Radical Crossover in Nitroxide Mediated "Living" Free Radical Polymerizations

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Abstract: The efficiency of exchange between the mediating nitroxide moieties at the termini of growing polymer chains during "living" free radical polymerizations has been probed by a series of crossover experiments using functionalized unimolecular initiators. The design of appropriately substituted initiators permitted the synthesis of specifically functionalized model polymers which could be readily distinguished using high-performance liquid chromatography (HPLC). Using these models, the mixture of macromolecules obtained from a 1:1 combination of disparate initiators was separated and identified. The results reveal that exchange of the mediating nitroxide free radicals is a facile process and at essentially all stages of the polymerization a nearly statistical mixture of crossover products is obtained. The HPLC techniques developed are also useful in evaluating the extent of chain termination in nitroxide mediated "living" free radical polymerizations.

Introduction

The field of "living" free radical polymerizations has witnessed explosive growth recently due to the great promise shown by these synthetically robust and simple procedures.[1] Of these procedures, those mediated by stable nitroxide free radicals, such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), are the most widely studied[2] and a variety of authors[3] have shown that the polymerization of styrene based monomers can be controlled to levels previously only obtained using anionic or cationic procedures.[4] Narrow polydispersity materials with controlled molecular weights,[5] chain ends,[6] and chain architectures[7] can be readily prepared by heating the neat monomer with a nitroxide based initiator at 120−130 °C under an inert atmosphere. Interestingly, well-defined random[8] and block[9] copolymers can be readily prepared from a variety of monomers, while the mild polymerization conditions also allow the polymerization of reactive monomers, such as sodium styrene sulfonate,[10] to give narrow polydispersity homopolymers with molecular weights approaching 10^6 amu.

The origin of this unprecedented control in free radical polymerizations is believed to be the reversible termination of the growing polymeric radical by the stable nitroxide free radical. This gives a dormant, or inactive species, **1**, in which the nitroxide is covalently bound to the polymer chain end. Under the polymerization conditions the carbon−oxygen bond is homolytically unstable and can undergo fragmentation to give a stable nitroxide free radical and the polymeric radical, **2**. Depending on the rate of recombination of this radical pair the polymeric radical, **2**, can then undergo chain extension with monomer to yield a similar polymeric radical, **3**, in which the degree of polymerization has increased. Recombination of **3** with the nitroxide then gives the dormant species, **4**, which has essentially the same structure as **1** and the cycle of homolysis−monomer addition−recombination can be repeated (Scheme 1). While this is the generally accepted blueprint for nitroxide mediated "living" free radical polymerizations a number of mechanistic questions remain unanswered. For example, it is not known if the nitroxide counter-radicals are associated with the same polymeric chain end during the course of the polymerization or if they are able to diffuse freely to the reaction medium.[11] In this paper we wish to report radical crossover experiments designed to probe the exchange of nitroxide free radicals at various stages during "living" free radical polymerizations.

Results and Discussion

Previously, it has been demonstrated that the chain ends of vinyl polymers can be accurately controlled using nitroxide mediated "living" free radical polymerizations.[6,13] This feature

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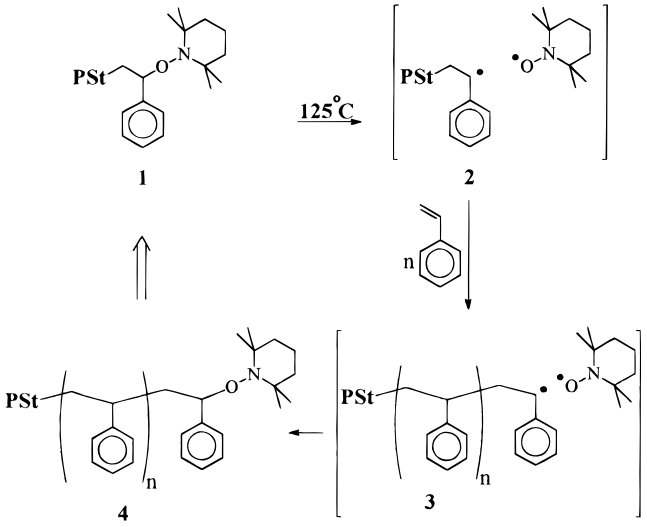
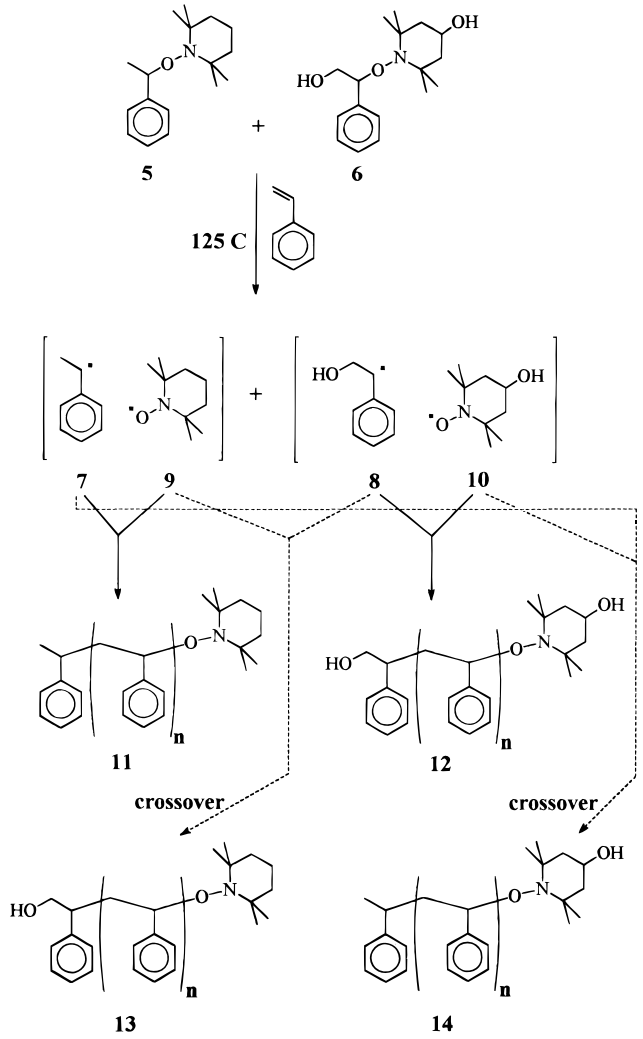
Scheme 1



is exploited in the design of crossover experiments to probe the potential diffusion of the mediating radical from the propagating chain end during "living" free radical polymerizations. The design of an appropriate crossover experiment is depicted in Scheme 2 and involves the use of two structurally similar unimolecular initiators which differ only in their substitution pattern. One derivative is unfunctionalized, **5**, while the unimolecular initiator, **6**, contains two hydroxy groups, one attached to the TEMPO unit and the second located at the β-carbon atom of the ethylbenzene unit. If a 1:1 mixture of **5** and **6** is used to initiate the "living" free radical polymerization of styrene, homolysis of the carbon−oxygen bond of **5** and **6** will lead to four radical species. Each of the radicals produced are chemically different and comprise a pair of initiating or propagating radicals, **7** and **8**, which are both based on ethylbenzene except that **8** has a hydroxy functionality attached to the β-carbon atom. Similarly, a pair of structurally similar mediating nitroxide radicals are produced, TEMPO, **9**, and 4-OH-TEMPO, **10**, which again differ by the presence of a single hydroxy group in **10**. If no escape of the mediating nitroxide radical from propagating chain end occurs, only two polystyrene derivatives will therefore be formed; **11**, which is derived from **5**, will have no hydroxy groups at the chain ends, while **12** contains a single hydroxy group at both chain ends. In contrast, if radical crossover does occur and the mediating nitroxide radicals are free to diffuse to the polymerization medium, four polystyrenes having different substitution patterns will be obtained. In addition to the "non-crossover" products, **11** and **12**, two monohydroxy functionalized polystyrenes, **13** and **14**, are obtained. Both **13** and **14** result from exchange, or crossover, of the nitroxides and differ in the placement of the single hydroxy chain end. Reaction of 4-OH-TEMPO, **10**, with the polymer chain derived from **7** gives **14** in which the hydroxy group is at the same chain end as the nitroxide unit. Alternatively, reaction of TEMPO, **9**, with the polymer chain derived from **8** gives **13** where the hydroxy group is at the opposite chain end to the nitroxide unit.

In either of the above scenarios a mixture of functionalized polystyrenes, having similar molecular weights but different chain end functional groups, is obtained. The separation and analysis of such a mixture is not a standard technique in polymer chemistry. However, a limited number of papers have appeared

Scheme 2



detailing the separation of polymeric materials using chromatographic techniques that are based on polarity, and not size, differences. For example, the purification and identification of dendrimers[14] has relied heavily on flash chromatography and high-performance liquid chromatography (HPLC), while McCarthy[15] has examined the separation of chain end functionalized polystyrene derivatives by thin-layer chromatography (TLC). To investigate the application of these separation techniques to the products in Scheme 2 the synthesis of all four possible model polymers, **11**, **12**, **13**, and **14**, was undertaken. This was accomplished by the synthesis of four different unimolecular initiators, **5**, **6**, **15**, and **16**, which vary in the number and placement of hydroxy functionalities (Figure 1). The preparation of the derivatives based on ethylbenzene, **5** and **15**, employed the synthetic approach recently described by Priddy

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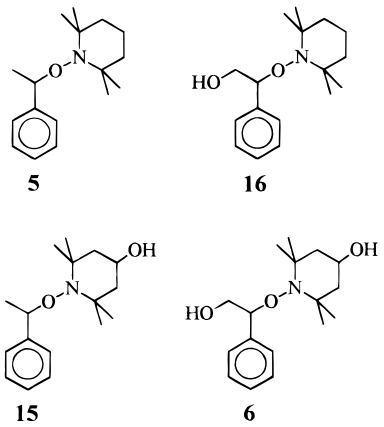
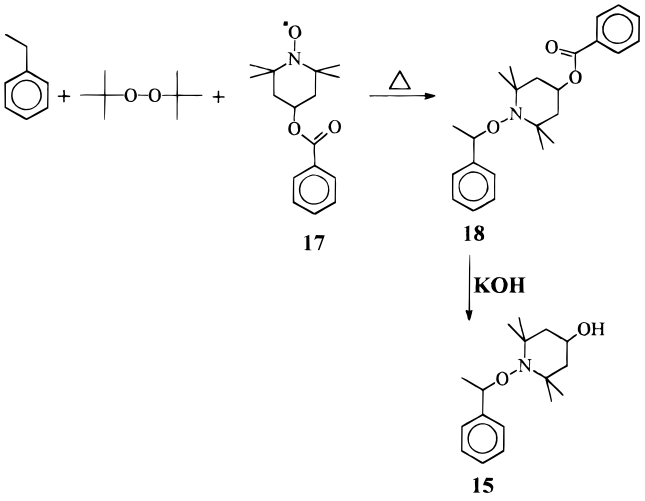


Figure 1. Structure of functionalized unimolecular initiators, **5**, **6**, **15**, and **16**, used for the preparation of the model chain end functionalized polystyrenes.

Scheme 3

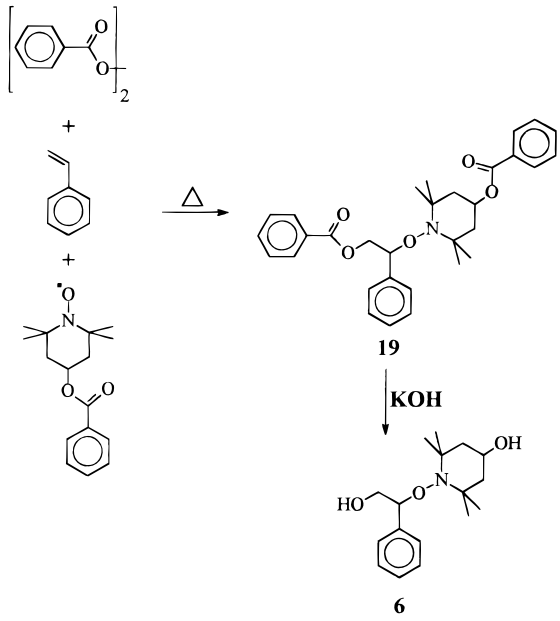


and Howell.[16] For example, a mixture of di-*tert*-butyl peroxide and 4-benzoyloxy-TEMPO, **17**, was heated at reflux in ethylbenzene for 16 h. This gave the alkylated TEMPO derivative, **18**, in 41% yield after purification which was then hydrolyzed with potassium hydroxide to give the desired monohydroxy derivative, **15**, in which the hydroxy group is located on the nitroxide ring (Scheme 3). In contrast, the derivatives in which the hydroxy group is located on the β-carbon, **6** and **18**, were both prepared by reaction of benzoyl peroxide with styrene and the appropriately functionalized TEMPO derivative. In this case, a mixture of benzoyl peroxide and 4-benzoyloxy-TEMPO is heated at 85 °C in excess styrene to give the diester, **19**, which on hydrolysis yields the desired dihydroxy derivative, **6**, in 34% yield over both steps (Scheme 4).

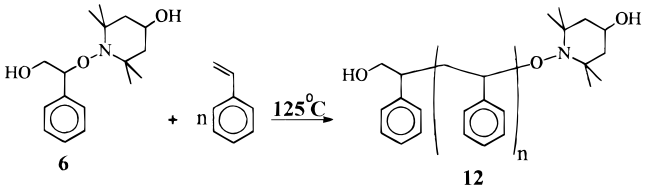
The preparation of the model polystyrene derivatives from the appropriately functionalized unimolecular initiators was then performed using standard "living" free radical polymerization conditions. The molecular weights of the model polymers, **11**−**14**, were controlled by the addition of specified equivalents of styrene to the corresponding unimolecular initiators and were approximately 3000 amu in each case. For example, reaction of **6** with 35 equiv of styrene at 125 °C for 48 h gave the dihydroxy-terminated polystyrene derivative, **12**, in 85% yield which was shown to have a molecular weight, M_n, of 2900 and a polydispersity of 1.09 (Scheme 5).

Significantly, examination of the model polystyrene macromolecules, **11**−**14**, by HPLC revealed substantially different elution times depending on the functional group/s at the chain

Scheme 4



Scheme 5



ends. Near baseline separation was observed between all four polymers with the shortest retention time peak (2.90 min) corresponding to the unfunctionalized polymer, **11**, while the peak with the longest retention time (5.80 min) corresponds to the polymer, **12**, with hydroxy groups at both chain ends. Surprisingly, the monohydroxy terminated polystyrenes, **13** and **14**, displayed different elution times even though they both contain a single hydroxy group and a single TEMPO unit. The presence of the hydroxy group and TEMPO unit at the same chain end of **14** results in a longer retention time (4.70 min) when compared to **13** (3.40 min). A possible reason for this difference is that the presence of the polar hydroxy and TEMPO functionalities at the same chain end results in increased interaction with the stationary phase when compared to the case where the hydroxy and TEMPO functionalities are at different chain ends. To determine the effect of molecular weight on elution times, model polystyrene macromolecules, **11**−**14**, with molecular weights of approximately 5000 and 7500 amu were prepared and examined under the same conditions. Near baseline was again observed between all the samples and only a slight reduction in retention times was observed. Therefore, slight variation in molecular weights for the model polymers, or the polystyrene derivatives produced during the crossover experiments, will not affect the analysis or identification of mixtures containing **11**−**14** at molecular weights less than 7500 amu. It should be noted that as the molecular weight increases above 7500 amu separation becomes progressively more difficult and above 10 000 amu is no longer possible. This is due to the influence of the chain ends becoming minimal at higher molecular weights, and the elution time of all the samples eventually becomes the same. For example, the elution time for the monohydroxy-terminated polystyrene, **14**, decreases from 4.70 min to 2.55 min as the molecular weight increases from 2 900 to 45 000 amu. A similar effect has been observed by

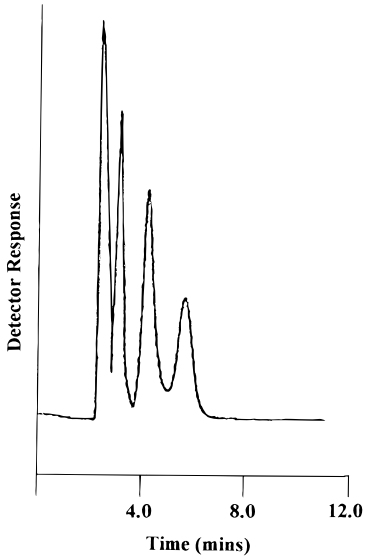


Figure 2. HPLC trace of the product mixture obtained from the polymerization of 35 equiv of styrene using a 1:1 combination of unimolecular initiators, **5** and **6**.

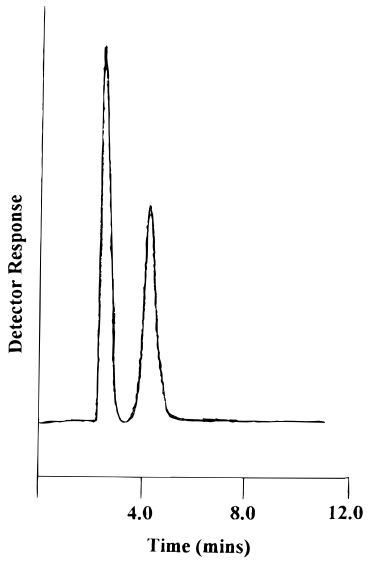
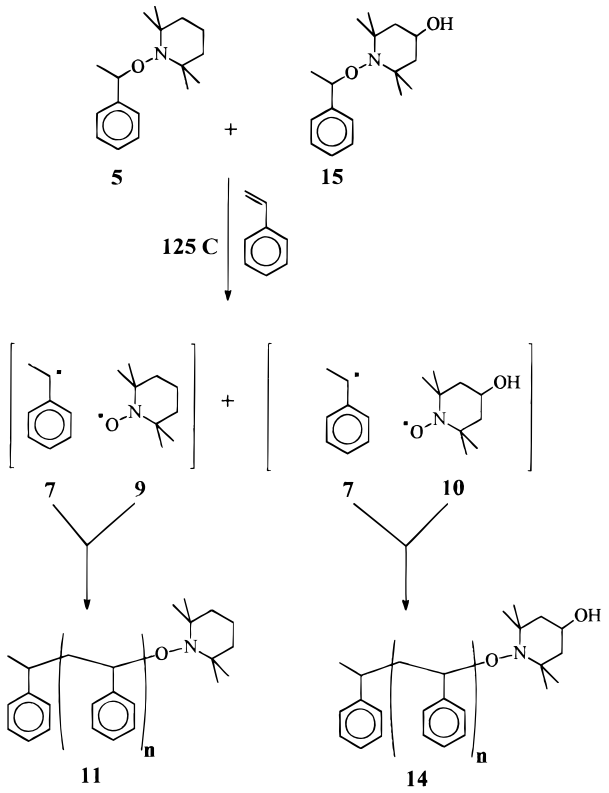


Figure 3. HPLC trace of the product mixture obtained from the polymerization of 40 equiv of styrene using a 1:1 combination of unimolecular initiators, **5** and **15**.

McCarthy[15] for the analysis of functionalized polystyrenes by thin-layer chromatography.

Crossover experiments were then performed using a 1:1 mixture of the unfunctionalized unimolecular initiator, **5**, and the dihydroxy initiator, **6**. As detailed above, if no radical exchange, or crossover, occurs HPLC analysis should show only two products, **11** and **12**. However, if crossover does occur, a statistical mixture of all four possible polystyrene derivatives should be obtained. The polymerization of 35 equiv of styrene with **5** and **6** was therefore conducted under standard "living" free radical polymerization conditions with samples being removed at 50 and 90% conversion. The mixture of polystyrene macromolecules obtained was found to have molecular weights, M_n, of 1600 (PD = 1.08) and 3100 (PD = 1.13), respectively, which indicates that controlled growth is occurring from the mixture of initiators. Interestingly, HPLC analysis of these samples showed that all four possible products were present in an approximately statistical ratio (Figure 2). Repetition of this experiment using 100 equiv of styrene gave essentially the same

Scheme 6



results at conversions ranging from 15% to 80%. From these results it can be concluded that the nitroxide free radicals are free to diffuse out of the reaction cage during "living" free radical polymerization and that statistical exchange of the chain ends occurs at an early stage of the polymerization.

To confirm the above results a modified crossover experiment was performed using a 1:1 mixture of the unfunctionalized initiator, **5**, and the monohydroxy derivative, **15**. In this case homolysis generates only three radical species, an initiating radical, **7**, and two different mediating nitroxide radicals, **9** and **10**. The commonality of **7** to both systems means that only two different polystyrene macromolecules, **11** and **14**, should be obtained (Scheme 6). Therefore, polymerization of 40 equiv of styrene with a 1:1 mixture of **5** and **15** gives a narrow polydispersity product (M_n = 3500, PD = 1.10) that was shown to contain only two peaks by HPLC analysis (Figure 3). These peaks correlate with the expected products, **11** and **14**, and the absence of other peaks or unknown products demonstrates the validity of the above crossover experiments.

In conclusion, a radical crossover experiment to probe the mobility of mediating nitroxide free radicals during "living" free radical polymerizations has been designed. To investigate the validity of this concept a series of unimolecular initiators having different hydroxy group substitution patterns as well as the corresponding polystyrene model polymers were synthesized. A HPLC technique was then developed which allowed the separation and identification of polystyrene macromolecules having different substitution patterns at the chain ends. Comparison of these model compounds with the product mixture obtained from the crossover experiments demonstrated conclusively that migration of the mediating nitroxide radicals during "living" free radical polymerizations is a facile process. The versatility and application of HPLC to other issues in "living" free radical polymerizations and telechelic polymers is currently being investigated.

Experimental Section

Nuclear magnetic resonance spectroscopy was performed on a Bruker AM 200 FT-NMR spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal reference. Gel permeation chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer with THF as the carrier solvent. Differential scanning calorimetry was performed on a Perkin Elmer DSC-7 calorimeter using a scanning rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperature was defined as the halfway point of transition heat flow. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica gel for flash chromatography was Merck Kieselgel 60 (230−400 mesh). High-pressure liquid chromatography experiments were conducted using a Waters 510 pump connected to a HP 1050 variable wavelength UV−vis detector and a Waters Microporosil 60A column (4.4 × 300 mm) using a 1:1 mixture of THF and isooctane as eluent. All solvents used for synthesis were dried and distilled in the appropriate manner before use; the commercial reagents were obtained from Aldrich and used without further purification. The unimolecular initiators, **5** and **16**, were prepared and purified as previously reported.[12]

4-(Benzoyloxy)-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (18). A solution of 4-benzoyloxy-TEMPO, (**17**, 8.00 g, 29.0 mmol) and di-*tert*-butyl peroxide (4.23 g, 29.0 mmol) in ethylbenzene (250 mL) was heated at reflux for 16 h, cooled, and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:4 hexane/dichloromethane gradually increasing to dichloromethane to give the ester, **18**, as a waxy solid (4.53 g, 41%). IR (neat) 2950, 1710, 1270, and 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.68, 1.16, 1.31, and 1.36 (each br s, 3H, C*H*$_3$), 1.49 (d, J = 7 Hz, 3H, C*H*$_3$), 1.40−2.00 (complex m, 4H), 4.78 (q, J = 7 Hz, 1H, C*H*), 5.21 (complex m, 1H, C*H*), 7.20−7.55 (complex m, 8 H, Ar*H*), and 7.99 (d of d, 2H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 21.16, 23.32, 34.10, 34.40, 44.67, 60.45, 60.73, 67.47, 83.39, 126.69, 127.01, 128.08, 128.31, 129.49, 130.61, 132.83, 145.13, and 166.17; mass spectrum (FAB) 381.

4-Hydroxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (15). To a solution of ester **18** (3.81 g, 10.0 mmol) in ethanol (100 mL) was added a solution of potassium hydroxide (1.12 g, 20.0 mmol) in water (5 mL). The reaction mixture was then heated at reflux under nitrogen for 16 h, cooled, and evaporated to dryness. The residue was partitioned between water (150 mL) and dichloromethane (150 mL) and the aqueous layer extracted with dichloromethane (2 × 50 mL). The combined organic extracts were then dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with dichloromethane gradually increasing to 1:19 ether/dichloromethane to give the alcohol, **15**, as a waxy solid (2.23 g, 81%). IR (neat) 3250, 2970, 1450, 1380, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.65, 1.08, 1.23, and 1.31 (each br s, 3H, C*H*$_3$), 1.48 (d, J = 7 Hz, 3H, C*H*$_3$), 1.20−1.90 (complex m, 4H), 3.92 (complex m, 1H, C*H*), 4.758 (q, J = 7 Hz, 1H, C*H*), and 7.20−7.33 (complex m, 5 H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 21.26, 23.39, 34.14, 34.45, 48.78, 48.88, 59.99, 60.20, 63.32, 83.30, 126.65, 126.95, 128.06, and 145.45; mass spectrum (FAB) 277.

4-(Benzoyloxy)-1-((2′-(benzoyloxy)-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (19). To a solution of benzoyl peroxide (2.29 g, 9.50 mmol) in distilled styrene (100 mL) was added 4-benzoyloxy-2,2,6,6-tetramethyl-1-piperidinyloxy (5.00 g, 18.9 mmol) and the solution heated at 90 °C under nitrogen for 20 h. After cooling the solution was evaporated to dryness and the reaction mixture purified by flash chromatography column eluting with 1:1 hexane/dichloromethane gradually increasing to dichloromethane to give the modified diester, **19**, as a pale yellow oil (3.70 g, 39%); IR (neat) 3100−2850, 1720, and 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70, 1.10, 1.24, 1.33 (each br s, 12H, C*H*$_3$), 1.35−1.95 (m, 4H, C*H*$_2$); 4.45 (ABq, J = 6 Hz, 1 H, C*H*H), 4.76 (ABq, J = 6 Hz, 1 H, CH*H*), 5.00 (ABq, J = 3 Hz, 1 H, C***H***), 5.16 (complex m, 1 H, C***H***), 7.25−7.50 (m, 11H, Ar*H*), 7.84 (B of ABq, J = 6 Hz, 2H, Ar*H*), and 7.93 (B of ABq, J = 6 Hz, 2H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 20.90, 21.22, 32.87, 34.10, 44.16, 44.80, 59.80, 60.63, 66.61, 67.22, 84.24, 127.71, 127.89, 128.18, 128.33, 128.42, 129.50, 129.71, 130.10, 132.88, 140.25, 166.13, and 166.327; mass spectrum (EI) *m*/*z* 501.

4-Hydroxy-1-((2′-hydroxy-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (6). To a solution of diester **19** (2.50 g, 5.00 mmol) in ethanol (50 mL) was added a solution of potassium hydroxide (800 mg, 14.0 mmol) in water (5 mL). The reaction mixture was then heated at reflux under nitrogen for 16 h, cooled, and evaporated to dryness. The residue was partitioned between water (150 mL) and dichloromethane (150 mL) and the aqueous layer extracted with dichloromethane (2 × 50 mL). The combined organic extracts were then dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with dichloromethane gradually increasing to 1:2 ether/dichloromethane to give the dialcohol, **6**, as a waxy solid (1.29 g, 88%). IR (neat) 3250, 2970, 1450, 1380, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10, 1.20, 1.25, and 1.41 (each br s, 3H, C*H*$_3$), 1.30−1.90 (complex m, 4H), 3.66 (complex m, 1H, C*H*), 3.93 (complex m, 1H, C*H*), 4.14 (ABq, J = 7 Hz, 1H, C*H*), 5.19 (ABq, J = 7 Hz, 1H, C*H*), and 7.25−7.33 (complex m, 5 H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 21.27, 21.57, 33.08, 34.74, 48.75, 49.93, 60.85, 61.84, 62.53, 69.00, 83.97, 126.91, 128.29, 128.67, and 138.70; mass spectrum (FAB) 293.

Radical Crossover Experiments. A mixture of the unfunctionalized initiator (**5**, 261 mg, 1.0 mmol) and the dihydroxy initiator (**6**, 293 mg, 1.0 mmol) was dissolved in styrene (8.32 g, 80.0 mmol) and heated at 125 °C under argon for 48 h. During this time, samples of the polymerization mixture were withdrawn at periodic intervals and evaporated to dryness. The polymeric mixture obtained was then analyzed by HPLC eluting with a 7:3 mixture of isooctane and tetrahydrofuran; the individual peaks were then compared with known, independently synthesized samples.

General Procedure for the Preparation of Specifically Functionalized Polystyrenes. The hydroxy functionalized initiator (**16**, 276 mg, 1.0 mmol) was dissolved in styrene (4.16 g, 40.0 mmol) and heated at 125 °C under argon for 48 h. The polymerization mixture, which solidified after ca. 24 h, was then dissolved in dichloromethane and precipitated into methanol (500 mL). The resulting solid was then collected by vacuum filtration and dried to give the hydroxy-terminated polystyrene, **13**, as a white solid (4.03 g, 90%): IR (neat) 3250, 3020, 2980, 1605, 1360, and 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15−0.40, 1.00−1.80, 2.50 (C*H*-TEMPO), 3.70 (C*H*$_2$OH), and 6.50−7.10.

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