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Maximizing polymer livingness in nitroxide-mediated miniemulsion polymerizations

M. Cunningham[a,*], M. Lin[a], C. Buragina[a], S. Milton[a], D. Ng[a], C.C. Hsu[a], B. Keoshkerian[b]

[a]*Department of Chemical Engineering, Queen's University, Kingston, Ont., Canada K7L 3N6*
[b]*Xerox Research Centre of Canada, 2660 Speakman Drive, Missiauga, Ont., Canada L5K 2L1*

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Abstract

Recent efforts to adapt nitroxide-mediated living radical polymerization chemistry to colloidal systems have shown considerable progress when miniemulsions are used. Miniemulsion SFRP in fact can yield higher conversions (>99%) and faster reaction rates than bulk SFRP. Much of the advantage of operating in miniemulsion arises from the inherent advantages of having a two phase system, in which the aqueous phase can be employed as a medium to introduce rate enhancing additives such as ascorbic acid to the reaction loci with a high degree of control. Additives such as ascorbic acid act by consuming excess nitroxide, and therefore directly influence the rate. Results on the effect of ascorbic addition on rate, molecular weight and livingness are presented. We have also begun to address the issue of high operating temperatures in TEMPO-mediated SFRP (~120–135 °C) that require a pressurized reactor. We have run experiments using TEMPO at 100 °C with slowly decomposing initiator added to maintain an appropriate free nitroxide concentration. Reasonable reaction rates are obtained, albeit with higher polydispersities (~1.6). Challenges and opportunities related to lower temperature operation are discussed.

Keywords: Polymer; Polymer science; SFRP

1. Introduction

Emulsion polymerization has long been an attractive process because of the numerous, practical advantages it offers in the manufacture of colloidal polymeric dispersions. Among those advantages are high monomer conversions, fast reaction rates and facile operation of the process. Recent efforts to adapt nitroxide-mediated living radical polymerization chemistry to colloidal systems have shown considerable progress when miniemulsions are used [1–20], but little real progress for true emulsion polymerization [21–23]. Nitroxide-mediated polymerizations, or stable free radical polymerizations (SFRP), have consistently displayed colloidal stability problems in emulsion. The reasons for this are beyond the scope of this work. Instead we have focused on understanding the issues involved in successfully adapting SFRP to miniemulsion polymerization. Fig. 1 shows the basic scheme for SFRP.

Our earlier work using SFRP in styrene miniemulsions revealed several potential issues and challenges, which we have been addressing in recent work. Included in these challenges were low reaction rates, unacceptably low final conversions (~60–70%) resulting from a levelling off in the polymerization rate, and the use of a volatile hydrophobe (or costabilizer) such as hexadecane in the formulation. We also witnessed significant variation in the initiator efficiency when bicomponent initiating systems (e.g. benzoyl peroxide, TEMPO) were used, depending on the choice of reaction conditions. Modelling studies revealed a further concern, that we were probably losing much of the livingness of the system (as much as 40–50% of our chains) under the conditions we were using. A question that arose was whether or not it would even be possible to achieve high or nearly complete conversions in SFRP miniemulsions in a reasonable reaction time, while at the same time preserving the livingness of the polymer. SFRP studies in bulk

* Corresponding author. Tel.: +1 613 533 2782; fax: +1 613 533 6637.
E-mail address: cunning@chee.queensu.ca (M. Cunningham).

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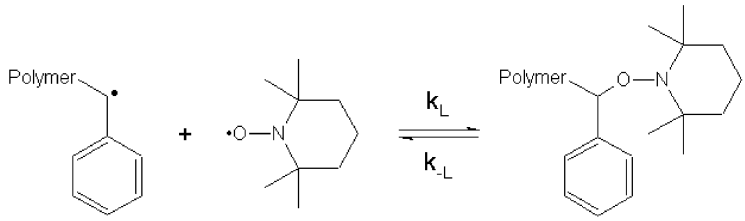

Fig. 1. Reversible activation–deactivation equilibrium of a polymeric radical by the nitroxide TEMPO.

polymerization have not been successful in achieving the combination of low reaction times with high conversion and a high degree of livingness. It will be shown that these foregoing issues have now been largely resolved. A final concern, more related to perception than purely technical causes, was that of operating at temperatures of ~135 °C. At these temperatures, the reactor is pressurized to about 300 kPa, and while operation is not difficult, the emulsion polymers industry has limited experience operating reactors under pressure.

2. Experimental methods

2.1. Chemicals

The following reagents were used as received from Sigma-Aldrich Canada Limited: benzoyl peroxde (BPO) (97%), TEMPO (98%), sodium dodecyl benzene sulfonate (SDBS) (tech.), L-ascorbic acid (99%) and hexadecane (HD) (99%). VA-085 ($C_{16}H_{32}Cl_2N_4O_4$) (Wako Chemical) was used as received. Styrene was washed three times with equal volume of 2 wt% NaOH solution to remove inhibitor. This was repeated using distilled water, followed by drying overnight over $CaCl_2$ and then vacuum distillation.

2.2. Synthesis of N-TEMPO [4-(1-naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl]

Following Jones et al. [24], a solution of 1-naphthoyl chloride (15 ml, 0.0985 mol) in anhydrous pyridine (25 ml) was added drop-wise to a 250 ml round bottom flask containing a stirred solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (OH-TEMPO; 12 g, 0.0725 mol) in anhydrous pyridine (75 ml) cooled in ice water. Nitrogen environment was maintained. After 18 h of stirring, water (9.5 ml) was added gradually, and the mixture was stirred for another 30 min. This mixture was poured into 300 ml ice water, and then extracted twice with 350 ml ethyl acetate and then washed with 270 ml dilute HCl (0.62 M), 270 ml saturated $NaHCO_3$, 270 ml water, and 270 ml brine (106.73 g NaCl, filtered) respectively. After a day of drying over Na_2SO_4, the solvent was evaporated with a rotating evaporator at 50 °C. The solid was recrystallized twice from ethyl acetate. Fig. 2 shows the structure of N-TEMPO.

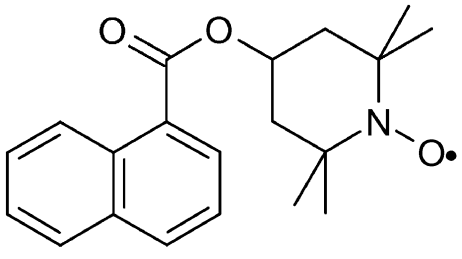

Fig. 2. Structure of N-TEMPO.

The alkoxyamine 4-naphthoyloxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (N-TEMPO-PhEt), used as an internal standard, is synthesized using a similar procedure, as reported in Scott et al. [25].

2.3. Polymerization

2.3.1. Synthesis of TEMPO-terminated macroinitiator

TEMPO-terminated macroinitiator (TTOPS [12]) was prepared by carrying out bulk styrene (40 ml) polymerization initiated by BPO (0.387 g, 1.60 mmol) and mediated with nitroxide (2.00 mmol) at 135 °C for 1 h to give a conversion of 4.2%. The M_n of the TTOPS was 1380 and polydispersity was 1.09.

2.3.2. Miniemulsion SFRP

The TTOPS solution was microfluidized with an aqueous solution (160 ml) of 0.09 M SDBS to give the miniemulsion, which was then poured into a 300 ml autoclave reactor that had been repeatedly purged with nitrogen, and then heated to the desired temperature set point. The polymerization was considered to begin when the temperature reached the set point. For the runs using ascorbic acid fed in semi-batch mode, a stream of known ascorbic acid concentration was added to the reactor at a rate of 10 ml/h for the duration of the experiment.

2.3.3. Low temperature miniemulsion SFRP

These runs were conducted in the same manner as above, except that VA-085 was added to the aqueous phase at the beginning of the experiment and the reactor temperature was 100 °C. VA-085 concentrations are reported based on the aqueous phase.

2.4. Characterization

Gravimetry is used to determine the conversion of all samples. It is the sole method used in batch polymerization runs. In semi-batch polymerization runs, conversion is determined with gas chromatography (GC) as well as gravimetry (Gravimetry is used to measure the mass of polymer, while monomer concentration is detected with GC. The combined mass gives the mass of initial monomer, thus eliminating the reliance of the technique on the accuracy of a mass balance). GC is performed with a Varian CP 3800, equipped with a Varian CP-8410 autosampler, a flame ionization detector, and a CP Sil coated WCOT Fused Silica capillary column.

2.4.1. Gel permeation chromatography

The molecular weight distribution (MWD) was obtained with gel permeation chromatography (GPC), using a Waters 2960 Separation Module connected to a Waters 410 Differential Refractometer. Five Waters Styragel columns (HR 0.5, 1, 3, 4 and 5E) were kept at 40 °C. Flow rate of the eluent, tetrahydrofuran (THF) was set at 1.0 ml/min. Polystyrene (PS) standards were used for calibration. Data were collected and processed using Waters Millenium software.

2.4.2. Particle size distribution

Particle size distributions were measured using a Malvern Mastersizer 2000 equipped with a Hydro 2000S optical unit. Styrene saturated water was used as the dispersant to minimize the diffusion of styrene from the particles.

2.5. Degree of livingness (DOL) measurement

Polymer samples were precipitated from solution using methanol and filtered to isolate the precipitate. The polymer was dissolved in chlorobenzene (0.012 M), mixed with N-TEMPO (50 equiv.), degassed with three freeze–thaw cycles, and heated at 123 °C for 154 min under nitrogen. The reaction mixture was added drop-wise into methanol to precipitate the polymer, which was again dissolved in THF. Following re-precipitation from methanol, the polymer was dried. To measure the alkoxyamine concentration, a Waters 474 Scanning Fluorescence Detector was added to the GPC in series after the differential refractometer (DRI). The alkoxyamine 4-naphthoyloxy-1-((1-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (N-TEMPO-PhEt), used as an internal standard, was dissolved in THF to give a concentration of 1.2×10^{-4} M. 10 ml of this solution was added to about 5 mg of each polymer sample, which was analyzed with GPC. Chromatograms of polystyrene (PS) standards and N-TEMPO-PhEt at different concentrations were collected from both detectors. From the fluorescence detector, the PS chromatograms allowed the area under a sample chromatogram to be corrected for the fluorescence of the PS backbone. The N-TEMPO-PhEt chromatograms allow calculation of the amount of alkoxyamine (NTEMPO-terminated chains) in the polymer sample from the corrected area. Chromatograms from both detectors were aligned, and processed with the same calibration curve using the N-TEMPO-PhEt peak. With this technique, the amount of NTEMPO-terminated chains in a sample could be determined. Further details can be found in Scott et al. [25].

Degree of livingness (DOL) is defined as the fraction of chains terminated with nitroxide, and can be calculated on either a mole or mass fraction basis. (In this paper, we report mole fraction.) DOL is determined using the living chain distribution obtained from the fluorescence detector, and the total chain distribution obtained from the DRI detector. Note that the fluorescence detector signal is proportional to the number of living chains, while the DRI detector is proportional to the mass of total chains, and therefore conversion of the DRI molecular weight distribution from a mass to number basis is required to determine the mole fraction DOL.

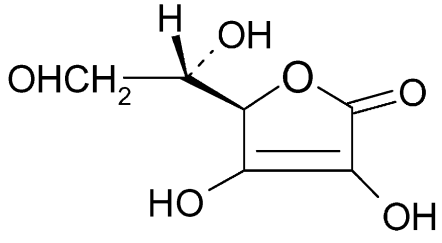

Fig. 3. Structure of L-ascorbic acid.

3. Results and discussion

3.1. Rate enhancement by ascorbic acid addition

A foremost priority was that of enhancing the polymerization rate, which we have chosen to do through indirect control of the free nitroxide (TEMPO) concentration. Because of the equilibrium nature of the activation–deactivation process (Fig. 1), a reduction in the nitroxide concentration results in an increase in the active polymeric radical concentration, thereby increasing the polymerization rate (Eqs. (1)–(3)).

$$R_p = k_p[M][\mathrm{Pn}\cdot] \quad (1)$$

$$K = [\mathrm{Pn}-N]/\{[\mathrm{Pn}\cdot][N\cdot]\} \quad (2)$$

$$R_p = k_p[M][\mathrm{Pn}-N]/\{K[N\cdot]\} \quad (3)$$

where R_p is the polymerization rate, [Pn·] is the active radical concentration, [Pn–N] is the inactive (dormant) chain concentration, [N·] is the free nitroxide concentration, and K is the equilibrium constant. Earlier efforts in our laboratory used camphor sulfonic acid (CSA) as a

rate-enhancing additive [10]. CSA did provide an increased rate but the gains were modest, and efforts to achieve greater rate enhancement through use of higher CSA concentrations resulted in increased polydispersities, indicating significant chain termination. Much better results are obtained using the water-soluble ascorbic acid to control the TEMPO concentration.

The structure of ascorbic acid is shown in Fig. 3. It is believed to directly consume TEMPO by reaction, although the exact mechanism is not known, and it is possible that the ascorbic acid also participates in other reactions. A saturated aqueous solution of TEMPO in water (pink in colour) becomes clear immediately upon addition of ascorbic acid, indicating rapid and complete consumption of the TEMPO. Ascorbic acid is readily oxidized, and can form one half of redox initiator systems.

Early experiments using ascorbic acid involved batch addition as we had done with CSA. However, the resulting molecular weight distributions were bimodal, with a broad, high molecular weight peak (formed at low conversions) as well as a narrower, low molecular weight peak. This uncontrolled polymerization was caused by consumption of much of the initial nitroxide by the ascorbic acid. Even when the amount of ascorbic acid was significantly reduced, effective rate enhancement while preserving low polydispersities proved elusive. It is worth noting that on an equimolar basis, ascorbic acid is much more effective at consuming TEMPO than is CSA. However, because ascorbic acid is water-soluble, it can be easily fed into the reactor in semi-batch mode thereby allowing greater control over the process. Judicious control of the ascorbic acid addition rate allows near-complete conversions to be obtained in as little as 2–3 h, while maintaining polydispersities $\sim$1.3, as shown in Fig. 4. Fig. 4 also shows a control run ([AA] = 0 M) in which pure water was fed into the reactor. The addition of water during polymerization increases the aqueous phase volume, and promotes greater partitioning of TEMPO into the aqueous phase from the organic phase. The effect is relatively minor but we do consistently see slightly higher conversions with water added compared to the batch case without water addition.

Fig. 4 shows that by adding ascorbic acid in semi-batch mode, the rate can be increased to give near complete conversions in $\sim$3 h. In view of the evolution of SFRP polymerizations and the widely held belief that their rates are inherently low, this is a remarkably fast polymerization. The rate enhancement effect is significant at 0.05 M ascorbic acid; increasing the concentration does little to further enhance the rate.

As shown in Fig. 5, the M_n increases linearly with conversion and the polydispersities are low (<1.2), suggesting a well-controlled polymerization. The experimental molecular weights are slightly lower than theoretical values, probably due to a small increase in chain number from thermally generated radicals. Once near complete conversion has been attained, continuing the reaction results in a slight increase in polydispersity arising from higher M_w, probably attributable to irreversible termination by combination.

For all experiments, coagulation was minimal. The particle size distribution was unimodal but broad, with a volume average mean of $\sim$120 nm. There was no noticeable change in the particle size distribution during the polymerizations. However, because of the broadness of the distribution, the presence of homogeneous nucleation cannot be discounted.

3.2. Degree of livingness (DOL) results

Although we were achieving narrow molecular weight distributions, as evidenced by the low polydispersities, we had concerns about the livingness of the system. It has been a widely held view that fast reaction rates in living radical polymerizations can only be achieved at the expense of high

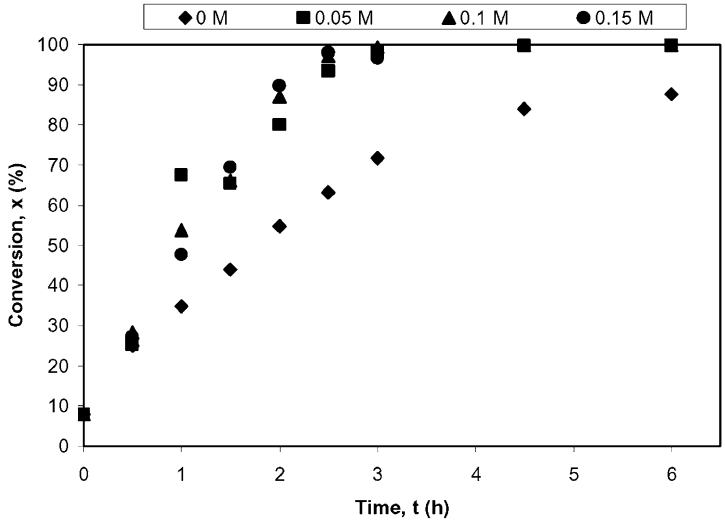

Fig. 4. Conversion-time profiles for semi-batch addition of ascorbic acid at various concentrations.

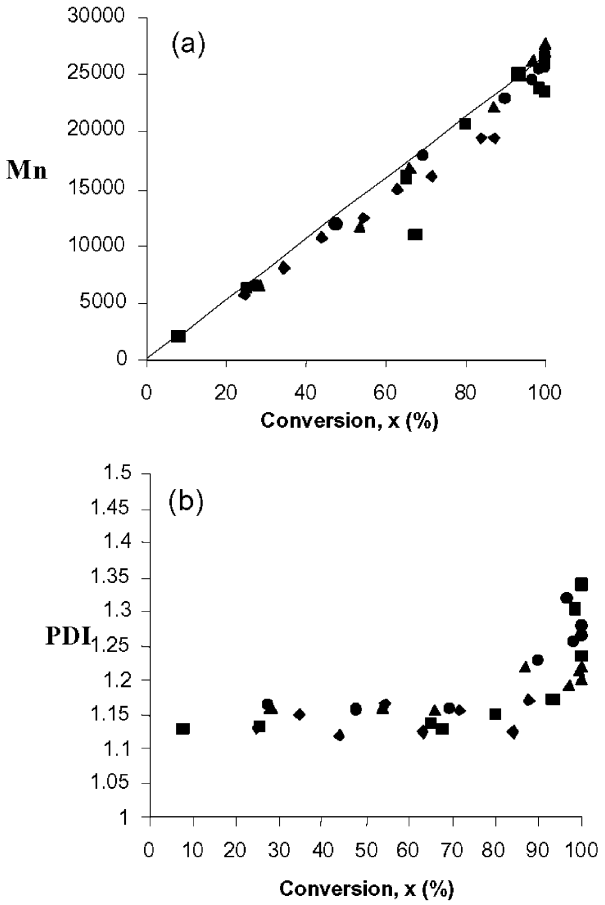

Fig. 5. (a) M_n versus conversion; (b) PDI versus conversion; for semi-batch miniemulsion SFRP involving TTOPS with ascorbic acid feed. (♦) 0 M; (■) 0.05 M; (▲) 0.10 M; (●) 0.15 M. Solid line is theoretical molecular weight.

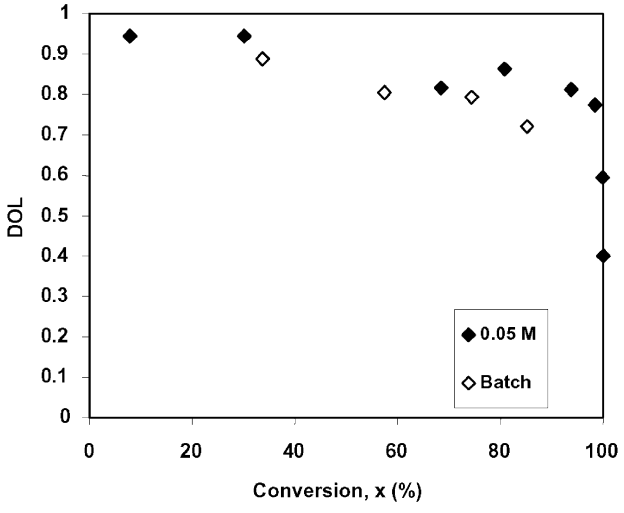

Fig. 6. Degree of livingness (DOL) for semi-batch run with ascorbic acid addition as a function of conversion. DOL = fraction of chains terminated with nitroxide.

radical–radical termination rates, and therefore fast reactions would inevitably be accompanied by poor livingness. To explore this issue, we have used a recently developed fluorescence-based technique to measure the livingness of the SFRP polymers. It will be shown that the livingness of SFRP polymers made using fast reactions is as good or even better than when slower reaction rates occur (Fig. 6). The explanation for this seemingly anomalous behaviour lies in the high rates of alkoxyamine disproportionation (hydrogen abstraction from a polymer chain end to yield unsaturated dead polymer and hydyoxylamine) that occur at 135 °C. By reducing reaction times, fewer chains are lost through disproportionation.

3.3. Miniemulsion SFRP at 100 °C

We have begun exploring the feasibility of running TEMPO-mediated SFRP miniemulsions at lower temperatures. Although TEMPO has not been previously used at $T < \sim 120$ °C and is typically used in the temperature range of 125–135 °C, we have conducted polymerizations at 100 °C. The objective of this work is not necessarily to determine if TEMPO is a suitable nitroxide at 100 °C, but rather to assess how much the conventional operating temperature range of a nitroxide can be expanded through control of the polymerization conditions.

There are incentives for working with TEMPO at lower temperatures. First, as previously noted the emulsion polymers industry has limited experience-operating reactors under pressure and therefore a process not requiring pressurized operation would be more attractive commercially. A variety of nitroxides have also been developed, with some of them being more suitable for lower temperature use, such as SG1 (made by Atofina; see Ref. [4] for example). However, TEMPO and its derivatives (e.g. 4-hydroxy-TEMPO) are inexpensive, readily available and thermally stable. In addition, the alkoxyamine disproportionation rates for TEMPO-terminated polystyrene chains are quite temperature sensitive [26], and thus lower temperature operation has the added benefit of dramatically reducing disproportionation rates and the formation of dead chains. At 135 °C, disproportionation is the major factor causing loss of livingness [13,14].

There are two major challenges in conducting TEMPO-mediated miniemulsion polymerizations at 100 °C. First is that the thermal polymerization rate of styrene at 100 °C is much lower than at 135 °C (approximately 25×), and it is now understood that the thermal initiation rate indirectly controls the overall polymerization rate through its role in determining the overall radical concentration. Excess nitroxide produced as a result of irreversible termination reactions accumulates in SFRP polymerizations; at higher temperatures (125–135 °C) this excess nitroxide is consumed by thermally generated radicals thereby allowing the polymerization to proceed at an acceptable rate. In the absence of significant thermal initiation however, nitroxide

accumulation will quickly suppress the polymerization altogether. We can consume excess nitroxide by adding either a radical generator (initiator) or a reagent like ascorbic acid that consumes the nitroxide. The challenge here lies in the precision required to maintain an optimal nitroxide level.

The second issue is not so easily overcome. At 100 °C, the activation rate of TEMPO-terminated chains is low, which will invariably lead to broadening of the molecular weight distribution. A narrow distribution in living radical polymerizations requires frequent activation–deactivation cycles so that all chains grow at about the same rate. If the activation rate is low, activation–deactivation cycles will be infrequent so that some chains will have experienced appreciable growth while others have not. It should be noted however, that these chains would still be living. An additional consequence of the low activation rate at 100 °C is that the active radical concentration will also be lower than at higher temperatures, and thus the polymerization rate will be decreased. (At lower temperatures, the equilibrium is shifted towards dormant chains, a result of the activation step before far more temperature sensitive than the deactivation step.) The two issues described above require discussion of the following question. Is it necessary (for a given application) that the MWD is narrow, or is it sufficient that the chains are living with a somewhat broader distribution? For many applications, there may be considerable latitude in the breadth of the MWD that will still yield acceptable performance in the final product.

We have begun preliminary experiments 100 °C using two different approaches. First is the addition of a carefully chosen initiator to the initial charge. The initiator should decompose at a rate that will provide enough radicals to consume excess nitroxide, but not so high as to consume too much nitroxide and lead to uncontrolled polymerization. We have used several different initiators. The initial concentration for any new initiator was chosen by matching the sum of radical generation rate for that initiator at 100 °C (calculated from decomposition rate data available in literature) plus the thermal initiation rate at 100 °C, to the thermal initiation rate at 135 °C. (See Refs. [13,14] for details on calculating the thermal initiation rate.) In this manner, the overall rate of radical generation at 100 °C was set equal to our normal runs at 135 °C. The initiator concentration could then be increased or decreased depending on the outcome of the experiment. The second approach was to add ascorbic acid to consume excess nitroxide in semi-batch mode as has previously been described. In this paper, we will present results only from the experiments in which initiator was added.

Fig. 7 shows the conversion versus time profile for SFRP miniemulsions run at 100 °C in which different concentrations of the water-soluble initiator VA-085 were added at the beginning of the experiment. The rate is quite sensitive to the VA-085 concentration, indicating that the active radical concentration is increased by the additional radicals being generated. For faster polymerizations (higher VA-085 concentrations), polydispersities were high (>2) and a nonlinear relationship between M_n and conversion was often observed, indicating an uncontrolled polymerization. However, for [VA-085] = 0.001 M, a linear relationship between M_n and conversion was observed. This linearity of this plot is characteristic of living radical polymerizations, but is does not require a high degree of livingness; only that the number of chains is constant with some living chains (i.e. a necessary but not sufficient condition for a living system). Fig. 8 shows the polydispersity profile for the run with [VA-085] = 0.001 M. The first point is the TTOPS. Immediately upon starting the miniemulsion polymerization with VA-085 present, the polydispersity increases to ~2, and then continually decreases to 1.4 at 80% conversion. These two figures are consistent with a living, but not well-controlled, polymerization. The high polydispersity early in the reaction is an expected consequence of the slow activation rate of chains that will lead to large variations in chain length at low times. At longer times, those variations diminish, as observed in the decreasing polydispersity.

The final and perhaps most interesting pieces of information are the DOL data for the run with [VA-085] = 0.001 M. At 50% conversion the DOL is 80%, and at

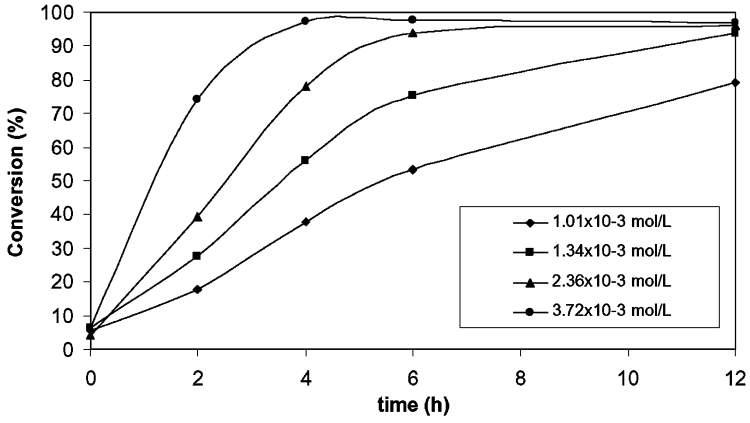

Fig. 7. Conversion versus time profiles at 100 °C with VA-085 added at various concentrations.

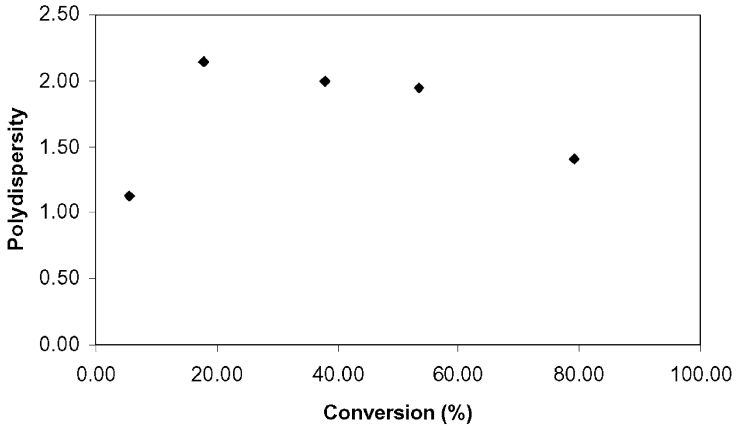

Fig. 8. Polydispersity for 100 °C run with VA-085 = 0.001 M.

80% conversion, DOL is 64%. In comparison to our most recent experiments at 135 °C presented here, these DOL results are lower. However, in a broader context, they compare favourably to results obtained within the past 1–2 years, and to bulk polymerizations. They also offer evidence of a much reduced formation rate of dead chains by disproportionation at 100 °C (consistent with Fukuda's results [26]), since a 12 h experiment at 135 °C will give very low DOL (<20%). Presumably the loss of livingness is due to bimolecular termination. Slower reactions (lower [VA-085]) should give higher livingness and lower polydispersity.

As stated earlier, the primary objective was not to necessarily develop a 100 °C process, but to explore the feasibility of extending the operating range of existing nitroxides by manipulating the excess nitroxide concentration. It appears that TEMPO could be used at temperatures much lower than 135 °C if slower polymerizations and somewhat higher polydispersities are acceptable. The broader implication is that the operating range of other nitroxides could also be expanded. Nitroxides typically used at 110–115 °C may be feasible for use at temperatures <100 °C.

4. Conclusion

While previous efforts in our laboratory used camphor sulfonic acid (CSA) as a rate-enhancing additive, we have obtained much better results using the water-soluble ascorbic acid to control TEMPO concentration. Since ascorbic acid is water-soluble, it can be easily added in semi-batch mode to obtain more precise control of the process. Judicious control of the ascorbic acid addition rate allows near-complete conversions to be obtained in as little as 2–3 h, while maintaining polydispersities ~1.3 or lower. With a fluorescence-based technique to measure the polymer livingness of the SFRP polymers, we have shown that the livingness of SFRP polymers made using fast reactions is as good or even better than when slower reaction rates occur, likely due to reduced living chain loss by disproportionation.

Although TEMPO has not been previously used at $T <$ ~120 °C, we have conducted polymerizations at 100 °C. Preliminary results are encouraging, with reasonable reaction rates and good livingness obtained, albeit with slightly higher polydispersities. It appears that TEMPO could be used at temperatures much lower than 135 °C, and other nitroxides could be used at temperatures lower than their conventional range.

Acknowledgements

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