 6.39 (d, 1 H, $J = 1.6$ Hz), 4.70 (s, 2 H), 4.10 (q, 1 H, $J = 6.72$ Hz), 1.63 (d, 3 H, $J = 7.23$ Hz). ^{13}C NMR: δ 169.69, 169.43, 153.44, 142.30, 141.30, 134.20, 131.55, 129.09, 128.92, 127.50, 127.34, 126.15, 126.10, 124.87, 124.20, 64.50, 36.75, 19.85. HRMS exact mass calcd for $[M + 1]^+$ $C_{19}H_{17}NO_3$, 307.1208; found, 307.1214.

***N*-Methyl-3-(1′-phenylethyl)maleimide, 9.** The alkoxyamine **3** (325 mg, 1.0 mmol) was dissolved in DMF (8 mL) and *N*-methylmaleimide (278 mg, 2.0 mmol) added, and the solution was purged with argon for 5 min. The reaction mixture was then heated at 100 °C for 2 h with stirring, and then the temperature was raised to 125 °C and monitored by TLC until all the alkoxyamine had reacted and elimination of nitroxide was complete. This usually required heating for 2−4 h at 125 °C. The DMF was then removed in vacuo, and the residue was purified by flash chromatography eluting with 3:1 hexanes/ethyl acetate. This gave the maleimide derivative, **9**, as a colorless oil (124 mg, 56%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.36−7.24 (m, 5 H), 6.24 (d, 1 H, $J = 1.39$ Hz), 4.02 (q, 1 H, $J = 7.25$ Hz), 2.96 (s, 3 H), 1.57 (d, 3 H, $J = 7.63$ Hz). ^{13}C NMR: δ 171.00, 170.70, 153.50, 141.54, 128.88, 127.47, 127.26, 126.02, 36.65, 23.75, 19.92. HRMS exact mass calcd for $[M + 1]^+$ $C_{13}H_{13}NO_2$, 215.0946; found, 215.0943.

***N*-Phenyl-3-(1-phenylethyl)maleic Anhydride, 10.** The alkoxyamine **3** (325 mg, 1.0 mmol) was dissolved in DMF (8 mL) and maleic anhydride (196 mg, 2.0 mmol) added, and the solution was purged with argon for 5 min. The reaction mixture was then heated at 100 °C for 2 h with stirring, and then the temperature was raised to 125 °C and monitored by TLC until all the alkoxyamine had reacted and elimination of nitroxide was complete. This usually required heating for 2−4 h at 125 °C. The DMF was then removed in vacuo, and the residue was purified by flash chromatography eluting with 3:1 hexanes/ethyl acetate. This gave the maleic anhydride derivative, **10**, as a colorless oil (281 mg, 54%). ^{1}H NMR (250 MHz, $CDCl_3$): δ; ^{1}H NMR (100 MHz, $CDCl_3$): δ 7.45−7.29 (m, 5 H), 6.58 (d, 1 H, $J = 2$ Hz), 4.20 (q, 1 H, $J = 6.5$ Hz), 1.65 (d, 3 H, $J = 6.5$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.12, 170.89, 152.83, 136.55, 131.48, 129.22, 128.91, 127.90, 127.72, 126.03, 46.12, 19.89. HRMS exact mass calcd for $[M + 1]^+$ $C_{12}H_9O_3$, 202.0630; found, 202.0636.

***N*-Phenyl-3-(1′-(4″-chloromethylphenyl)ethyl)maleimide, 11.** The alkoxyamine, **21** (373 mg, 1.0 mmol), was dissolved in DMF (8 mL) and *N*-phenylmaleimide, **4** (346 mg, 2.0 mmol), added, and the solution was purged with argon for 5 min. The reaction mixture was then heated at 100 °C for 2 h with stirring, and then the temperature was raised to 125 °C and monitored by TLC until all the alkoxyamine had reacted and elimination of nitroxide was complete. This usually required heating for 2−4 h at 125 °C. The DMF was then removed in vacuo, and the residue was purified by flash chromatography eluting with 3:1 hexanes/ethyl acetate. This gave the maleimide derivative, **11**, as a colorless oil (281 mg, 86%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.45−7.29 (m, 9 H), 6.41 (d, 1 H, $J = 1.56$ Hz), 4.58 (s, 2 H), 4.12 (q, 1 H, $J = 6.47$ Hz), 1.63 (d, 3 H, $J = 5.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.56, 169.23, 153.01, 141.61, 136.58, 131.45, 129.16, 128.99, 127.90, 127.66, 126.19, 125.82, 45.80, 36.46, 19.74. HRMS exact mass calcd for $[M + 1]^+$ $C_{19}H_{16}ClNO_2$, 325.0869; found, 325.0863.

General Procedures for Polymer Modification Reactions. The alkoxyamine-terminated polystyrene, **12**, $M_n = 4400$, PDI = 1.08 **(**1.00 g, 0.227 mmol), was dissolved in degassed DMF (5.0 mL) and *N*-phenylmaleimide, **4** (157 mg, 0.909 mmol, 4.0 equiv), added. The reaction mixture was then heated at 120 °C under argon for 4 h. After this time, the reaction mixture was precipitated into methanol (300 mL), and the precipitate was collected and dried to give **13** (0.94 g, 92%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.2−6.5 (m, ArH), 6.05 (s, 1H, alkene H), and 2.2−1.2 (m, alipH); $M_n = 4400$, PDI = 1.08. For all other polymers, the yield was typically 90−95%, and no change in the molecular weight or polydispersity was detected. Changes in the NMR spectra were consistent with the replacement of the alkoxyamine chain end with a *N*-phenylmaleimide group.

***N*-(4-Pyrenylbutyl)maleimide, 16.** A solution of Ph_3P (1.91 g, 7.2 mmol) in THF (140 mL) was cooled to −78 °C, and diethyl azodicarboxylate (1.15 mL, 7.27 mmol) was added for 1−2 min. The yellow reaction mixture was then stirred for 5 min, 4-pyrenebutanol, **15** (2.19 g, 7.9 mmol), added portionwise, and stirring continued until it was completely dissolved. Neopentyl alcohol (0.35 g, 4 mmol) and maleimide, **14** (0.69 g, 7.2 mmol), were added sequentially to the reaction mixture as solids, and the resulting suspension was allowed to remain at −78 °C for 10 min, during which time all of the maleimide dissolved. The cooling bath was then removed, and the reaction mixture was stirred overnight at room temperature. The yellow solution was concentrated and purified by flash chromatography eluting with hexane/ethyl acetate, 7:3, and the maleimide derivative, **16**, isolated as a bright yellow solid (1.93 g, 75%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.79 (m, 4H), 3.35 (t, 2H, $J = 7.58$ Hz), 3.57 (t, 2H, $J = 7.58$ Hz), 6.63 (s, 2H), 7.81−8.25 (m, 9H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 22.51, 28.77, 32.86, 37.66, 123.30, 124.69, 124.82, 124.86, 125.04, 125.11, 125.79, 126.62, 127.25, 127.28, 127.49, 128.61, 129.90, 130.92, 131.45, 133.97, 136.19, 170.79. HRMS exact mass calculated for $[M + 1]^+$ $C_{24}H_{19}NO_2$, 353.1416; found, 353.1427.

2,2,5-Trimethyl-3-(1-(4′-(4″-pyrenebutyloxy)methyl)phenylethoxy)-4-phenyl-3-azahexane, 18. Pyrenebutyric acid (0.80 g, 2.8 mmol), triphenylphosphine (0.73 g, 2.8 mmol), diisopropylazodicarboxylate (DIAD) (0.56 g, 2.8 mmol), and 2,2,5-trimethyl-3-(1-(4′-hydroxymethyl)phenylethoxy)-4-phenyl-3-azahexane[18] (1.0 g, 2.8 mmol) were mixed in THF (20 mL) and stirred under argon for 20 h. The solution was extracted with water/dichloromethane, and the organic phase was dried ($MgSO_4$). It was filtered, concentrated, and purified with flash column chromatography (petroleum ether gradually increasing to 1:1 petroleum ether/dichloromethane) to give the labeled initiator **18** as a light yellow foam (1.0 g, 57%). ^{1}H NMR (250 MHz, $CDCl_3$, both diastereomers): δ 8.2−7.7 (m, 18H), 7.5−7.1 (m, 18H), 4.93 (d, 4H, $J = 9.5$ Hz), 4.66 (q + q, 2H, $J = 6.5$ Hz), 3.41 (d, 1H, $J = 10.8$ Hz), 3.4 (m + m, 4H), 2.35 (m + m, 2H), 2.30 (m + m, 2H), 1.62 (d, 3H, $J = 6.8$ Hz), 1.54 (d, 3H, $J = 7.0$ Hz), 1.31 (d, 3H, $J = 6.3$ Hz), 1.04 (s, 9H), 0.92 (d, 3H), 0.77 (s, 9H), 0.54 (d, 3H, $J = 6.5$ Hz), 0.22 (d, 3H, $J = 6.5$ Hz). ^{13}C NMR (63 MHz, $CDCl_3$, both diastereomers): δ 173.02, 131.45, 131.11, 128.07, 127.48, 127.38, 127.01, 126.70, 126.22, 125.82, 124.89, 124.80, 123.35, 66.25, 33.96, 32.74, 28.45, 28.27, 26.85, 21.59. Elemental analysis: $C_{43}H_{47}NO_3$ requires C, 82.5; H, 7.57; and N, 2.24%. Found: C, 82.4; H, 7.46; and N, 2.01%.

General Procedure for the Polymerization of Styrene. Styrene and the pyrene-labeled alkoxyamine, **18**, were placed in a vial with a stirrer bar. The vial was degassed (three times) and sealed, and the polymerizations were heated at 120 °C for 6 h. For lower conversions shorter reaction times were used. The polymer was then dissolved in dichloromethane and purified by precipitation in methanol (three times). The pure polymer **19** was analyzed by GPC, NMR, and UV−vis.

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