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Kinetics of Nitroxide Mediated Radical Polymerization of Styrene with Unimolecular Initiators

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Summary: This study examined the kinetics of nitroxide-mediated radical polymerization of styrene with unimolecular (alkoxyamine) initiators. Control of polymerization rate and polymer molecular weight in unimolecular nitroxide-mediated radical polymerization was studied by looking at the effects of the three main factors: initiator concentration, temperature, and initiator molecular weight on polymerization rate, molecular weight and polydispersity. In addition, the behavior of the unimolecular initiating systems was compared to that of the corresponding bimolecular system. The effective TEMPO concentration and degree of self-initiation of styrene were proved to be significant in dictating magnitudes of molecular weight averages and widths of molecular weight distribution.

Keywords: alkoxyamine; controlled radical; kinetics; polymerization; styrene

Introduction

Controlled radical polymerization (CRP) has attracted much attention over the last two decades. This has in large part been due to the fact that it has allowed a high degree of flexibility in producing polymers with controlled architectures because of its applicability to a wide range of monomer types with varying functional groups. The different types of CRP may be used in varying reaction media, and under appropriate reaction conditions lead to good control over the macromolecular structures.[1] This has made CRP an effective methodology in the development of polymers for a variety of applications in fields such as nano-technology and bio-materials.[2,3]

Nitroxide-mediated radical polymerization (NMRP) is one of the most attractive CRP techniques. It stands out from other CRP techniques because of the relative simplicity of its mechanism and the ease of purifying reagents. Based on the different synthetic strategies, NMRP can be addressed using two types of initiation methods: ‘‘unimolecular’’ and ‘‘bimolecular’’. In unimolecular NMRP, the propagating radicals form primarily from decomposition of a preformed alkoxyamine at elevated temperature. In bimolecular NMRP, the radicals are generated by the decomposition of a conventional initiator in the presence of monomer and nitroxyl radical. The conventional initiator radical produced from thermal decomposition of the initiator reacts with monomer and the styryl radical formed then reacts with nitroxyl radicals leading to in-situ formation of alkoxyamine, which then becomes the core for the NMRP mechanism.[4]

There is a reasonable understanding of unimolecular initiator systems in terms of mechanism, and several kinetic models have been developed.[5–10] However, most of the prior experimental studies have focused on polymerization at relatively

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low monomer conversions. At high monomer conversion levels issues that complicate the analysis may arise and thus make interpretation of results less straightforward. For example, in NMRP of styrene, self-initiation of styrene is important for maintaining reasonable conversion rates, as the radicals produced balance those lost through termination and this maintains the active radical concentration at useful levels. At high conversion, this effect tails off because of the reduction of monomer concentration. There is little information to relate how this affects the maximum conversion levels possible for different combinations of reaction variables. Therefore, a primary objective of the work described in this paper was to extend the understanding of the unimolecular system over the whole conversion range.

In addition, detailed experimental studies regarding the effect of varying reaction conditions have not been carried out. In order to utilize CRP to make useful materials, proper selection of reaction conditions is needed to ensure reliable control over the polymerization process and hence the properties of resulting polymers. Therefore, the second objective of this work was to investigate the effects of reaction variables on a unimolecular system, which will in turn be used to refine predictive kinetic models.[8,10]

Previous studies[11] have indicated certain advantages of unimolecular systems over the corresponding bimolecular systems at low conversion, such as comparable polymerization rate, more predictable molecular weight and narrower molecular weight distributions. This needed to be confirmed and other conflicting results between bimolecular and unimolecular initiators needed to be reconciled.

Experimental Part

Materials

Styrene (99%) and TEMPO (98%) were purchased from Aldrich. Styrene was washed three times with a 10 w/v% sodium hydroxide solution and three times with distilled water, dried over calcium chloride and distilled under vacuum just prior to use. Benzoyl peroxide (BPO) (98.5%) was obtained from Elf Atochem. Both TEMPO and BPO were used as received without further purification. Tetrahydrofuran (HPLC grade) was purchased from EMD Chemicals. Ethanol, dichloromethane and acetone were obtained from VWR. All the solvents were used as received.

Preparation of Unimolecular Initiator

TEMPO (0.1 mol/l) was dissolved in styrene (120 mL) in a flask. The solution was then degassed by bubbling N_2 through it for about 1 hour and then heated to 95 °C over a period of about 25 mins (oil bath temperature) while maintaining an N_2 atmosphere. A solution of benzoyl peroxide (molar ratio of TEMPO/BPO = 1.2) in styrene (40 mL) was made and degassed by bubbling N_2 through it at room temperature. The degassed BPO solution was added dropwise into the TEMPO/styrene solution over a period of 20 min, which gave a pale yellow solution. The oil bath was maintained at 95 °C for about 1h, and then the reaction flask was removed from the oil bath. The bath temperature was then increased to 125 °C, and once the temperature stablized, the flask was returned to the oil bath. The reaction solution was maintained at 125 °C for a further 3.5 hours. The solution was cooled to room temperature and then concentrated by rotary evaporator ($T = 35\,°C$, $P = 1$ mbar). Subsequently, the residue was dissolved in the minimum amount of methylene chloride. This product was precipitated dropwise from an excess of ethanol (the volume ratio of product solution to ethanol was 1:10). The mixture was stirred vigorously during precipitation. The precipitate was then separated by filtration. Dissolving-precipitation-filtration steps were repeated several times until the product appeared ivory colored. Then the purified product was thoroughly dried in a vacuum oven ($P = 27$ Inches Hg vacuum) at 65 °C. Yield was then determined gravimetrically by comparing the product mass to the initial reagent amount. Molecular weight was determined by size exclusion chromatography.

Synthesis of Polystyrene

Polymerizations were completed in borosilicate glass ampoules (capacity ~4 ml). Reagents were weighed, mixed and 1-2 ml aliquots were pipetted into ampoules. Ampoules were then degassed by several vacuum-freeze-thaw cycles, sealed under vacuum and then immersed in a silicone oil bath at a certain temperature. Ampoules were removed at selected time intervals to ensure a well-defined conversion versus time plot. Once removed from the bath, the ampoules were quenched in liquid nitrogen to stop the polymerization. Ampoules were then thawed at ambient temperature over about 5 minutes (per ampoule), weighed, and opened. The contents were dissolved in dichloromethane, and poured into a flask containing ethanol to precipitate the polymer. The polymer samples were air-dried to remove the bulk of the volatiles and then vacuum-dried at 65 °C until a constant weight was reached.

Characterization

Monomer conversion was determined by gravimetry (the mass ratio of the isolated polymer to the monomer feed). In the calculations, the mass of initiator was subtracted from both that of the total monomer feed and the mass of final polymer residue. Average molecular weights and polydispersity (PDI) were obtained by size exclusion chromatography (SEC) which used tetrahydrofuran (THF) as the mobile phase. The GPC was equipped with three PLgel 10 μm MIXED-B columns (Polymer Laboratories Inc.) and a multi-detector system (Viscotek TDA 302): refractive index (RI), low angle laser light scattering (LALLS) and right angle laser light scattering (RALLS), as well as an intrinsic viscosity detector (IV-DP viscometer differential pressure). The molecular weights were determined by multi-detector calibration using narrow molecular weight distribution poly(styrene) standards and Viscotek Omnisec 3.2 software. Mole fractions of polymer with respect to retention volume in GPC samples were obtained as derived data from the molecular weight analysis by the Omnisec 3.2 software.

Factorial Design

In order to obtain a better understanding of how the kinetic behavior was affected by reaction variables, three factors (Temperature (T), Initiator concentration [I] and initiator molecular weight (Mn(I))) at two levels of each factor were studied. The details of factor levels examined are summarized in Table 1.

Results and Discussion

Effect of Initiator Concentration

The effect of initiator concentration on the polymerization rate (at 140 °C, initiator $M_n \approx 2000$ g/mol) is illustrated in Figure 1.

As can be seen, below 65–75% conversion, the polymerization rates using two initiator concentrations can not be distinguished. Above 75% conversion, it can be seen from Figure 1 that the lower initiator concentration led to a slightly higher polymerization rate and a higher final monomer conversion level. It was found in the studies overall that first order reaction kinetics were followed (indicated by linear ($\ln[M]_o/M$ vs time plots) up to about 70% monomer conversion. Above that level there was a tail off in reaction rates, the extent of which depended on the level of initiator added. This can be explained by the fact that as polymer concentration increases, the radical con-

Table 1.
Summary of factor levels in experiments.

	Factor Levels		
	−	0	+
T(°C)	120	130	140
[I] (mol/l)	0.030	0.040	0.050
M_n(I) (g/mol)	≈2000	≈3000	≈6000

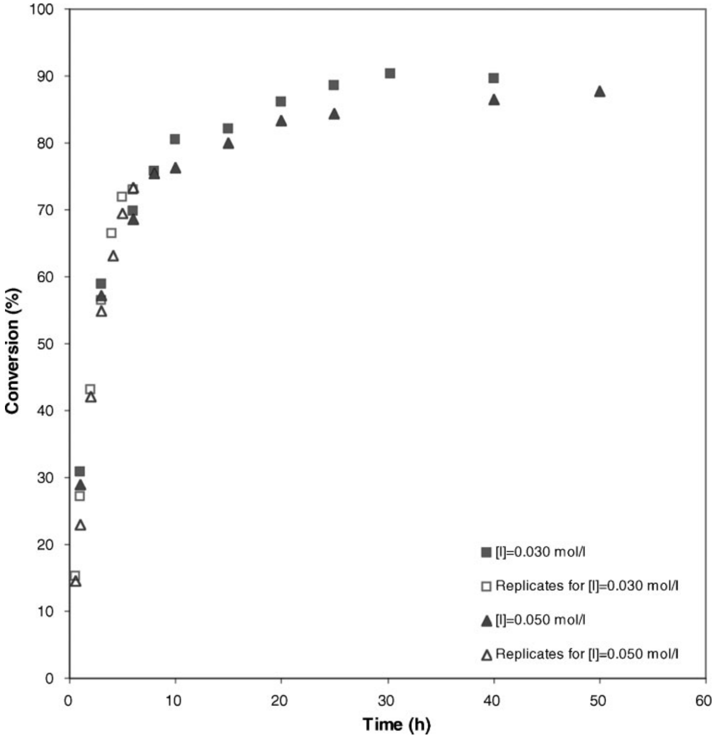

Figure 1.
Conversion vs. time plot, effect of initiator concentration, T = 140°, $M_n(I) \approx 2000$ g/mol.

centrations drop because of termination to form dead polymer chains. Initially this is balanced by radical formation through thermal initiation of styrene but as monomer is consumed the degree of new radical production drops, which would then lead to the drop in radical concentration and so it would be expected that true first order kinetics would not be followed for the whole reaction.

It can also be seen that the tail off in rate was more marked for cases where the higher initiator concentration was used. Consider the fact that in the overall mechanism the propagation reaction competes for radicals with the associative reaction (equilibrium step) (Scheme 1).

$$P_n * + [M] \xrightarrow{k_p} P_{n+1} *$$

$$P * + NO * \xleftrightarrow{K} P - ON$$

Scheme 1.
Main reactions of P^* in the NMRP mechanism.

The rates of the two main reactions involving radicals are the rate of propagation (1) and rate of deactivation (2).

$$R_p = k_p[P^*][M] \tag{1}$$

$$R_d = k_d[P^*][NO^*] \tag{2}$$

Due to the consumption of propagating chains by termination, $[P^*]$ drops as polymerization proceeds. Correspondingly, the equilibrium condition must be maintained and so TEMPO builds up ($[NO^*]$ increases). During the course of reaction [M] drops, and this reduces R_p and the rate of radical production from thermal initiation. Therefore as reaction proceeds, the relative magnitude of R_d increases with respect to R_p. Eventually the concentrations of reacting species will reach a level where there is no measurable propagation because the deactivation reaction will dominate. If we have a higher level of $[NO^*]$ at the start of the reaction, the point at which polymerization "ceases" should be lower with respect to fractional conversion of monomer because the associative reaction will be even more favored relative to propagation. In such a situation, a unimolecular system with higher effective TEMPO concentration would be expected to have a lower polymerization rate at high monomer conversion levels, exactly as confirmed by Figure 1.

Figure 2 shows number and weight average molecular weights, M_n and M_w, of polymer produced using different concentrations of initiator for reactions at 120 °C and 140 °C with the lower initiator molecular weight (Note that the average molecular weights displayed in the figures in this paper are those for the polymer formed during reaction, i.e. they are the measured values for samples, from GPC measurements, minus the molecular weight averages of the initiator). It is evident that M_n increases linearly with conversion. This indicates that the experiment approached an ideal situation in CRP where the initiation was fast and the termination was minimized.

At the temperatures studied, it was noted that the molecular weights obtained for the polymer products were lower for the higher initiator concentrations (0.050 mol/l). The inverse relationship between M_n of polymer formed and initiator concentration has been noted previously and in ideal CRP, the relationship shown in Equation 3 should be followed.[1]

$$M_n = \frac{[M]_0 - [M]_t}{[I]_0} \times M_0 \tag{3}$$

M_n is the number average molecular weight of polymer, $[M]_0$ is monomer concentration at time $t = 0$, $[M]_t$ is monomer concentration at time t, $[I]_0$ is initiator concentration at time $t = 0$, and M_0 is the molecular weight of the monomer unit.

A comparison was carried out between the experimental molecular weight data, obtained from GPC analysis, and the theoretical values for molecular weight, calculated by Eq. 3. Results for selected experiments are presented in Figure 3.

For data collected from experiments carried out at 120 °C, the ratio (R) of the theoretical molecular weight to experimental molecular weight was only slightly larger than 1 (e.g., for the cases in Figure 3, when $M_n(I) \approx 2000$ g/mol, $R = 1.1$ and for $M_n(I) \approx 6200$ g/mol, $R = 1.01$).

A likely reason for the deviation from unity may be due to the fact that it is assumed in the calculation of [I] that all molecules in the initiator batch will be capped with a nitroxide. In reality this is not to be expected since some of the batch will be dead chains formed by normal radical chain termination in the synthesis of the initiator and so the true concentration of initiator molecules will be less. Significant deviations from ideal molecular weight development trends with respect to higher levels of conversion were seen for samples obtained from the experiments at 140 °C (see Figure 3). This is likely because of a higher degree of styrene self-initiation (see below for a more detailed explanation).

Effect of Temperature

Radical polymerization processes are known to be sensitive to temperature, and in most cases, an increase in temperature will increase polymerization rate. This was observed for this work with the unimolecular initiators. Figure 4 shows the effect of temperature on polymerization rate in the presence of a low molecular weight initiator ($M_n \approx 2000$ g/mol). As shown, at higher temperature, the polymerization rate is significantly higher.

If we consider the general kinetic details in NMRP, the reversible activation process gives

$$K = \frac{k_a}{k_d} = \frac{[NO^*][P^*]}{[P-ON]} \tag{4}$$

where K is the equilibrium constant, k_d and k_a are the deactivation and activation rate constants, respectively, $[P^*]$ is propagating radical concentration, $[X^*]$ is nitroxyl radical concentration, and [P-X] is the capped polymer radical concentration.

Polymerization rate is determined by the propagation rate constant k_p and the

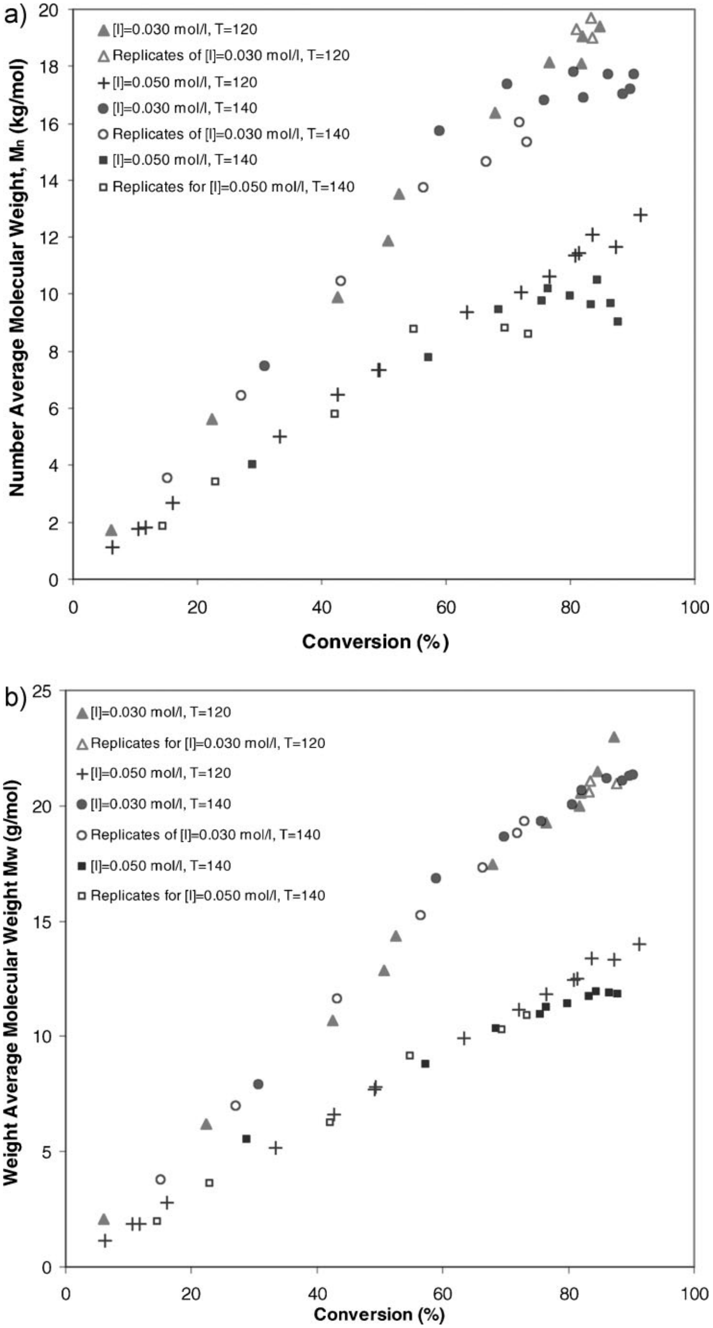

Figure 2.

Effect of initiator concentration and temperature, (a) M_n vs. conversion; (b) M_w vs. conversion, $M_n(I) \approx 2000$ g/mol.

active radical concentration (as described in Eq. (1)). Increasing temperature will increase the propagation rate constant (k_p). In addition, dissociation of C–ON bond is an endothermic process. As a result, increase in temperature will enhance the rate of dissociation of C–ON relative to that of the associative reaction, namely, K

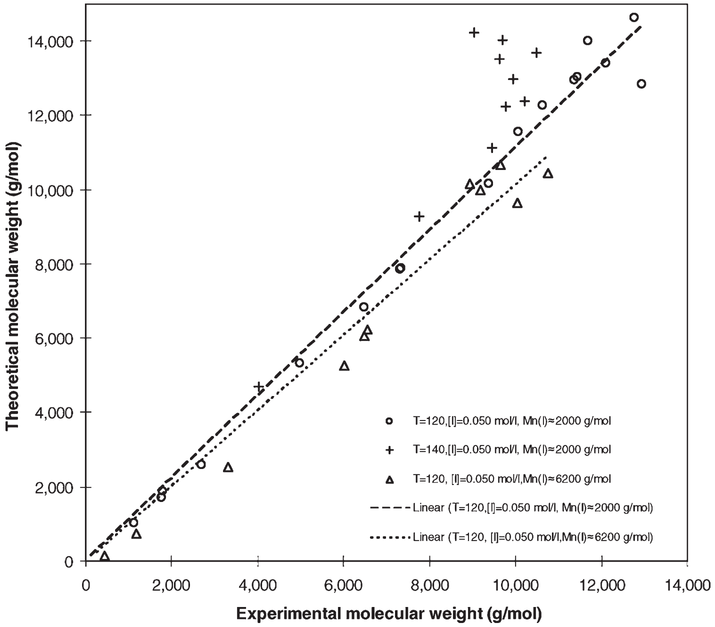

Figure 3.
Comparison of theoretical and measured molecular weights of polymers.

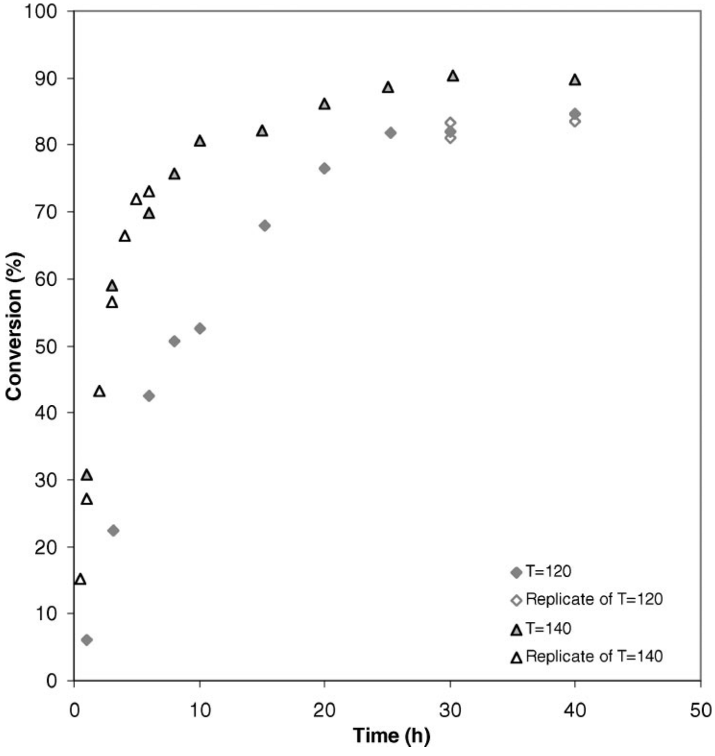

Figure 4.
Conversion vs. time plot, effect of temperature, $M_n(I) \approx 2000$ g/mol, $[I]_o = 0.030$ mol/l.

will increase. Since k_p increases and an increase in K will lead to higher $[P^*]$, the overall result of increased temperature is to increase the polymerization rate.

The effect of temperature on molecular weight development can be seen in Figure 2. It is apparent that, for a given initiator concentration, over much of the conversion range, temperature does not have a significant effect on molecular weight. The fact that similar molecular weights are obtained at different temperature levels can be explained by relating to the concept of "run length per activation cycle (RLPAC)[12,13]" (Eq. 5).

$$RLPAC = \frac{R_p}{R_d} = \frac{k_p[M][P^*]}{k_d[X^*][P^*]} = \frac{k_p[M]}{k_d[X^*]} \qquad (5)$$

The number of monomer units added to the polymer chain within a certain period depends on the ratio of rate of propagation to deactivation. If deactivation is faster, then fewer monomer units can be added to the polymer chain in a given time period. Increasing temperature not only increases the propagation rate (k_p increases), but also increases the deactivation rate (both k_d and $[X^*]$ increase). As a result, the ratio of R_p/R_d will not show a significant change if the changes in the competing factors balance. This presumably explains the slight effect of temperature on molecular weight as observed in the experiments for monomer conversion levels up to about 60%.

A notable plateau in M_n values with respect to monomer conversion (while M_w increased with conversion) was observed for higher temperature above 60% conversion. As can be seen in Figure 2, below 60% conversion, temperature had no effect on the trends in M_n vs. conversion but above 70% conversion, the results from the higher temperature showed a plateau in M_n values with respect to increasing conversion. In contrast, M_w values for given levels of conversion at the two temperatures increased with conversion through the whole range. A similar observation has been made by an earlier study for the bimolecular initiator system[12].

The reasons for this can be ascertained by comparing data obtained from GPC results for normalized mole fraction vs. retention volume at different conversion levels for both temperatures, as shown in Figures 5 and 6.

At both temperatures, the peaks in the traces were observed to shift to higher molecular weight (lower retention volume) with increasing conversion, showing that the polymer chains are growing steadily. The differences in the low molecular weight tails (high retention volume) of the derived data from GPC traces at the two temperatures represent the reason for the differences in number average MW trends. It can be seen that the mole fractions of low MW chains are larger for the polymer made at the higher temperature, which indicated that a higher proportion of low molecular weight oligomers was formed at 140 °C. The probable reason for the higher proportion of oligomeric species in products of reaction at 140 °C stems from the fact that self-initiation is faster at higher temperatures. A higher mole fraction of low MW species likely balances any increase in the peak MW and this causes the leveling off in M_n. In this situation, the mass of the low molecular fractions would still be low relative to the total mass of polymer and so it would have less effect on the incremental increases for M_w, as is seen in the results of Figures 2, 5 and 6. This subsequently leads to an increasing polydispersity with conversion at the higher temperature.

Effect of Initiator Molecular Weight

Initiator molecular weight was studied as another experimental factor in order to assess if variation in the size of initiator molecule would lead to any unusual kinetic behavior. Figure 7 shows conversion vs. time data for 120 °C using two initiators with different molecular weights at a concentration of 0.030 mol/L.

As illustrated, there were no significant differences in the conversion vs time profiles for the reactions using the different initiators at the same concentration. This

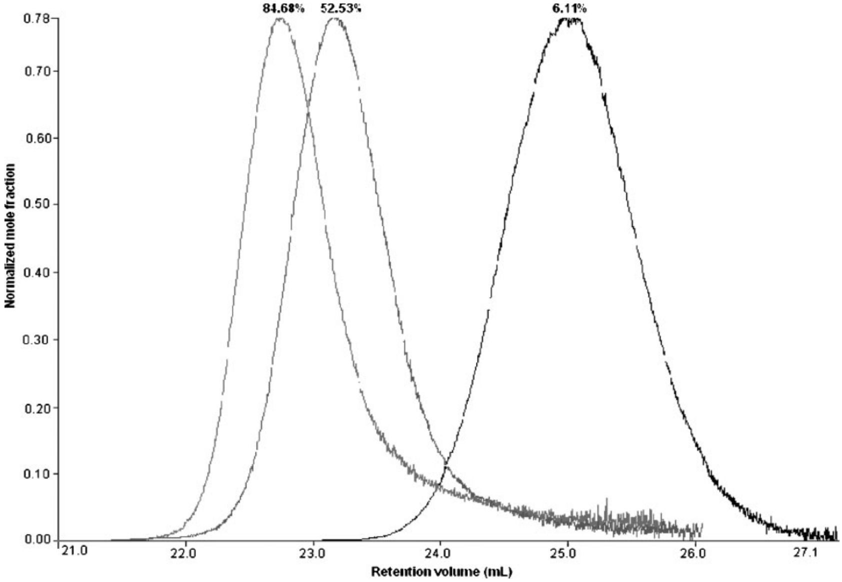

Figure 5.
Normalized mole fraction vs. retention volume, T = 120°, $M_n(I) \approx 2000$ g/mol, [I] = 0.030 mol/l

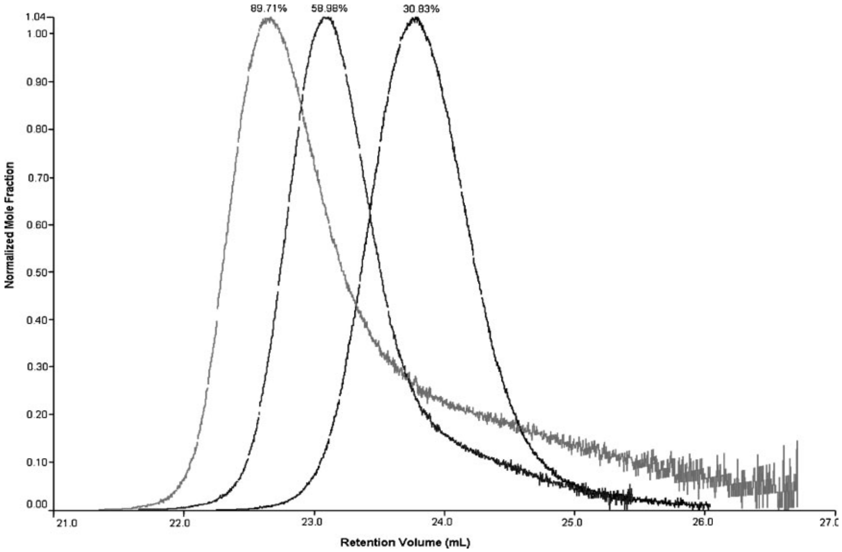

Figure 6.
Normalized mole fraction vs. retention volume, T = 140°, $M_n(I) \approx 2000$ g/mol, [I] = 0.030 mol/l

was despite the fact that for a given batch of reaction solution, higher molecular weight (MW) initiator will take up a larger proportion in the initial mixture volume. Therefore, in order to prepare a mixture with the same initiator concentration, the amount of monomer initially needed would be less for the solutions with the higher MW initiator. For example, in the experiments illustrated, the initial monomer concentration in the mixture with the higher MW initiator is 27% lower than that in the

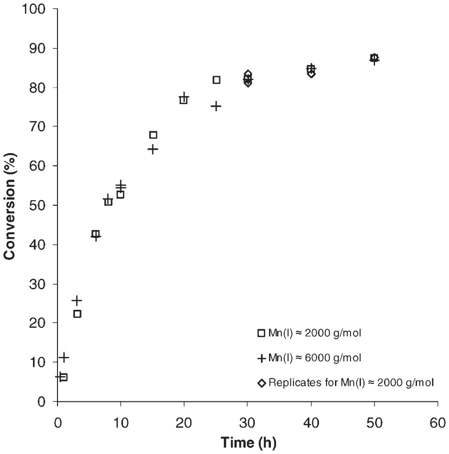

Figure 7.
Conversion vs. time plot, effect of initiator molecular weight, T = 120 °C, $[I]_0 = 0.030$ mol/l.

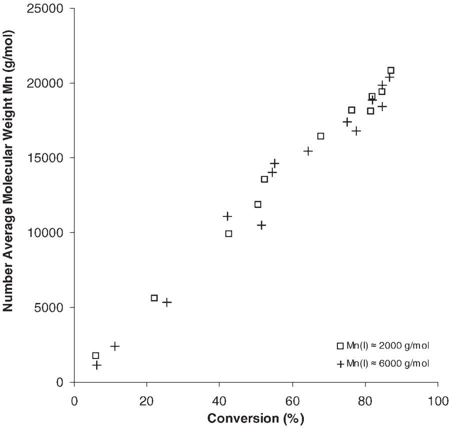

Figure 8.
Effect of initiator molecular weight, T = 120 °C, $[I]_0 = 0.030$ mol/l. M_n vs. conversion

mixture with the lower MW initiator. Nevertheless, if first order kinetics is followed, then the fractional conversion vs time profiles should be the same at the two conditions.

The increase in molecular weight of the resulting polymer with conversion should also be proportional to the concentration of monomer consumed and inversely proportional to the effective TEMPO concentration (Eq. 3). Thus it would be expected that, if the true concentrations of nitroxide were the same for reactions using low and high molecular weight initiators, then the incremental increases in MW should be higher for the reaction using the lower molecular weight initiator (because its initial monomer concentration is greater). This is not observed for the measured molecular weights, where, for the equivalent reactions with the two weights of initiator, the incremental increases in molecular weight are essentially the same for reactions at a given temperature and initiator concentration, as illustrated in Figure 8. A possible reason for this could be that the active alkoxyamine concentrations for the two initiators are unlikely to be exactly the same. It was assumed in the execution of the studies that moles of alkoxyamine in a reaction were simply represented by the mass of initiator divided by the molecular weight of the initiator. Such a calculation does not take into account the fact that some of the initiator sample will be dead polymer. Scott et al. [14], have demonstrated that the proportion of dead polymer increases with conversion in a typical NMRP system. Given this and the fact that higher levels of monomer conversion were required to make the initiator with MW of about 6000, than those with MW of about 2000, the initiator with MW of 6000 would likely have a higher proportion of dead polymer. This should lead to higher incremental increases when using the high MW initiator, thus balancing to some extent the differences that would stem from different initial monomer concentrations. In addition, the measured molecular weights for the initiators by GPC are not exact and so because of this there would be significant uncertainty in the initial initiator concentration value. Furthermore, this means that the real initiator concentrations with regards to nitroxyl level would likely not be exactly the same in the different experiments. This introduces considerable uncertainty to the calculations by Equation 3, which can also help rationalize why the measured MW values were similar for both initiator types in Figure 8. Overall, the molecular weight of initiator can be considered to have little effect on polymerization rate and molecular weight development in the present study.

Comparison with Bimolecular Initiation

A comparison of styrene polymerizations using bimolecular and unimolecular systems was carried out, using reagent concentrations similar to those reported by Nabifar et al.[12]. The results for conversion vs. time in both reactions are presented in Figure 9.

It can be seen that below 70% conversion, the rates of monomer conversion were essentially the same for both unimolecular and bimolecular systems. Above 70% conversion, the results showed that the reaction with unimolecular initiator slows down more than the bimolecular reaction. One reason that may explain this difference is that the true concentration of nitroxyl controller is less in the bimolecular system than in the unimolecular. This can be explained by a loss of TEMPO in side reactions in the bimolecular system. The bimolecular system involves a multi-step initiation, which leads to various side reactions.[15,16] So the total concentration of effective TEMPO is actually lower than that of the TEMPO initially added to the reaction mixture. In a unimolecular system this is not an issue and the total concentration of effective alkoxyamine is close to that determined for the reaction mixture preparation.

The fact that the effective nitroxide concentration is higher in unimolecular NMRP is seen in the molecular weight evolution trends of the two systems. In the molecular weight vs. conversion plots of Figure 10, both of the systems show linear trends, indicating that they are both controlled; the unimolecular system, however, has a lower molecular weight for given levels of conversion. From the M_n data collected, it

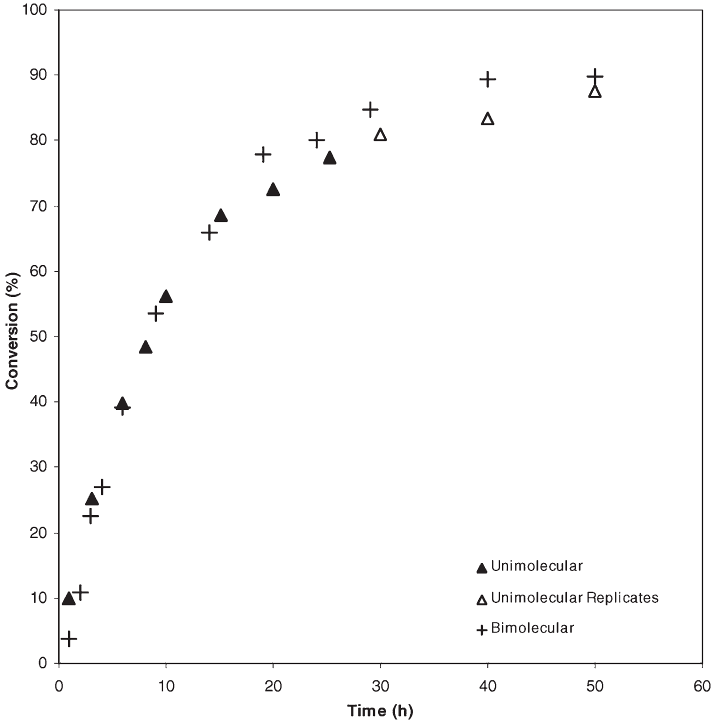

Figure 9.
Conversion vs. time plot; comparsion of NMRP of styrene at 120 °C between a unimolecular system with $[I]_0 = 0.040$ mol/l and a bimolecular system with $[TEMPO] = 0.040$ mol/l, and $[TEMPO]/BPO] = 1.1$.

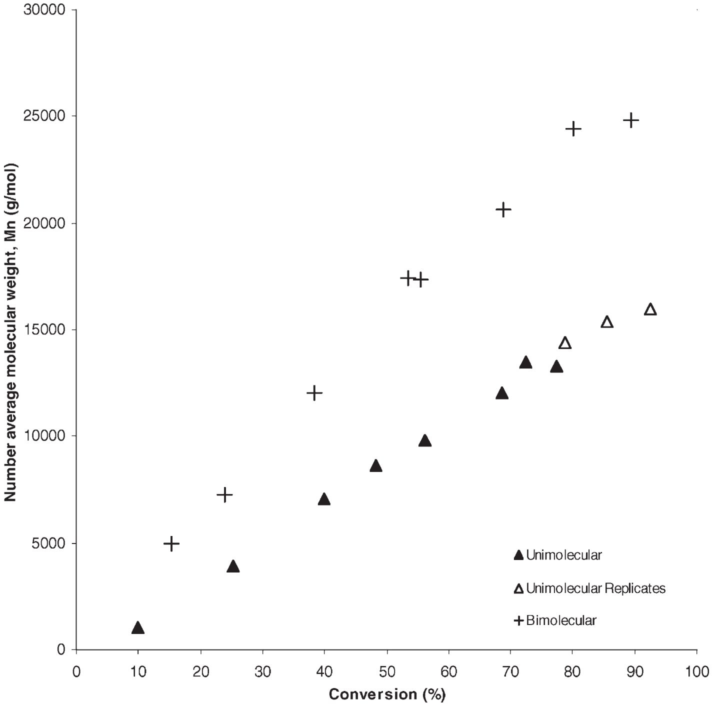

Figure 10.

Molecular weight vs. conversion plot, comparsion of NMRP of styrene at 120 °C between a unimolecular system with $[I]_0 = 0.040$ mol/l and a bimolecular system with $[TEMPO] = 0.040$ mol/l, and $[TEMPO]/BPO] = 1.1$.

was calculated, using Equation 3, that the effective alkoxyamine concentration observed for the bimolecular system would be about 0.03 mol/l as opposed to 0.04 mol/l as planned for the experiment.

Given the evidence shown above concerning the effect of changing initiator concentration, the MW trends for the bimolecular case support the theory that effective initiator (controller) concentration is lower. In turn we can also relate the higher rates observed at high conversion levels for the bimolecular case to the lower concentrations of alkoxyamine.

Conclusions

This study has assessed the kinetic behavior of a controlled radical polymerization system with a unimolecular initiator. The experimental studies examined the reaction through the whole conversion range, and a comparison with the corresponding bimolecular system has been made.

Initiator concentration was found to have no effect on polymerization rate at low conversions as was reported in earlier studies. At high conversion, polymerization rate was observed to have an inverse dependence on initiator concentration. In addition, as has been found previously, higher initiator concentration led to lower molecular weights. It was confirmed that M_n is inversely proportional to the effective TEMPO concentration when reactions were run at 120 °C, in keeping with standard theories relating to NMRP mechanism.

As expected, increasing temperature led to higher polymerization rates. For given levels of initiator, molecular weights were found to be largely unaffected by the temperature of reaction in contrast to what is observed for standard free radical polymerizations. This was rationalized by considering that the RLPAC would not change significantly with temperature. At high conversion levels for samples produced at higher temperatures, M_n showed a plateau in values with respect to monomer conversion. This was because increasing temperature increases the rate of self-initiation, leading to higher proportions of new radicals throughout the course of polymerization. In general, the temperature studies show that although higher temperature leads to faster polymerization rates, the control of the polymerization is poorer because of the effect that enhanced thermal initiation has on the polydispersity of the polymer products.

Initiators produced from different batches, with different molecular weight and polydispersity, showed only slight effects on polymerization rate and molecular weight. This indicates that initiator produced in different batches can be used in the same polymerization study since it will not bring significant changes in a kinetic study.

In addition, the kinetic behavior of a unimolecular NMRP process was compared with a bimolecular system. Differences in rates and molecular weight trends could be explained by considering that the unimolecular system had a higher effective nitroxyl concentration. This in turn confirmed the loss of TEMPO by side reactions in bimolecular initiation. Thus the research supports the earlier proposal that unimolecular initiation is the preferred methodology for producing polymer with more predictable molecular weights.[11]

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