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Stable Free Radical Miniemulsion Polymerization

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Abstract: Stable emulsions of polystyrene have been prepared by nitroxide-mediated living-radical miniemulsion polymerization. Optimization of the ratios and amounts of surfactant, cosurfactant, and nitroxide provided both good latex properties and good living-radical chemistry. Results were superior to those obtained in comparable bulk polymerizations. Conversions of 87% were obtained in 6 hours at 135°C without the use of a rate accelerant and the molecular weight distributions were typically in the 1.1 range.

Introduction

Stable free radical polymerization (SFRP) is one type of living-radical polymerization in which the initiated polymer chains are reversibly capped by a stable free radical, for example, a nitroxide radical, as shown in Scheme 1. The reversible capping by nitroxide is the key to the SFRP process enabling control over molecular weight and molecular weight distribution. Detailed mechanistic and kinetic studies of the SFRP process have been published.[1,2,3,4]

One of the attractive features of the SFRP process is that it produces a dormant polymer, which under the appropriate conditions can be used for further polymerization or chemical manipulation to yield complex architectures.[5] Most polymer synthesis by the SFRP process reported in the literature has been done in the bulk.[6,7,8,9,10] While convenient and practical for small-scale laboratory reactions, a bulk polymerization process is not

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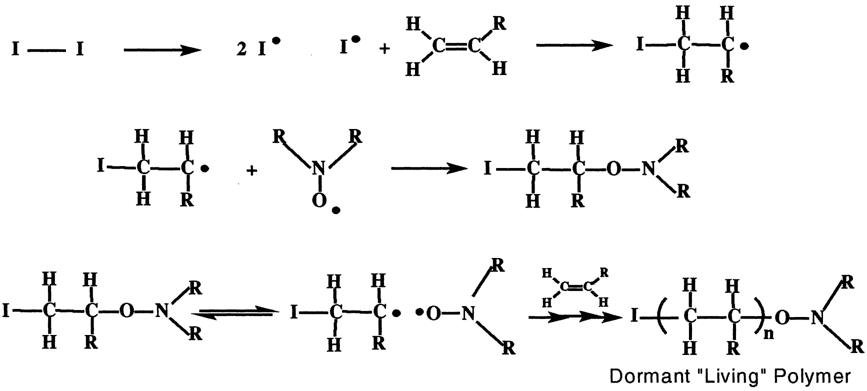
necessarily the process of choice for large-scale commercialization efforts. In most cases the heat transfer and kinetic benefits of an emulsion process are more desirable. And to go one step further it would be very intriguing to be able to make inexpensive block copolymers by an emulsion process, a goal we are working towards.



Scheme 1. Reaction Scheme for the SFRP process

Clearly, however, the development of a stable free radical emulsion polymerization process presents many new challenges. The kinetics of the SFRP process are quite different from conventional free radical polymerization kinetics and it is difficult to predict the outcome of combining a living-radical polymerization with an emulsion process. Under bulk polymerization conditions the rates of polymerization and the degree of control are dependent on the level of free nitroxide or excess nitroxide in the reaction solution. This can be readily determined since the reaction medium is homogeneous. The same cannot be said for an emulsion reaction medium. Even at the outset it can be anticipated that the partitioning of the nitroxide between the aqueous phase and the micelle will be problematic.

To further complicate an SFRP emulsion polymerization process, bulk reactions have shown that temperatures up to 135°C are required to get the polymerization to proceed at a reasonable rate thus requiring the development of an emulsion process above the boiling point of water. One group's earlier attempts to perform SFR emulsion polymerization were unsuccessful leading them to conclude that for emulsion polymerization to be successful, a living-radical system needs to be developed that operates at ambient temperatures.[11] However, a recent paper by Marestin et *al.*[12] reports stable polystyrene latexes, in the presence of nitroxides, can be prepared at temperatures in the 135°C range.[13] Polystyrene was prepared at 37% conversion in 36 hours at solids contents of 5% or less. The number average molecular weights were typically 10K or less with the molecular weight distributions in the 1.3-1.7 range. The particle size distributions were broad and/or bimodal. These initial results are encouraging but illustrate the challenges that still need to be addressed and resolved to develop a viable emulsion nitroxide-mediated living-radical polymerization process. For example, shorter reaction times, higher conversions, higher solids content, higher molecular weights, better control over polydispersity, and an understanding of particle formation, as well as, the actual livingness of the system, are necessary. The challenges highlighted in the Marestin[12] paper have prompted us to communicate our work on a stable free radical miniemulsion polymerization process we have been studying which begins to address many of these issues.

Experimental

All polymerizations were performed at 20% solids loading using potassium persulfate (KPS) as the initiator and 2,2,6,6-tetramethylpiperidinyloxy radical (TEMPO) as the nitroxide stable free radical agent. Cosurfactant hexadecane (HD) was used in combination with the surfactant sodium dodecylbenzenesulfonic acid, sodium salt (SDBS). The amount of SDBS employed was in the typical range for emulsion polymerizations, 0.5-2 wt% (based on the aqueous phase). All polymerizations were done in a 300 mL Parr reactor at 135°C. The Parr reactor was degassed with argon prior to starting the reaction. Particle sizes were determined by light scattering using a Nicomp instrument. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters/Millipore liquid chromatograph equipped with Ultrastyragel® columns of pore size 10^4Å, 2x500Å and 100Å. A flow rate of 0.8 mL/min was used with tetrahydrofuran as the elutant.

Results and Discussion

The initial goal of this work was to demonstrate that a stable latex containing living polymer could be prepared using a miniemulsion process. The monomer chosen for investigation was styrene, as it has been well studied under bulk conditions. In a conventional miniemulsion polymerization process small monomer droplets are formed using a high shear device followed by nucleation within these droplets. The monomer droplets are stabilized by surfactants or by a combination of surfactants and a cosurfactant (hexadecane or cetyl alcohol).[14,15] A similar approach was used for the SFRP miniemulsion study. For the initial experiments 0.35 wt% of SDBS and 0.9 wt% of hexadecane was used. The molar TEMPO:KPS ratio was 1.2:1, which is a typical ratio for a bulk polymerization. The initial latex was milky white and stable, as were all subsequent samples taken during the polymerization. After 6 hours at 135°C no reactor fouling or agglomeration was evident. The initial number average particle size of the latex particles was about 90 nm, as was the final particle size. While these initial

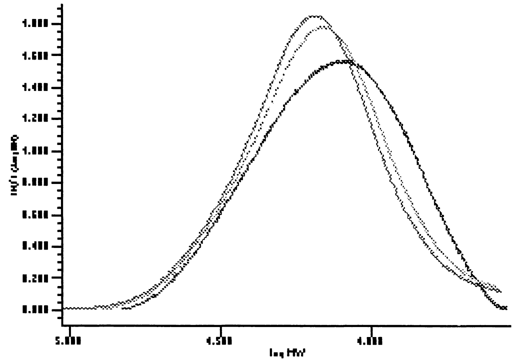


Figure 1. GPC traces after 2, 4, and 6 hours for a SFR miniemulsion polymerization at 135 °C

formulations provided stable latexes, examination of the characteristics of the polymer as a function of time suggested that the polymerizations were not proceeding via a living-radical polymerization mechanism. Samples taken from the reaction mixture every two hours for six hours and analyzed by GPC (Figure 1) did not show the expected shifts in the molecular weight distribution to higher molecular weights as a function of time, characteristic of a living system. The molecular weight distributions (polydispersity) were in the 1.6 range, broad for polystyrene by SFRP standards. The amount of nitroxide used was clearly insufficient under these miniemulsion polymerization conditions to yield a living-radical polymerization.

A series of experiments were performed where the level of nitroxide was increased. It was found that during these experiments it was also necessary to modify the surfactant conditions. An intermediate set of conditions was found (1.4 wt% SDBS, 3.6 wt% hexadecane, TEMPO:KPS 2.4:1) that indicated living behavior but gave poor latex stability. The GPC traces (Figure 2) for 2, 4 and 6 hour samples show that while part of the molecular weight distribution moves to higher molecular weights as a function of time there is a higher molecular weight component that does not shift. This suggests that only a portion of the chains is living. It is assumed that the high molecular weight chains grew by a conventional free radical process since they were present very early on in the

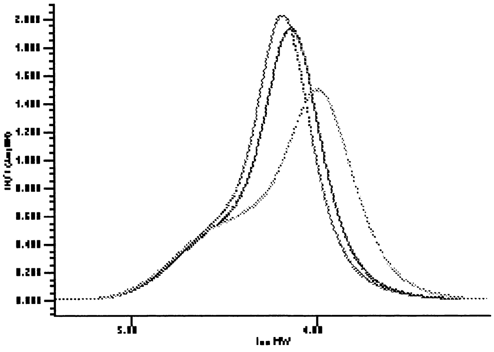


Figure 2. GPC traces after 2, 4, and 6 hours for a SFR miniemulsion polymerization of styrene at 135 °C.

polymerization. The initial latex was stable with a number average particle size of 30 nm. However, after 2 hours there was fouling observed on the walls of the reactor and the stirrer that became progressively worse over time. The final latex had a bimodal distribution of particles. The observation that some of the chains were living was encouraging. However, the latex stability was reduced. Further optimization of both the latex parameters and the nitroxide was necessary.

A second series of designed experiments were conducted in order to determine if formulation and reaction conditions existed that would enable both good SFRP chemistry and good latex properties. This study showed that both requirements could be met by using 0.7 wt% SDBS, 3.6 wt% hexadecane, and a TEMPO:KPS ratio of 2.9:1. Figure 3 shows the molecular weight distributions (PDs) for a 3 hour and a 6 hour polymer sample. It is important to look at the shape of the curves and the shifting of the curves as a function of time. The molecular weight distributions are Gaussian in shape with little or no tailing. The PD of the final product is 1.1 and the number average molecular weight is 14,000. In fact, further reactions demonstrated that styrene SFR miniemulsion polymerization PDs can be obtained that are typically in the 1.1 range and in many cases as low as 1.08. Number average molecular weights of 35,000 have been achieved with PDs of 1.2 . In addition to obtaining Gaussian, narrow molecular weight distributions the entire molecular weight distribution shifts to higher molecular weights as a function of

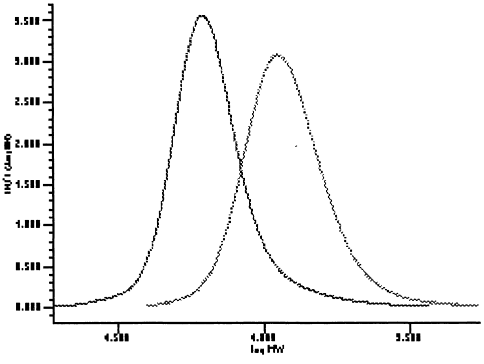


Figure 3. Optimized SFR miniemulsion polymerization of styrene at 135°C sampled after 3 and 6 hours.

time, a necessary characteristic of a living system.

The conversion of the final polymer sample shown in Figure 3, as determined by gas chromatography, after 6 hours was 87%. Compared to bulk polymerizations described in the literature, this is a very short reaction time to achieve 87% conversion especially since no rate accelerant, such as camphorsulfonic acid, is required.[16,17] Equally important, the stable milky white latex was obtained with no reactor fouling or agglomeration and the final number average particle size was 50 nm.

Conclusions

Although this study resulted in a set of suitable miniemulsion polymerization conditions for a nitroxide-based living-radical polymerization process many fundamental questions still need to be addressed. Studies are ongoing to understand important issues such as the effect of particle size and nitroxide partitioning on the polymerization mechanism and kinetics. Future work also involves chain extending the polystyrenes prepared by miniemulsion to demonstrate that the polymers can be used for block copolymer synthesis. We are also looking at performing these emulsion polymerizations at temperatures below 100°C. While we have had some successful at doing this, it has come at the expense of increased reaction times. Work is continuing to reduce the reaction times and the results of this work will be published in the near future.

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