Limitations in the Synthesis of High Molecular Weight Polymers via Nitroxide-Mediated Controlled Radical Polymerization: Experimental Studies

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ABSTRACT: Limitations associated with preparing high molecular weight polystyrene (PS) by nitroxide-mediated controlled radical polymerization have been tested by considering the role of unimolecular initiator concentration on active polymer radical concentration and thus degree of polymerization. Recent theories ignoring autopolymerization effects lead to the conclusion that, at low monomer conversion, the number-average molecular weight, M_n, scales with the −2/3 power of unimolecular initiator concentration. Bulk polymerizations were done using either α-methylstyryl di-*tert*-butyl nitroxide (A−T) as unimolecular initiator or PS macroinitiator made from A−T. These initiators allow relatively low reaction temperature (77, 87, or 97 °C) and moderate, but not eliminate, the contribution of autopolymerization or thermal initiation of polymerization. By varying unimolecular initiator concentration over nearly 4 orders of magnitude, well-controlled PS, with polydispersity index ≤ 1.4, can be made with M_n values in the range 114 000−238 000 g/mol using either A−T as initiator or a PS macroinitiator. For conditions yielding controlled PS, in general the experimental M_n−initiator concentration data afforded good agreement with the −2/3 power-law expression and allowed estimation of the equilibrium constant for the capping−uncapping reaction. However, attempts to make controlled, higher molecular weight PS by further reducing initiator concentration resulted in loss of control due to autopolymerization effects. The impact of autopolymerization in producing well-controlled PS was evident from studies yielding a nearly constant conversion as a function of macroinitiator concentration.

Introduction

Controlled radical polymerization, also called living free radical polymerization, has been shown over the past decade by both academic studies and industrial research to have great potential for the production of polymers with controlled architecture.[1−29] Examples include not only homopolymers with well-defined, relatively monodisperse chain lengths and functionalized chain ends but also polymers of complex structure, including star polymers,[16] hyperbranched or dendritic polymers,[9,15,16,19] microgels,[12] and polymer brushes,[21] as well as a range of copolymers.[5,7,9−11,14,15,17,19,20,23−27] Many of these materials cannot be synthesized with precision via conventional free radical polymerization, e.g., block copolymers, while others cannot be made by any conventional polymerization method; e.g., although addition-type block copolymers can be made via anionic polymerization, addition-type gradient copolymers cannot generally be made by any method other than controlled radical polymerization. Controlled radical polymerization also has advantages over conventional radical polymerization based on certain fundamental issues, e.g., autoacceleration of polymerization rate at high bulk conversion.[30−32]

The subset of controlled radical polymerization called nitroxide-mediated controlled radical polymerization (NM-CRP) is more environmentally benign than the other widely studied, controlled radical polymerization method called atom transfer radical polymerization (ATRP) due to the presence of heavy metals in the ATRP reaction scheme. However, in the case of NM-CRP, which is typically done at relatively high polymerization temperature, almost all of the polymers that have been made were of low-to-moderate chain length, with molecular weight (MW) commonly less than 80 000 g/mol. There are very few reports[2,8,18] indicating the production of polymers via NM-CRP with MWs significantly in excess of 100 000 g/mol where the MW is still controlled, i.e., with polydispersity remaining below 1.5 and average chain length growing with increasing conversion. There are many reasons to be interested in the production of relatively high MW polymers via NM-CRP, including the fact that commercial applications of addition-type polymers often require high MW materials. Also, in the case of polymers that may be made only via NM-CRP, some of the most interesting physical properties, e.g., microphase separation of gradient copolymers,[33−35] may be accessible only at relatively high MWs.

The approach that we have employed for testing the limits of controlled, high MW polymer via NM-CRP is to consider the impact of unimolecular initiator concentration, C_0, at low monomer conversion. (An associated report focusing on mechanistic modeling analysis of the limits related to the synthesis of high MW polymers via NM-CRP is given in ref 36.) Recent analyses of NM-CRP kinetics by Fischer and co-workers[37,38] and by Fukuda et al.,[39] which consider the contributions of unimolecular initiation, propagation, reversible capping, and termination steps (see Scheme 1), lead to the conclusion that, in the limit of very low, uncapped stable radical concentration, the uncapped polymerizing radi-

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Scheme 1. NM-CRP Reaction Mechanism without Autopolymerization[a]

I. Initiation (very rapid) $A\text{-}T \rightarrow A^{\cdot} + T^{\cdot}$

$A^{\cdot} + M \rightarrow P_1^{\cdot}$

II. Propagation $P_x^{\cdot} + M \xrightarrow{k_p} P_{x+1}^{\cdot}$

III. Reversible Uncapping/Capping $P_x\text{-}T \overset{K_e}{\rightleftarrows} P_x^{\cdot} + T^{\cdot}$

IV. Termination $P_x^{\cdot} + P_y^{\cdot} \xrightarrow{k_t} D_x + D_y$ or D_{x+y}

[a] A−T is the unimolecular initiator, $A^{\bullet}$ is the initiated radical, $T^{\bullet}$ is the stable radical, M is monomer, $P_x^{\bullet}$ is polymer radical with x repeat units, $P_x{-}T$ is the capped polymer, D_x is terminated "dead" polymer with x repeat units, k_p is the propagation rate parameter, K_e is the equilibrium constant for reversible uncapping/capping, and k_t is the termination rate parameter. Note: in the description of the kinetics in the text, all A−T is assumed to lead to polymer radical.

cal concentration, $[P^{\bullet}]$, is given by

$$[P^{\bullet}] = (K_e C_0/3k_t)^{1/3} t^{-1/3} \tag{1}$$

where K_e is the equilibrium constant for the reversible capping−uncapping reaction, k_t is the termination rate parameter, and t is the polymerization time. These analyses can be extended to consider the relationship between C_0 and the number-average degree of polymerization, DP_n, achievable via NM-CRP:

$$DP_n = ([M]_0 - [M])/C_0 \tag{2}$$

where $[M]_0$ and $[M]$ are monomer concentrations at initiation of polymerization and polymerization time t, respectively. Equation 2 indicates that under the circumstance of low values of C_0 high DP_n values may be achieved at low monomer conversion, possibly reducing the impact of thermal initiation of polymerization that can result in a loss of control of the polymerization.[40] Employing the fact that the rate of polymerization is given by

$$-d[M]/dt = k_p[P^{\bullet}][M] \tag{3}$$

in conjunction with eq 1 and recalling that in the limit as $z \rightarrow 0$, $\exp(-z) = 1 - z$, then eq 2 may be rewritten as

$$DP_n = 1.5[M]_0 k_p (K_e/3k_t)^{1/3} t^{2/3} C_0^{-2/3} \tag{4}$$

in the limit of low conversion. Under such conditions, DP_n may be expected to reach high values with a substantial reduction in C_0 via the proportionality of DP_n to $C_0^{-2/3}$.

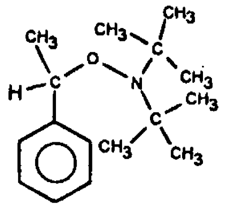
Fukuda et al.'s analysis[39] of NM-CRP kinetics has additionally considered the circumstance in which thermal initiation of polymerization is not ignored, which is relevant for styrene polymerization. Under this circumstance, these workers noted "the system will sooner or later reach the stationary state."[39] Upon achievement of the stationary state condition ($d[P^{\bullet}]/dt = d[T^{\bullet}]/dt = 0$), $[P^{\bullet}]$ is defined strictly by the relative rates of thermal initiation and termination, i.e., $[P^{\bullet}] = (R_{ti}/k_t)^{1/2}$ where R_{ti} is the rate of thermal initiation. Reference 36 considers the more general case, where thermal initiation is not ignored but where the stationary state has not necessarily been reached. Regardless of which kinetic picture is considered, that disregarding the possibility of thermal initiation (with $DP_n \sim C_0^{-2/3}$) or that considering the possibility of thermal initiation *without* achievement of the stationary state, it is obvious that one route for testing the limit of high MW polymer production via NM-CRP is through a severe reduction in unimolecular initiator concentration. While such an approach may not prove attractive from a commercial sense, it nevertheless tests the limits of high MW polymer synthesis via NM-CRP and additionally allows for the determination of the impact of autopolymerization or thermal initiation of polymerization[4,6,8,10] in causing a loss of control in NM-CRP-based processes.

Here we provide an experimental test of the applicability of such an approach using the low MW, unimolecular initiator A−T, first employed by Catala et al.[41] in the NM-CRP synthesis of polystyrene (PS) at moderate temperature. By choosing this unimolecular initiator, it is possible to undertake studies of styrene polymerization at temperatures well below 100 °C, where autopolymerization is greatly reduced relative to the temperatures of 120−125 °C often employed in NM-CRP syntheses.[42] In turn, this permits sufficiently long polymerization times for the production of high MW PS while maintaining control of polymerization. In particular, we demonstrate the controlled polymerization of high MW PS, up to at least 150 000 g/mol and possibly up to 238 000 g/mol, from batch, bulk polymerizations of styrene with A−T. Additionally, by employing moderate MW macroinitiator made from NM-CRP synthesis of PS using A−T as unimolecular initiator, controlled synthesis of high MW PS is demonstrated with number-average molecular weight, M_n, well in excess of 100 000 g/mol. Thermal initiation of styrene polymerization at the moderate polymerization temperatures used here disallows the controlled synthesis of yet higher MW PS.

Experimental Section

Materials. Styrene (Aldrich, 99%) was deinhibited using *tert*-butylcatechol inhibitor remover (Aldrich) and CaH_2 before use.

Initiator A−T (α-methylstyryl di-*tert*-butyl nitroxide) was produced by coupling the chemically generated carbon radical of *sec*-phenylethyl bromide with di-*tert*-butyl nitroxyl radical.[43] Specifically, A−T was synthesized as follows. Hydrazine (9.35 g, 290 mmol) was added to (1-bromoethyl)benzene (2.70 g, 14.5 mmol) and sonicated in an ultrasonic bath for 30 min. The reaction mixture was diluted with diethyl ether (150 mL), the layers were separated, and the hydrazine layer was washed with diethyl ether (50 mL). The combined organics were washed with 10% aqueous KOH (50 mL) followed by aqueous saturated sodium chloride solution (50 mL) and then dried over magnesium sulfate. The solvent was removed in vacuo, yielding 1-phenylethylhydrazine (1.54 g) as a viscous oil.



A-T

In a separate flask, lead dioxide (2.11 g, 8.83 mmol) and di-*tert*-butyl nitroxide (0.706 g, 4.41 mmol) were suspended

Table 1. Number-Average Molecular Weight and Polydispersity Index Data for 6.5 h, Batch Polymerizations as a Function of Polymerization Temperature and Unimolecular Initiator (A−T) Concentration

	$T = 77$ °C		$T = 87$ °C		$T = 97$ °C	
concn (mol/L)	$M_n \times 10^3$ (g/mol)	PDI	$M_n \times 10^3$ (g/mol)	PDI	$M_n \times 10^3$ (g/mol)	PDI
7.0×10^{-6}	298	1.52	315	1.56	277	1.55
1.3×10^{-5}	304	1.52			282	1.56
2.6×10^{-5}	302	1.54	301	1.50	291	1.54
5.1×10^{-5}	165	1.54	304	1.51	286	1.56
1.03×10^{-4}	126	1.48	267	1.52	240	1.58
2.05×10^{-4}	45	1.38	182	1.47	228	1.58
4.1×10^{-4}			121	1.31	171	1.54
8.2×10^{-4}	8	1.28	78	1.16	134	1.32
1.64×10^{-3}			38	1.21	96	1.14
3.28×10^{-3}			17	1.15	43	1.23
6.56×10^{-3}			6.9	1.17	13	1.22
1.31×10^{-2}			3.1	1.15	8.8	1.13

Table 2. Number-Average Molecular Weight and Polydispersity Index Data for 3.0 h, 87 °C, Batch Polymerizations as a Function of Unimolecular Initiator (A−T) Concentration

concn (mol/L)	$M_n \times 10^3$ (g/mol)	PDI	concn (mol/L)	$M_n \times 10^3$ (g/mol)	PDI
2.6×10^{-5}	296	1.49	4.1×10^{-4}	48	1.25
5.1×10^{-5}	238	1.43	8.2×10^{-4}	38	1.23
1.03×10^{-4}	154	1.34	1.64×10^{-3}	23	1.21
2.05×10^{-4}	85	1.20			

in toluene (7.5 mL) and sonicated for 30 min. This nitroxyl mixture was cooled to −78 °C, and the 1-phenylethylhydrazine suspended in toluene (5.0 mL) was added by cannula in portions. An additional aliquot (7.5 mL) of toluene was added to the hydrazine flask for rinsing, and the resulting solution was also cannulated into the nitroxyl suspension. The reaction mixture was allowed to stir overnight while slowly warming to room temperature. The mixture was then diluted with diethyl ether (100 mL) and filtered through a plug of Celite, which was then washed with diethyl ether (200 mL). The combined organics were evaporated in vacuo to give a yellow oil. Purification by flash chromatography (hexanes:ethyl acetate = 95:5) afforded A−T (0.63 g, 60%). ^{1}H NMR ($CDCl_3$): 1.04 (s, $C(CH_3)_3$, 9 H), 1.31 (s, $C(CH_3)_3$, 9 H), 1.46 (d, $J = 6.8$ Hz, $CHCH_3$, 3 H), 4.82 (q, $J = 6.8$ Hz, $CHCH_3$, 1 H), 7.21−7.33 (m, *aromatic Hs*, 5H).

Methods. Number-average molecular weight (M_n) and polydispersity index (PDI) were determined by gel permeation chromatography on a Waters Breeze instrument equipped with three Waters columns (Styragel HMW 2, HMW 6E, and HR4) using tetrahydrofuran as the eluent and a Waters 2410 differential refractometer as the detector. Twenty-two PS standards (1320−775 000 g/mol) were used for calibration.

Polymerizations. Styrene (9.09 g, 0.0873 mol) and A−T were combined in a test tube and purged under a N_2 atmosphere for 30 min. The test tube was then sealed with a rubber septum and then placed in an oil bath that had been preheated to the polymerization temperature. The A−T concentrations used in batch polymerizations at 77, 87, and 97 °C for 6.5 h are shown in Table 1. Additional samples were prepared as described above and polymerized at 87 °C for 3 h using A−T concentrations shown in Table 2. The resulting polymer solution was precipitated in methanol and dried at 110 °C under vacuum for several hours. Fractional conversion for each polymerization was determined gravimetrically.

Polymerizations were also undertaken via a chain extension using a PS macroinitiator. The PS macroinitiator was synthesized by combining styrene (18.18 g, 0.1746 mol) and A−T (0.184 g, 7.39×10^{-4} mol) in a test tube. Following a 30 min N_2 purge, the test tube was sealed and placed in an 87 °C oil bath, and the sample was polymerized for 3.5 h. The resulting polymer solution was precipitated in methanol and dried at 110 °C under vacuum for several hours to yield the desired PS macroinitiator.

Table 3. Number-Average Molecular Weight and Polydispersity Index Data for 3.0 h, 87 °C, Batch Polymerizations via Chain Extension Using a PS Macroinitiator (M_n = 18 200 g/mol, PDI = 1.23)

concn (mol/L)	$M_n \times 10^3$ (g/mol)	PDI	concn (mol/L)	$M_n \times 10^3$ (g/mol)	PDI
2.6×10^{-5}	267	1.52	4.1×10^{-4}	70	1.21
5.1×10^{-5}	218	1.52	8.2×10^{-4}	45	1.21
1.03×10^{-4}	154	1.49	1.64×10^{-3}	34	1.21
2.05×10^{-4}	114	1.27			

For the chain extension, styrene (9.09 g, 0.0873 mol) and varying amounts of PS macroinitiator (shown in Table 3) were heated together at 87 °C in sealed test tubes for 3.0 h, following a 30 min N_2 purge. The polymer solution was precipitated as previously described. Fractional conversion for these chain extensions was also determined gravimetrically.

Results and Discussion

The M_n and PDI data resulting from the NM-CRP syntheses of PS are provided in Tables 1 and 2 as functions of unimolecular initiator concentration. The data in Table 1 are for 6.5 h syntheses at 77, 87, and 97 °C while the data in Table 2 are for 3.0 h syntheses at 87 °C.

Table 1 reveals a strong temperature dependence of M_n when the polymerizations remain reasonably well controlled, i.e., for systems in which PDI < 1.5. For example, at a C_0 value of 8.2×10^{-4} mol/L, the M_n values of the 6.5 h polymerization product increase from 8000 to 78 000 to 134 000 g/mol as the temperature is increased from 77 to 87 to 97 °C, respectively. This significant rise in M_n with polymerization temperature is opposite the effect obtained with conventional free radical polymerization[31,32] and can be explained by the strong temperature dependence of the reversible polymer-radical capping−uncapping step in the NM-CRP mechanism, leading to less time spent in the capped state with increasing polymerization temperature. (See Scheme 1.) Fractional conversion is also observed to increase dramatically with increasing temperature, from less than 1% to 7.9% to 16.1% as polymerization temperature is increased from 77 to 87 to 97 °C, respectively. As expected for a NM-CRP process, the ratios of fractional conversion obtained at different polymerization temperatures are approximately the same as the ratios of M_n values. This latter point is further supported by data for other controlled conditions, e.g., at a unimolecular initiator concentration of 1.64×10^{-3} mol/L the ratio of M_n obtained at 87 °C to that obtained at 97 °C is 0.40, in good agreement with the ratio of 0.41 for the fractional conversions (6.8%/16.5%) at the same two temperatures.

Further inspection of Table 1 indicates that it is possible to maintain approximate control of these 6.5 h polymerizations at 87 and 97 °C up to M_n values of at least 120 000−135 000 g/mol by employing low levels of unimolecular initiator, 4.1×10^{-4} mol/L at 87 °C and 8.2×10^{-4} mol/L at 97 °C. Attempts to achieve higher M_n values by decreasing the concentration of unimolecular initiator below those values, an approach suggested by eq 4, were positive but were accompanied by a loss of the controlled nature of the polymerization. This is evidenced both by the PDI values of ~1.5 or higher and by the much reduced dependence of M_n on initiator concentration at very low concentration. These results can be rationalized by the presence of thermal initiation of polymerization which is enhanced at higher polymerization temperature. With polymerizations of equal reaction time, this will allow for loss of control at higher C_0 in the higher temperature polymerization system.

The results above allow for an approximate determination of the extent to which the activation rate (rate of initiation of polymerization via alkoxyamine dissociation followed by rapid monomer addition) must greatly exceed the rate of autopolymerization in order to maintain a living and controlled process, a point that has been considered by Souaille and Fischer.[40] In the case of the 6.5 h polymerizations at 87 and 97 °C, the activation rates at the lowest values of C_0 where control is maintained are 1.9×10^{-7} and 9.8×10^{-7} M s^{-1}, respectively. (Data allowing calculation of the dissociation rate parameter for A–T, needed to determine the activation rates, are found in ref 42.) Catala et al.[41] have reported that the rate of formation of thermally initiated styrene radicals in bulk styrene is 1.6×10^{-8} M s^{-1} at 100 °C, 6×10^{-9} M s^{-1} at 90 °C, and 2×10^{-9} M s^{-1} at 80 °C. This indicates that the ratio of activation rate to thermal initiation needed to maintain a controlled polymerization for 6.5 h is in the neighborhood of 40–100.[44]

There was relative difficulty in achieving any substantial level of conversion at 77 °C over 6.5 h. Maximum conversion levels of 2.5–2.8% were observed for the three lowest unimolecular initiator concentrations where the polymerization was uncontrolled; thus, the conversion levels were more indicative of the conversion achievable via autopolymerization than by that achievable via NM-CRP. In contrast, for the two unimolecular initiator concentrations in Table 1 where polymerization was controlled, fractional conversions were 1.0% or less. The very low conversion levels in the controlled polymerizations and the very limited range of unimolecular initiator concentration over which controlled, nonoligomeric PS is obtained can be rationalized by the strong temperature dependence of the reversible capping–uncapping step in the case of the A–T-based NM-CRP synthesis of PS. The data suggest that, in the absence of rate enhancement promoters,[8] a practical minimum temperature for obtaining controlled, moderate MW PS via the use of the A–T-based NM-CRP polymerization method is near 77 °C.

A comparison of Table 2 with Table 1 indicates that the use of a shorter polymerization time, 3.0 h vs 6.5 h at 87 °C, can result in a controlled polymer at lower unimolecular initiator concentration. In particular, with a 3.0 h polymerization at 87 °C, PS may be synthesized in a controlled manner with M_n values at least up to 150 000–160 000 g/mol by use of a 1.03×10^{-4} mol/L A–T concentration. The polymer synthesized with the next lower initiator concentration, 5.1×10^{-5} mol/L, also is indicative of a controlled polymerization, with M_n of 238 000 g/mol and PDI of 1.43, albeit one very close to losing control. In contrast, when the polymerization time is extended to 6.5 h at these two unimolecular initiator concentrations, uncontrolled products with PDI ~ 1.5 are achieved. This loss of control between 3.0 and 6.5 h may be explained by the cumulative effects of thermal initiation of polymerization at 87 °C, leading at sufficiently long time to an uncontrolled polymerization.

Figures 1 and 2 provide comparisons of the dependence of M_n obtained in the 87 and 97 °C polymerizations described in Tables 1 and 2 as a function of $C_0^{-2/3}$.

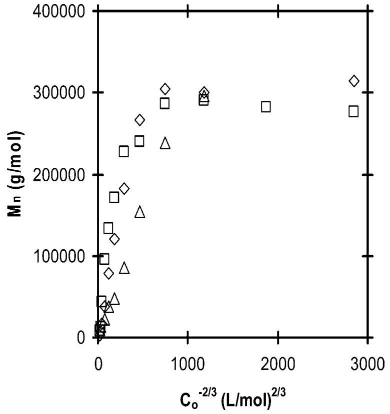


Figure 1. Number-average molecular weight, M_n, as a function of unimolecular initiator concentration, C_0, to the −2/3 power for batch polymerizations at $T = 87$ °C for $t = 3.0$ h (△) and $t = 6.5$ h (◇) and at $T = 97$ °C for $t = 6.5$ h (□).

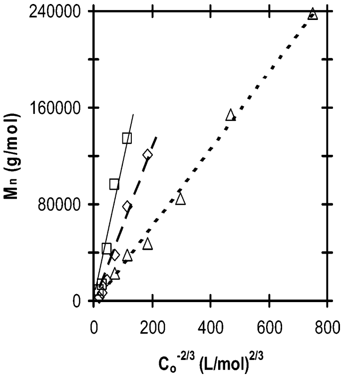


Figure 2. Number-average molecular weight, M_n, as a function of unimolecular initiator concentration, C_0, to the −2/3 power for the controlled, batch polymerization data (with PDI < 1.5) at $T = 87$ °C for $t = 3.0$ h (△) and $t = 6.5$ h (◇) and at $T = 97$ °C for $t = 6.5$ h (□). Best fits of experimental polymerization data at $T = 87$ °C for $t = 3.0$ h (- - -) and for $t = 6.5$ h (— — —) and at $T = 97$ °C for $t = 6.5$ h (—) are constrained to go through the origin of the figure.

In the case of Figure 1, which presents data over the full range of unimolecular initiator concentration investigated in this study, there is substantial curvature in each of the three plots at very high M_n values, ultimately leading to a near plateau of the M_n data at high values of $C_0^{-2/3}$, i.e., at very low unimolecular initiator concentration. This strong deviation from the expected −2/3 power-law dependence at very high MW is consistent with the loss of control of polymerization via autopolymerization effects. Figure 2 shows the M_n data for the 87 and 97 °C polymerizations as a function of $C_0^{-2/3}$ over a narrower range than that shown in Figure 1. In this regime, it appears, via PDI results (PDI < 1.5), that the polymerizations have remained under control. Within error, the three data sets in Figure 2 provide good fits to the −2/3 power-law dependence, indicating consistency with the theoretical frameworks of Fischer[37,38] and of Fukuda[39] that lead to eq 1 and thereby to eq 4.

It is worth noting that, even in the absence of autopolymerization, perfect agreement with the proportionality of M_n to $C_0^{-2/3}$ may not be expected in NM-CRP syntheses undertaken here. This is due in part to the fact that the value of k_t in eq 4 is not independent of polymerization time. In reality, k_t is a function of the chain lengths of polymer/oligomer radicals participating in the termination reaction as well as the overall

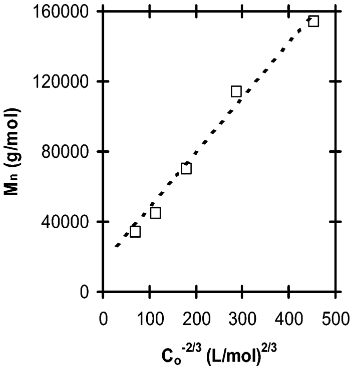


Figure 3. Number-average molecular weight, M_n, as a function of macroinitiator concentration, C_0, to the $-2/3$ (□) power when batch NM-CRP is done via chain extension at 87 °C for 3.0 h using a PS macroinitiator (M_n = 18 200 g/mol, PDI = 1.23). The best fit (- - -), constrained to go through M_n = 18 200 at $C_0^{-2/3} = 0$, is determined only for the polymerization products that are considered to be controlled; i.e., the highest M_n datum point (with PDI > 1.4) is not included in the fit.

polymer concentration, i.e., conversion. (Greater details regarding the chain length and polymer concentration dependencies of k_t may be found in refs 31, 32, 45, and 46.) However, given the low conversion levels achieved in the polymerizations undertaken here, it is expected that the error resulting from this assumption is relatively small. A similar conclusion was reached recently by Yoshikawa et al.,[28] who, in a study at low conversion and relatively high unimolecular initiator concentration leading to the production of low MW PS, found good agreement between experimental conversion levels achieved in synthesis of PS via NM-CRP to those expected from Fukuda's theory leading to eq 1.

A second factor that may contribute error to the $M_n \sim C_0^{-2/3}$ relationship is related to the fact that this proportionality assumes that conversion levels are infinitesimal. While this is not strictly the case, maximum conversion levels for the samples for which polymerization control is maintained were 8.0% for the 87 °C, 6.5 h synthesis and 16.5% for the 97 °C, 6.5 h synthesis, which are sufficiently low to introduce only small deviations from the relationship being tested.

Table 3 and Figure 3 show the resulting M_n and PDI values obtained by using a relatively low MW PS macroinitiator (originally made from the A$-$T initiator in a bulk styrene polymerization at 87 °C) as the unimolecular initiator. The PS macroinitiator had M_n = 18 200 g/mol and PDI = 1.23 and was added at a variety of low concentrations to styrene and polymerized at 87 °C, resulting in production of high MW PS via chain extension.

It is apparent from the PDI values in Table 3 that control of polymerization can be maintained for M_n values at least as high at 114 000 g/mol; however, with low macroinitiator concentrations yielding M_n values in excess of 150 000 g/mol, control of the polymerization is lost. Apparently, at chain extension times of 3.0 h, a macroinitiator concentration of 2.05×10^{-4} mol/L is sufficient so that thermal initiation of homopolymerization does not cause loss of the pseudoliving nature of the polymerization. Substantial reduction of the macroinitiator concentration below that level clearly provides too little of the stable radical to maintain control even with the modest level of thermal initiation of polymerization present at 87 °C.

Figure 3 compares the dependence of M_n obtained in the chain extension studies at 87 °C on the PS macroinitiator concentration to the $-2/3$ power. Over the range of M_n values for which the polymerization remains controlled, the data approximately fit the $-2/3$ power-law expression. Also included in the figure is the datum point for the polymerization yielding an M_n value of 154 000 g/mol, where the PDI indicates the loss of polymerization control. This latter datum point demonstrates approximate agreement with the best fit of the controlled polymerization data to the $M_n \sim C_0^{-2/3}$ relationship.

It is interesting to note that for all concentrations of PS macroinitiator employed here the resulting fractional conversion was nearly constant, ranging from a low of 1.9% to a high of 2.3%. An essentially constant conversion level regardless of unimolecular initiator concentration at identical polymerization times has been observed in other NM-CRP studies, notably by Catala et al.[41] in their A$-$T-based synthesis of PS at 90 °C. Clearly, the combination of eqs 1 and 3 suggests that, at low conversion, fractional conversion should be proportional to $C_0^{1/3}$. The near constancy in conversion level with substantial variation in unimolecular initiator concentration observed here in the case of the PS macroinitiator and in other studies[41] does not disprove the basic kinetic pictures developed by Fischer[37,38] and by Fukuda.[39] Instead, it points to the important role that autopolymerization can play even in circumstances where the NM-CRP polymerizations apparently remain controlled. Autopolymerization may even be relevant at low polymerization temperature conditions afforded through the use of new unimolecular initiators; Drockenmuller and Catala[47] recently reported on the development of a new unimolecular initiator allowing NM-CRP synthesis of PS at 60 °C and found that the thermal polymerization rate was 10% of that ascribed to the controlled radical polymerization.

A final noteworthy point associated with the current study is that it is possible to use the data in Figures 2 and 3 (all at low conversion) along with eq 4 (valid at low conversion) to determine the value of the equilibrium constant associated with the capping/uncapping reactions of the polystyrene/di-*tert*-butyl nitroxide involved the NM-CRP process. Using the slope of each of the plots in Figures 2 and 3 along with the bulk styrene molar concentration and polymerization time, values of $k_p(K_e/k_t)^{1/3}$ can be directly determined. The data associated with the 3.0 h, 87 °C polymerization in Figure 2 yield $k_p(K_e/k_t)^{1/3} = 6.3_8 \times 10^{-4}$ M$^{-1/3}$ s$^{-2/3}$, in excellent agreement with the value of $6.2_4 \times 10^{-4}$ M$^{-1/3}$ s$^{-2/3}$ obtained from the 3.0 h, 87 °C polymerization in Figure 3 and in reasonable agreement with the value of $7.5_7 \times 10^{-4}$ M$^{-1/3}$ s$^{-2/3}$ obtained from the 6.5 h, 87 °C polymerization in Figure 2. By averaging these values and using k_p = 572 M^{-1} s^{-1} obtained from ref 32 and k_t estimated to be 1.0×10^8 M^{-1} s^{-1}, a value of $K_e = 1.6 \times 10^{-10}$ M is obtained at 87 °C. Adjusting for the temperature dependences of k_p and k_t with activation energy values from refs 32 and 48, a value of $K_e = 8.7 \times 10^{-10}$ M is obtained at 97 °C. These values of K_e in the range $10^{-10}-10^{-9}$ M may be seen to be reasonable on the basis of comparison to recently calculated K_e values for other NM-CRP capping/uncapping reactions. In particular, for cleavage of PS/TEMPO, Fukuda et al.[49] have reported that $K_e = 7.8 \times 10^{-12}$ M at 114 °C and 2.1×10^{-11} M at 125 °C, where the growth of the PS chain is known to be slow. In contrast, Drockenmuller and Catala[50] have reported values of (5.1–5.2) × 10^{-10} M for K_e in a 90 °C, NM-CRP synthesis of PS mediated by *N*-β-sulfinyl alkoxyamine, which yields a relatively rapid, controlled growth of PS similar to that found in the present study. A more critical analysis of the appropriate values of K_e associated with our experimental study and other contributing factors, e.g., autopolymerization, not explicitly considered in the analysis here is provided in ref 36.

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