# "Living" Free-Radical Polymerizations in the Absence of Initiators: Controlled Autopolymerization

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ABSTRACT: The autopolymerization of styrene, styrenic derivatives, and styrene/(meth)acrylate comonomer mixtures in the presence of stable nitroxide free radicals has been shown to be a "living" process. Molecular weight can be controlled by varying the ratio of vinyl monomer to TEMPO and low-polydispersity materials are obtained. Significantly, a definite incubation period is observed during these polymerizations, and the length of this incubation period increases with increasing amounts of TEMPO. The structures of the in situ generated unimolecular initiators which are formed during this incubation period correspond to those expected from a Mayo mechanism for the autopolymerization of styrene. The isolated and purified adducts, **4** and **5**, were shown to be effective unimolecular initiators leading to low-polydispersity, controlled molecular weight polymers.

## Introduction

The synthesis of well-defined macromolecules by "living" free-radical techniques has witnessed explosive growth during the last few years due to its commercial and academic importance.[1] One of the most widely studied approaches to "living" free-radical polymerizations involves the use of stable nitroxide free radicals such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO).[2] The role of the nitroxide in these systems is to mediate the reactivity of the growing polymer chain by forming a thermally unstable alkoxyamine chain end. Dissociation of the alkoxyamine chain end under the polymerization conditions regenerates the radical chain end, which can then add more monomer units before being capped again by the nitroxide. This thermally reversible capping reaction dramatically reduces the concentration of radical chain ends in the polymerization mixture and leads to a significant degree of "living" character. Accurate control over molecular weight,[3] chain ends,[4] and macromolecular architecture[5] has been observed for a variety of monomer/comonomer systems,[6] with polydispersities typically well below the theoretical limiting value of 1.50 for conventional free-radical processes.

Initiating systems for "living" free-radical polymerizations can be conveniently divided into two classes: bimolecular systems in which a mixture of a traditional radical initiator, such as benzoyl peroxide (BPO), is used in conjunction with a stable nitroxide free radical;[7] and unimolecular systems where a preformed alkoxyamine derivative containing both a latent initiating group and nitroxide in a 1:1 stoichiometry is employed.[8] Typically, "living" free-radical polymerizations are conducted in the bulk by simply heating a mixture of monomer and initiator at 125 °C for extended periods of time. However, for styrene-based monomers the elevated temperatures and long reaction times may result in additional radical species being formed by autopolymerization.[9] While significant formation of these autopolymerization radicals is undesirable when bimolecular or unimolecular initiating systems are employed, these radicals could be captured with added nitroxides to give "in-situ" unimolecular initiators. It may therefore be possible to conduct "living" free-radical polymerizations in the absence of added initiating systems relying only on added nitroxide radicals to mediate the polymerization. Preliminary work in the autopolymerization of styrene in the presence of TEMPO has been reported almost simultaneously by Georges[10] and Matyjaszewski.[11] Differing results were obtained, with one group reporting polydispersities of 2.0−2.5 while under similar conditions the other group obtained polymers with polydispersities in the range 1.20−1.30. While this manuscript was in preparation, Fukuda[12] also demonstrated that a constant supply of initiating radicals (i.e. thermal initiation or autopolymerization) may be required for nitroxide-mediated "living" free-radical polymerizations to be successful. Due to this minor discrepancy and the potential importance of autopolymerization in nitroxide-mediated "living" free-radical polymerizations, we wish to report our studies on the autopolymerization of styrenic derivatives in the presence of nitroxides.

## Experimental Section

Nuclear magnetic resonance spectroscopy was performed on a Bruker AM 300 FT-NMR spectrometer using deuterated chloroform as solvent and tetramethylsilane as internal reference. Gel permeation chromatography was carried out on a Waters chromatograph (four Waters Styragel HR columns, HR1, HR2, HR4, and HR5E in series) connected to a Waters 410 differential refractometer with THF as the carrier solvent. Molecular weights were determined using polystyrene standards. Infrared spectra were recorded on a Perkin-Elmer IR-44 as thin films or NaCl pellets. 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). 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. Mass spectra were obtained on a HP 5988A mass spectrometer using a direct insert probe and EI ionization. All reagents and solvents were used as received.

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**General Procedure for Autopolymerization Experiments.** A solution of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (156 mg, 1.0 mmol) in styrene (20.8 g, 200.0 mmol) was heated at 125 °C under argon for 20 h. During this time the solution became colorless and the viscosity increased substantially. Samples of the polymerization mixture were withdrawn at periodic intervals, and conversion was determined by $^1$H NMR spectroscopy while molecular weights were determined by GPC. Reactions were typically run to ca. 80−90% conversion and the solidified reaction mixture was then dissolved in dichloromethane (80 mL), and precipitated in methanol (1000 mL), and the resulting solid was isolated by vacuum filtration and dried to give the polymer as a white solid (16.3 g, 78%): IR (neat) 3250, 3020, 2980, 1605, 1360, 1050 cm$^{-1}$; $^1$H NMR (CDCl$_3$) 1.00−2.20, 6.30−7.10. The polymerizations of *p*-chlorostyrene, *p*-methoxystyrene, and *p*-methylstyrene as reported in Table 1 were conducted under identical conditions.

The polymerizations of comonomer mixtures of styrene with *p*-(chloromethyl)styrene, methyl methacrylate, or *tert*-butyl acrylate were performed under identical conditions except that the polymerization time was increased to 36 h.

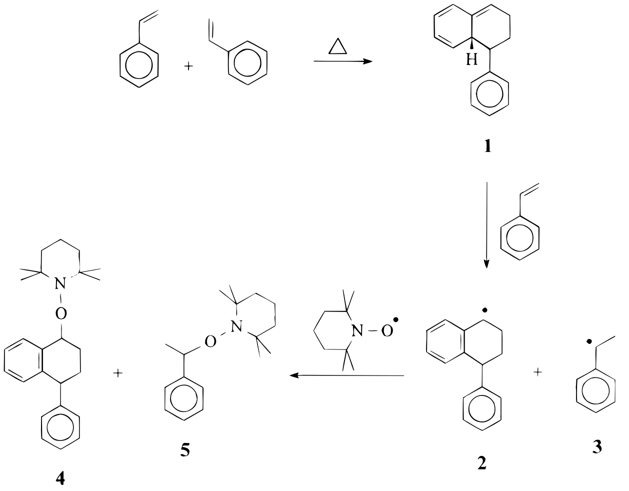
**Isolation of Major Initiating Species.** A solution of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (7.80 g, 50 mmol) in styrene (52.0 g, 500 mmol) was heated at 125 °C under argon for 18 h. The reaction mixture was cooled and evaporated to dryness. GPC analysis of the crude product revealed that no significant degree of polymerization had occurred during the reaction. The crude product was then purified by flash chromatography eluting with 1:1 hexane/dichloromethane gradually increasing to dichloromethane and finally 1:9 diethyl ether/dichloromethane. This gave three major products which were further purified as detailed below. The highest $R_f$ major product was purified by flash chromatography eluting with 1:2 hexane/dichloromethane gradually increasing to dichloromethane to give the ethylbenzene derivative, **5**, as a colorless solid, mp 45−47 °C (600 mg, 5%): IR (neat) 2950, 1490, 1390, 1375, 1040 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.64, 1.05, 1.16, and 1.36 (each br s, 12 H, C$H_3$), 1.23−1.58 (m, 6 H, C$H_2$), 1.44 (d, $J$ = 7 Hz, 3 H, CH(C$H_3$)), 4.76 (q, $J$ = 7 Hz, 1 H, C$H$(CH$_3$)), 7.25−7.35 (m, 5 H, Ar$H$); $^{13}$C NMR (CDCl$_3$) $\delta$ 17.22, 20.34, 23.55, 31.59, 34.49, 40.37, 59.66, 83.10, 126.59, 126.74, 127.97, 145.84; mass spectrum (EI) $m/z$ 261.

The second major product was further purified by flash chromatography eluting with 1:2 hexane/dichloromethane gradually increasing to dichloromethane to give the tetrahydronaphthalene derivative, **4**, as a colorless oil (3.2 g, 18%): IR (neat) 2950, 1495, 1380, 1050 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.92 and 1.04 (each br s, 6 H, C$H_3$), 1.10−1.60 (complex m, 12 H), 1.80−2.30 (complex m, 4 H), 4.14 and 4.27 (each t, $J$ = 2 Hz, 1 H), 5.06 and 5.18 (each ABt, $J$ = 2 Hz, 1 H), 6.95−7.30 (complex m, 9 H, Ar$H$), 7.83 and 7.91 (ABq, 1 H, Ar$H$); $^{13}$C NMR (CDCl$_3$) $\delta$ 17.52, 20.90, 21.10, 28.67, 29.27, 30.28, 33.67, 34.74, 40.63, 45.83, 46.31, 60.18, 60.70, 78.22, 78.97, 125.36, 125.69, 126.32, 126.93, 127.74, 128.45, 128.86, 129.03, 129.18, 129.87, 130.95, 138.01, 138.52, 140.20, 147.57; mass spectrum (EI) $m/z$ 363.

The third major product was further purified by flash chromatography eluting with 1:4 hexane/dichloromethane gradually increasing to 1:9 diethyl ether/dichloromethane to give the bis(alkoxyamine) derivative, **8**, as a colorless oil (2.8 g, 26%): IR (neat) 2960, 1480, 1395, 1375, 1035 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.50 (br s, 3 H, C$H_3$), 0.89−1.48 (complex m, 33 H), 3.82 (t, $J$ = 7 Hz, 1 H, C$H$), 4.35 (t, $J$ = 7 Hz, 1 H, C$H$), 4.79 (t, $J$ = 7 Hz, 1 H, C$H$), 7.25−7.35 (m, 5 H, Ar$H$); $^{13}$C NMR (CDCl$_3$) $\delta$ 17.11, 20.20, 20.37, 32.75, 34.03, 39.64, 40.61, 59.78, 79.40, 85.17, 127.14, 127.57, 128.13, 142.53; mass spectrum (EI) $m/z$ 416.

**Polymerization of Styrene Using Isolated Adducts.** The purified adducts **4**, **5**, or **8** (1.0 mmol) were dissolved in styrene (15.6 g, 150.0 mmol) and heated at 125 °C under argon for 36 h, during this time the viscosity of the polymerization mixture increased substantially and eventually solidified. The solidified reaction mixture was then dissolved in dichloromethane (60 mL), precipitated in methanol (1000 mL), and the resulting solid isolated by vacuum filtration and dried to give the polymer as a white solid (yields were 80−90%): IR (neat) 3250, 3020, 2980, 1605, 1360, and 1050 cm$^{-1}$; $^1$H NMR (CDCl$_3$) d 1.00−2.20 and 6.30−7.10.

**Scheme 1**

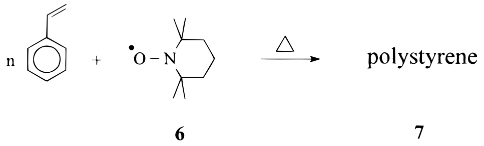


## Results and Discussion

The thermal autopolymerization of styrene and styrenic derivatives has been known since 1839 and is still a source of much controversy and research.[9] The most widely accepted mechanism for the spontaneous generation of radicals from styrene was first proposed by Mayo in 1968 and involves an initial [4 + 2] Diels−Alder reaction between two molecules of styrene.[13] This gives the nonaromatized Mayo adduct, **1**, which cannot undergo a thermal 1,3-sigmatropic shift due to symmetry considerations and therefore undergoes a molecular-assisted homolysis reaction with another molecule of styrene to give the aromatized radical, **2**, and the radical, **3**, derived from styrene. Under normal thermal polymerization conditions, **2** and **3** would give uncontrolled polymerization, leading to high-molecular-weight, high-polydispersity polystyrene. In the presence of nitroxides however, the opportunity exists to control this autopolymerization by the trapping of **2** and **3** with TEMPO to give the alkoxyamines **4** and **5** (Scheme 1). Interestingly, the structure of **5** is exactly the same as that of the unimolecular initiator obtained from the reaction of ethylbenzene with a mixture of di-*tert*-butyl peroxide and 2,2,6,6-tetramethylpiperidinyl-1-oxy. In a similar fashion, **4** is also a secondary benzylic alkoxyamine and may function as a unimolecular initiator for the “living” free-radical polymerization of styrene. This “in situ” generation of unimolecular initiators by the reaction of nitroxides, such as TEMPO, with the radicals generated by the autopolymerization of styrene may permit well-defined vinyl polymers to be prepared with controlled molecular weights and low polydispersity by “living” free-radical polymerizations in the absence of initiators.

To investigate this question 200 molar equiv of styrene was heated at 125 °C with 1 molar equiv of TEMPO, **6**, under nitrogen for 20 h. During this time, the TEMPO color slowly faded, after which the polymerization mixture became increasingly more viscous and eventually solidified. Purification of the crude polymer by precipitation into methanol gave the polystyrene, **7**, in 78% yield which was shown to have a molecular weight ($M_n$) of 20 100 and a polydispersity of 1.26 (Scheme 2). Significantly, the experimental molecular weight compares favorably with the theoretical

**Scheme 2**



molecular weight of 19 000 which is calculated on the assumption that the degree of polymerization (DP) is equal to the molar ratio of styrene to TEMPO coupled with a ca. 90% conversion.[14] In agreement with the initial results of Georges,[15] the molecular weight ($M_n$) was observed to evolve in a nearly linear fashion with conversion, which is indicative of a "living" process (Figure 1).

The ability to control the molecular weight was further examined by heating styrene with various amounts of TEMPO at 125 °C. As shown in Figure 2, the experimentally determined molecular weights agree closely with the theoretical molecular weights up to 40 000 amu, with variations typically less than 15%. The polydispersities for the macromolecules were also very low, typically between 1.15 and 1.35 for molecular weights less than 40 000 amu. At styrene/TEMPO ratios of greater than 400:1, notable deviations from this behavior were observed, with experimental molecular weights being lower than the theoretical molecular weights and polydispersities increasing to ca. 1.40–1.50. Significantly, these values are still less than the theoretical limiting value of 1.50 for conventional free-radical polymerizations. This increase in polydispersity with molecular weight and the close agreement between the experimental and theoretical molecular weights (<40 000 amu) are similar to those observed for unimolecular initiators and suggest that unimolecular initiators are being generated "in situ" during the autopolymerization of styrene in the presence of nitroxides.[14] The polydispersities were also found to increase with polymerization temperature; for example, the polymerization of a 200:1 mixture of styrene and TEMPO at 145 °C was found to give polystyrene with a polydispersity of 1.65. It should be noted that the behavior of these nitroxide-mediated autopolymerizations is, in all cases, dramatically different from that observed for autopolymerizations in the absence of added nitroxides. A comparison of GPC traces for the polymer, **7** ($M_n$ = 20 100, PD = 1.26), with that for an "uncontrolled" autopolymerization ($M_n$ = 220 000, PD = 2.35) shows a significant reduction in polydispersity for the nitroxide-mediated case (Figure 3). It should be noted that the shape of the GPC curve for **7** is asymmetric with a pronounced tailing at lower molecular weights, and similar curves were observed for essentially all the nitroxide-mediated autopolymerization products. At high conversions, typically ca. 95%, the proportion of this tail increases significantly and leads to an associated increase in the polydispersity of the sample; for this reason, autopolymerizations were routinely run to ca. 85–90%. This low molecular-weight tail is believed to be due to polymer chains formed by autopolymerization after consumption of all the added nitroxide as well as minor amounts of termination products. These results demonstrate that linear polystyrene, with accurately controlled molecular weights and low polydispersities, can be prepared in the absence of initiators by the autopolymerization of styrene in the presence of predetermined amounts of TEMPO. The observation of low polydispersities is in agreement with the earlier work of Matyjaszewski.[11]

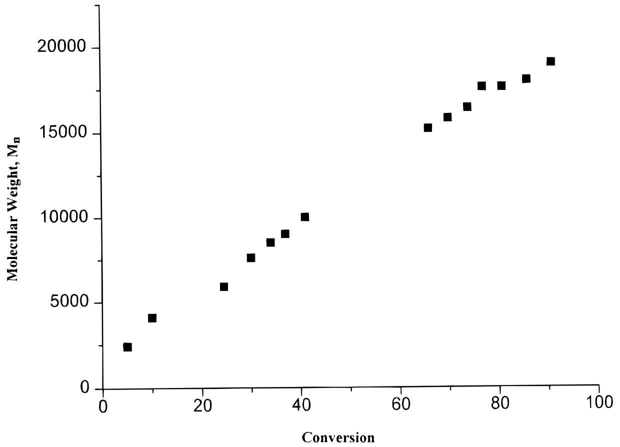


**Figure 1.** Plot of molecular weight, $M_n$, for the unpurified polymer, **7**, versus percent conversion for the reaction of 200 molar equiv of styrene with 1 molar equiv of TEMPO at 125 °C.

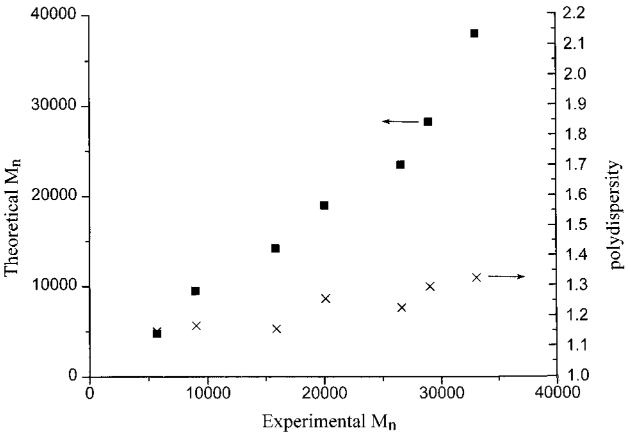


**Figure 2.** Variation in polydispersity with experimentally determined molecular weights, $M_n$, and the relationship between experimental and theoretical molecular weights for the autopolymerization of styrene at 125 °C using varying amounts of added TEMPO.

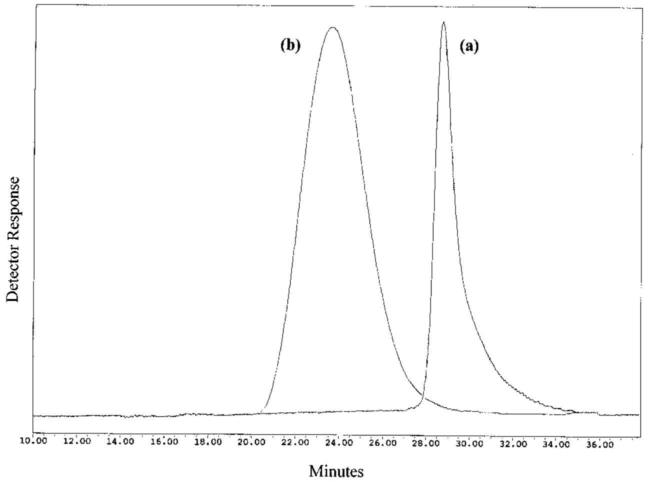


**Figure 3.** Comparison of GPC traces for (a) the product obtained from the reaction of 200 equiv of styrene with TEMPO at 125 °C with (b) the product obtained from the autopolymerization of styrene at 125 °C in the absence of added TEMPO.

The nature of these nitroxide-mediated autopolymerizations was further probed by examining the relationship between conversion and reaction time. A plot of reaction time versus conversion for a series of styrene: TEMPO molar ratios at 125 °C is shown in Figure 4.

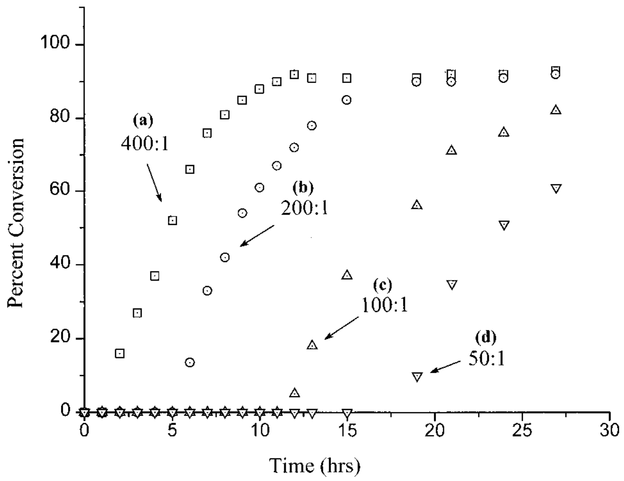
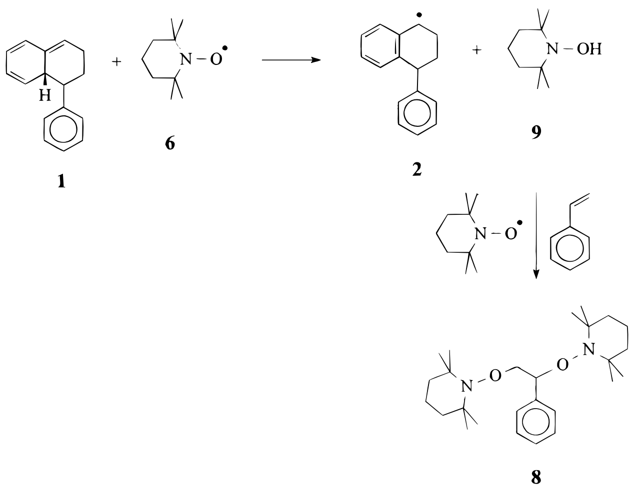


**Figure 4.** Percent conversion as a function of time for the polymerization of styrene at 125 °C with varying molar amounts of TEMPO: (a) 400:1; (b) 200:1; (c) 100:1; (d) 50:1.

As also observed by Matyjaszewski and co-workers,[11] all of the styrene/TEMPO polymerization mixtures showed a definite incubation period. Interestingly, polymer formation could not be detected during these incubation periods, and the length of this incubation time showed a marked dependence on the amount of TEMPO present in the polymerization mixture, with increasing amounts of TEMPO leading to longer incubation times. For example, the incubation time was observed to increase from ca. 1.5 to 18 h as the molar ratio of styrene to TEMPO ratio decreased from 400:1 to 50:1. After this incubation period, the polymerizations were observed to occur with rates of conversion similar to that observed for normal nitroxide-mediated “living” free-radical polymerizations. A possible reason for this observed behavior is that the radicals generated spontaneously by autopolymerization are trapped by TEMPO in the initial stages of the reaction to give “in situ” generated unimolecular initiators. In the presence of excess TEMPO, these initiators do not lead to significant amounts of polymerization and an incubation period is observed. However, as the reaction proceeds, the excess TEMPO is consumed, and at this point the polymerization reaction effectively starts and the rate of conversion is similar to that found for well-defined unimolecular initiators. The increase in incubation time with increasing TEMPO concentration can be rationalized by the necessity to generate a greater number of radicals by autopolymerization. Increasing, or decreasing, the polymerization temperature was also observed to result in a corresponding decrease, or increase, respectively, in the incubation time.

To account for this novel behavior, the spontaneously generated radicals formed during the autopolymerization of styrene must be effectively trapped by TEMPO to give adducts which are capable of acting as unimolecular initiators under typical “living” free-radical polymerization conditions (i.e. 125−130 °C for 20−48 h). To investigate the nature of these initiating species, and hence the structure of the spontaneously generated radicals, 10 equiv of styrene was heated with 1 equiv of TEMPO at 130 °C. The reaction was stopped at 18 h which is within the incubation time for this styrene/TEMPO ratio. Removal of the excess styrene gave a complex mixture of components from which three major products could be separated by repeated flash chromatography. These were isolated and identified as the ethylbenzene derivative **5**, the bis-TEMPO adduct **8**, and the tetrahydronaphthalene derivative **4**. The isolation of **4** and **5** is in agreement with the Mayo mechanism for the autopolymerization of styrene. A $[4 + 2\pi]$ Diels−Alder cycloaddition between two styrene molecules gives the adduct, **1**, which then undergoes an assisted loss of a hydrogen atom to generate the radical, **2**. Trapping of **2** by TEMPO then gives the tetrahydronaphthalene derivative, **4** (Scheme 1). It should be noted that in this system, unlike the conventional autopolymerization of styrene, two different molecules may assist in this loss of a hydrogen atom. If a molecule of styrene abstracts the hydrogen, a secondary ethylbenzene radical, **3**, is formed, which can then be trapped by TEMPO to give **5**. Conversely, a TEMPO radical can abstract the hydrogen atom to give the *N*-hydroxy derivative, **9**, which presumably undergoes addition to styrene followed by a second trapping reaction with TEMPO to give the bis-TEMPO adduct, **8** (Scheme 3).

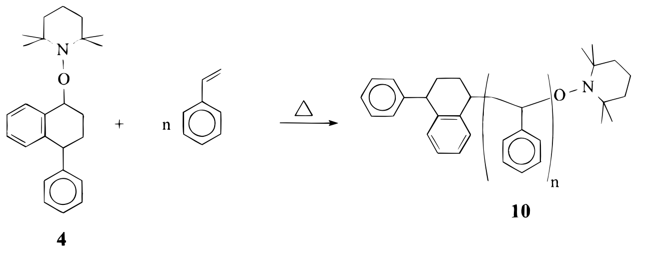
### Scheme 3



The same bisadduct, **8**, has also been identified as the major product in the reaction of a 1:1 mixture of styrene and TEMPO at 130 °C by Scaiano.[16] The formation of **8** as a significant product for the above model reaction should therefore be viewed in the context that the relative concentration of TEMPO, **1**, in a 10:1 reaction mixture is extremely high. This favors H-abstraction by **1** to give the *N*-hydroxy derivative, **9**, which leads to **8**. Under more typical polymerization conditions, the concentration of TEMPO is significantly less and therefore the formation of **8** would be expected to be less favored. To investigate this point, the reaction of 200 equiv of styrene with TEMPO was conducted at 130 °C for 3.5 h. Again the reaction was stopped during the incubation period and a similarly complex mixture of products was obtained. In this case, the bis(alkoxyamine) derivative, **8**, was a minor constituent, with the major product being **4**. These results are similar to, though not the same as, to those reported by Moad[17] for the autopolymerization of styrene in the presence of nitroxides at 100 °C under rigorous experimental and purity conditions. In this elegant series of experiments, only the adducts **4** and **8** were observed in the reaction mixture, with no detectable amounts of **5**. This change in product distribution may be due to the differences between our typical 'living' free-radical polymerization conditions and those used by Moad.[17]

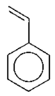
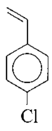
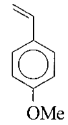
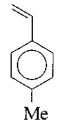
It was instructive to examine the efficiency of the three “in situ” generated TEMPO adducts **4**, **5**, and **8** as unimolecular initiators for the controlled polymerization of styrene. It has previously been shown by

**Scheme 4**



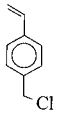
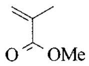
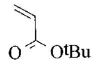
Priddy[18] and others[8] that the ethylbenzene derivative, **5**, is an efficient unimolecular initiator for "living" free-radical polymerization leading to controlled molecular weights and very low polydispersities (1.10−1.20). In a similar fashion, the tetrahydronaphthalene derivative, **4**, was shown to give controlled molecular weight polystyrene derivatives with low polydispersities (1.10−1.20) under standard "living" free-radical conditions. For example, heating a mixture of **4** and 150 equiv of styrene at 125 °C for 36 h gave a polystyrene derivative, **10**, which was shown to have a molecular weight, $M_n$, of 14 000 and a polydispersity of 1.11 (Scheme 4). This compares favorably with the theoretical molecular weight of 14 500[14] and demonstrates that **4** can act as an efficient unimolecular initiator for "living" free-radical polymerizations. Interestingly, this behavior would be predicted based on recent results which demonstrate that attachment of the TEMPO group to a secondary benzyl carbon leads to "living" character in nitroxide-mediated systems while attachment to a primary benzylic carbon does not.[8] Under identical conditions the bis-TEMPO adduct, **8**, was observed to give poor molecular weight control and higher polydispersities when compared to **4**. For example, heating a mixture of **8** and 150 equiv of styrene at 125 °C for 36 h gave a polystyrene derivative which was shown to have a molecular weight, $M_n$, of 9500 and a polydispersity of 1.55. This behavior can be rationalized by the fact that **8** contains two different alkoxyamines, a secondary benzylic moiety which leads to efficient initiation and low-polydispersity polymers (PD = 1.1−1.2) and a primary alkoxyamine group which is moderately stable under the polymerization conditions and therefore leads to inefficient initiation and polydisperse polymers (PD = 2.0−2.5).[8] Therefore **8** acts as a difunctional initiator in which one initiating site is efficient and gives controlled growth while the other site is not efficient and leads to uncontrolled growth. The combination of these two initiating units in the same molecule then leads to the observed increase in polydispersity when **8** is compared to either **4** or **5**.

**Table 1. Molecular Weight ($M_n$) and Polydispersity for Purified Polymers Obtained from the Polymerization of Styrenic Monomers in the Presence of TEMPO at 125 °C under Argon for 20 h**

| Monomer | Ratio[a] | $M_n$[b] | PD |
|---|---|---|---|
|  | 50 | 5 700 | 1.15 |
| | 100 | 9 000 | 1.17 |
| | 150 | 15 900 | 1.16 |
| | 200 | 20 700 | 1.18 |
| | 200 | 20 100 | 1.26 |
| | 250 | 26 600 | 1.23 |
| | 300 | 29 000 | 1.30 |
| | 300 | 27 500 | 1.20 |
| | 400 | 35 000 | 1.33 |
| | 500 | 37 000 | 1.28 |
| | 600 | 38 500 | 1.43 |
| | 800 | 48 000 | 1.49 |
| | 1000 | 60 500 | 1.46 |
|  | 100 | 10 500 | 1.26 |
| | 200 | 20 000 | 1.29 |
| | 300 | 31 500 | 1.18 |
| | 400 | 35 000 | 1.22 |
| | 500 | 40 500 | 1.24 |
|  | 100 | 11 000 | 1.19 |
| | 200 | 17 000 | 1.25 |
| | 300 | 26 500 | 1.31 |
| | 400 | 34 000 | 1.34 |
|  | 100 | 9 500 | 1.30 |
| | 200 | 21 000 | 1.24 |
| | 300 | 28 500 | 1.29 |
| | 400 | 36 500 | 1.32 |

[a] Molar ratio of monomer to TEMPO. [b] Polystyrene equivalent molecular weights.

**Table 2. Molecular Weight ($M_n$) and Polydispersity for Purified Polymers Obtained from the Polymerization of Comonomer Mixtures in the Presence of TEMPO at 125 °C under Argon for 36 h**

| Comonomer | Feed[a] | Ratio[b] | $M_n$[c] | PD |
|---|---|---|---|---|
|  | 1:9 | 200 | 22 000 | 1.24 |
| | 2:8 | 200 | 25 000 | 1.38 |
| | 3:7 | 200 | 24 000 | 1.45 |
| | 4:6 | 200 | 29 200 | 1.52 |
|  | 1:9 | 150 | 14 000 | 1.22 |
| | 2:8 | 150 | 14 500 | 1.22 |
| | 3:7 | 150 | 13 000 | 1.31 |
| | 4:6 | 150 | 12 000 | 1.35 |
|  | 1:9 | 150 | 14 500 | 1.23 |
| | 15:85 | 150 | 15 000 | 1.20 |
| | 25:75 | 150 | 16 500 | 1.18 |
| | 50:50 | 150 | 11 500 | 1.45 |

[a] Molar feed ratio of comonomer to styrene. [b] Molar ratio of total monomers to TEMPO. [c] Polystyrene equivalent molecular weights.

The ability to control the autopolymerization of other styrenic derivatives and comonomer mixtures was then examined under the same conditions as those reported above. For example, a mixture of *p*-chlorostyrene (200 molar equiv) and TEMPO was heated at 125 °C for 20 h and the solidified polymerization mixture dissolved in dichloromethane and precipitated into methanol. This gave the poly(*p*-chlorostyrene) homopolymer in 80% yield, which was shown to have a molecular weight, $M_n$, of 20 000 and a polydispersity of 1.29. The controlled autopolymerization of a range of other substituted styrene derivatives was also observed under the same polymerization conditions (Table 1). It should be noted that pentafluorostyrene was not observed to give significant amounts of polymer under prolonged heating at 125 °C in the presence of TEMPO. This behavior is fully consistent with the decreased ability of pentafluorostyrene to undergo autopolymerization via a Mayo mechanism.[19]

Copolymerization of styrene with a variety of comonomers, such as methyl methacrylate, was also found to lead to well-defined random copolymers in the absence of added initiators (Table 2). In accord with the results obtained for the "living" free-radical polymerization of styrene with acrylates or methacrylates in the presence of unimolecular initiators, such as **5**,[6] the polydispersities of the random copolymers prepared by autopolymerization were also observed to increase with decreasing amounts of styrene. Interestingly, for the same molar ratio of total monomers to TEMPO, the incubation time was found to increase with increasing amounts of the acrylate or methacrylate comonomer. This variation in incubation times for the same molar ratio correlates with a dilution of the styrene monomer by the acrylate or methacrylate comonomers which do not undergo significant autopolymerization.[9] This leads to a reduction in the rate of radical formation by autopolymerization and hence an increase in incubation time. A similar effect is apparent in the autopolymerization of styrene in admixture with inert solvents such as chlorobenzene.

In conclusion, the preparation of well-defined styrenic polymers by nitroxide-mediated “living” free-radical procedures has been shown to be a facile process in the absence of initiators for a variety of styrene derivatives and comonomer mixtures. The self-generated free radicals formed during autopolymerization are effectively trapped by the added nitroxide to give “in-situ” unimolecular initiators, which leads to controlled polymer formation, though the degree of control is not as great as for unimolecular[8] or bimolecular[7] initiating systems. A well-defined incubation period is also observed in these processes, which is consistent with a proposed mechanism involving a Mayo intermediate. Copolymerization of styrene with acrylate or methacrylate comonomers in the absence of initiators was also shown to be a “living” process, and the results obtained were in agreement with those observed for polymerizations involving unimolecular initiators. The importance of this autopolymerization reaction to nitroxide-mediated “living” free-radical procedures involving unimolecular and bimolecular systems is currently under investigation.

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