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Nitroxide Mediated Living Radical Polymerization in Miniemulsion

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Summary: The introduction of the aqueous phase into a living radical polymerization increases the complexity of the kinetics by creating the possibility of species partitioning between the aqueous and organic phases, and introducing aqueous phase reactions which could play a significant role particularly in chain initiation and/or particle nucleation. We have conducted a series of styrene miniemulsion polymerizations in which the solubility of initiator and nitroxide have been systematically varied. Experiments were run using either water-soluble (potassium persulphate) or oil-soluble (benzoyl peroxide) initiator, and either TEMPO or 4-hydroxy-TEMPO. These two nitroxides vary considerably in their water solubility. The effects of initiator and nitroxide solubility in water on conversion-time behaviour, molecular weight and initiator efficiency are presented.

Introduction

Emulsion-based polymerizations offer several reaction engineering advantages over homogeneous polymerizations such as bulk and solution, and are therefore an attractive option for suitable systems. Living (or controlled) radical polymerization has been used to produce a variety of polymeric materials with designed microstructures not previously attainable with free radical polymerizations, including narrow molecular weight distribution homopolymers, di-block and tri-block polymers, as well as more complex morphologies such as brush, star and comb polymers. Adapting living radical polymerization to emulsion-based systems would enhance its versatility, make it more economically viable, and open up possibilities for applications is aqueous coatings and dispersions. Miniemulsion polymerization provides a simpler system than emulsion polymerization for studying living radical polymerizations, as it: (1) removes the need for transport of the controlling agent (e.g. nitroxide) through the aqueous phase from droplets to particles; and (2) largely eliminates the complexities of the particle nucleation step in emulsion polymerization (some degree of

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homogeneous nucleation probably occurs). Nitroxide mediated polymerizations (SFRP) in heterogeneous systems have recently been reported in emulsion [1-4] and miniemulsion [4-13].

Experimental Part

Reagents: Benzoyl peroxide (BPO), hexadecane, 2,2,6,6 tetramethy-1-piperidinyloxy (TEMPO), 4-hydroxy-2,2,6,6-tetramethypiperidinyloxy (OH-TEMPO) (Sigma Aldrich Ltd Canada) and potassium persulfate (KPS) (Fisher Scientific) were used as received. Styrene (Sigma Aldrich Ltd Canada) was washed three times with a 2% wt NaOH solution to remove the inhibitor and then was washed three times with distilled water. Washed styrene was dried on calcium chloride overnight and then distilled under vacuum and refrigerated until use.

Polymerization: The aqueous phase consisted of SDBS (0.88g, 2.5mmol) and deionized water (120mL) and the organic phase consisted of hexadecane (5.4g, 0.024mol), nitroxide (0.70 mmol) and styrene (33mL). All reagents were mixed and passed twice through a Microfluidizer-110S (Microfluidics International Corporation) operating at 40 psi-inlet pressure to obtain a miniemulsion. The initiator (0.41 mmol) was added to either the aqueous or organic phase, depending on its solubility. The latex was then poured into a 300mL-autoclave reactor. The reactor was purged with nitrogen to remove oxygen. The latex was heated to 135°C for 6 hours. Samples were withdrawn every 90 minutes.

Characterization: Conversion was determined gravimetrically. Molecular weight and polydispersity were determined by size exclusion chromatography with a Waters 2690 Separations Module equipped with a Waters 410 Differential Refractometer, Waters Styragel columns and an on-line degasser. Data analysis was performed using Millennium 2010 software. A calibration curve was constructed from monodisperse polystyrene standards ranging from 8.7×10^2 to 2.8×10^6 AMU. The eluant was tetrahydrofuran flowing at 1mL/min and at temperature of 30°C.

Results

A sytematic study of the effects of initiator and nitroxide solubility in styrene miniemulsion polymerization has been undertaken. Different initiator concentrations and nitroxide:initiator ratios have been studied. In this manuscript, the results from one set of conditions are presented. Either BPO (oil-soluble) or KPS (water-soluble) was used as initiator, and either TEMPO or OH-TEMPO was used to mediate the polymerization. OH-TEMPO is considerably more water-soluble than TEMPO (Table 1).

Table 1. Measured partition coefficients for TEMPO and OH-TEMPO between styrene and water at 25, 90, 120 and 135°C, and the effects of hexadecane, polystyrene and SDBS on nitroxide partitioning. 95% confidence intervals are shown for each measured value. From reference [10]. Reproduced with permission of John Wiley and Sons.

System	**P_j (mole% mole%$^{-1}$)**			
	25°C	**90°C**	**120°C**	**135°C**
TEMPO	711.5 ± 10.5	900.7 ± 45.4	718.3 ± 8.5	652.2 ± 40.6
OH-TEMPO	2.9 ± 0.2	11.0 ± 0.5	13.8 ± 0.4	14.3 ± 1.4
TEMPO with added hexadecane	-	-	-	593.9 ± 23.6
TEMPO with added polystyrene	-	-	-	640.9 ± 30.1
OH-TEMPO with added SDBS	-	-	-	14.1 ± 2.4

With bimolecular initiating systems in SFRP miniemulsions, the water solubility of the initiator and of the nitroxide play an important role in progress of the polymerization. At a nitroxide:initiator of 1.7, little difference was observed in the conversion-time profiles when different initiator or nitroxide was used (Figures 1a, 2a, 3a, 4a). This insensitivity is caused by thermal polymerization playing a major role in determining the rate, and has been widely observed in nitroxide mediated styrene polymerizations. For all runs, the final polydispersities were <1.3. The number of chains initiated and the Mn vs conversion profiles are however strongly affected by the choice of initiator and nitroxide. For TEMPO-mediated runs, Mn is higher at a given conversion for the BPO-initiated runs than for the KPS-initiated runs, signifying more chains have been initiated with KPS (Figure 1b). When TEMPO is used, the Mn plots are linear with conversion and have an intercept near zero, signifying expected behaviour for a living polymerization. For the OH-TEMPO-mediated runs, the Mn versus conversion profiles are nearly independent of initiator type, indicating the same number of chains is initiated for either initiator (Figure 2b). Furthermore, the plots of Mn versus conversion display a rapid increase initially, followed by a period of linear growth.This suggests the polymerization was less controlled in the early stages, and is probably due to low OH-TEMPO concentration in the particles since the OH-TEMPO is known to substantially partition into the aqueous phase.

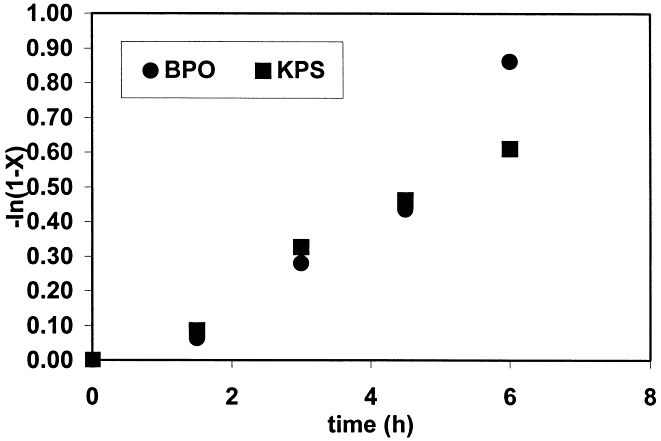

Figure 1a. Effect of initiator type on conversion for TEMPO-mediated runs.

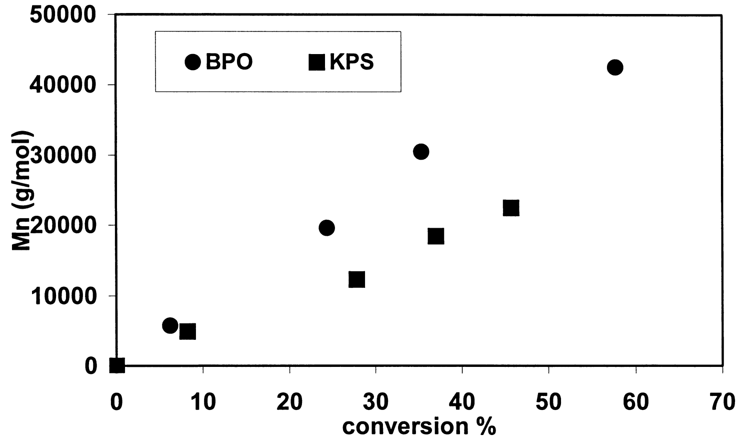

Figure 1b. Effect of initiator type on Mn for TEMPO-mediated runs.

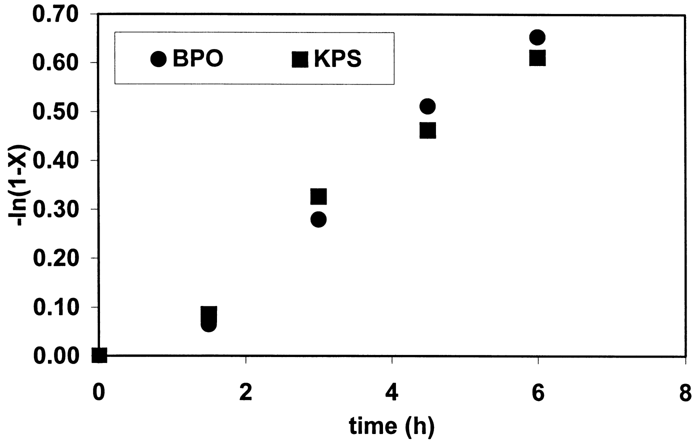

Figure 2a. Effect of initiator type on conversion for OH-TEMPO-mediated runs.

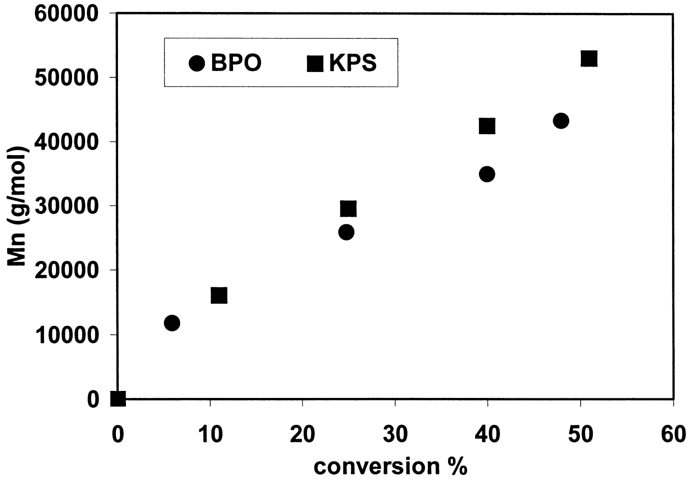

Figure 2b. Effect of initiator type on Mn for OH-TEMPO-mediated runs.

Examination of the BPO-initiated runs shows that the molecular weights are very similar at a given converion, regardless of nitroxide type (Figure 3b). However, for the KPS-initiated runs, the OH-TEMPO runs have higher molecular weight at a given conversion (fewer chains initiated) than the TEMPO-mediated runs (Figure 4b).

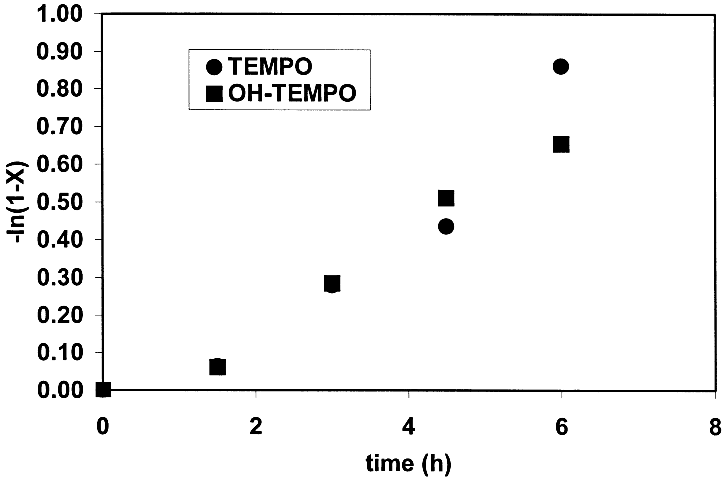

Figure 3a. Effect of nitroxide type on conversion for BPO-initiated runs.

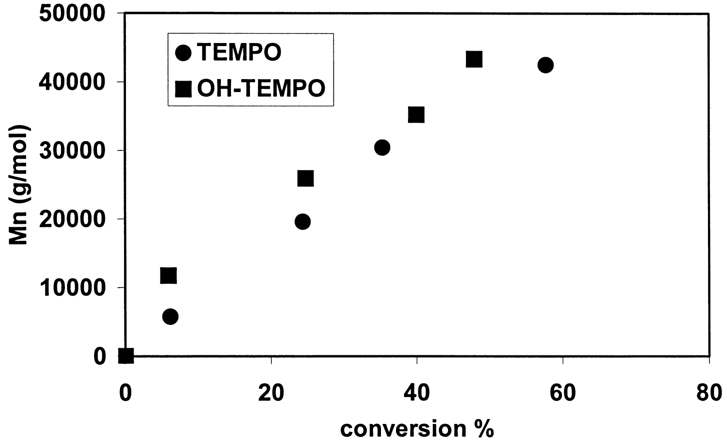

Figure 3b. Effect of nitroxide type on Mn for BPO-initiated runs.

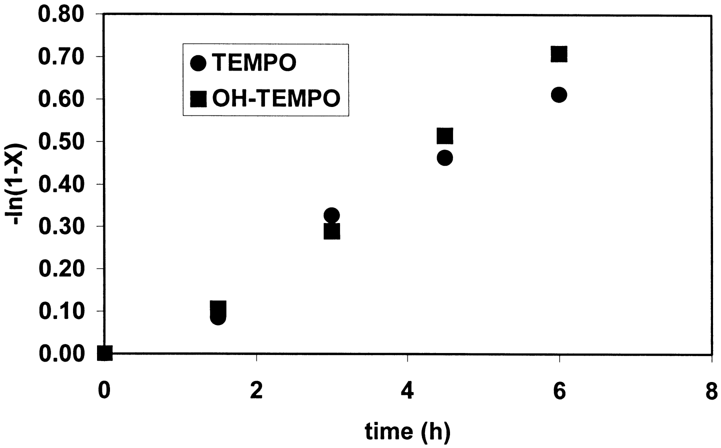

Figure 4a. Effect of nitroxide type on conversion for KPS-initiated runs.

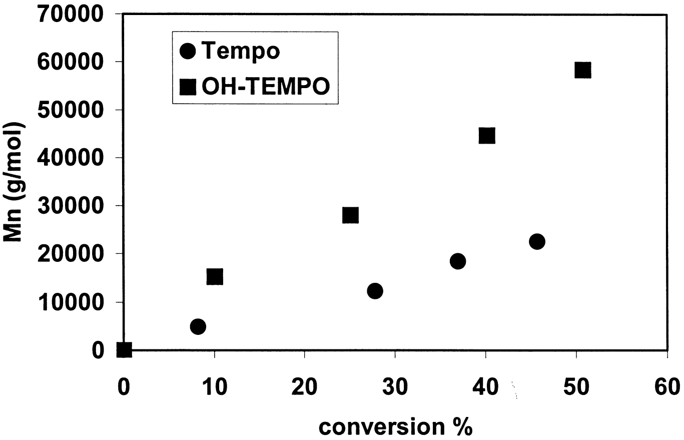

Figure 4b. Effect of nitroxide type on Mn for KPS-initiated runs.

Figures 5 and 6 show the number of chains as a function of conversion for TEMPO-mediated and OH-TEMPO-mediated runs respectively. The TEMPO-mediated runs initiated by BPO have a nearly constant number of chains, while TEMPO-mediated runs initiated by KPS show a small increase in chain number at low conversions. Nearly twice as many chains are nucleated when KPS is used. The OH-TEMPO-mediated runs show a low initial number of chains that gradually increases up to ~30-40% conversion. Interestingly the number of chains is essentially the same for both nitroxides when OH-TEMPO is used.

Consideration of the aqueous phase events is critical to understanding these results. Upon initiator decomposition in the aqueous phase, oligomeric radicals grow in the aqueous phase until they reach sufficient length to enter a micelle or particle, or they react with the nitroxide to yield a dormant chain that remains either remains water-soluble or enters a particle. SFRP reactions are quite sensitive to the free nitroxide concentration, and loss of a portion of the nitroxide into the aqueous phase from the reaction locus (particles) can seriously affect the course of the polymerization. Depending on the water solubility of the monomer, a nitroxide-capped radical may be capable of exit if it is fixed to a short oligomeric radical. The fate of living but dormant oligomeric radicals in the aqueous phase is more complex. If the monomer or living oligomer concentration in the aqueous phase is high enough, propagation of the dormant chain can continue in the aqueous phase until the macroradical becomes hydrophobic and enters a particle. If however aqueous monomer concentrations are low, propagation may be slow with the result that those chains remain as oligomers in the aqueous phase (they do not enter particles) thereby reducing the apparent number of chains in the system. Aqueous oligoradicals may also undergo irreversible termination with other aqueous radicals.

The continuous growth in chain number for the OH-TEMPO-mediated runs suggests that relatively water-soluble OH-TEMPO-capped oligomers remain in the aqueous phase during the early stages of polymerization. They gradually enter particles as the polymerization progresses. When TEMPO is used, the oligomers are more hydrophobic. With BPO as initiator, the oligoradicals are most hydrophobic, and all initially-formed radicals enter the particles at the outset of polymerization. When KPS is used, the oligoradicals will be more hydrophilic, which may explain the moderate but observable increase in the number of chains at low conversions (Figure 5).

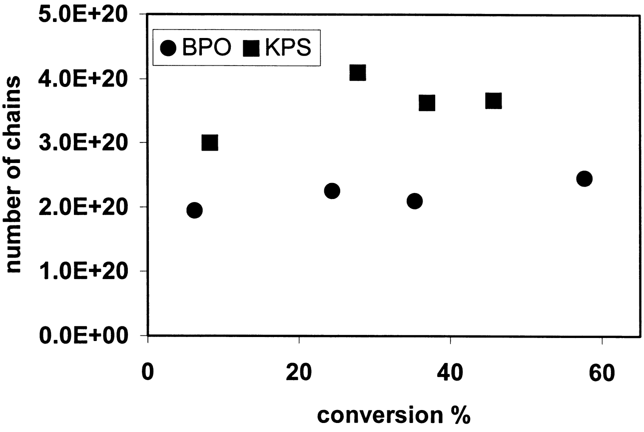

Figure 5. Number of chains versus conversion for TEMPO-mediated runs.

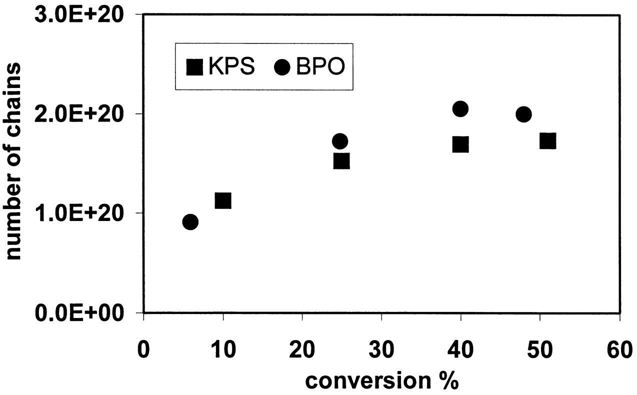

Figure 6. Number of chains versus conversion for OH-TEMPO-mediated runs.

Conclusion

At a nitroxide:initiator ratio of 1.7, rate differences are small regardless of the type of nitroxide and initiator used. However molecular weight is significantly affacted by the choice of initiator and nitroxide. No major effect of initiator type on number of chains was observed for OH-TEMPO mediated runs, but with TEMPO-mediated runs, KPS initiation resulted in more chains (lower Mn) than BPO.The nitroxide type had little effect on the number of chains for BPO-initiated runs but when KPS was used the nitroxide type was important, with TEMPO gives more chains (lower Mn) than OH-TEMPO. The number of chains was approximately constant when TEMPO was used, but gradually increased for OHTEMPO-mediated runs. The observed effects of nitroxide and initiator type are related to the aqueous phase kinetics and initiator efficiency. When more hydrophilic oligoradicals are produced (using OH-TEMPO or KPS), some of these remain in the aqueous phase in the early stages of polymerization. With more hydrophobic oligoradicals are produced (using BPO and TEMPO), no growth in the number of chains is seen, suggesting most of the oligoradicals partition into the particle phase from the outset of polymerization.

[1] S.A.F. Bon, M. Bosveld, B. Klumperman, A.L. German, *Macromolecules* **1997**, 30, 324-326.
[2] C. Marestin, C. Noel, A. Guyot, J. Claverie, *Macromolecules* **1998,** 31, 4041-4044.
[3] J. Cao, J. He, C. Li, Y. Yang, *Polymer Journal* **2001**, 33,75-80.
[4] M. Lansalot, B. Charleux, J.-P. Vairon, R. Pirri, P. Tordo, *Polym Prepr (Am Chem Soc, Div Polym Chem)* **1999**, 40, 317-318.
[5] T. Prodpran, V.L. Dimonie, E.D. Sudol, M.S. El-Aasser, *Proceedings of the American Chemical Society, Division of Polymeric Materials: Science and Engineering* **1999,** 80, 534-535.
[6] P.J. MacLeod, B. Keoshkerian, P. Odell, M.K. Georges, *Proceedings of the American Chemical Society, Division of Polymeric Materials: Science and Engineering* **1999**, 80, 539-540.
[7] C. Farcet, M. Lansalot, B. Charleux, R. Pirri, J.-P. Vairon, *Macromolecules* **2000**, 33, 8559-8570.
[8] T. Prodpran, V.L. Dimonie, E.D. Sudol, M.S. El-Aasser, *Macromol Symp* **2000**, 155, 1-14.
[9] G. Pan, E.D. Sudol, V.L. Dimonie, M.S. El-Aasser, *Macromolecules* **2001**, 34, 481-488.
[10] J.W. Ma, M.F. Cunningham, K.B. McAuley, B. Keoshkerian, M.K. Georges, *Journal of Polymer Science A: Polymer Chemistry* **2001**, 39, 1081-1089.
[11] K. Tortosa, J.-A. Smith, M.F. Cunningham, *Macromol. Rapid Commun.* **2001**, 22, 957-961.
[12] M.F. Cunningham, M. Xie, K.B. McAuley, B. Keoshkerian, M.K. Georges, to appear in *Macromolecules.*
[13] B. Keoshkerian, P.J. MacLeod, M.K. Georges, *Macromolecules* **2001**, 34, 3594-3599.