

End-Group Fidelity in Nitroxide-Mediated Living Free-Radical Polymerizations

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ABSTRACT: In this study, new nitroxides based on the 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy skeleton were used to examine chain-end control during the preparation of polystyrene and poly(*t*-butyl acrylate) under living free-radical conditions. Alkoxyamine-based initiators with a chromophore attached to either the initiating fragment or the mediating nitroxide fragment were prepared, and the extent of the incorporation of the chromophores at either the initiating end or the propagating chain end was determined. In contrast to 2,2,6,6-tetramethyl piperidinoxy (TEMPO), the incorporation of the initiating and terminating fragment into the polymer chain was extremely high. For both poly(*t*-butyl acrylate) and polystyrene with molecular weights less than or equal to 70,000, incorporations at the initiating end of greater than 97% were observed. At the terminating chain end, incorporations of greater than 95% were obtained for molecular weights less than or equal to 50,000. The level of incorporation tended to decrease slightly at higher molecular weights because of the loss of the alkoxyamine propagating unit, which had important consequences for block copolymer formation. These results clearly show that these new α -H nitroxides could control the polymerization of vinyl monomers such as styrene and *t*-butyl acrylate to an extremely high degree, comparable to anionic and atom transfer radical polymerization procedures. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 4749–4763, 2000

Keywords: living free-radical polymerization; alkoxyamines; nitroxide; chain-end functionality

INTRODUCTION

The control of structures on a nanometer scale is becoming an important topic in all aspects of science.¹ It is anticipated that polymeric materials will play a crucial role in many areas of nanoscale science and, because of the small size scales involved, the structure of the polymer will assume an increasingly significant role. Factors such as molecular weight, chain ends, polydispersity, and architecture will become pivotal in determining the performance of polymeric materials on these reduced size scales. It is, therefore, an important

goal to develop methods for controlling the structure of functionalized macromolecules with as high a degree of fidelity as possible.² Living polymerization techniques offer one of the best opportunities to achieve this level of control, and for vinyl polymers, a number of different strategies— anionic, cationic, and free-radical—are available.³ Although living anionic procedures are the most widely studied, a considerable amount of recent effort has been devoted to the development of living free-radical procedures because of their potential advantages.

In all three variations of living free-radical procedures—atom transfer radical polymerization,⁴ reversible addition-fragmentation chain transfer (RAFT),⁵ and nitroxide-mediated⁶—numerous groups have demonstrated strategies for control-

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ling molecular weight,⁷ chain-end functional groups,⁸ polydispersity,⁹ and macromolecular architecture.¹⁰ Even though it is increasingly important to understand these polymerization processes in greater detail, detailed investigations into the absolute structure of the polymers produced with these novel techniques are lacking. In particular, the identification and quantification of unwanted side reactions, such as autoinitiation¹¹ and various termination processes (i.e., radical coupling, chain transfer, and disproportionation),¹² are especially critical for the formation of block copolymers because any one of these unwanted side reactions can lead to the formation of homopolymers.

To study the retention of chain-end functional groups for nitroxide-mediated living free-radical processes, the incorporation of chromophore units into the structure of the alkoxyamine-based unimolecular initiator is the method of choice. Working with azo-labeled 2,2,6,6-tetramethylpiperidinoxy (TEMPO) derivatives, Priddy et al.¹³ reported that the end-group purity decreased with molecular weight and conversion. More importantly, high levels of chain-end incorporation, greater than 80%, was only achieved for very low molecular weights (<10,000). The degree of fidelity for the propagating or nitroxide-derived chain end was shown to be even worse, with the value of 60–80% being significantly lower than for the initiating chain end. In similar work, with pyrene as the chromophore,¹⁴ TEMPO-based alkoxyamines were shown to give levels of incorporation between 90 and 95% for the polymerization of styrene, although the molecular weights were again low, about 10,000. Both of these results demonstrate that the fidelity of TEMPO-mediated living free-radical procedures does not approach 100%, even in the best systems. This is not surprising given the long polymerization times (16–48 h) and polydispersities (1.1–1.3) typically obtained for TEMPO-mediated living free-radical procedures.

Recently, alternate nitroxide structures have been introduced that show a number of key advantages when compared with the initial TEMPO systems. For example, nitroxides bearing a hydrogen on the α -carbon, such as those based on the 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxo skeleton (**1**), were shown to have significantly faster kinetics, give lower polydispersities, and be able to polymerize a wide range of monomers such as acrylates and 1,3-dienes. The universal nature of these new nitroxides¹⁵ and the emerging impor-

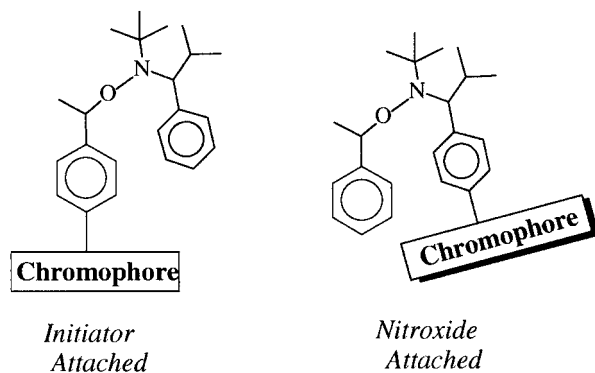
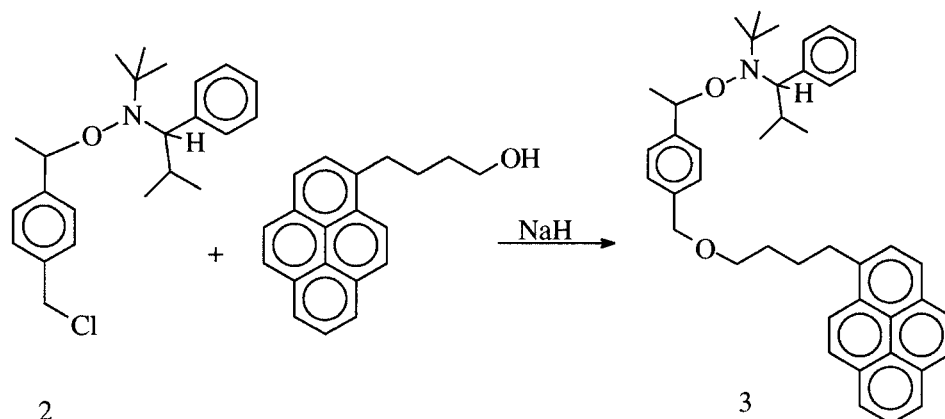


Figure 1. Possible structures for the attachment of chromophores to alkoxyamine-based initiators.

tance of alkoxyamines based on **1** for preparing nanoscopically defined polymeric materials¹⁶ prompted a thorough examination of the polymerization fidelity for these novel systems.

RESULTS AND DISCUSSION

For alkoxyamine-based unimolecular initiators, two modes of attachment of the chromophore to the alkoxyamine skeleton are possible. In one, a chromophore is attached to the initiating fragment, and in the other, the structure involves attaching the chromophore to the mediating nitroxide radical (Fig. 1). In selecting a synthetic strategy for the preparation of an alkoxyamine labeled at the initiating chain end, the ready availability of *p*-chloromethyl styrene and the corresponding alkoxyamine (**2**) suggested the use of 4-pyrenebutanol as the chromophoric unit. Therefore, the reaction of **2** with the anion of 4-pyrenebutanol gave the desired labeled alkoxyamine 4-(4'-pyrenebutoxymethyl)-2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (**3**) in an 84% yield (Scheme 1).¹⁷ One of the advantages of alkoxyamine-based initiators is their stability under a variety of reaction conditions as well as normal purification and handling procedures. This allowed the initiator (**3**) to be stored at room temperature and fully characterized with standard procedures. As shown in Figure 2, the ¹H NMR spectrum of **3** could be fully assigned and confirmed the introduction of a single pyrene chromophore. Alternatively, the aminomethyl-substituted derivative [4-(aminomethyl)-2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane; **4**] could be treated with dansyl chloride (**5**) to give the corresponding fluorescently labeled initi-



Scheme 1

ator 4-phenyl-2,2,5-trimethyl-3-[1-(5'-dimethylaminophenyl)sulfonamido methyl]phenylethoxy]-3-azahexane (**6**; Scheme 2).

With the desired initiators, **3** and **6**, having been obtained, polymerizations with styrene and *t*-butyl acrylate were performed under standard conditions. Two variables, the molar ratio of initiator to monomer and the monomer conversion, were examined in an effort to determine how the chain-end fidelity varies with increasing molecular weight and extent of reaction.

For polystyrene, vials of different molar ratios of styrene and **3** were sealed under argon and heated at 120 °C for 6 h; this typically resulted in conversions of 75–90% (Scheme 3). To ensure that all small molecule impurities were removed, the crude polymer (**7**) was purified by repeated precipitation (at least three times) and analyzed by gel permeation chromatography (GPC) with a diode array UV detector. In this way, the presence of extraneous chromophores, not attached to the polystyrene chain, could be negated. All of the

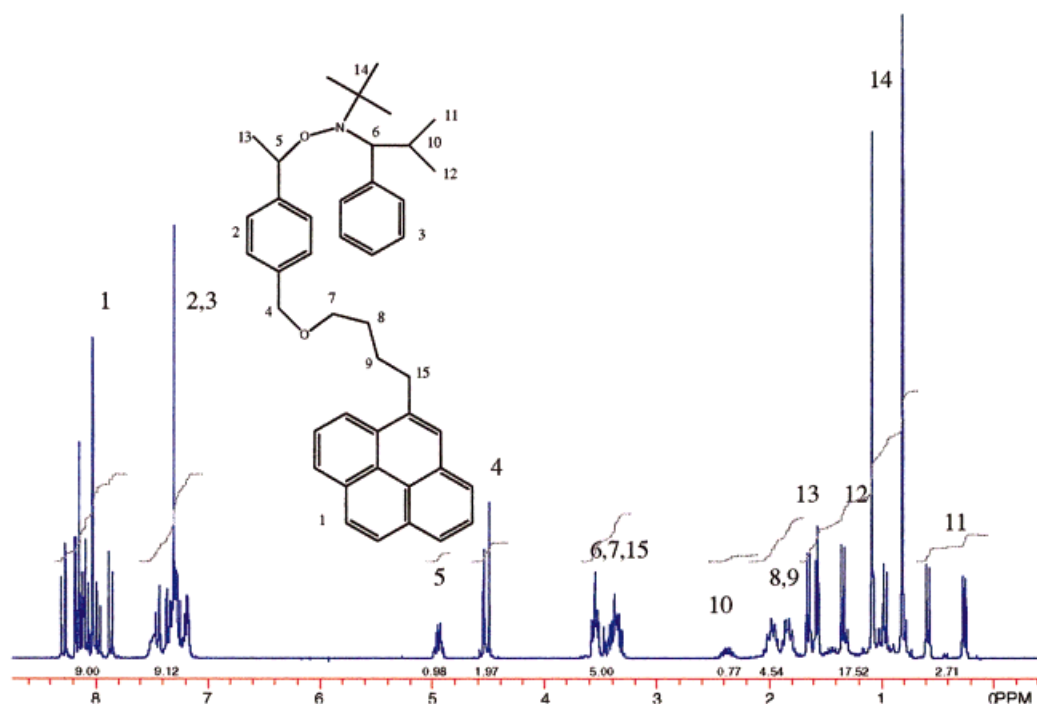
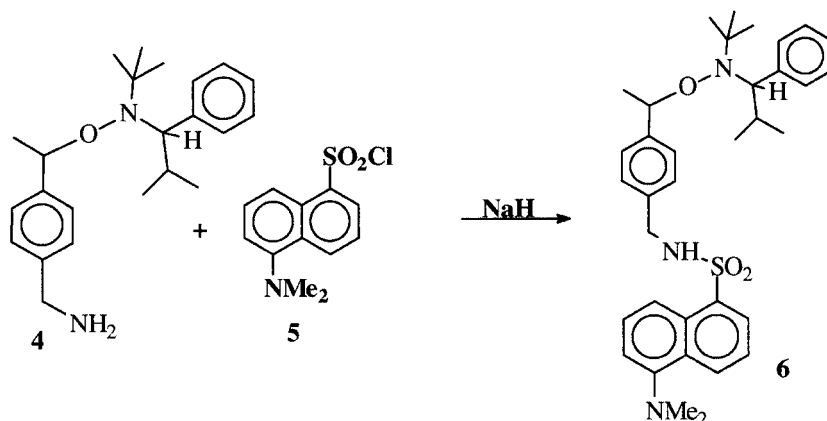


Figure 2. ^1H NMR (250-MHz) spectrum of pyrene-labeled alkoxyamine (**3**). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 2

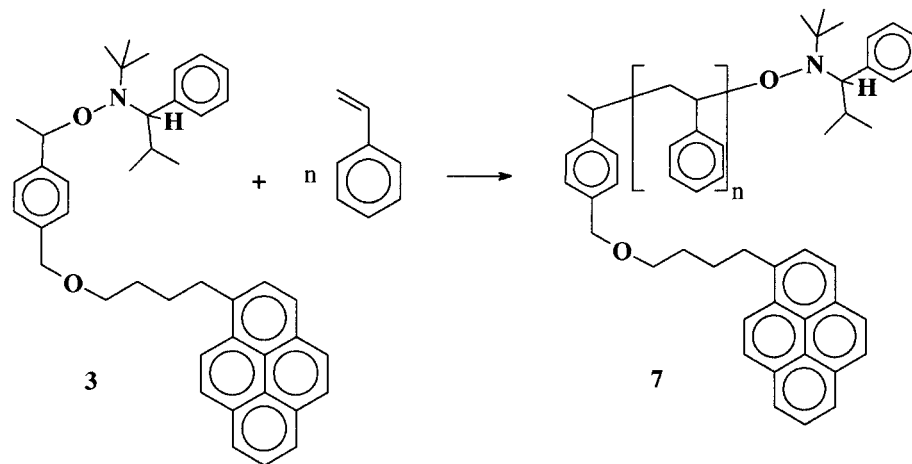
samples prepared were shown to have number-average molecular weights (M_n) that were within 10% of the theoretical molecular weights, and the polydispersities were between 1.05 and 1.15, which demonstrates the controlled nature of living free-radical polymerizations initiated with **3**.

For the monomer conversion studies, a 500/1 ratio of styrene to **3** was chosen, and a series of identical polymerizations were stopped at reaction times ranging from 0.5 to 6 h. In this way, samples were obtained with conversions ranging from 16 to 80%, and as before, molecular weights and polydispersities were indicative of a living process. The fidelity of the polymerization process was then examined via the determination of the extent of pyrene incorporation at the initiating chain end for both sets of samples. To accomplish this, the absorbances of the initiator (**3**) and the polymers were measured at 344 nm, and the ex-

tinction coefficients were calculated for a range of different concentrations. The ratio of these experimentally determined extinction coefficients then allowed the relative percentage of pyrene incorporated at the chain ends to be determined and the end-group fidelity to be assessed (Figs. 3 and 4).

Poly(*t*-butyl acrylate)

In a similar fashion, *t*-butyl acrylate was polymerized, in the presence of **3** and 0.05 equiv of **1**, in sealed vials under argon at 120 °C for 36 h (Scheme 4).¹⁵ In this case, the residual monomer was removed by evaporation, and the crude polymer (**8**) was purified by repeated precipitation into methanol. GPC overlays of the poly(*t*-butyl acrylates) with a range of molecular weights are shown in Figure 5 and once again demonstrate



Scheme 3

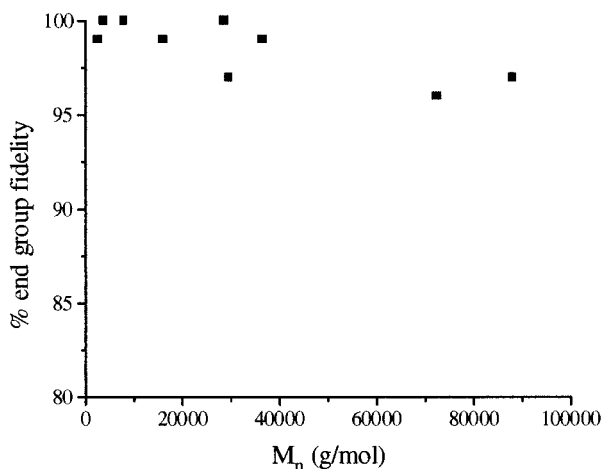


Figure 3. Initiator end-group fidelity against molecular weight for polystyrene prepared from **3** with different molecular weights at 120 °C for 6 h.

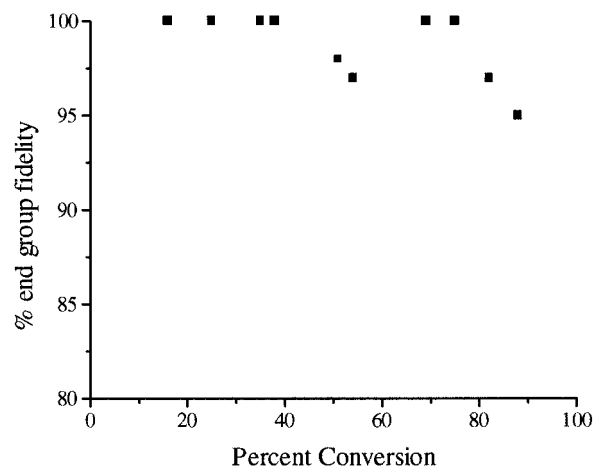


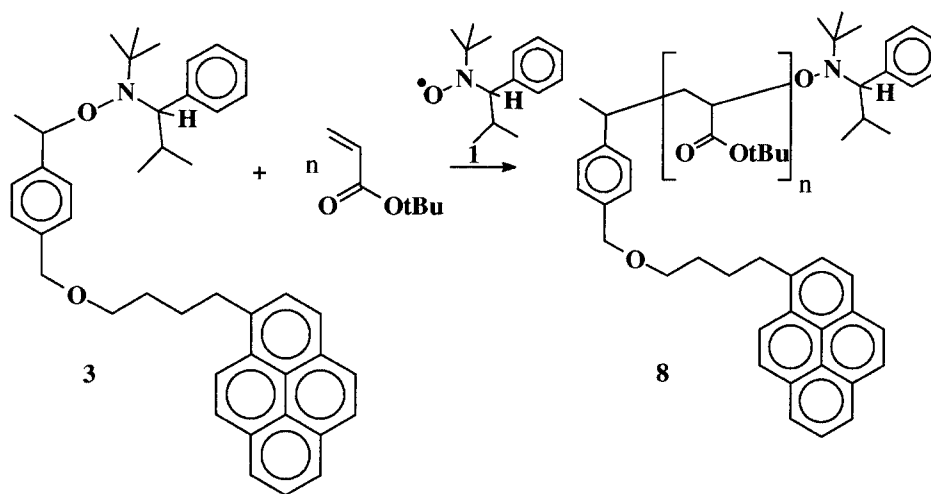
Figure 4. Initiator end-group fidelity for the polymerization of 500 equiv of styrene with **3** at 120 °C to different conversions.

the low polydispersities and controlled molecular weights that can be obtained for nitroxide-mediated living free-radical polymerizations of acrylates mediated by these new nitroxides.

The monomer conversion studies were performed with a system containing a 500/1 ratio of *t*-butyl acrylate to **3**, and the samples were removed at 3–36 h, resulting in conversions ranging from 13 to 82%. For both experimental series, that is, molecular weight and conversion, the incorporation of the pyrene chain end was determined in the same fashion as before, and the results are depicted in Figures 6 and 7.

All of these experiments clearly showed that for both polystyrene and poly(*t*-butyl acrylate)

prepared by nitroxide-mediated living free-radical polymerization in the presence of **3**, the incorporation of the initiating fragment into the polymer chain was extremely high. Incorporations of greater than 97% were observed for molecular weights less than or equal to 70,000, and only at molecular weights approaching 100,000 was a slight decrease observed. This was not surprising given the small amount of initiator present in these high molecular weight systems. At these low concentrations, even minor amounts of autopolymerization/extraneous polymerization¹¹ could have a significant effect and lead to an apparent decrease in initiator incorporation. However, even at 100,000 amu, the level of chain-



Scheme 4

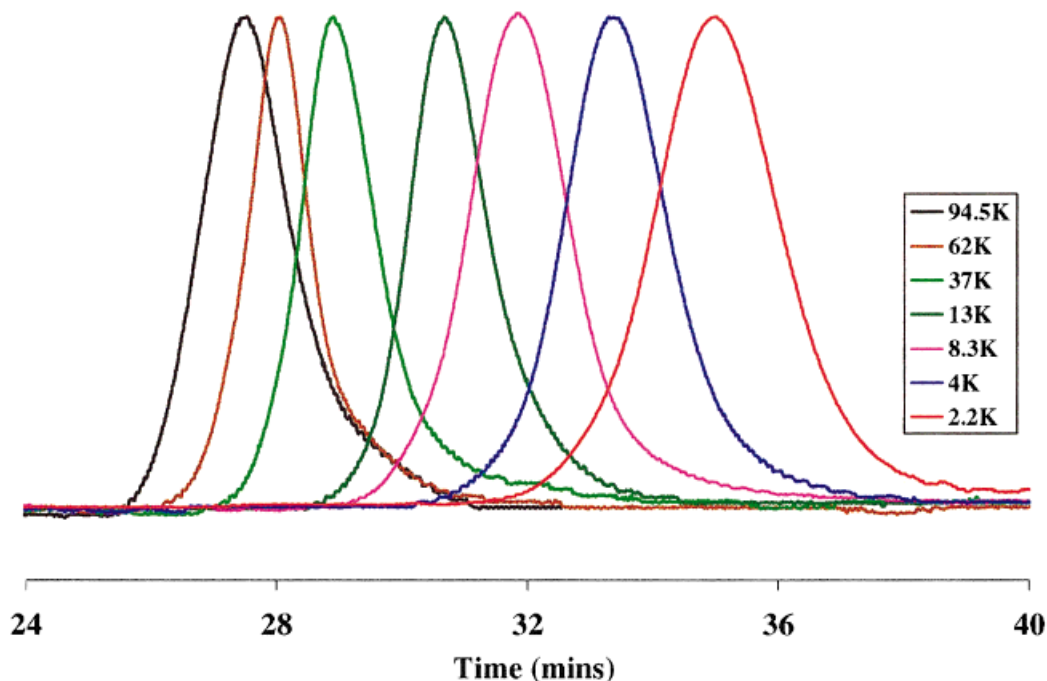


Figure 5. GPC overlay of poly(*t*-butyl acrylate) prepared from various ratios of *t*-butyl acrylate, **3**, and **1**.

end incorporation for functionalized initiators was about 95% or greater. These results were further confirmed by an examination of the relationship between functional group incorporation and conversion for the respective 500/1 polymerization systems. In each case, there was no significant decrease in the incorporation of the initiating unit with increasing conversion, and 98–

100% incorporation was observed even at high conversions. We also examined the effect of the pyrene unit on the polymerization process examined by conducting similar experiments in the presence of the corresponding dansyl derivative (**6**). Analogous results were obtained for **6** with levels of incorporation of between 97 and 100%, which demonstrates that the pyrene or dansyl

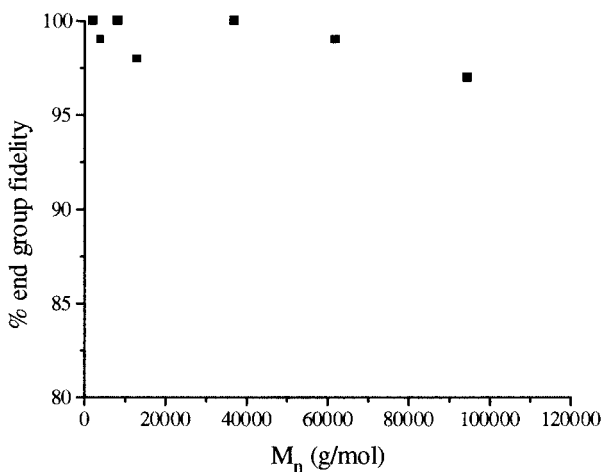


Figure 6. Initiator end-group fidelity for the polymerization of *t*-butyl acrylate in the presence of **3** and 0.05 equiv of **1** at 120 °C for 36 h.

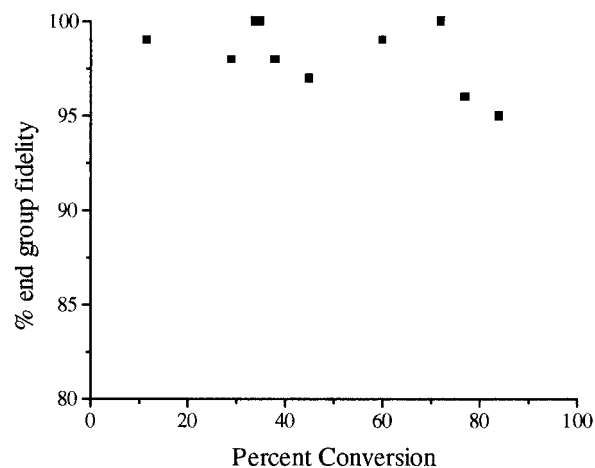
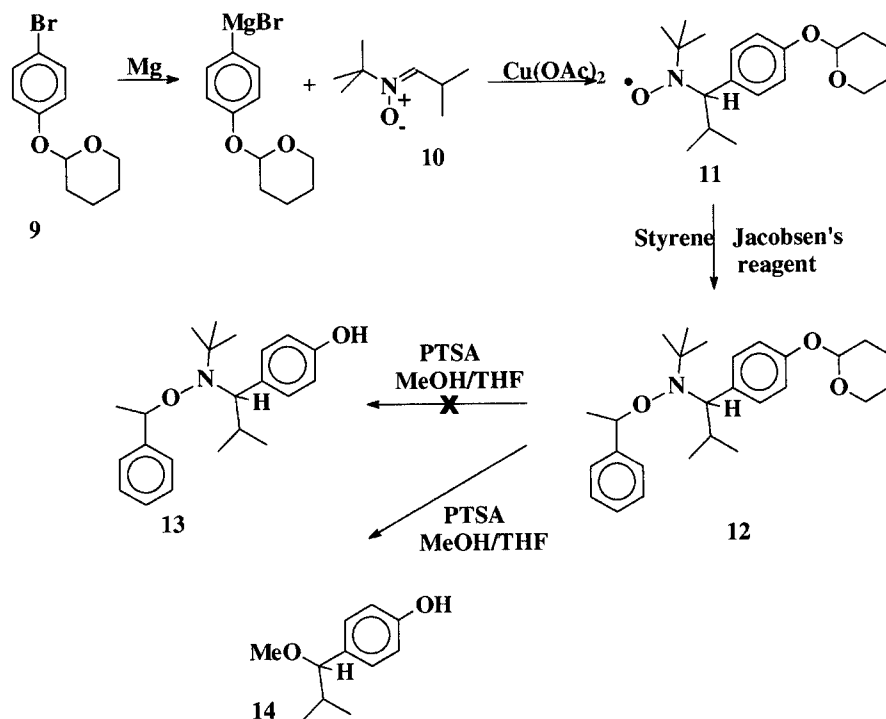


Figure 7. Initiator end-group fidelity for the polymerization of 500 equiv of *t*-butyl acrylate with **3** and 0.05 equiv of **1** at 120 °C for various reaction times.



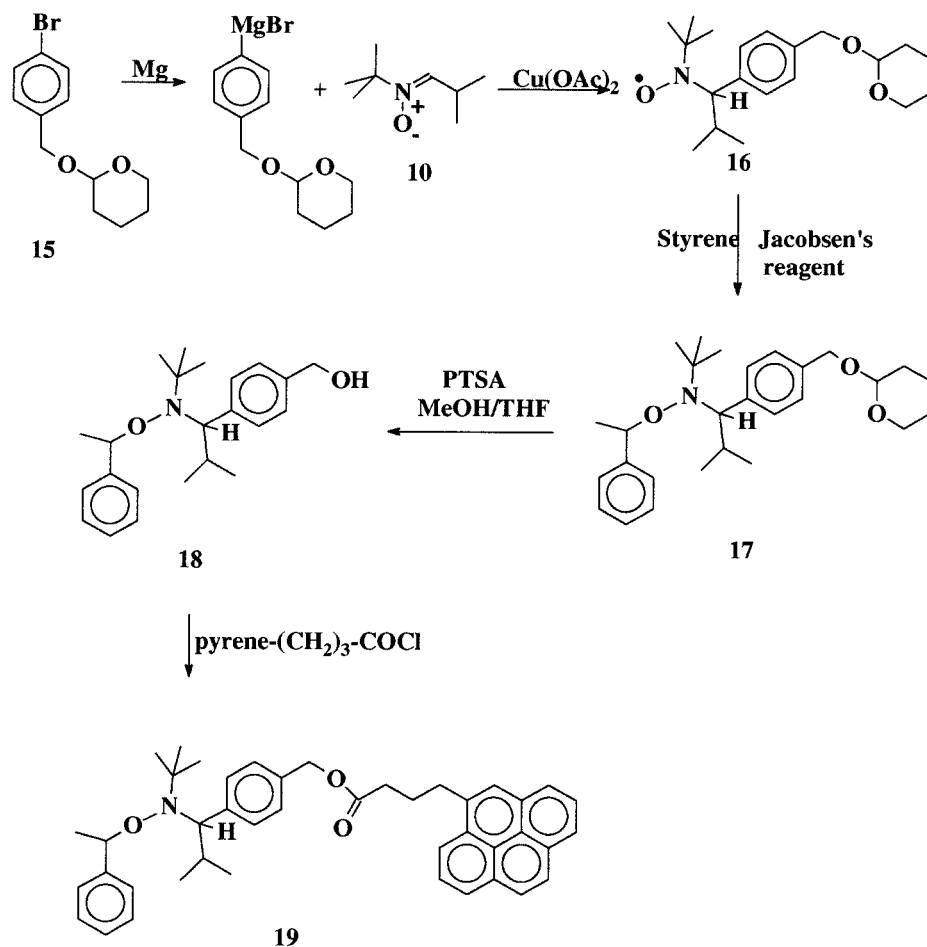
Scheme 5

end groups had no effect on the polymerization and further reinforces the versatile nature of the nitroxide-mediated process and its compatibility with different functional chain ends.

Propagating Chain End

Although the synthesis of the alkoxyamine derivatives labeled at the initiating end were straightforward, the preparation of alkoxyamine-based initiators in which the mediating nitroxide free radical was labeled with a chromophore proved to be a more synthetically demanding task. Initial attempts at employing pyrene-labeled nitro or aldehyde derivatives at the beginning of the synthesis proved to be unsuccessful because of unwanted side reactions during the Grignard addition step. This inability to carry a pyrene chromophore through the synthesis then prompted a protection/deprotection strategy to be adopted, with the chromophore being added at the nitroxide or alkoxyamine stage. To this end, bromoanisole was converted into a Grignard reagent and used in an analogous way to phenyl magnesium bromide in the synthesis of **3**. Deprotection of the methyl group to a phenolic group can be accomplished by the addition of boron tribromide.¹⁸ However, this and other deprotection

procedures were tried repeatedly with no success, and only decomposition was observed. To overcome this problem, a protecting group that could be removed under milder conditions, such as a tetrahydropyran THP group, was employed in place of the methoxy group. In this case, the Grignard reagent was prepared from commercially available 2-(4-bromophenoxy)tetrahydro-2H-pyran (**9**) and reacted with the nitron (*N*-*tert*-butyl- α -isopropyl nitron; **10**) to give the nitroxide [2,2,5-trimethyl-4-(tetrahydropyran-2-yloxy)phenyl-3-azahexane-3-nitroxide; **11**], which after coupling with styrene yielded the THP-protected alkoxyamine, 2,2,5-trimethyl-3-[1-(4'-tetrahydropyran-2-yloxy)phenylethoxy]-4-phenyl-3-azahexane (**12**; Scheme 5). In this case, deprotection under mild conditions also resulted in decomposition, and no detectable amounts of the desired phenol (**13**) were observed. Instead, the cleavage product (**14**) was obtained in a high yield. Presumably, the electron-donating phenolic group activated the C—N bond to nucleophilic displacement by methanol in the reaction mixture, resulting in cleavage. Further support for this decomposition pathway was obtained from deprotection reactions performed with 2-butanol as a solvent, which was reported to have a higher degree of selectivity than meth-

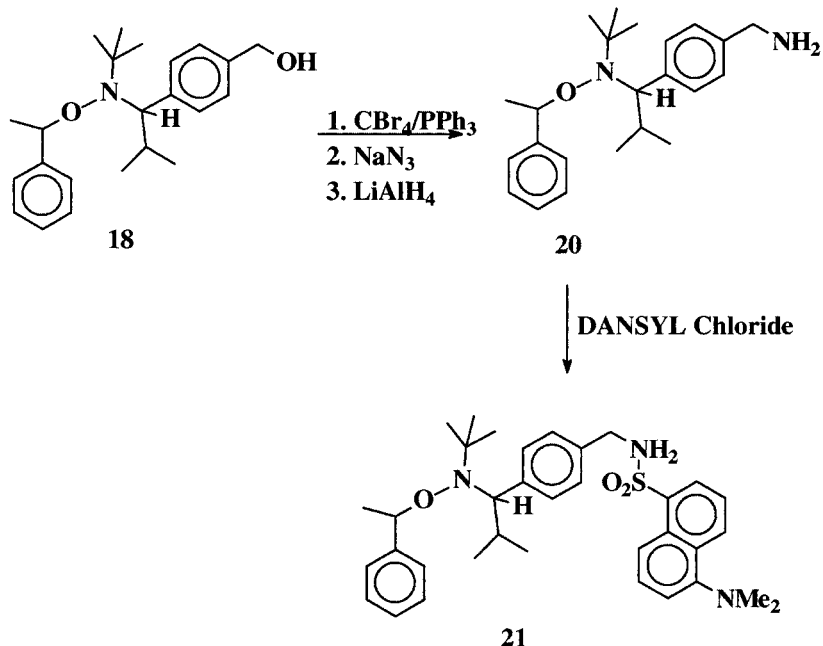


Scheme 6

anol;¹⁹ however, decomposition to the ether was again observed.

To overcome this problem, a spacer group was introduced between the OH functional group and the phenyl ring in an attempt to negate the electronic effects of the phenolic group. As a result, the starting material, 4-bromobenzyl alcohol, was protected as the THP derivative [4-(tetrahydropyranyloxymethyl)phenylbromide; **15**] and the corresponding Grignard derivative coupled with the nitroxide, as described previously (Scheme 6). This gave the nitroxide [2,2,5-trimethyl-4-(4'-tetrahydropyranyloxymethyl)phenyl-3-azahexane-3-nitroxide; **16**], which was added to styrene in the presence of Jacobsen's reagent to give the protected alkoxyamine, 2,2,5-trimethyl-3-[1-(4'-tetrahydroxypranylmethyl)phenylethoxy]-4-phenyl-3-azahexane (**17**), in high yields.¹⁷ In this case, deprotection under standard conditions proved to be successful, and the desired hydroxymethyl derivative, 2,2,5-trimethyl-3-[1-(4'-hy-

droxymethyl)phenylethoxy]-4-phenyl-3-azahexane (**18**), was obtained in a 94% yield after purification. The coupling of 4-pyrenebutyric acid to the initiator (**18**) was accomplished with diisopropylazodicarboxylate as a catalyst or by reaction with the corresponding acid chloride. This gave the desired chromophore-labeled alkoxyamine, 2,2,5-trimethyl-3-[1-(4'-(4''-pyrenebutyloxy)methyl)phenylethoxy]-4-phenyl-3-azahexane (**19**), in which a pyrene group was attached to the nitroxide fragment, and characterization by a variety of techniques confirmed the proposed structure. Attempts to couple **5** with the hydroxymethyl derivative (**18**) proved to be unsuccessful because of the facile hydrolysis of the sulfonate linkage. In this case, the corresponding aminomethyl derivative, 2,2,5-trimethyl-3-[1-(4'-aminomethyl)phenylethoxy]-4-phenyl-3-azahexane (**20**), was prepared with standard chemistry and coupled with **5** to give the stable dansyl derivative, 4-(5'-dimethylaminonaphthylsulfonamidomethyl)phenyl-2,2,5-



Scheme 7

trimethyl-3-(1-phenylethoxy)-3-azahexane (**21**), in a 91% yield after purification (Scheme 7).

Having obtained the initiators in which the mediating nitroxide radical was labeled with a chromophore, we performed analogous studies with styrene and *t*-butyl acrylate to determine the fidelity of the mediating chain end. For polystyrene, the molecular weight range examined was 6100–93,000 g/mol, and for the conversion studies, a 500/1 molar ratio of styrene to **19** was again chosen. Samples were obtained with conversions ranging from 20 to 76%.

In a similar fashion, *t*-butyl acrylate was polymerized in the presence of **19** and 0.05 equiv of the corresponding nitroxide in sealed vials under argon at 120 °C for 36 h. The purification was performed as earlier, and the molecular weight range examined was 4500–141,000 g/mol, whereas for the systems containing a 500/1 ratio of *t*-butyl acrylate to **19**, the samples were obtained with conversions ranging from 19 to 96%.

From these two series of samples, the extinction coefficients of the initiator and the polymers were determined at 344 nm in the same manner as for the functionalized initiating chain-end derivatives (Figs. 8–11). Both sets of experiments showed that for polystyrene and poly(*t*-butyl acrylate), the end-group fidelity of the polymer chain was extremely high, with the level of incorporation being slightly lower for the propagating

chain end than for the initiating chain end. This increased fidelity for the initiating chain end was understandable, given that only a single reaction led to the insertion of the chromophore at the initiating chain end. In contrast, a large number of cleavage/insertion/coupling cycles occurred for the propagating chain end, and the probability of errors being introduced was significantly higher. This was exacerbated at higher molecular weights, and there was some indication that the

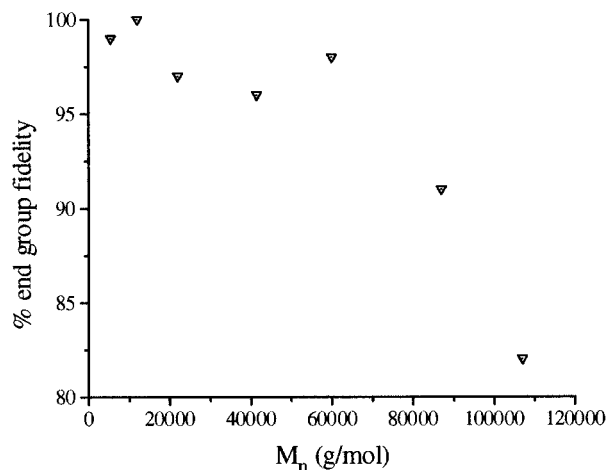


Figure 8. Alkoxyamine end-group fidelity for the polymerization of styrene in the presence of various amounts of **19** at 120 °C for 6 h.

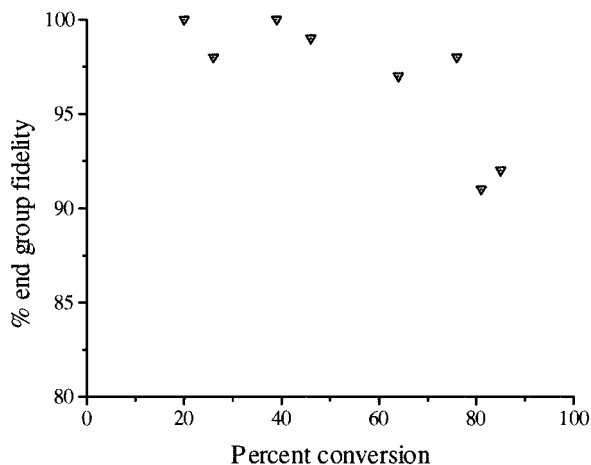


Figure 9. Alkoxyamine end-group fidelity for the polymerization of 500 equiv of styrene in the presence of **19** at 120 °C for reaction times ranging from 0.5 to 6 h.

chain-end fidelity decreased with molecular weight, especially for molecular weights in excess of 75,000. This was in full agreement with the low initiator concentrations in these polymerizations and the greater influence of minor termination reactions.

CONCLUSIONS

The fidelity of living free-radical polymerizations using alkoxyamines based on new and improved

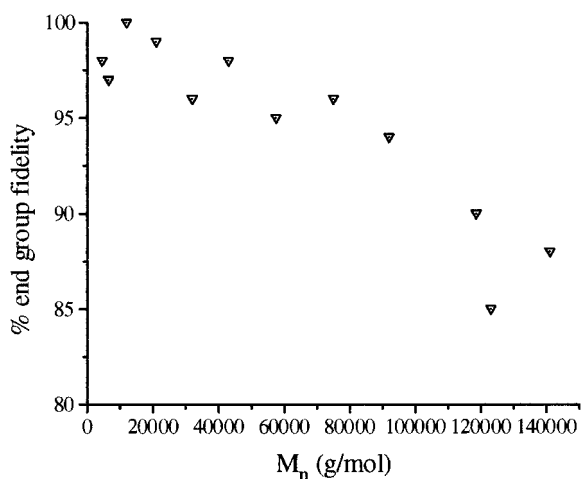


Figure 10. Alkoxyamine end-group fidelity for the polymerization of various amounts of *t*-butyl acrylate in the presence of **19** and the corresponding nitroxide (0.05 equiv) at 120 °C for 36 h.

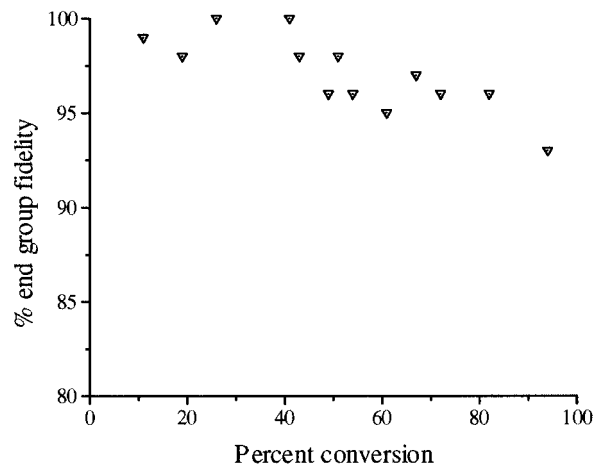


Figure 11. Alkoxyamine end-group fidelity for the polymerization of 500 equiv of *t*-butyl acrylate with **19** and 0.05 equiv of the corresponding nitroxide at 120 °C for times ranging from 3 to 24 h.

α -hydrido nitroxides such as **1** was studied. The experiments clearly showed that for polystyrene and poly(*t*-butyl acrylate), the incorporation of the initiating and terminating fragments into the polymer chain was extremely high. Therefore, the synthesis of telechelic polymers with molecular weights less than or equal to 70,000–100,000 should be extremely facile with these new alkoxyamines. Similarly, the high retention of the alkoxyamine group at the propagating chain end for molecular weights less than 50,000 suggests that the synthesis of well defined block copolymers should be an efficient process. However, at higher molecular weights the loss of the alkoxyamine group may lead to the formation of dead starting homopolymer, thereby compromising block copolymer purity. These results clearly show that this new class of alkoxyamines can control the polymerization of polystyrene and poly(*t*-butyl acrylate) efficiently with degrees of control approaching anionic or atom transfer radical polymerization procedures.

EXPERIMENTAL

Analytical thin-layer chromatography was performed on Merck plates coated with silica gel 60 F₂₅₄. The silica gel for flash chromatography was Merck Silica Gel 60 (230–400 mesh, ASTM). ¹H NMR and ¹³C NMR spectra were recorded in chloroform-*D* solutions with a Bruker AM 250 spectrometer at 250 MHz for ¹H NMR and 62.9

MHz for ^{13}C NMR. Ultraviolet–visible (UV–vis) absorption spectroscopy was measured on a Hewlett–Packard 8452A diode array spectrophotometer. GPC was performed in tetrahydrofuran (THF) on a Waters chromatograph equipped with four 5- μm Waters columns (300 \times 7.7 mm) connected in series with increasing pore size (100, 1000, 100,000 and 1,000,000 Å). A Waters 410 differential refractometer and a 996 photodiode array detector were employed. The polystyrene molecular weights were calculated relative to linear polystyrene standards, whereas the poly(*t*-butyl acrylate) molecular weights were calculated relative to poly(*t*-butyl acrylate) standards.

3

4-Pyrene butanol (2.2 g, 8.0 mmol) was dissolved in dry THF (50 mL) under an argon atmosphere, sodium hydride (1.0 g, 42 mmol) was added, and the reaction mixture was stirred at room temperature for 30 min. The chloromethyl alkoxyamine (**2**; 3.0 g, 8.0 mmol) was added, and the reaction was refluxed 16 h under argon. The reaction mixture was then evaporated to dryness, extracted with dichloromethane, washed with water, dried, filtered, and concentrated. The crude product was purified by flash chromatography, eluting with 8/2 petroleum ether/dichloromethane to give the labeled derivative (**3**) as a light-yellow gum (4.3 g, 84%).

^1H NMR (250 MHz, CDCl_3 , both diastereomers, δ): 8.2–7.7 (m, 18H), 7.5–7.1 (m, 18H), 4.95 (q+q, 2H, $J = 6.5$ Hz), 4.5 (d, 4H, $J = 7.5$ Hz), 3.41 (d, 1H, $J = 10.8$ Hz), 3.4 (m+m, 4H), 2.35 (m+m, 2H), 1.7 (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): 145.13, 144.38, 142.51, 142.30, 137.60, 136.90, 131.52, 131.06, 131.00, 129.84, 128.71, 127.56, 127.50, 127.42, 127.30, 127.20, 127.07, 126.57, 126.39, 126.25, 125.78, 125.17, 125.14, 124.68, 123.52, 83.35, 82.51, 72.94, 72.87, 70.28, 70.07, 60.56, 60.49, 33.34, 32.08, 31.72, 29.89, 29.85, 28.49, 28.32, 24.72, 23.19, 22.23, 22.03, 21.21, 21.15. ELEM. ANAL. Calcd. for $\text{C}_{43}\text{H}_{49}\text{NO}_2$: C, 84.4%; H, 8.07%; N, 2.29%. Found: C, 84.6%; H, 7.89%; N, 2.52%.

4

The azido derivative¹⁷ (2.50 g, 6.6 mmol) was dissolved in anhydrous THF and cooled to 0 °C.

Lithium aluminum hydride (0.24 g, 6.6 mmol) was added portionwise, and the reaction mixture was stirred for 1 h. It was then filtered, extracted with water/dichloromethane, and dried (MgSO_4). The crude product was purified with flash column chromatography, eluting with dichloromethane gradually increasing to 1/9 methanol/dichloromethane to give **4** as a colorless foam (1.95 g, 83%). ^1H NMR (250 MHz, CDCl_3 , both diastereomers, δ): 7.5–7.1 (m, 18H), 4.7 (q+q, 2H, $J = 7.5$ Hz), 3.6 (s+s, 4H), 3.1 (d, 1H, $J = 10$ Hz), 3.0 (d, 1H, $J = 10$ Hz), 2.2 (m, 1H), 1.4 (d, 3H, $J = 7.5$ Hz), 1.4 (d, 3H, $J = 7.5$ Hz), 1.0 (d, 3H, $J = 5$ Hz), 0.81 (s, 9H), 0.6 (d, 3H, $J = 5$ Hz), 0.8 (m, 1H), 0.5 (s, 9H), 0.3 (d, 3H, $J = 6.5$ Hz), 0.0 (d, 3H, $J = 6.5$ Hz). ^{13}C NMR (63 MHz, CDCl_3 , both diastereomers, δ): 144.42, 143.64, 142.45, 142.26, 142.06, 141.33, 131.00, 130.94, 127.36, 127.19, 126.86, 126.81, 126.38, 126.17, 53.26, 82.39, 72.20, 60.48, 60.43, 46.24, 32.03, 31.70, 28.43, 28.26, 24.69, 23.18, 22.15, 21.97, 21.14.

6

To the amino derivative **4** (0.2 g, 0.56 mmol) dissolved in anhydrous THF (10 mL), **5** (0.17 g, 0.62 mmol) and pyridine (0.049 g, 0.62 mmol) were added. The reaction was then heated for 5 h under reflux, concentrated, and purified by flash column chromatography, eluting with 1/4 dichloromethane/petroleum ether gradually increasing to 1/9 diethyl ether/dichloromethane to give the dansyl derivative (**6**) as a yellow solid (0.26 g, 79%). ^1H NMR (250 MHz, CDCl_3 , both diastereomers, δ): 8.3–6.4 (m, 30H), 4.6 (q+q, 2H, $J = 7.5$ Hz), 3.8 (s+s, 4H), 3.1 (d, 1H, $J = 10$ Hz), 3.0 (d, 1H, $J = 10$ Hz), 2.7 (s, 12H), 2.1 (m, 1H), 1.4 (d, 3H, $J = 7.5$ Hz), 1.4 (d, 3H, $J = 7.5$ Hz), 1.0 (d, 3H, $J = 5$ Hz), 0.81 (s, 9H), 0.6 (d, 3H, $J = 5$ Hz), 0.8 (m, 1H), 0.5 (s, 9H), 0.3 (d, 3H, $J = 6.5$ Hz), 0.0 (d, 3H, $J = 6.5$ Hz). ^{13}C NMR (63 MHz, CDCl_3 , both diastereomers, δ): 152.09, 145.52, 144.73, 142.32, 142.14, 135.15, 134.70, 130.96, 130.85, 130.55, 129.97, 129.85, 129.71, 128.45, 127.66, 127.61, 127.35, 127.20, 127.11, 126.35, 126.19, 123.77, 118.75, 115.24, 83.12, 82.09, 72.19, 60.45, 53.40, 47.21, 45.41, 32.01, 31.74, 28.40, 28.23, 24.61, 23.16, 22.03, 21.90, 21.10. ELEM. ANAL. Calcd. for $\text{C}_{35}\text{H}_{45}\text{N}_2\text{O}_3\text{S}$: C, 73.3%; H, 7.90%; N, 4.88%. Found: C, 73.0%; H, 7.96%; N, 5.03%.

11

4-(Tetrahydro-2H-pyranoxo)phenyl magnesium bromide (5.3 g, 20 mmol) was added dropwise to a

solution of **10** (1.4 g, 10 mmol) in THF (15 mL). The mixture was stirred overnight at room temperature under argon. Saturated ammonium chloride (5 mL) and water (10 mL) were added, and the reaction mixture was extracted with diethylether. The organic layers were dried with magnesium sulfate and filtered, and after concentration, the crude hydroxylamine was dissolved in a mixture of methanol (50 mL), concentrated ammonium hydroxide (4 mL), and copper acetate [Cu(OAc)₂; 0.25 g, 1.3 mmol]. The solution was initially orange, and after aeration for 30 min, the color became green. The solution was then concentrated and dissolved in chloroform (50 mL) and water (50 mL). The aqueous layer was extracted with chloroform, and the organic layers were collected and washed with saturated sodium bicarbonate. They were dried with magnesium sulfate and concentrated. The crude product was purified by flash column chromatography, eluting with 20/1 hexane/ethyl acetate. The product (**11**; 2.0 g, 63% yield) was obtained as an orange oil.

12

A mixture of toluene and ethanol (1/1; 100 mL) was bubbled with air for 1 h. Styrene (1 g, 9.6 mmol), **11** (2.0 g, 6.2 mmol), [*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato]-manganese(III)chloride (1.1 g, 1.6 mmol), and sodium borohydride (0.71 g, 19 mmol) were added in that order. Air was bubbled into the mixture for 13 h while stirring was continued. The product was filtered on a layer of silica on sand to remove the solids. The organic solution was concentrated and purified by flash column chromatography, eluting with 16/1 petroleum ether/ethyl acetate to give **12** (2.10 g, 79%). ¹H NMR (250 MHz, CDCl₃, both diastereomers, δ): 7.5–7.1 (m, 18H), 5.2 (m, 2H), 4.79 (q+q, 2H, *J* = 6.5 Hz), 3.90 (q, 4H, *J* = 7.5 Hz), 3.5 (m+m, 4H), 3.41 (d, 1H, *J* = 10.8 Hz), 3.29 (d, 1H, *J* = 10.8 Hz), 2.35 (2m, 2H), 1.8 (m+m, 8H), 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).

15

4-Bromobenzylalcohol (2.45 g, 13 mmol) and 3,4-dihydro-2H-pyran (1.1 g, 13 mmol) were mixed in dichloromethane (10 mL), and six drops of concentrated HCl were added. The reaction mixture was stirred for 16 h, extracted with water, dried

(MgSO₄), and concentrated to give the desired bromide (**15**) as a colorless oil (3.4 g, 98%) that was purified by distillation. ¹H NMR (250 MHz, CDCl₃, δ): 7.4 (ABq, 4H, *J* = 8.5 Hz), 4.5 (s, 2H), 4.5 (d of d, 1H, *J* = 12.5 Hz), 3.7 (d of m, 2H), 1.6 (complex m, 6H). ¹³C NMR (63 MHz, CDCl₃, δ): 137.41, 131.57, 131.43, 129.38, 128.51, 121.33, 97.84, 68.05, 64.45, 62.15, 30.53, 25.44, 19.32.

16

4-(Tetrahydropyranyloxymethyl)phenyl magnesium bromide was prepared from distilled **15** (3.8 g, 13 mmol) and added dropwise to a solution of **10** (1.8 g, 13 mmol) in THF. The mixture was stirred overnight at room temperature under argon. Saturated ammonium chloride (2 mL) and water (10 mL) were added, and the reaction mixture was extracted with diethylether. The organic layers were dried with magnesium sulfate and filtered, and after concentration, the crude hydroxylamine was dissolved in a mixture of methanol (50 mL), concentrated ammonium hydroxide (4 mL), and Cu(OAc)₂ (0.25 g, 1.3 mmol). The solution was initially orange, and after aeration for 30 min, the color became green. The solution was then concentrated and dissolved in chloroform (50 mL) and water (50 mL). The aqueous layer was extracted with chloroform, and the organic layers were collected and washed with saturated sodium bicarbonate, dried with magnesium sulfate, and concentrated. The crude product was purified by flash column chromatography, eluting with 5% diethylether in dichloromethane to give **16** as an orange oil (2.7 g, 62%).

17

A mixture of toluene and ethanol (1/1; 60 mL) was bubbled with air for 1 h. Styrene (1.0 g, 9.6 mmol), **16** (2.0 g, 6.0 mmol), (*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato)manganese(III) chloride (1.0 g, 1.4 mmol), and sodium borohydride (0.70 g, 19 mmol) were added. Air was bubbled through the reaction mixture for 13 h while stirring was continued. The product was filtered through a layer of silica/sand to remove the solids. The organic solution was concentrated and purified by flash column chromatography, eluting with petroleum ether gradually increasing to 1/1 petroleum ether/dichloromethane to give the alkoxyamine (**17**; 1.5 g, 60%). ¹H NMR (250 MHz, CDCl₃, both diastereomers, δ): 7.5–7.1 (m, 20H), 4.9 (q+q, 2H, *J* = 6.5 Hz), 4.41 (d, 4H,

$J = 12.5$ Hz), 4.29 (d, 4H), 3.50 (m+m, 8H), 3.41 (d, 1H, $J = 10.8$ Hz), 3.29 (d, 1H, $J = 10.8$ Hz), 2.35 (2m, 2H), 1.62 (d, 3H, $J = 6.8$ Hz), 1.63 (m+m, 4H), 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): 130.89, 128.33, 128.04, 127.79, 127.46, 127.27, 127.02, 126.71, 126.59, 126.22, 97.75, 83.49, 71.99, 68.82, 62.09, 60.39, 32.06, 30.62, 28.45, 28.26, 25.54, 24.60, 23.09, 21.96, 21.18, 19.39.

18

17 (1.3 g, 3.0 mmol) was dissolved in methanol (50 mL) and THF (30 mL). Paratoluene sulfonic acid (0.056 g, 0.3 mmol) was added, and stirring was continued for 20 h. Sodium bicarbonate (1.0 g) was added to neutralize the acid, and the reaction mixture was filtered and concentrated to the alcohol (**18**; 1.0 g, 94%), which was used without further purification. ^1H NMR (250 MHz, CDCl_3 , both diastereomers, δ): 7.5–7.1 (m, 18H), 4.9 (q+q, 2H, $J = 6.5$ Hz), 4.4 (d, 4H, $J = 12.6$ Hz), 3.41 (d, 1H, $J = 10.8$ Hz), 3.29 (d, 1H, $J = 10.8$ Hz), 2.35 (2m, 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): 141.79, 138.70, 131.16, 128.55, 128.05, 127.64, 127.30, 126.99, 126.65, 126.19, 126.10, 125.91, 83.48, 82.76, 71.83, 65.35, 60.52, 32.04, 31.68, 30.52, 28.44, 28.24, 24.60, 23.05, 22.08, 21.92, 21.11, 21.00

19

Pyrenebutyric acid (0.8 g, 2.8 mmol), triphenylphosphine (0.73 g, 2.8 mmol), diisopropylazodicarboxylate (0.56 g, 2.8 mmol), and **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 derivative (**19**) as a light-yellow foam (1.0 g, 57%). ^1H 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).

$J = 6.8$ 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. ELEM. ANAL. Calcd. for $\text{C}_{43}\text{H}_{47}\text{NO}_3$: C, 82.5%; H, 7.57%; N, 2.24%. Found: C, 82.4%; H, 7.46%; N, 2.01%.

20

The azidomethyl derivative (1.7 g, 4.5 mmol), prepared from the hydroxymethyl-substituted alkoxyamine (**18**) as described previously,¹⁷ was dissolved in anhydrous THF (25 mL), and the reaction mixture was cooled to 0 °C. Lithium aluminum hydride (0.17 g, 4.5 mmol) was added portionwise, and the reaction mixture was stirred for 1 h at room temperature. It was filtered and extracted with water/dichloromethane, and the combined extracts were dried (MgSO_4). The crude product was purified by flash column chromatography, eluting with 1/1 petroleum ether/dichloromethane gradually increasing to 1/4 methanol/dichloromethane to give **20** as a colorless foam (1.3 g, 82%). ^1H NMR (250 MHz, CDCl_3 , both diastereomers, δ): 7.5–7.1 (m, 18H), 4.7 (q+q, 2H, $J = 7.5$ Hz), 3.6 (s+s, 4H), 3.1 (d, 1H, $J = 10$ Hz), 3.0 (d, 1H, $J = 10$ Hz), 2.2 (m, 1H), 1.4 (d, 3H, $J = 7.5$ Hz), 1.4 (d, 3H, $J = 7.5$ Hz), 1.0 (d, 3H, $J = 5$ Hz), 0.81 (s, 9H), 0.6 (d, 3H, $J = 5$ Hz), 0.8 (m, 1H), 0.5 (s, 9H), 0.3 (d, 3H, $J = 6.5$ Hz), 0.0 (d, 3H, $J = 6.5$ Hz).

21

To a mixture of **20** (1.3 g, 3.7 mmol) and **5** (1.09 g, 4 mmol) dissolved in anhydrous THF (20 mL), pyridine (0.32 g, 4.0 mmol) was added, and the reaction mixture was heated at reflux under nitrogen for 18 h. The mixture was concentrated and purified by flash column chromatography, eluting with petroleum ether gradually increasing to dichloromethane. This gave the desired dansyl-labeled derivative (**21**) as a light-yellow solid (1.50 g, 69%). ^1H NMR (250 MHz, CDCl_3 , both diastereomers, δ): 8.3–6.4 (m, 30H), 4.6 (q+q, 2H, $J = 7.5$ Hz), 3.8 (s+s, 4H), 3.1 (d, 1H, $J = 10$ Hz), 3.0 (d, 1H, $J = 10$ Hz), 2.6 (s, 12H), 2.1 (m, 1H), 1.4 (d, 3H, $J = 7.5$ Hz), 1.4 (d, 3H, $J = 7.5$ Hz), 1.0 (d, 3H, $J = 5$ Hz), 0.81 (s, 9H), 0.6 (d, 3H, $J = 5$ Hz), 0.8 (m, 1H), 0.5 (s, 9H), 0.3 (d, 3H, $J = 6.5$ Hz).

= 6.5 Hz), 0.0 (d, 3H, $J = 6.5$ Hz). ^{13}C NMR (63 MHz, CDCl_3 , both diastereomers, δ): 131.19, 130.55, 129.82, 128.43, 120.06, 126.96, 126.68, 126.16, 123.19, 118.76, 115.22, 47.20, 45.42, 31.59, 28.40, 28.21. ELEM. ANAL. Calcd. for $\text{C}_{35}\text{H}_{45}\text{N}_2\text{O}_3\text{S}$: C, 73.3%; H, 7.90%; N, 4.88%. Found: C, 73.4%; H, 7.67%; N, 4.95%.

General Procedure for the Polymerization of Styrene

Styrene and the pyrene-labeled alkoxyamine (**3**) 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 was analyzed by GPC, NMR, and UV-vis.

General Procedure for the Polymerization of *t*-Butyl Acrylate

t-Butyl acrylate, the pyrene-labeled alkoxyamine (**3**), and the corresponding nitroxide (**1**; 0.05 equiv) were placed in a vial with a stirrer bar. The vial was degassed and sealed, and the polymerizations were heated at 120 °C for 36 h. For lower conversions, shorter reaction times were used. The polymer was then dissolved in dichloromethane, evaporated to dryness, and purified by precipitation from dichloromethane to hexane. The pure polymer was analyzed by GPC, NMR, and UV-vis.

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