

4-Acetoxy Styrene Nitroxide-Mediated Controlled Radical Polymerization: Comparison with Styrene

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ABSTRACT: The nitroxide-mediated controlled radical polymerization (NM-CRP) of 4-acetoxy styrene with an alkoxyamine was analyzed by a combined experimental and modeling approach. At low nitroxide concentrations, thermal initiation was significant, and control of the polydispersity was poor, as was observed previously for styrene. A continuum model based on the method of moments was used to regress the parameters for the reversible nitroxide uncoupling/coupling reactions (activation energy of uncoupling), thermal initiation (activation energy of initiation), and termination (frequency factor of recombination). The model was able to capture the molecular weight averages and the polydispersity index as a

function of time and the nitroxide concentration qualitatively and quantitatively. Using this mechanistic framework, we developed kinetic Monte Carlo models that allowed the molecular weight distributions to be predicted explicitly in good agreement with experimental data. A comparison of the NM-CRP of 4-acetoxy styrene and styrene is provided to illustrate the effect of the acetoxy substituent. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 740–750, 2010

Key words: kinetics (polym.); living polymerization; computer modeling; polystyrene

INTRODUCTION

Recently, there has been a high demand for multi-component polymeric materials with well-defined microstructures.^{1–3} By controlling chain architecture, one can tailor the physical properties of a material for specific applications. To synthesize such materials, a controlled method of polymerization is necessary to maintain a low polydispersity index (PDI) and, at the same time, to control the molecular weight and composition of a material. A true controlled or living polymerization, such as anionic polymerization, is characterized by the lack of a self-termination reaction; because there is no biradical termination reaction, uniform chain lengths are obtainable.^{4,5} Because chains are initiated and terminated at the same time and there is no randomness

that is associated with biradical termination, the polymer formed is monodisperse. Although these methods have shown the ability to create novel materials,^{6,7} the types of monomers that are polymerizable with anionic polymerization are restricted because of the presence of incompatible substituent groups. This poses significant problems, particularly in copolymerizations where multiple monomer types are polymerized together. Additionally, these syntheses generally require stringent purification methods, which makes these methods impractical compared to free-radical methods.

An alternative route for the synthesis of high-molecular-weight, low-polydispersity polymers is the use of a pseudo-living method. These methods, referred to as a class as *living free-radical polymerizations* (LFRPs), are generally variants of conventional free-radical polymerizations in which biradical termination still exists but is suppressed by the presence of a stable transient radical species.⁸ The stable radical in these processes reversibly terminates propagating radical chains, which reduces the probability of biradical termination and allows uniform chain growth similar to that in living methods. Because of this, the polymerization time is significantly increased but allows chains to propagate at a more uniform rate; this decreases the PDI considerably compared to conventional free-radical polymerization.

Additional Supporting Information may be found in the online version of this article.

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Different types of LFRPs have been shown to successfully synthesize well-defined, near-monodisperse polymers and copolymers in the literature.⁸ These methods include nitroxide-mediated controlled radical polymerization (NM-CRP),^{3,9,10} atom transfer radical polymerization (ATRP),^{7,11} and reverse addition fragmentation chain transfer (RAFT) polymerization.^{12,13} In each of these variants of LFRP, a stable transient radical species reversibly terminates, or caps, chains; this, thereby, prevents them from undergoing biradical termination. The differences among these methods reside in the choice of the stable radical species; in NM-CRP, a stable nitroxide is used, whereas in ATRP, a transition-metal/ligand complex is used, and in RAFT, a thiocarbonylthio agent is used as a reversible chain-transfer agent.

Among these methods, NM-CRP is one of the most widely used for the polymerization of styrenic monomers and is commonly used because of its ability to polymerize numerous types of monomers and its ease of synthesis compared to other methods of LFRP.¹ Most commonly, these syntheses are conducted in a similar manner to conventional free-radical polymerization with the addition of a stable nitroxide radical, such as 2,2,6,6-tetramethyl-1-piperidinyloxy.^{14,15} Typically, these polymerizations must be conducted at relatively high temperatures ($\sim 120^\circ\text{C}$) to allow for sufficient uncoupling of the nitroxide. This is particularly detrimental in the polymerization of styrenic monomers, as it is known that these monomers undergo significant amounts of thermal polymerization at temperatures approaching 100°C and higher. The thermal polymerization of styrene has been studied extensively and is thought to proceed through the two-step mechanism first proposed by Mayo.¹⁶ To reduce the effect of thermal polymerization, it is desirable to use a nitroxide that is capable of uncoupling at lower temperatures to reduce the impact of thermal polymerization. A unimolecular initiator, α -methylstyryl di-*tert*-butyl nitroxide (A-T), has been used to conduct the polymerization of styrene.^{9,17} Upon heating, this initiator forms a propagating alkyl radical and a stable nitroxide radical in a 1 : 1 stoichiometric ratio. In these studies, A-T was shown to successfully control the polymerization of styrene at temperatures below 100°C . Additional studies in our laboratory used mechanistic modeling tools to analyze the effect of side reactions on the production of the high-molecular-weight polymer with this system.¹⁸

We sought to use this unimolecular initiator in conjunction with our mechanistic modeling framework to analyze the NM-CRP of another styrenic monomer, 4-acetoxystyrene, to evaluate the kinetics of its polymerization via NM-CRP and compare its behavior to that of styrene. Although there are few reports regarding the polymerization kinetics of 4-acetoxystyrene in the literature, it is commonly poly-

merized as an intermediate in the formation of poly(4-hydroxystyrene), which is commonly used in photoresists.^{19,20} Additionally, 4-acetoxystyrene has been polymerized with NM-CRP in both homopolymerization and its copolymerization with styrene to form novel copolymers.^{10,21,22} It was observed in these studies that 4-acetoxystyrene exhibited an increased rate of propagation compared to styrene in both the homopolymerization and copolymerization studies. This was later confirmed by the work of Li et al.,²³ who used pulsed-laser polymerization to directly measure the propagation rate coefficient for 4-acetoxystyrene free-radical polymerization. Their findings were consistent with the previous observations that 4-acetoxystyrene propagated at a higher rate compared to styrene, and they accounted for this increase using arguments based on Hammett substituent effects, namely, that the electron-withdrawing character of the acetoxy group accounted for decreased radical stability. They also examined thermal polymerization, and a mechanistic model was used to fit the rate parameters for thermal initiation and termination. It was determined that in addition to a higher rate of propagation, the rate coefficient for 4-acetoxystyrene thermal initiation was higher than that of styrene and the rates of termination were lower than those of styrene within the temperature range studied. In this study, we conducted NM-CRP experiments of 4-acetoxystyrene to quantify the kinetics of the reversible coupling reaction using mechanistic modeling and to compare the coupling kinetics to those of styrene.

In this study, we used two modeling frameworks to analyze 4-acetoxystyrene NM-CRP. The first of these frameworks was based on the method of moments; similar constructs have been used successfully in previous studies in our laboratory to describe various polymerization and depolymerization systems. These models have been able to provide a high level of detail, including conversion and molecular weight averages. However, without assumptions regarding the shape of the distribution, the moment-based models are unable to predict the full molecular weight distribution (MWD). To provide a higher level of detail of the system, models based on a stochastic simulation algorithm have been developed. This methodology, referred to as kinetic Monte Carlo (KMC), has been used to study various catalytic systems and a small number of polymerization systems.²⁴⁻²⁷ Because KMC polymerization models are able to explicitly keep track of chains, size distributions can be generated.

EXPERIMENTAL

We prepared the 4-acetoxystyrene monomer (Sigma-Aldrich, St. Louis, MO) by mixing it with calcium

hydride overnight to remove water, followed by gravity filtration. The monomer was then deinhibited by vacuum distillation to remove phenothiazine. A–T was prepared as described in the literature for styrene NM-CRP.⁹ We carried out the batch polymerization by reacting approximately 200 mg of 4-acetoxystyrene with A–T in 3-mL glass ampules (Wheaton, Millville, NJ) in duplicate. A–T concentrations ranged between 0.00082 and 0.000026 mol/L. To achieve such low concentrations, a dilution series was created from a stock solution. Samples were purged with argon for approximately 2 min and flame-sealed via a propane torch. A Techne SBL-2D fluidized sand bath and a digital temperature controller (Burlington, NJ) were used to maintain isothermal conditions. Polymerization was conducted for 3 or 6.5 h at a temperature of 87°C and for 6.5 h at 97°C over the A–T concentration range specified previously. Reaction vessels were suspended inside the sand at a constant depth and, after the reaction, were quenched in a second sand bath at room temperature. After cooling, the contents of the ampule were extracted in 5 mL of tetrahydrofuran overnight to dissolve the resulting polymer.

For molecular weight values, we prepared the samples by passing them through a 0.2- μm filter using a syringe. A dual-detector size exclusion chromatography (SEC) method was used; refractive-index (RI) and light-scattering (LS) detectors were used in tandem to provide two measures of the MWD for a particular sample. Separation was achieved through the use of four Styragel SEC columns (HR 0.5, 1, 3, and 4). A dual-detector system housed in a Waters (Milford, MA) 2695 Separation Module SEC consisting of a Waters 410 differential refractometer (RI detector) and a Wyatt Instruments Dawn EOS 690-nm laser photometer multiangle LS detector (Santa Barbara, CA) was used. Measurements were conducted at 35°C with an injection volume of 100 μL . The acquisition software for the RI detector was Waters Millennium 3.05.01, and that for the LS detector was Wyatt ASTRA 4.90.07.

The RI detector was calibrated with 10 narrow molecular weight polystyrene standards (840–800,000 Da) to create a universal calibration curve. With Mark–Houwink parameters for 4-acetoxystyrene in tetrahydrofuran of $K = 1.75 \times 10^{-4}$ dL/g and $a = 0.64$, MWDs were obtained from the RI detector. Previous literature reports have questioned the accuracy of RI measurements on poly(4-acetoxystyrene),²¹ so MWDs were also obtained from an LS detector. Because the LS detector molecular weights did not rely on a calibration, they were regarded as primary measurements. The differential index of refraction, dn/dc , where n is the index of refractions and c is concentration, value necessary for these measurements was previously determined as 0.14 mLg⁻¹.²³ Although LS molecular weight data were regarded to

be more exact because they did not rely on a calibration, number-average molecular weights were slightly lower than the true values because of the truncation of the low-molecular-weight tail during integration. To compensate for this effect, the number-average molecular weights used in model fitting were determined with the LS weight-average weights along with PDI data determined by RI measurements.

MODEL DEVELOPMENT

Mechanistic chemistry

The reactions included in the NM-CRP mechanism were based on previous work that studied the NM-CRP of styrene with the A–T initiator.¹⁸ The base reactions included within our modeling framework are shown in Figure 1: (1) initiator dissociation, (2) initiator association, (3) initiator radical addition, (4) chain propagation, (5) nitroxide coupling, (6) nitroxide uncoupling, (7) termination by disproportionation, and (8) termination by combination.

With a mechanistic framework, we determined in our previous work¹⁸ with styrene NM-CRP that two key side reactions compromised the living behavior of the system: thermal polymerization and chain transfer to monomer. Thermal initiation is responsible for the continuous production of radicals during the course of a polymerization. Although chain transfer to monomer was shown to have a minor effect on the molecular weight averages obtained in NM-CRP, it is generally regarded as a fundamental reaction within the free-radical polymerization framework and, therefore, was included. These reactions were included with the base reactions to form a similar mechanism to that used to model styrene NM-CRP. These reactions are shown in Figure 2: (9) thermal radical formation, (10) thermal radical addition, (11) chain transfer to monomer, and (12) monomeric radical addition.

Moment-based model development

To model this system, the method of moments was used to provide a detailed picture of the kinetics and molecular weight dependence on the alkoxyamine concentration. This construct has been used successfully in the modeling of various polymerization and depolymerization systems, and the development of the moment equations has been discussed in detail in the literature.^{18,28,29} The key moment equations are repeated here in the Supporting Information. The reactions were formulated at the mechanistic level, and the rate coefficients were specified on a per event basis in the Arrhenius form [$k = A \exp(-E_a/RT)$, where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature]. A strategy was used to categorize chains by end

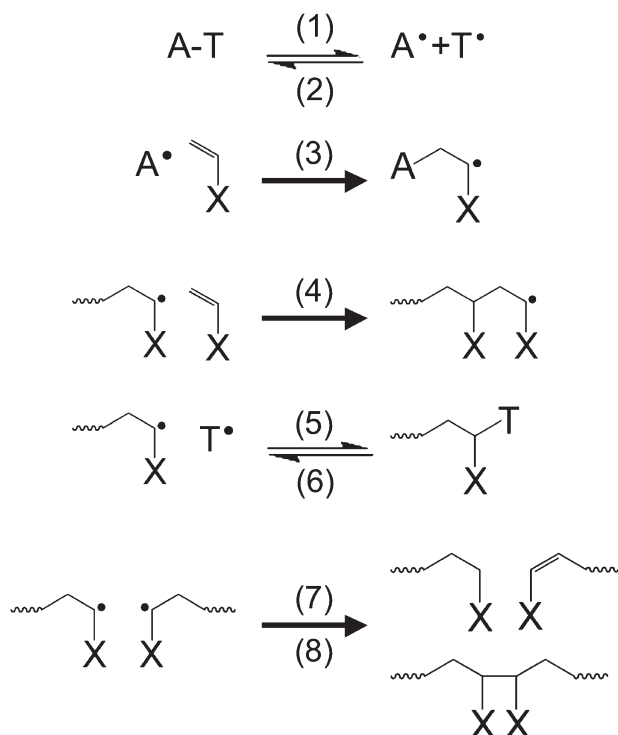


Figure 1 Base reactions included in the 4-acetoxystyrene NM-CRP model.

groups, as shown in Figure 3. These include ends initiated by A derived from A-T, nitroxide capped ends (T), saturated ends (h), unsaturated ends (H), chains initiated by thermal radicals (R), and chains initiated by monomeric radicals (M).

The termination rate coefficients were defined according to the International Union of Pure and Applied Chemistry (IUPAC) preferred equation: $R_t = 2(k_{tc} + k_{td})[P\cdot]^2$, where R_t is the rate of termination, $[P\cdot]$ is the total radical concentration, k_{tc} is the rate coefficient of termination by combination, and k_{td} is the rate coefficient of termination by disproportionation. In our previous study,²³ we assumed that the thermal initiation of 4-acetoxystyrene underwent a two-step reaction similar to that of styrene, in which a dimer was formed through a Diels-Alder reaction, which then reacted with another monomer to form two propagating radicals.^{30,31} It was also assumed that this mechanism could be described with a third-order reaction with respect to the monomer concentration. PERL scripts were used to generate lists of moment equations, which were then compiled in C and solved with the DASSL stiff differential equation solver.³² Parameter fitting was conducted with generalized regression software.³³

KMC model development

KMC models were developed on the basis of the stochastic simulation algorithm first developed by Gil-

lespie.³⁴ Instead of species concentrations, these models track discrete particles in a microscopic-scale homogeneous reaction volume representative of the complete system. Additionally, these models are based on a simple iterative procedure that does not involve the solution of coupled differential equations. The reaction channels shown in Figures 1 and 2 occur on a microscopic basis and occur stochastically on the basis of reaction probabilities:

$$\sum_{v=1}^{\mu-1} P_v < r_1 < \sum_{v=1}^{\mu} P_v \quad (1)$$

where μ is the index of the selected reaction channel, P_v is the probability of the v th reaction channel, and r_1 is a random number uniformly distributed between 0 and 1. The probabilities for each reaction are determined on the basis of its fraction of the total rate of reaction:

$$P_v = \frac{R_v}{\sum_{v=1}^M R_v} \quad (2)$$

where R_v is the stochastic rate of the v th reaction and M is the total number of distinct reactions. The time interval between reactions (τ) is determined as follows:

$$\tau = \frac{1}{\sum_{v=1}^M R_v} \ln\left(\frac{1}{r_2}\right) \quad (3)$$

where r_2 is a second random number uniformly distributed between 0 and 1.

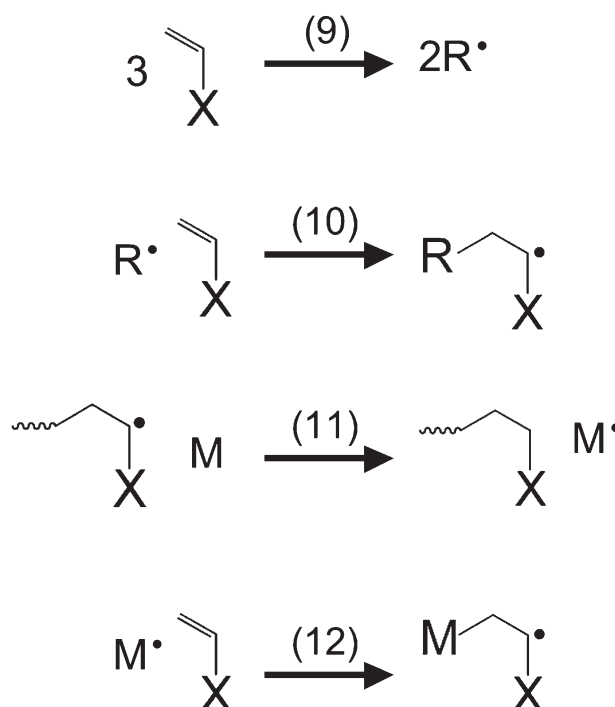


Figure 2 Side reactions included in the NM-CRP model.

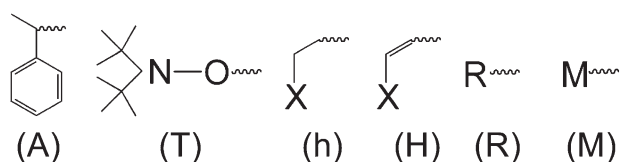


Figure 3 Chain ends tracked in the NM-CRP moment-based model.

Because the reaction rates in KMC are represented discretely, they must be converted from macroscopic values on a per volume basis to stochastic rates on the basis of the total number of molecules within the scaled reaction volume. To accomplish this, macroscopic concentrations need to be converted to the total number of molecules within the scaled volume (V), and rate coefficients must be converted accordingly:

- $k^{\text{MC}} = k^{\text{exp}}$, first-order reactions
- $k^{\text{MC}} = \frac{k^{\text{exp}}}{VN_A}$, second-order reactions between different species
- $k^{\text{MC}} = \frac{2k^{\text{exp}}}{VN_A}$, second-order reactions between same species
- $k^{\text{MC}} = \frac{6k^{\text{exp}}}{(VN_A)^2}$, third-order reactions between same species

where k^{MC} represents a KMC rate coefficient, k^{exp} represents a continuum rate coefficient, and N_A is Avogadro's number.

RESULTS AND DISCUSSION

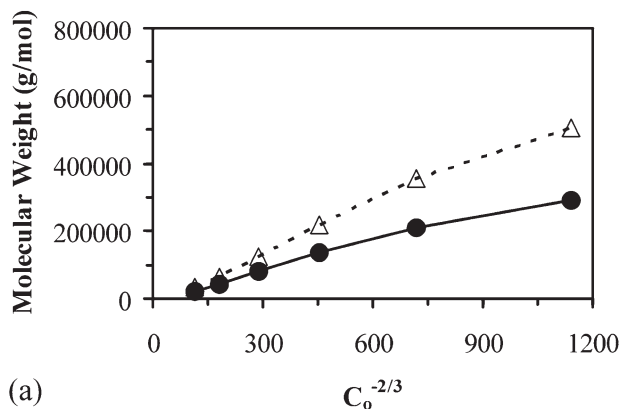
Identification of the governing kinetic parameters: The moment-based model

First, the moment-based model was used to identify the values of key kinetic parameters governing the NM-CRP of 4-acetoxystyrene. The number- and weight-average molecular weights for polymerization at 3 and 6.5 h measured experimentally are plotted against the initial A-T concentration to the $-2/3$ power, as shown in Figure 4. Analogous studies of styrene NM-CRP exhibited the same type of qualitative behavior; in the absence of side reactions, the number-average molecular weight is expected to have a linear dependence on the initial initiator concentration to the $-2/3$ power.^{9,18} Although this was observed for samples with high concentrations of A-T for both reaction times, samples with low initiator concentrations at 3 and 6.5 h exhibited a bendover, after which the molecular weights began to approach a constant value after a threshold initiator concentration was reached. This was previously attributed to the marked presence of thermal initiation; despite lower polymerization temperatures, the NM-CRP of styrene was still susceptible to a loss of

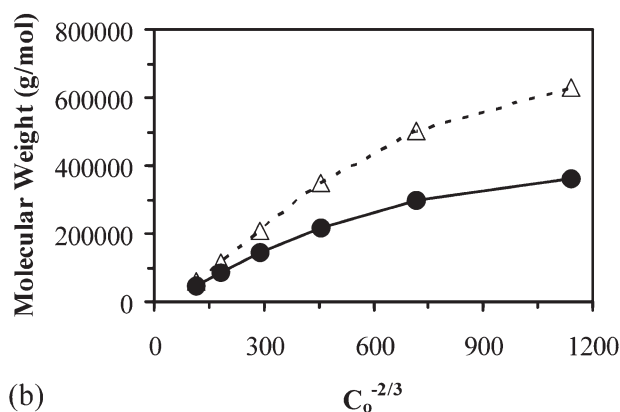
control at these particular conditions, and the same behavior was observed here for 4-acetoxystyrene.

Using these data, we then used our modeling framework to fit the activation energy of uncoupling governing the reversible nitroxide exchange reaction (reaction 6 in Fig. 1), activation energy for thermal initiation (reaction 9 in Fig. 2), and frequency factor for recombination (reaction 8 in Fig. 1). The parameters for other reactions were determined in our previous study involving 4-acetoxystyrene pulsed-laser polymerization and thermal polymerization studies or derived from literature values for styrene. A summary of all of the rate parameters is shown in Table I.

It was assumed, as it was for our previous styrene modeling studies, that no branch formation occurred, that recombination accounted for 85% of the total termination rate, and that the activation



(a)



(b)

Figure 4 Comparison of the model fit and data for 4-acetoxystyrene NM-CRP at 87°C for (a) 3 and (b) 6.5 h: (●) number-average molecular weight (M_n) and (△) weight-average molecular weight (M_w) as a function of the nitroxide concentration (C_0). Parameters for nitroxide uncoupling (activation energy of uncoupling), termination by combination and disproportionation [frequency factor for combination and frequency factor for disproportionation (fixed with disproportionation as 15% of the total termination rate)], and thermal initiation (activation energy of initiation) were fitted. M_w was determined from LS measurements, whereas M_n was determined from RI PDI values. Fitted model results are shown as lines: (—) M_n and (---) M_w .

TABLE I
Kinetic Parameters Used in the 4-Acetoxy styrene NM-CRP Modeling

Reaction	Reaction number in figure 1 or 2	Frequency factor (s^{-1} , $L mol^{-1} s^{-1}$, or $L^2 mol^{-2} s^{-1}$)	Activation energy (kJ/mol)
Initiator uncoupling	1	3.8×10^{14a}	120.0 ^a
Initiator coupling	2	1.65×10^{10b}	6.3 ^c
Initiator radical addition	3	4.97×10^{7d}	32.5 ^d
Thermal initiation	9	1.35×10^{3e}	97.1 ± 1.0^f
Propagation	4, 10, 12	1.79×10^{7e}	28.7 ^e
Nitroxide uncoupling	6	3.8×10^{14a}	123.8 ± 3.5^g
Nitroxide coupling	5	1.65×10^{10b}	6.3 ^h
Chain transfer to monomer	11	2.31×10^{6i}	53.0 ⁱ
Termination by combination	8	$1.07 \pm 0.17 \times 10^{10g}$	6.3 ^c
Termination by disproportionation	7	1.88×10^{9j}	6.3 ^c

All rate coefficients were assumed to be of the Arrhenius form [$k = A \exp(-E_a/RT)$] and were for elementary steps on a per event basis.

^a Styrene uncoupling parameter for di-*tert*-butyl-nitroxide.³⁸ The initiator uncoupling and coupling parameters were based on styrene because A in Figure 1 was a styrene radical.

^b Same value used for styrene.

^c Styrene termination activation energy at reactivity ratio ambient pressure.³⁵

^d Determined with the IUPAC rate constant of propagation for styrene³⁹ with $r_1 = 0.86$ for styrene/4-acetoxy styrene cross-propagation.⁴⁰

^e Determined in the thermal polymerization study of Li et al.²³

^f The fitted value was similar to that determined in the thermal polymerization study of Li et al.²³

^g Fitted in this study.

^h Same value used for initiator coupling.

ⁱ Determined by Hui and Hamielec³¹ for styrene.

^j Fixed at 15% of the total termination rate.

energy for termination was equal to that of styrene, 6.3 kJ/mol. Although we regressed a value of the frequency factor for recombination in our previous study, it was an average value over a broad conversion range that did not necessarily reflect the higher rate coefficients of termination characteristic of low-conversion polymerization³⁵ that was maintained here. Thus, the frequency factor for recombination was allowed to be a parameter. In addition, because the thermal initiation reaction was a sequence of multiple steps and not a single elementary step, the overall activation energy was also included as a parameter because the value regressed at higher temperatures in our previous study may not have been extensible to the lower temperatures studied here.

The results of the model fitting are shown in Figure 4. The model was clearly able to capture the molecular weight values and the polydispersity both qualitatively and quantitatively. To obtain this agreement, the fitted equilibrium constant (K) for uncoupling/coupling was determined to be $2.08 \times 10^{-13} M$ at 87°C, which was an order of magnitude less than that for styrene NM-CRP ($K = 10^{-12} M$). The conversion values studied here were low, so the parameters reported in Table I for the uncoupling/coupling reactions were valid in the absence of any significant diffusion effects that might have been present at high conversion. There was a slight increase in the fitted thermal initiation activation energy, which was determined as 97.1 kJ/mol, com-

pared to the previously fitted value of 90.4 kJ/mol. The fitted values for the termination frequency factors were determined to be 1.07×10^{10} and $1.88 \times 10^9 L mol^{-1} s^{-1}$ for recombination and disproportionation, respectively, which was an increase of a factor of six compared to the average values used previously over wider conversion ranges.

Validation of the kinetic parameters: Extension to higher temperatures and prediction of MWD

To validate the kinetic parameters, we first used the moment-based model to predict the behavior of the 4-acetoxy styrene NM-CRP at a higher temperature, 97°C. The model was able to predict the experimental results with excellent agreement over the entire initiator concentration range, as shown in Figure 5 for a reaction time of 6.5 h. The reaction was clearly less living under these conditions, as the bendover in the molecular weight averages occurred at a higher initiator concentration, and the plateau that was indicative of thermal polymerization was more evident.

We next carried out KMC simulations using the kinetic parameters obtained from the moment-based modeling to predict the full MWD, which could not be attained by the method of moments without making an assumption about the type of distribution.³⁶ In all of the simulation results reported here, a value of 10^{11} monomer molecules was chosen to scale the

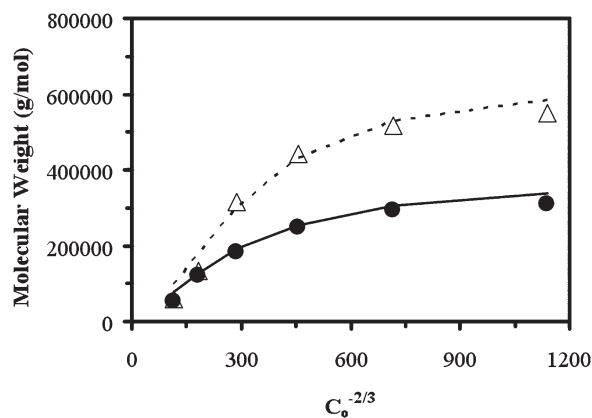


Figure 5 Comparison of the model predictions and experimental data for 4-acetoxystyrene NM-CRP at 97°C for 6.5 h: (●) number-average molecular weight (M_n) and (△) weight-average molecular weight (M_w) as a function of the nitroxide concentration (C_0).

KMC volume. This value was selected on the basis of a series of studies with an increasing number of monomers initially in the reaction system until agreement with the radical concentrations reported by the moment-based model was obtained. KMC simulation predictions of the MWD were compared against the experimental results obtained via SEC-LS measurements for a reaction time of 6.5 h at different initiator concentrations and a temperature of 87°C. The simulation results provided excellent agreement with the experimental results, as shown in Figure 6. The KMC simulations were able to capture very well the increase in the polydispersity of the MWD as the initiator concentration decreased.

Comparison of the livingness of 4-acetoxystyrene and styrene

With a validated set of kinetic parameters in hand, we next compared the behavior of 4-acetoxystyrene and styrene. To assess the livingness of 4-acetoxystyrene, we first examined the fractions and molecular weight values of different types of chains output by the model, as shown in Figure 7 for 6.5 h of polymerization at 87°C across a broad range of initiator concentrations. These figures are analogous to those reported for styrene by Kruse et al.¹⁸ in Figures 8 and 12. At a high initiator concentration, shown in Figure 7(a), the system was composed nearly entirely of capped chains initiated by A-T; this indicated that the majority of the chains were initiated at the onset of the polymerization and were well controlled, as evidenced by the trends in the molecular weight averages. At an intermediate initiator concentration, shown in Figure 7(b), the majority of chains were capped but at a lower degree of livingness compared to those shown in Figure 7(a) as the fraction of dead polymer increased significantly with a corresponding decrease in the frac-

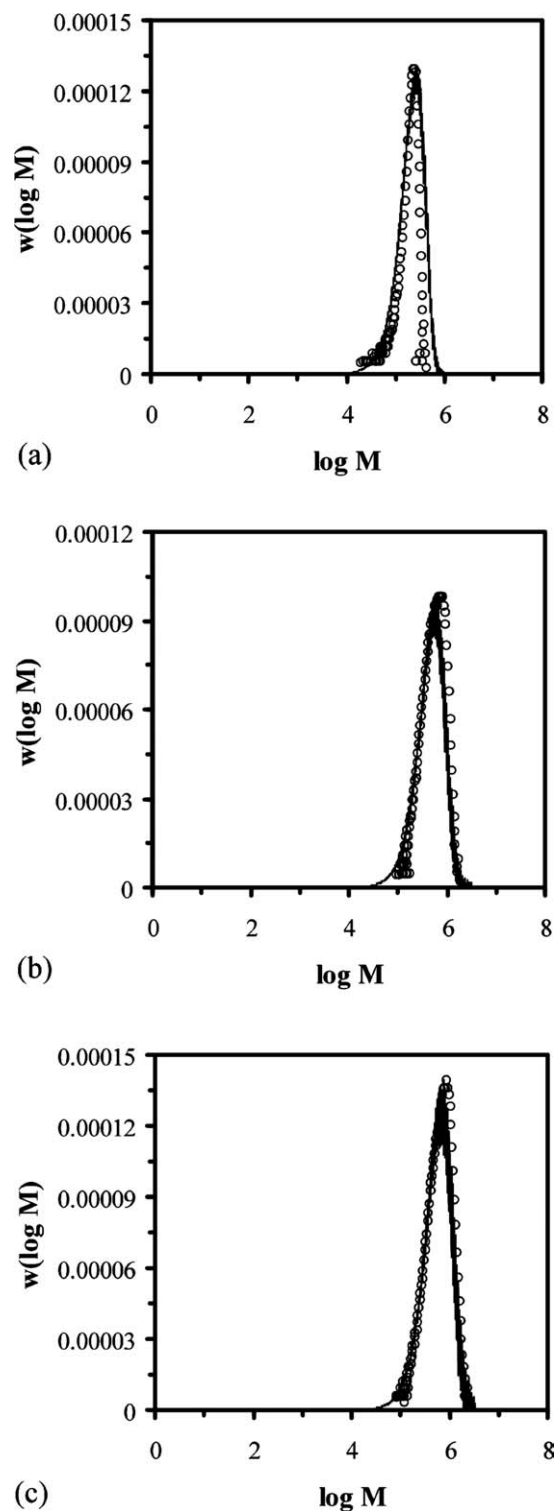


Figure 6 Comparison of predictions by KMC simulations and experimental MWDs of 4-acetoxystyrene NM-CRP at 87°C for 6.5 h with initiator (A-T) concentrations of (a) 0.000205 (PDI = 1.44), (b) 0.000052 (PDI = 1.87), and (c) 0.000026 mol/L (PDI = 1.84). Experimental results determined by SEC-LS are shown as symbols, and KMC results are shown as lines. w represents weight and M is molecular weight.

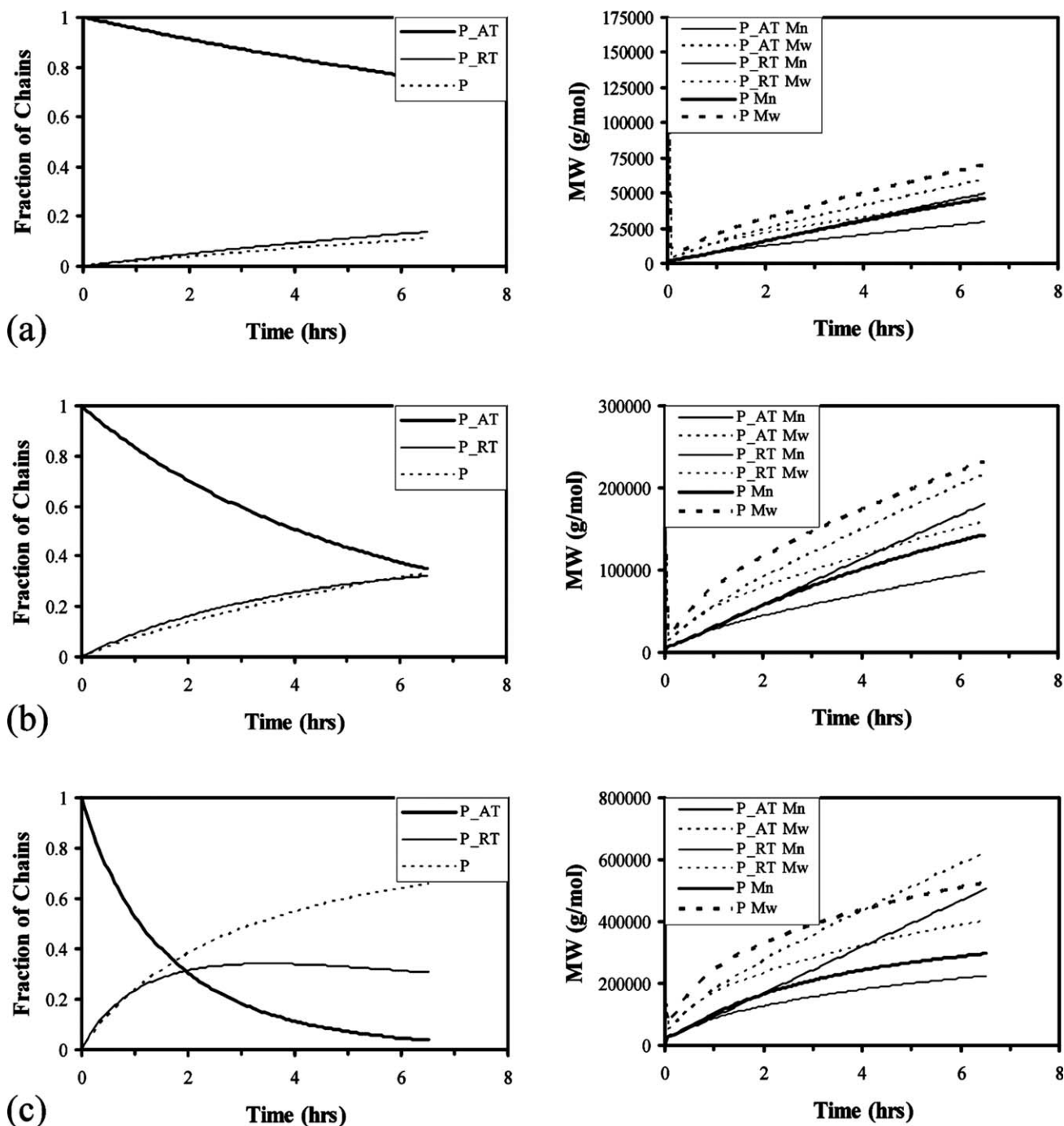


Figure 7 Chain fractions and molecular weight averages for polymerizations at 87°C for 6.5 h with initiator concentrations of (a) 0.00082, (b) 0.000205, and (c) 0.000052 mol/L. P_AT denotes capped chains initiated by the alkoxyamine, P_RT denotes capped chains initiated by thermal radicals, and P designates the aggregate dead polymer. MW is the molecular weight.

tion of capped chains. Although the A-T fraction exhibited control over molecular weight, this chain fraction was gradually replaced with high-polydispersity, dead polymer over the course of the reaction. At an initiator concentration of 0.000052 mol/L, which was significantly lower than typically used in NM-CRP, the polymerization was essentially uncontrolled from the onset. Although the A-T chains exhibited control, as shown in Figure 7(c), the system

possessed a low degree of livingness as high-polydispersity, dead polymer constituted the majority of the chains in the system.

The KMC simulations also allowed the MWDs of the chain fractions shown in Figure 7 to be predicted. These are plotted in Figure 8. As shown in Figure 8(a), at a high initiator concentration of 0.00082 mol/L, the A-T chains composed the majority of the chains, consistent with a high degree of

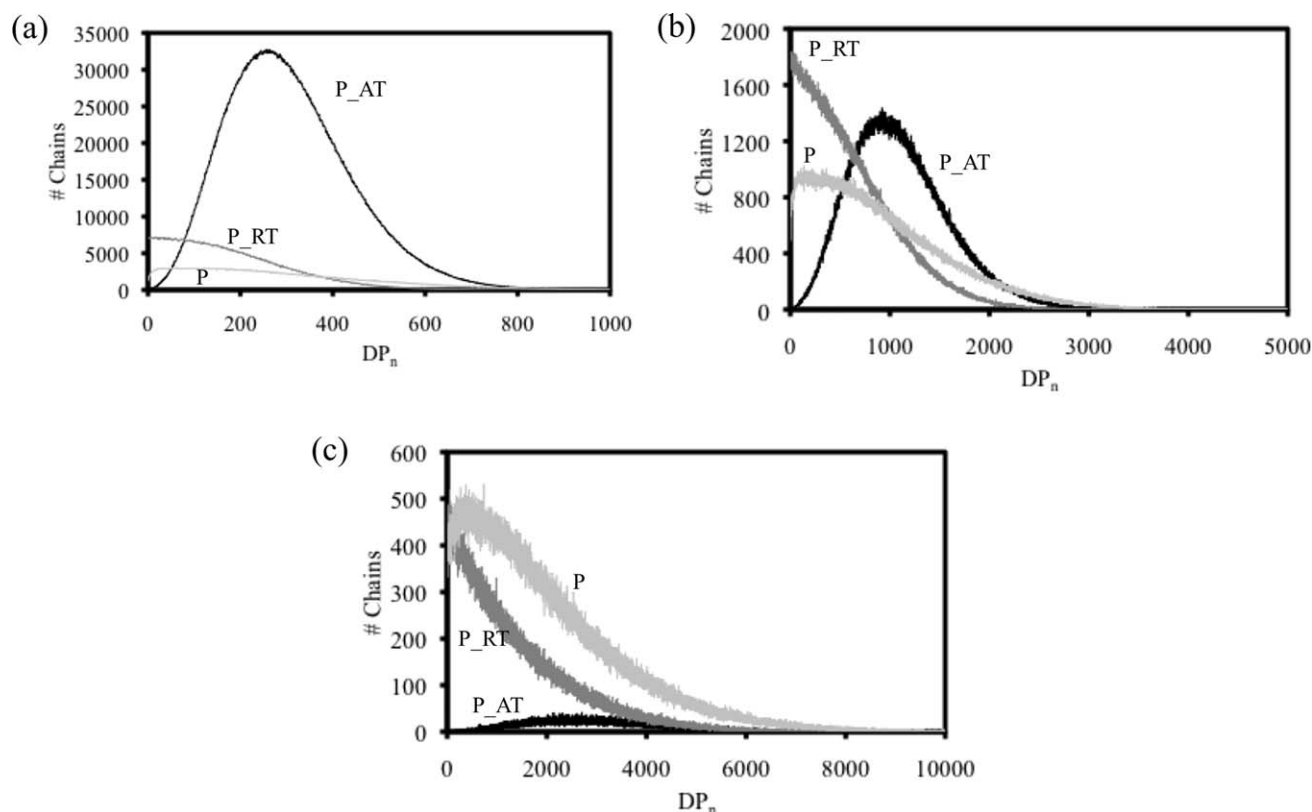


Figure 8 MWDs for chain fractions of polymerization at 87°C for 6.5 h with initiator concentrations of (a) 0.00082, (b) 0.000205, and (c) 0.000052 mol/L. P_AT denotes capped chains initiated by the alkoxyamine, P_RT denotes capped chains initiated by thermal radicals, and P designates the aggregate dead polymer. DP_n is the number-average degree of polymerization.

livingness. Compared to the other chains, the distribution of A–T chains exhibited a peak as these chains were initiated at the onset of polymerization. In contrast, the capped chains initiated thermally, R–T, and dead polymer chains were continuously generated over the course of polymerization. As the initiator concentration decreased, the A–T chains existed as a measurable fraction, as shown in Figure 8(b,c). However, the systems were dominated by dead polymer and R–T chains, and the resulting overall MWDs grew broader, as revealed in Figure 6.

The livingness of 4-acetoxystyrene was directly compared to styrene at the same conditions, as shown in Figure 9. A comparison of 4-acetoxystyrene and styrene NM-CRP at 6.5 h with a moderate initiator concentration of 0.000205 mol/L indicated that 4-acetoxystyrene possessed a higher fraction of living chains compared to styrene. Under these reaction conditions, styrene lost control at about halfway through the polymerization, whereas 4-acetoxystyrene was able to maintain control throughout the polymerization with a decreasing fraction of capped chains. The slight increase in the activation energy for the uncapping reaction for 4-acetoxystyrene compared to styrene equated to a threefold decrease in

the value of the dissociation rate constant. This accounted for a significant difference in the livingness between the two systems, as 4-acetoxystyrene chains remained capped to a more significant extent compared to styrene over the course of polymerization and exhibited a higher degree of control over a longer polymerization time. Although very elegant multiparameter correlations exist to predict the combined effect of polar, steric, and stabilization effects in alkoxyamine C–ON bond homolysis,³⁷ the quantities that are necessary to use these correlations were not all available for the 4-acetoxy substituent. Our experimental results offer an interesting target for researchers who are interested in further validating or developing correlations for the bond strengths of nitroxides.

CONCLUSIONS

Using a mechanistic modeling framework in conjunction with experimental studies, we analyzed the bulk NM-CRP of 4-acetoxystyrene. Using a construct based on the method of moments that was previously used in our study of styrene NM-CRP, we formulated a mechanistic model that contained base reactions, including propagation, termination, and

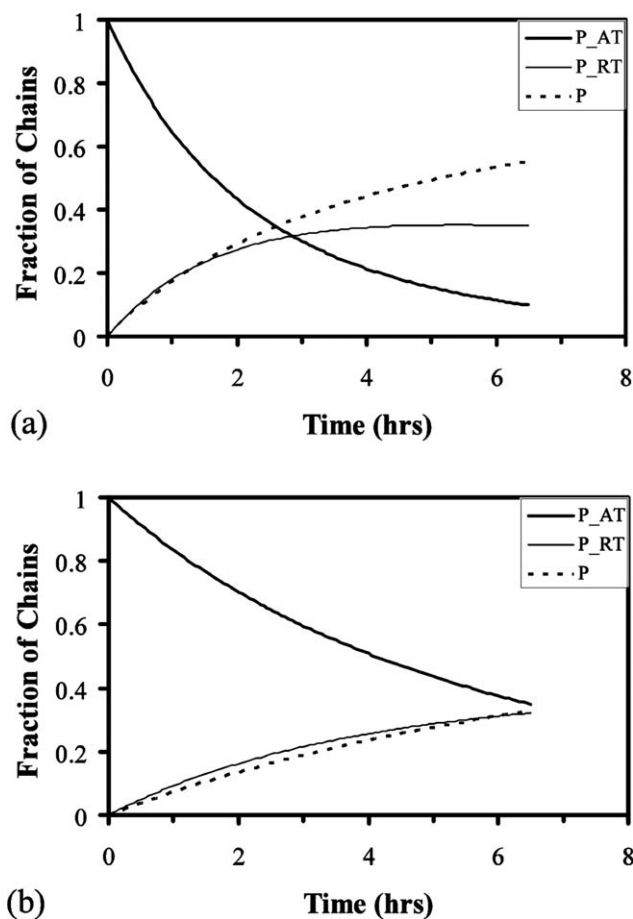


Figure 9 Comparison of chain fractions for (a) styrene and (b) 4-acetoxystyrene with an initiator concentration of 0.000205 mol/L after 6.5 h of polymerization at 87°C.

nitroxide coupling, and side reactions of thermal initiation and chain transfer to monomer. With this model and the parameters used in a previous study of 4-acetoxystyrene thermal polymerization and with the fitting of a parameter for the nitroxide uncoupling reaction, the activation energy for thermal initiation, and the frequency factor for recombination, the model was able to capture the experimental data extremely well. KMC simulations were also used to examine the NM-CRP system in even greater detail. KMC simulations were carried out that used 10^{11} monomers, and the simulated MWDs were compared to the experimental distributions produced via SEC-LS; and accurate predictions were obtained.

The ability of the modeling approach used here to provide insight into detailed characteristics of the polymer chains was aptly demonstrated by analysis of the fractions of chains of different types and their respective molecular weights and MWDs in detail. Up to intermediate conversions, the system remained controlled, and the majority of the chains were capped, initiated by A at the onset of polymerization, and maintained a low polydispersity throughout the course of the reaction. Only at the

lower initiator concentrations did the system lose control and approach the behavior of a pure thermally initiated system in which the chains were predominantly terminated chains. Additionally, the model was used to quantify the livingness of 4-acetoxystyrene NM-CRP compared to styrene. An order of magnitude decrease in the equilibrium constant for 4-acetoxystyrene coupling compared to styrene on the basis of a higher activation energy for uncoupling accounted for a significant increase in the livingness of the system. For similar reaction conditions, 4-acetoxystyrene polymerization remained controlled throughout the entire time range, whereas styrene remained controlled for approximately half.

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