# Nitroxide-Mediated Miniemulsion Acrylate Polymerization

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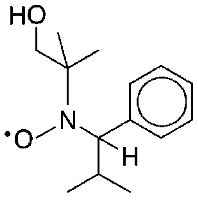
The development of living-radical polymerizations in the past 9 years has been impressive, resulting in a new way of thinking about free radical polymerization.[1] However, ultimately, living-radical polymerization will be judged on how commercially successful it becomes. Of the three main living-radical polymerizations, our group at Xerox has focused on the stable free radical polymerization (SFRP) process, and the vast majority of our studies have been done under bulk conditions.[2] While this process has served us and others well in developing and understanding the SFRP process, it is doubtful it will ever be the process of choice for large-scale manufacturing. As a consequence, focus has shifted to developing an SFRP emulsion process. Since the SFRP process is typically performed at 135 °C, well above the boiling point of water, some unique problems have made this task rather difficult as evidenced by the first two papers in this area. Finding the right conditions and combination of reagents to affect a stable high-temperature emulsion to date has been elusive.[3,4] However, as has been reported by Professor El-Aasser's group at Leihigh[5] and our group at Xerox,[6] an SFRP process can be successfully performed at high temperatures under miniemulsion conditions. Work at a lower temperature SFRP process has been reported by Lansalot et al., although conversions have been limited to 70% and polydispersities are broad, both probably a consequence of the low temperature that was used.[7]

For the miniemulsion process to be successful, a number of goals must be achieved. The miniemulsion lattices must be stable at high temperature, conversion must be 99% plus, reaction time needs to be relatively short, and the system must be compatible with a variety of monomers. We have recently reported on a modified SFRP miniemulsion process in which we have been able to polymerize styrene to 99% plus conversions while still maintaining a high degree of livingness by using a preformed TEMPO-terminated oligomer as the initiator.[8] In this communication, we demonstrate that by further modifying the miniemulsion polymerization process acrylates can be polymerized in a living fashion under high-temperature miniemulsion conditions while maintaining latex stability.

We studied two approaches to performing miniemulsion polymerization of acryaltes. The first centered on the use of a nitroxide-terminated polystyrene oligomer as the initiator for the miniemulsion. Nitroxide **1**, reported by Hawker et al.[9] to work well with acrylates, was reacted with benzoyl peroxide and styrene underbulk conditions at 135 °C for 15 min to give a polystyrene oligomer, $M_n = 1156$ and PD = 1.15, as estimatedby gel permeation chromatography (GPC) calibrated with polystyrene standards.



**(1)**

A miniemulsion was prepared[8] by emulsifing a solution of the oligomer (1.2 g) and hexadecane (1.2 g) in *n*-butyl acrylate (30 mL) with a solution of sodium dodecylbenzenesulfonate (2.4 g) in water (120 mL). To 5 mL of this emulsion was added a small amount of TEMPO [7 drops of a solution of TEMPO (28 mg) in *n*-butyl acrylate (4 mL)].[10] Heating the reaction mixture to 135 °C for 3 h resulted in polymer with $M_n = 11\ 816$ and polydispersity (PD) = 1.27. Monomer conversion was 86%. A visual inspection of the inside of the reactor vessel showed no fouling, a qualitative indication of the stability of the latex.

Having demonstrated that a stable SFRP miniemulsion nitroxide-mediated polymerization could be performed at 135 °C with *n*-butyl acrylate with nitroxide **1**, we were interested to see whether the same could be done with TEMPO as the nitroxide. There are economical reasons for wanting to use a nitroxide like TEMPO. However, it is well-known that polymerization of acrylates with TEMPO under bulk SFRP conditions proceeds poorly.[11] The polymerizations typically go to about 10% conversion or less and then shut down due to a buildup of excess nitroxide which inhibits the polymerization. Addition of compounds, such as acetol or simple sugars, which can produce small amounts of ene−diols in solution that react with the excess nitroxide, enable the acrylate polymerizations to proceed.[12] In the same class of materials is ascorbic acid, which has been reported to react very quickly ith nitroxides.[13] In the case of the polystyrene miniemulsion polymerization we reported earlier,[8] it was observed that no additives, such as camphorsulfonic acid, required under bulk conditions to speed up the polymerization, are required in the miniemulsion system.[14] We speculate this is due to a partitioning of excess free nitroxide between the organic and aqueous phases, reducing the amount of free nitroxide in the organic phase where the polymerization occurs. This would suggest that the polymerization of acrylates with TEMPO would be possible under miniemulsion conditions if there were a small amount of an efficient nitroxide destroyer, such as ascorbic acid, in the aqueous phase. This would help to reduce the amount of excess free nitroxide in the organic phase by shifting the equilibrium partitioning of the free nitroxide toward the aqueous phase.

Miniemulsions were prepared in a similar manner detailed above, the only difference being that alkoxyamine **2** (0.40 g), terminated with TEMPO, was used instead of the nitroxide **1**-terminated polystyrene oligomer. Heating these miniemulsions to 135 °C for typically 4−6 h resulted in oligomer products, as indicated by GPC analysis, with conversions of 8% or less. However, when the same emulsions were heated to 135 °C with a small amount of ascorbic acid in the

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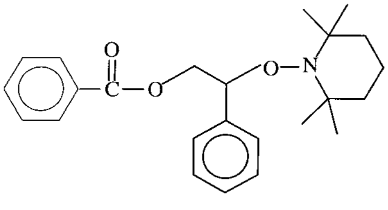

(2)

**Table 1. Number-Average Molecular Weights and Polydispersities for the Molecular Weight Distributions in Figure 1**

| sample | time (h) | $M_n$ | PD |
|---|---|---|---|
| i | 1 | 8 838 | 1.87 |
| ii | 2 | 10 290 | 1.82 |
| iii | 3 | 12 494 | 1.62 |

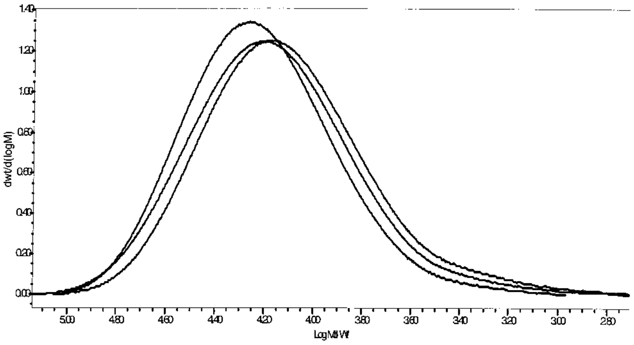

**Figure 1.** GPC plot of poly(*n*-butyl acrylate) prepared with alkoxyamine **2** as the initiator. The three distributions are for 1, 2, and 3 h polymerizations, going from right to left.

aqueous phase ($4.5 \times 10^{-6}$ mol of ascorbic acid per 5 mL of emulsion), polymerization occurred with conversions, after 3 h, typically between 60 and 65%. GPC analysis of the polymer products showed an incremental increase in molecular with time (Table 1, Figure 1). Polydispersities were broader than when nitroxide **1** was used, but the polymers are living as seen by the incremental increase in molecular weight with time. Chains growth is fastest in the first hour, then slows, and continues in a more consistent manner after that. The faster increase in molecular weight early in the polymerization may be due to the higher concentration of ascorbic acid in the reaction mixture in the first hour. Or the faster rate is due to the ease of diffusion of TEMPO from the organic to the aqueous phase in the early stage of the polymerization before an increase in viscosity in the micellular droplets restricts its flow. It is also possible that the actual explanation may be a combination of both these arguments.

The rate of polymerization can be controlled by varying the amount of ascorbic acid. An increase in ascorbic acid gives a higher molecular weight in a given time. Thus, for the emulsion formulation described above after 3 h at 135 °C, polymers with $M_n$'s of 1519, 8930, and 12 740 are obtained when $5.3 \times 10^{-7}$, $1.1 \times 10^{-6}$, and $2.1 \times 10^{-6}$ mol of ascorbic acid is used, respectively (Figure 2). However, if too much ascorbic acid is used, greater than $8.8 \times 10^{-6}$ mol, a bimodal molecular weight distribution results. The high molecular weight distribution occurs due to uncontrolled polymerization of some chains as consequence of a deficiency of nitroxide. When this occurs, it does so in the first hour of the polymerization, again when the mobility of the nitroxide between the two phases is unrestricted. While these results are instructive, more work needs to be performed in this area to confirm exactly what is happening.

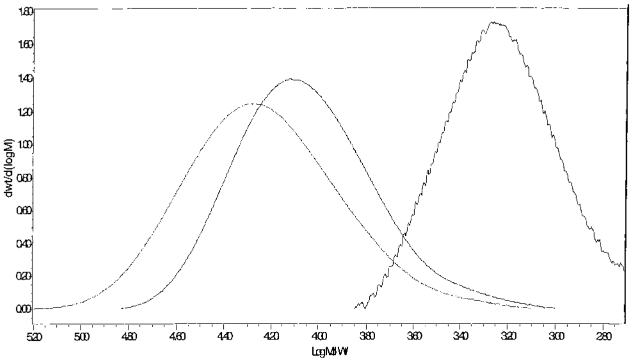

**Figure 2.** GPC plot of poly(*n*-butyl acrylate) prepared with alkoxyamine **2** as the initiator, with $5.3 \times 10^{-7}$, $1.1 \times 10^{-6}$, and $2.1 \times 10^{-6}$ mol of ascorbic acid going from right to left.

In summary, we report that acrylates can be polymerized by an SFRP miniemulsion process to yield stable lattices, thus expanding the list of monomers that can be polymerized by this technique. While better polydispersities are obtained with nitroxide **1**, TEMPO, which has an economical advantage, can also be used. Work is continuing to achieve 100% conversion in these polymerizations and to see how well they will function to make a variety of block copolymer under miniemulsion conditions.

## References and Notes

(1) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (b) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901. (c) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5555.

(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. *Macromolecules* **1994**, *27*, 7228.

(3) Bon, S. A. F.; Bosveld, M.; Klumperman, B.; German, A. L. *Macromolecules* **1997**, *30*, 324.

(4) Marestin, C.; Nöel, C.; Guyot, A.; Claverie, J. *Macromolecules* **1998**, *31*, 4041.

(5) Prodpran, T.; Dimonie, V.; Sudol, E. D.; El-Aasser, M. S. *Macromol. Symp.* **2000**, *155*, 1.

(6) MacLeod, P.; Barber, R.; Odell, P. G.; Keoshkerian, B.; Georges, M. K. *Macromol. Symp.* **2000**, *155*, 31.

(7) Farcet, C.; Lansalot, M.; Charleux, B.; Pirri, R.; Vairon, J. P. *Macromolecules* **2000**, *33*, 8559.

(8) Keoshkerian, B.; MacLeod, P.; Georges, M. K. *Macromolecules* **2001**, *34*, 3594.

(9) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904.

(10) Georges, M. K.; Veregin, R. P. N.; Daimon, K. *ACS Symp. Ser.* **1998**, *685*, 170.

(11) Georges, M. K.; Odell, P. G.; Listigovwers, N. A.; Quinlan, M. H. *ACS Symp. Ser.* **1998**, *713*, 80.

(12) Keoshkerian, B.; Georges, M. K.; Quinlan, M.; Veregin, R. P. N.; Goodbrand, B. *Macromolecules* **1998**, *31*, 7559.

(13) Plaeos, C. M.; Dais, P. *J. Chem. Soc., Chem. Commun.* **1977**, 345.

(14) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. *Macromolecules* **1994**, *27*, 7228.

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