Determination of Alkoxyamine Concentrations in Nitroxyl-Mediated Styrene Polymerization Products

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ABSTRACT: A fluorescence method is presented for measuring the concentration of TEMPO-terminated chains in polystyrene samples prepared by controlled free radical polymerization. Exchange of TEMPO with a naphthoyloxy derivative is used to fluorescence-label those alkoxyamine-terminated polymer chains that are capable of further styrene addition. Determination of the fluorophore concentration in the exchanged polymer provides an accurate assessment of the concentration of alkoxyamine-terminated chains within a given sample. Fractionation of samples by gel permeation chromatography and simultaneous analysis by differential refractive index and fluorescence provides a measure of the distribution of nitroxyl-terminated chain ends as a function of molecular weight. This method is demonstrated on a series of polystyrene samples synthesized under various polymerization conditions.

Introduction

Nitroxyl-mediated free radical polymerization techniques are valued for their reported ability to prepare polymers with a narrow molecular weight distribution[1] and block copolymer structure.[2,3] Reversible termination of macroradicals by a nitroxyl such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) limits the concentration of propagating radicals to levels where radical termination is inhibited to a greater extent than is monomer addition, thereby generating pseudo-living polymerization conditions.[4] However, it is generally accepted that irreversible termination occurs in these systems, giving rise to a composition distribution that includes alkoxyamine-terminated (dormant) and polymerization-inactive chain populations.[5,6]

At present, the alkoxyamine-terminated chain population produced by nitroxyl-mediated polymerization (NMP) is determined through chain extension[2] and/or by nuclear magnetic resonance analysis.[7,8] However, chain extension methods provide a qualitative description of the amount of alkoxyamine-terminated polystyrene chains, while the accuracy of NMR integration is insufficient to quantify the dormant chain concentration in high molecular weight materials. A third method reported by Zhu et al. used a UV−vis chromophore-labeled initiator/mediator to quantify alkoxyamine contents in an NMP polystyrene.[9] However, details of this method and its utility are not available.

Nitroxyl-exchange experiments have been used to characterize the reactivity of a variety of alkoxyamine systems.[10,11] Recently, Turro et al. employed this technique to generate a fluorescent polystyrene through exchange of TEMPO with a naphthoyloxy analogue, N-TEMPO (Scheme 1).[12] We now wish to present our adaptation of this approach for the determination of the concentration of dormant polystyrene chains in the presence of irreversibly terminated chains.

In this report we disclose the experimental conditions required for quantitative chain labeling as well as details on a fluorescence technique for determining the number of dormant chains per gram of material. This method is validated by GC analysis and subsequently demonstrated on a series of miniemulsion NMP polystyrene samples for which the molecular weight and polydispersity are known. Finally, a GPC method for characterizing the distributions of molecular weight and dormant chain populations is presented. The emphasis of this paper lies on the experimental methodology through which dormant chain populations can be characterized.

Experimental Section

Materials. The following reagents were used as received from Sigma-Aldrich (Oakville, Ontario): 1-naphthoyl chloride (97%), 4-hydroxy-TEMPO (98%) [4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy], TEMPO (98%) [2,2,6,6-tetramethylpiperidinyloxy], copper powder (99%), copper(II) bromide (99%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (99%), (1-bromoethyl)benzene (98%), SDBS (80%) [sodium dodecylbenzenesulfonate], and hexadecane (99%). Tetrahydrofuran (Aldrich, 99.9+%) and styrene (Aldrich, 99%) were distilled prior to use, while pyridine (Aldrich, 99+%) was distilled over CaH_2.

4-Naphthoyloxy-2,2,6,6-tetramethylpiperidinyloxy (N-TEMPO) was prepared according to the method of Jones et al.[13] The unimolecular initiators **1**, **2**[14] as well as **3**, **4**[15] were prepared and purified as previously reported (Chart 1).

Instrumentation. Nuclear magnetic resonance spectroscopy was performed on a Bruker Avance 300 MHz spectrometer in $CDCl_3$ with chemical shifts referenced to tetramethylsilane. Bulk fluorescence measurements were acquired in cyclohexane using a Photon Technology International model QM-1 fluorimeter with a xenon lamp. Gas chromatography (GC) analysis was performed using a Hewlett-Packard 5890 series II gas chromatograph with a flame ionization detector. Polystyrene molecular weight distributions were recorded using a Waters 2960 separations module equipped with Styragel HR 5, HR 4, HR 3, HR 1, and HR 0.5 columns (Waters Corp., Mississauga, Ontario) using THF as the carrier solvent (30 °C, 1 mL/min). Calibration of the GPC was done using monodisperse polystyrene standards. A Waters 410 differential refractometer was operated in series with a Waters 474

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Scheme 1

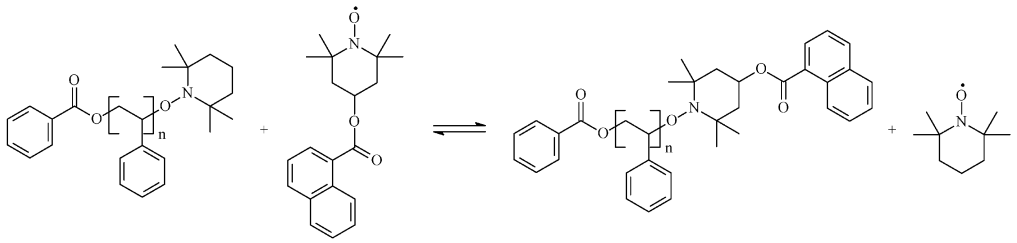
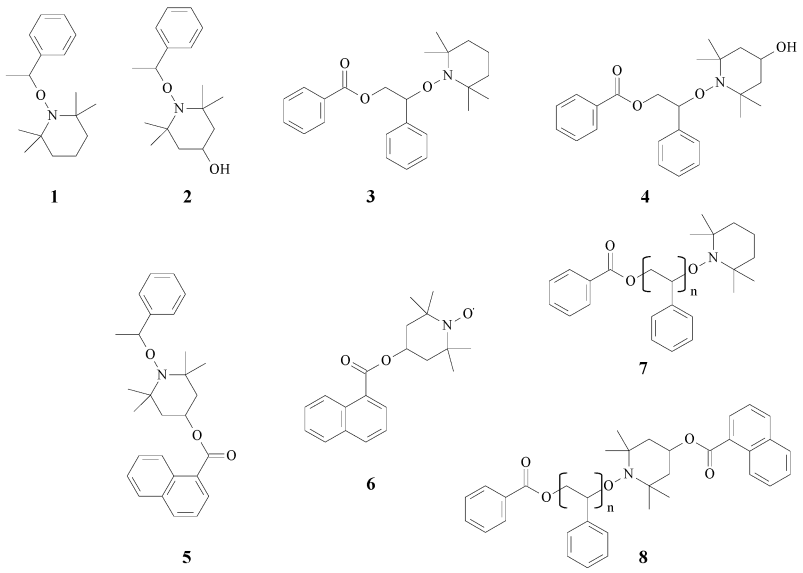


Chart 1. Structures Used in This Investigation



scanning fluorescence detector. All GPC fluorescence measurements used an excitation wavelength of 280 nm and an emission wavelength of 355 nm.

4-Naphthoyloxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (5). A solution of 1-naphthoyl chloride (5.5300 g, 29.0 mmol) in pyridine (16 mL) was added dropwise under nitrogen to a solution of **2** (3.2100 g, 11.6 mmol) in pyridine (12 mL) at 0 °C. This solution was stirred at 0 °C for 17.5 h. The reaction solution was then quenched with 2.0 mL of water, diluted in ice water (120 mL), and extracted with ethyl acetate (3 × 60 mL). The organic layers were combined and washed with dilute HCl (1 × 110 mL), saturated potassium bicarbonate (1 × 110 mL), water (1 × 110 mL), and brine (1 × 110 mL). The organic phase was dried and concentrated in vacuo to yield yellow oil that was diluted in hexanes (5 mL) and charged to an alumina column. The column was eluted with a 95% hexanes/5% ethyl acetate solution, and the eluent was concentrated in vacuo to yield clear oil that was recrystallized from ethanol to give white crystals (4.3050 g, 86% yield). ^{1}H NMR: δ 0.75, 1.25, 1.39, 1.42 (s, 12H, N−C(C*H*$_3$)$_2$−), 1.53 (d, 3H, C*H*$_3$−CH(Ar)−O−), 1.65−2.20 (m, 4H, −C(CH$_3$)$_2$−C*H*$_2$−CH(OC=O−)−C*H*$_2$−C(CH$_3$)$_2$−), 4.82 (q, 1H, CH$_3$−C*H*(Ar)−O−), 5.40 (m, 1H, −C(CH$_3$)$_2$−CH$_2$−C*H*(OC=O−)−CH$_2$−C(CH$_3$)$_2$−), 7.25, 7.35, 7.55, 7.64, 7.90, 8.05, 8.15, 8.90 (m, 12H, Ar−*H*). Required for $C_{28}H_{33}NO_3$ (EI, M^+): *m*/*e* 431.2460; found: *m*/*e* 431.2472.

Styrene NMP. An aqueous solution (120 mL) of SDBS (0.88 g) was added to a solution of distilled styrene (33 mL) and hexadecane (4.37 g) and the desired quantity of **3** or **4**. The aqueous and organic phases were mixed and homogenized using a microfluidizer (Microfluidics 110S, 3 bar). The miniemulsion was transferred to a 300 mL, stainless steel, autoclave (Autoclave Engineers), degassed by nitrogen purging, and heated to 135 °C under nitrogen. Samples of the polystyrene emulsion were taken periodically, and the monomer conversion was determined gravimetrically after removing residual styrene and correcting for hexadecane content.

Table 1. GC and Fluorescence Method Comparison for a NMP Polystyrene[a]

polymerization time (h)	styrene conv (%)	polystyrene M_n	polydispersity	fluores moles **8**/g polymer (×10^5)	GC moles **8**/g polymer (×10^5)
1.5	22	8 800	1.29	10.5	9.9
3.0	43	13 800	1.24	5.5	5.1
6.0	56	17 800	1.29	3.4	3.4
12.0	63	20 000	1.34	2.2	2.4

[a] Miniemulsion polymerization, [**3**] = 0.020 M, 135 °C.

The NMP of styrene to produce the data within Table 1 was typical of the polymerization procedure used throughout this work. Water, SDBS, styrene, and hexadecane in the quantities listed above were mixed with **3** (0.295 g, 0.773 mmol) prior to microfluidization. The resulting miniemulsion transferred to the reactor, degassed, and heated to 135 °C. Samples withdrawn after 1.5, 3.0, 6.0, and 12.0 h of polymerization were dried in vacuo and analyzed for monomer conversion and molecular weight distribution.

N-TEMPO Exchange of 1. A solution of **1** (0.012 M) in chlorobenzene was degassed by three freeze/pump/thaw cycles and heated at 123 °C for 154 min under nitrogen in the presence of 50 mol equiv of N-TEMPO. Conversion was monitored by fluorescence intensity and GC analysis of **1** (19095Z-221 HP-SIMDIST megabore column) using a heating profile of 80 °C for 20 min, ramp to 100 °C at 2 °C/min, hold for 55 min, ramp to 280 °C at 10 °C/min, and hold for 5 min.

N-TEMPO Exchange of Polystyrene and Method Validation. Polystyrene samples were purified by dissolution/precipitation (THF/methanol) and dried in vacuo at 60 °C overnight. M_n results from GPC analysis were used to estimate the number of chains ends per gram of polystyrene within a given sample. Based on this estimate, a 5 wt % solution of polystyrene in chlorobenzene containing a 50:1 excess of N-TEMPO:polymer chain ends was prepared. The solution was

degassed by three freeze/pump/thaw cycles and heated to 123 °C for 154 min under nitrogen.

An example of the exchange procedure is provided for the sample withdrawn at 1.5 h from the NMP reaction summarized by Table 1. NMP polystyrene (**7**, 0.123 g, $M_n = 8813$, PD = 1.289) and N-TEMPO (**6**, 0.227 g, 0.70 mmol) were dissolved in chlorobenzene (2.33 g, 20.7 mmol). The mixture was degassed and heated under nitrogen to 123 °C for 154 min to yield the labeled product, **8**.

Exchanged samples for which method validation was undertaken were charged with a known quantity of acetophenone after cooling to room temperature. This was used subsequently as an internal standard for GC analysis. The solution was then precipitated into methanol, and the polymer was isolated by filtration using a 0.22 μm Teflon filter paper. The filtrate was then analyzed by GC (Supelco SPB-1 microbore column) to determine TEMPO and acetophenone concentrations using a heating profile of 50 °C for 3 min, ramp to 150 °C at 10 °C/min, ramp to 280 °C at 12 °C/min, and hold for 15 min. The labeled polystyrene was purified by dissolution/precipitation (THF/methanol), filtered using a 0.22 μm Teflon filter paper, and dried in vacuo at 60 °C for 12 h.

Joint GPC Molecular Weight/Fluorescence Analysis. A 2.3 mM solution of **5** in THF was used as solvent for the polystyrene samples to generate GPC solutions containing an internal fluorescence standard. Polystyrene (~10.0 mg) and this standard solution (10.0 mL) were mixed in precisely known quantities. Additional fluorescence calibration standards of **5** in THF were analyzed to transform the fluorescence detector output into alkoxyamine concentration. Correction for the dead time between the fluorescence and refractive index detectors was accomplished by synchronizing the maximum fluorescence and refractive index signals for **5** in each sample. Analysis of refractive index output gave the weight fraction of polystyrene chains as a function of molecular weight.[16] Transformation of the fluorescence signal to the absolute number of moles of **8** as a function of time was achieved using a calibration based on standard solutions of **5**.

Results and Discussion

Nitroxyl-Exchange Conditions. An accurate determination of the dormant chain population within a NMP polystyrene requires that all TEMPO-terminated polymer chains be exchanged with the naphthoyloxy derivative, **6**. This is accomplished by activating the alkoxyamine in the presence of a large excess of **6** under conditions where chain deactivation by disproportionation is minimized. Upon reaching an equilibrium condition, a system containing a 50:1 molar ratio of **6**:**1** should convert 98% of **1** into its fluorescent derivative **5**, assuming that these compounds are of comparable thermodynamic stability.

Based on the work of Marque et al., the first-order rate constant for homolytic dissociation of the C−O bond of **1** in *tert*-butylbenzene at 123 °C is approximately 4.3×10^{-2} min^{-1}.[17] Therefore, 92 min equates to 5.7 half-lives of **1** at 123 °C, which we consider to be the minimum time required for a nitroxyl-exchange reaction of **1** to reach equilibrium. This result was tested by heating **1** in the presence of 50 mol equiv of **6** at 123 °C for 154 min. Both fluorescence and GC analysis confirmed that 98.3% of **1** was converted to the desired naphthoyloxy derivative, **5** (Figure 1). We are therefore confident that these reaction conditions can be extended to polystyrene, converting approximately 98% of TEMPO-terminated polystyrene **7** into its fluorescent derivative, **8**.

Determination of Dormant Chain Concentrations. Fluorescence emission spectra for labeled polystyrene **8**, the model compound **5**, and unlabeled NMP polystyrene **7** are illustrated in Figure 2. Integrations

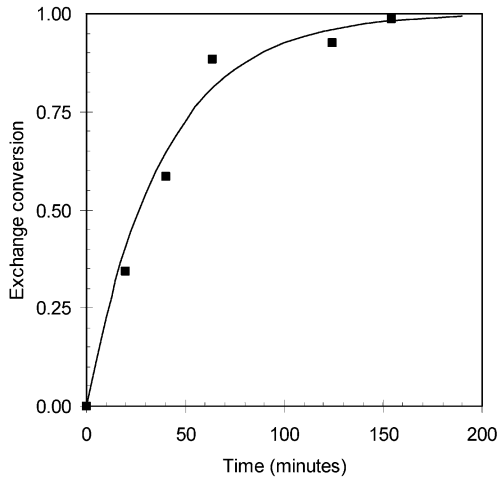


Figure 1. Conversion of **1** to **5** vs time as determined by fluorescence ($[\mathbf{1}]_0 = 0.012$ M, $[\mathbf{6}] = 0.60$ M, chlorobenzene, 123 °C; − = regression).

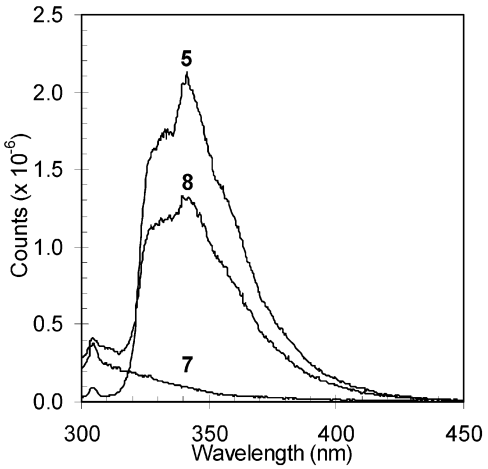


Figure 2. Emission spectra of **5**, NMP polystyrene **7**, and labeled polystyrene **8** ($\lambda_{excitation} = 280$ nm).

of the emission spectrum of **8** from 325 to 375 nm were corrected for the weak fluorescence of styrene mers in order to isolate the contribution of labeled chain ends. An instrument calibration based on standard solutions of **5** was then applied to derive an absolute measure of the fluorophore concentration in unknown solutions of **8**. The calibration demands that the quantum yields of compounds **5** and **8** are equivalent. This bulk fluorescence method provides a measure of the number of dormant chain ends per gram of polystyrene, as listed in Table 1 for a series of NMP materials derived from a single polymerization experiment.

Given that the nitroxyl-exchange labeling procedure involves activation of the alkoxyamine, there is a possibility of terminating dormant chains by disproportionation. In particular, the 50-fold excess of nitroxyl used in the exchange process could conceivably accelerate this irreversible termination process. However, studies of the disproportionation of **1** have shown the process to be first-order with respect to alkoxyamine and independent of the concentration of added nitroxyl.[6] Ohno et al. have suggested that **1** disproportionates at a greater rate than its polymeric analogue **7**,[6] suggesting that deactivation of dormant chains under the exchange conditions employed is negligible.

Experimental evidence of the retention of alkoxyamine concentrations during labeling exchange is provided in

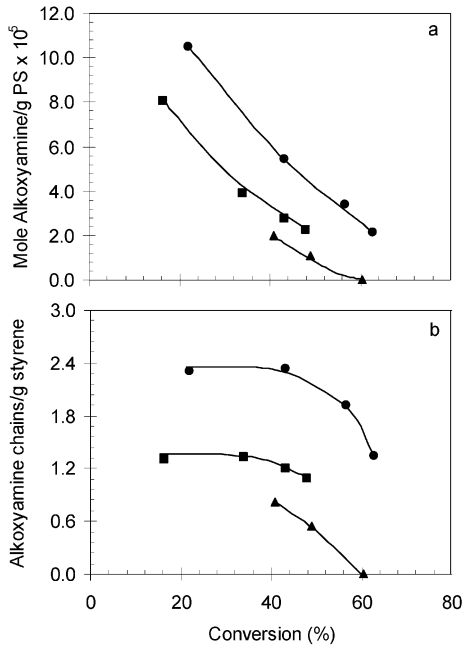


Figure 3. Bulk alkoxyamine contents of NMP polystyrenes initiated by **3**: (a) moles **8**/g polystyrene; (b) moles **8**/g total styrene (monomer + polymerized); ▲, [**3**] = 0.007 M; ■, [**3**] = 0.014 M; ●, [**3**] = 0.020 M.

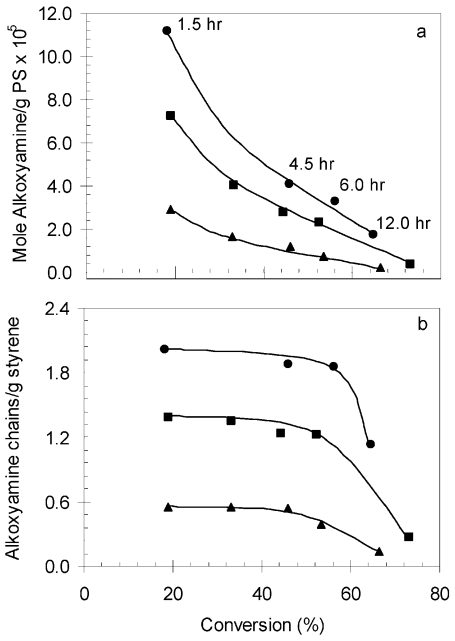


Figure 4. Bulk alkoxyamine contents of NMP polystyrenes initiated by **4**: (a) moles **8**/g polystyrene; (b) moles **8**/g total styrene (monomer + polymerized); ▲, [**4**] = 0.007 M; ■, [**4**] = 0.014 M; ●, [**4**] = 0.020 M.

Table 1. GC analysis for the amount of TEMPO liberated by the exchange process accounts for the TEMPO displaced by N-TEMPO as well as that produced by alkoxyamine disproportionation. Although the exchanges were performed under oxygen-free conditions, air oxidation of the hydroxylamine derived by disproportionation would occur rapidly during product workup. Agreement of the GC measurement of released TEMPO and the fluorescence measurement of **8** indicates that chain deactivation was not significant under the prescribed labeling conditions. Further confirmation of this fact is provided in Figure 1, which demonstrates that fluorescence derived from **5** reached a stable plateau after 154 min, rather than declining due to alkoxyamine disproportionation.

Polystyrene Series Analysis. Six series of NMP polystyrenes were analyzed for total dormant chain content using the bulk fluorescence method detailed above. These materials were prepared by miniemulsion polymerization of styrene using different concentrations (0.007, 0.014, and 0.020 M) of two alkoxyamine initiators, **3** and **4**. Given that Ma et al. discovered significant differences in the conversion and molecular weights of polystyrenes produced using TEMPO and 4-hydroxy-TEMPO-mediated systems,[18] further analysis of the extent of chain deactivation in these processes was of interest.

Figures 3 and 4 illustrate the evolution of alkoxyamine end-group concentrations for these series of miniemulsion polymerizations. The results indicate that at equivalent styrene conversions the number of alkoxyamine-terminated polystyrene chains per gram of polymer was similar for the two initiation systems (Figures 3a and 4a). As expected, alkoxyamine end-group concentrations were higher in those polymerizations employing greater initiator (**3**, **4**) loadings, and they declined with monomer conversion. This decline in a mass-based alkoxyamine concentration (moles **8**/g polystyrene) is a consequence of not only irreversible termination but also chain growth.

Using the recorded monomer conversion, an alkoxyamine concentration based on the total mass of styrene within the system can be derived. Given that the polymerizations were conducted under batch conditions, the total mass of styrene (monomer + polymerized) remained constant throughout the reaction. Therefore, the decline of an alkoxyamine concentration based on moles **8**/g styrene reflects only the extent of chain termination. As shown in Figures 3b and 4b, significant irreversible chain termination occurred in all experiments, with the extent of deactivation increasing notably beyond 40% styrene conversion.

While the bulk method of measuring alkoxyamine concentrations proved to be useful for monitoring the evolution of chain termination in NMP systems, the distribution of dormant chains with respect to molecular weight was also of interest. Therefore, we undertook a more thorough analysis of these samples in which GPC fractionation was used to record the distributions of molecular weight and alkoxyamine termini among polymer chains. In particular, the NMP series employing 0.020 M of **4** as initiator (Figure 4) was examined.

Joint GPC Molecular Weight/Fluorescence Analysis. The differential refractive index and fluorescence intensity profiles for a NMP polystyrene and its nitroxyl-exchanged derivative are presented in Figure 5. The data demonstrate that no detectable changes to molecular weight distribution resulted from the labeling of dormant polymer chains. A correction for polystyrene fluorescence was developed to isolate the emission intensity derived from the labeled alkoxyamine. In general, this correction amounted to less than 5% of the measured fluorescence intensity for the samples analyzed in this work.

Figure 6 presents the distribution of molecular weight and alkoxyamine content for NMP materials initiated by a 0.020 M organic-phase concentration of **4**. The dormant chain population at a given molecular weight is represented by the absolute number of moles of alkoxyamine passing through the detector. Concentra-

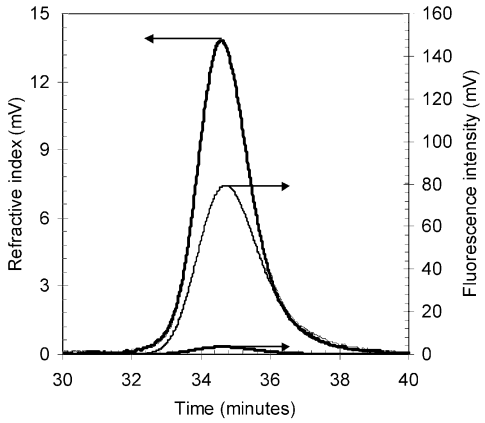


Figure 5. GPC refractive index and fluorescence signals for NMP polystyrene: thick line, unexchanged; thin line, exchanged.

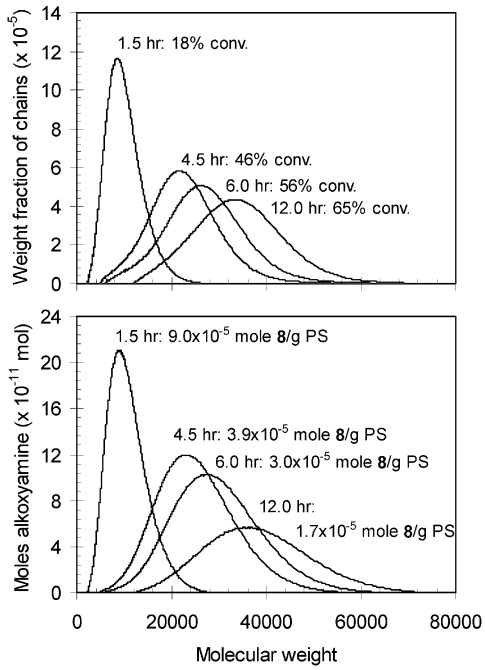


Figure 6. Evolution of molecular weight/alkoxyamine distributions for an NMP polystyrene initiated by [**4**] = 0.020 M.

tions of polystyrene solutions were prepared gravimetrically with great care, thereby facilitating direct comparisons of sample responses. We note that integrations of the fluorescence distribution produced by these samples are consistent with bulk fluorescence measurements (Figure 4), thereby providing confidence in the ability of the GPC technique to correlate with the bulk fluorescence spectrometer method.

The GPC fractionated samples demonstrate the extent of molecular weight distribution broadening with increasing time/conversion. Of particular interest is the corresponding broadening of the dormant chain population, as it encompassed the entire distribution of molecular weight. This indicates that dormant chains were not simply those of highest molecular weight or longest polymerization time, as may be expected from an ideal NMP process. Rather, polymerization activity exists for chains of all molecular weight, and NMP must involve significant chain transfer to generate dormant chains of relatively young age. This process is likely to involve alkoxyamine disproportionation to release a hydroxylamine that is readily oxidized to the corresponding nitroxyl and/or bimolecular radical termination to produce the nitroxyl directly. In either case, polymerization would be arrested were it not for thermal autoinitiation to generate styrenic radicals that are subsequently mediated by liberated nitroxyl. This mechanism has been proposed by several researchers with an interest in the dynamics of NMP processes of styrene.[6,19] A comprehensive discussion of the influence of polymerization conditions on molecular weight and alkoxyamine distributions will be the focus of a forthcoming publication.

Conclusions

The fluorescence labeling of nitroxyl-terminated polystyrene provides a means of quantifying the dormant chain populations in an NMP sample. Analysis using a conventional spectrofluorimeter provides a direct measure of the number of moles of alkoxyamine per gram of polymer, which can be transformed into other variables of interest using such information as monomer conversion. GPC fractionation and analysis by online refractive index and fluorescence detectors provide information regarding the distribution of molecular weight and dormant chain ends.

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