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Rate-Enhanced Nitroxide-Mediated Miniemulsion Polymerization

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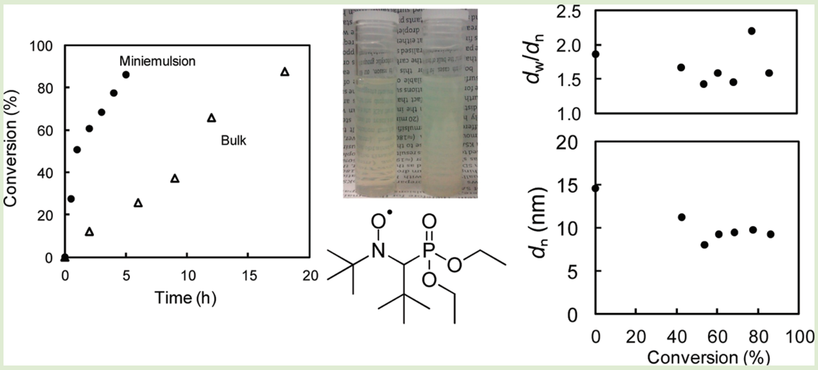
Supporting Information



ABSTRACT: A novel approach is presented whereby nitroxide-mediated radical polymerization (NMP) is conducted in an aqueous heterogeneous system at an initial polymerization rate an order of magnitude greater than the corresponding bulk system, accompanied by an improvement in the level of control over the molecular weight distribution. NMP of styrene mediated by *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) at 90 °C was performed in a miniemulsion with exceptionally small particles of number-average diameter ~10 nm, generated by ultrasonication combined with in situ surfactant formation. The results are discussed in terms of the effects of compartmentalization, nitroxide partitioning (exit/entry), and a rate-enhancing effect of oleic acid. These findings illustrate that it is possible to significantly improve the performance of an NMP process by the exploitation of intrinsic effects of heterogeneous systems.

Nitroxide-mediated radical polymerization (NMP)[1] is one of the most well-known methods of controlled/living radical polymerization (CLRP).[2] One of the challenges with NMP is to increase the polymerization rate (R_p) while maintaining good control (narrow molecular weight distribution (MWD)) and livingness (end-functionality). In a homogeneous system (bulk/solution), a higher R_p tends to lead to (partial) loss of control/livingness. R_p can be increased (often with a concomitant decrease in control) by use of a rate-enhancing additive, for example, acetic anhydride or organic acids such as camphorsulfonic acid.[3] Another technique is to add a high-temperature radical initiator, which provides a continuous supply of radicals.[4] Extensive work has also been carried out on the development of novel nitroxides to enable NMP to be conducted at lower temperatures (equivalent to increased R_p at normal NMP temperatures).[1b,5] The past decade has witnessed impressive developments in the field of CLRP in dispersed systems for polymer and polymeric nanoparticle synthesis.[6] CLRP in dispersed systems is inherently more complex than their homogeneous counterparts (bulk/solution) due to a range of intrinsic features associated with heterogeneity, for example, reactant partitioning and phase transfer events[7] and interface-[8] and compartmentalization effects.[9] Ultimately, one strives to understand and exploit these phenomena so that the efficiency of a CLRP process in terms of control of the MWD, the livingness as well as R_p, can be improved.

It is an intriguing prospect to exploit intrinsic effects of aqueous dispersed NMP to increase R_p while maintaining good control/livingness. In this regard, compartmentalization effects and nitroxide partitioning effects are of utmost interest. Compartmentalization effects originate in the physical confinement of reactants within discrete spaces (nanoreactors), and comprise segregation effects and the confined space effect.[9,10] The segregation effect refers to two species located in separate particles being unable to react, whereas the confined space effect refers to how two species react more rapidly in a small particle than in a large particle, as described in detail for NMP based on theoretical work.[10,11] In the absence of nitroxide partitioning, segregation of propagating radicals may lead to reduced termination rates (increased livingness and higher R_p) and the deactivation rate may increase due to the confined space effect (leading to better control, i.e., narrower MWDs, but lower R_p).[9,10] Depending on the relative magnitudes of the segregation effect and the confined space effect, the level of control and R_p may increase or decrease.[11f] In addition, the

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fluctuation in the number of nitroxide radicals between different particles can lead to less control and higher R_p.[22] The magnitude of the confined space effect on deactivation is reduced if the nitroxide is able to exit into the continuous phase and is nonexistent if the nitroxide diffuses freely between particles.[9,11b,g,12] Experimental data of NMP in aqueous dispersed systems include examples of systems where (i) the behavior is similar to in bulk,[13] (ii) R_p is lower than in bulk with good control/livingness,[14] and (iii) R_p is higher than in bulk but control/livingness is (partially) lost.[8a,f,15] To the best of our knowledge, there are to date no examples of heterogeneous NMP systems where R_p is considerably higher than in the corresponding homogeneous system without significant loss of control/livingness.

Herein we describe a novel approach whereby NMP is conducted in an aqueous heterogeneous system at an initial polymerization rate an order of magnitude greater than the corresponding bulk system, accompanied by an improvement in the level of control. NMP of styrene mediated by *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) was performed in a miniemulsion with exceptionally small particles of a number-average diameter ~10 nm, generated by ultrasonication combined with in situ surfactant formation.

The in situ surfactant technique for miniemulsion formation is based on the generation of surfactant at the oil–water interface by reaction between a hydrophobic organic acid in the oil phase and a base in the aqueous phase.[16] This approach enables the preparation of miniemulsions without use of high energy mixing devices. In the present work, the in situ surfactant technique was employed in conjunction with ultrasonication at a high surfactant content (based on our recently reported approach[17]) to generate miniemulsions with exceptionally small droplets. Styrene-in-water miniemulsions were generated using oleic acid and potassium hydroxide (n_{COOH}/n_{OH} = 1:2) with 120 wt % oleic acid relative to styrene and 5.2 wt % styrene relative to water. This surfactant content is much higher than in a normal miniemulsion, but lower than in a typical microemulsion. The oil phase contained 10 wt % hexadecane and a SG1-terminated polystyrene macroinitiator (PSt-SG1; M_n = 1380 g/mol, M_w/M_n = 1.18) and 10 mol % free SG1 relative to PSt-SG1 (Table S1, Supporting Information). The initial miniemulsion was transparent, with no phase separation or changes in the degree of transparency at room temperature for at least three weeks. Figure 1 shows conversion–time data for polymerization at 90 °C (the St/SG1 system has previously been shown to proceed well at this relatively low temperature[18]), as well as data for the corresponding bulk polymerization. The bulk polymerization was slow, reaching 88% conversion in 18 h. The miniemulsion polymerization displays an exceptionally high R_p, the initial R_p being close to 12 times higher than in bulk. In both cases, the M_n values are close to the theoretical values ($M_{n,th}$) (Figure 2), but the control is superior in miniemulsion with M_w/M_n = 1.17–1.21 to be compared with M_w/M_n > 1.2 in bulk (Figures 2 and S1 of the SI). It is noted that M_n > $M_{n,th}$ at the highest conversion levels in miniemulsion, indicating a reduction in the number of polymer chains (most likely due to bimolecular termination by combination). Figure 3 shows number-average particle diameters (d_n) versus conversion, revealing that the particles are extremely small, with d_n ≈ 10 nm to high conversion. These particles are markedly smaller than what is normally obtained in a miniemulsion[19] and more akin to a microemulsion.[20] However, the particle size distributions based on weight and intensity, as well as TEM analysis, reveal that larger particle are also present (Figures 4 and S2 of the SI). The emulsions generally became somewhat less transparent on polymerization but remained translucent (Figure 4).

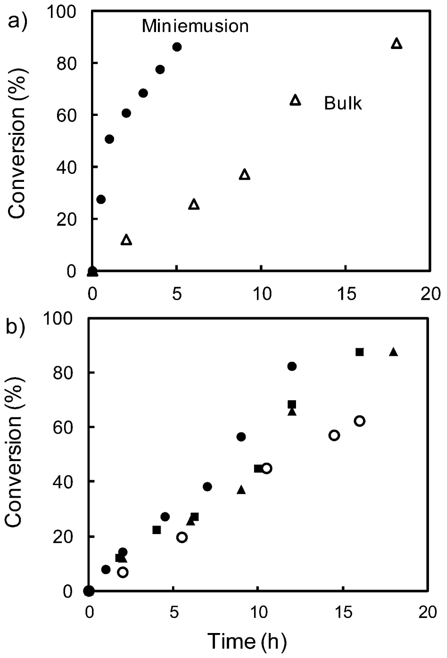

Figure 1. Conversion vs time data for NMP of styrene (a) using a PSt-SG1 macroinitiator ($[\text{PSt-SG1}]_0$ = 0.06 M in the organic phase; 10 mol % free SG1 rel. to PSt-SG1) in (●) a miniemulsion (based on ultrasonication and in situ generation of potassium oleate; 120 wt % oleic acid relative to styrene) and (△) bulk at 90 °C; (b) using a PSt-SG1 macroinitiator in bulk (▲; $[\text{PSt-SG1}]_0$ = 0.06 M), and solutions comprising (●) 120 wt % oleic acid relative to styrene, (■) 8 wt % oleic acid and 112 wt % toluene relative to styrene, and (○) toluene ($[\text{PSt-SG1}]_0$ = 0.025 M in all solution polymerizations, and 10 mol % free SG1 relative to PSt-SG1 for all four polymerizations (see text and SI for full details).

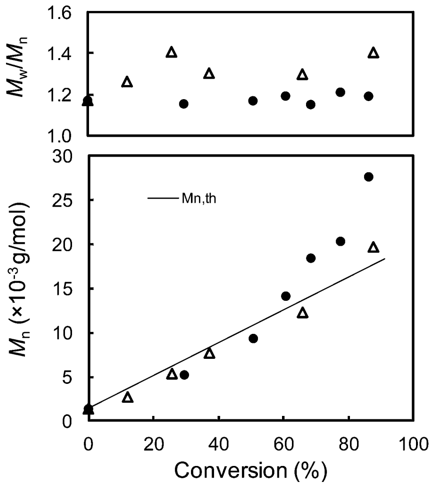

Figure 2. M_n and M_w/M_n vs conversion for NMP of styrene using a PSt-SG1 macroinitiator in (●) miniemulsion and (△) bulk at 90 °C (see Figure 1 caption for details).

Considering the rapid polymerization in miniemulsion, the high level of control over the MWD is quite remarkable. This intriguing behavior may originate in a number of separate

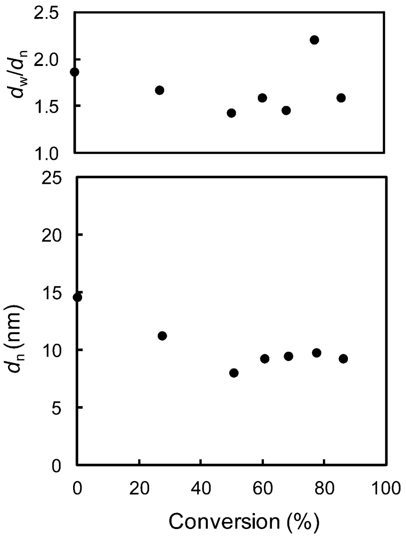

Figure 3. d_n and d_w/d_n vs conversion for NMP of styrene using a PSt-SG1 macroinitiator in miniemulsion and bulk at 90 °C (see the Figure 1 caption for details).

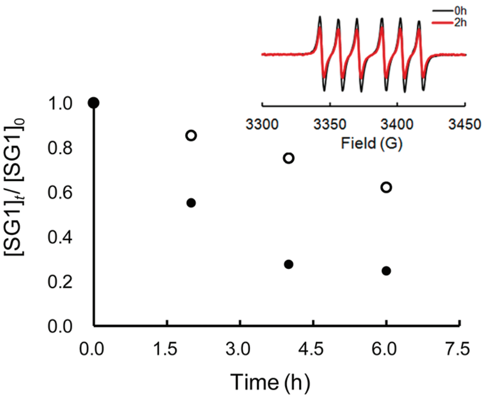

Figure 5. Relative concentrations of nitroxide SG1 as functions of time for solutions of SG1 (5.5 mM) in oleic acid (●) and *tert*-butylbenzene (○) at 90 °C as measured by EPR. The inset shows EPR spectra in oleic acid.

effects, for example, compartmentalization, nitroxide partitioning, and oleic acid functioning as a rate-enhancing additive. Electron paramagnetic resonance (EPR) spectroscopy was used to monitor the SG1 concentration versus time at 90 °C for solutions of SG1 in *tert*-butyl benzene and oleic acid, respectively (Figure 5). The rate of disappearance of SG1 was approximately twice as high in oleic acid as in *tert*-butyl benzene, with a half-life of ~3 h. This is much lower than previously reported for SG1 (half-life 15 h at 120 °C[21]) for reasons that are not clear. These data suggest that the presence of oleic acid in the miniemulsion may have caused an increase in R_p. However, homogeneous (solution) NMP conducted using the same organic phase composition as in miniemulsion (120 wt % oleic acid relative to styrene) revealed only a very moderate increase in R_p relative to the corresponding bulk and toluene solution NMPs, and the effect of 8 wt % oleic acid (diluted with toluene to eliminate concentration effects) was even smaller (Figure 1b). The control over the MWDs was good for 8 wt % oleic acid, whereas control/livingness was largely lost for 120 wt % oleic acid (Figures 6 and S3 and S4 of the SI). It is thus apparent that the high R_p and good control/livingness in miniemulsion cannot be explained simply by oleic acid influencing the SG1 concentration.

On the basis of theoretical work on compartmentalization effects in NMP in the absence of nitroxide partitioning (exit/entry), R_p decreases with decreasing particle size,[10,11] in sharp contrast to the present results. However, if the nitroxide is able to undergo exit to a significant extent, the situation is quite different.[9,11b,g,12] Nitroxide exit counteracts the confined space effect on deactivation, thereby causing an increase in R_p. In the

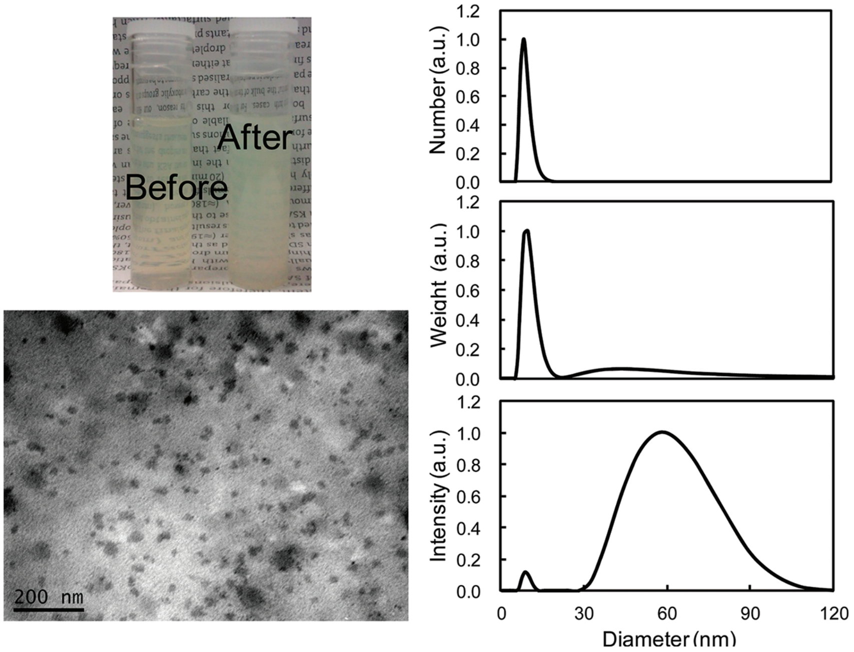

Figure 4. Photos before/after polymerization, TEM image (scale bar = 200 nm) and DLS particle size distributions for NMP of styrene at 90 °C with a PSt-SG1 macroinitiator ($[\text{PSt-SG1}]_0$ = 0.06 M in organic phase; 10 mol % free SG1 relative to PSt-SG1) in a miniemulsion based on ultrasonication and in situ generation of potassium oleate; 120 wt % oleic acid relative to styrene (conversion = 77%).

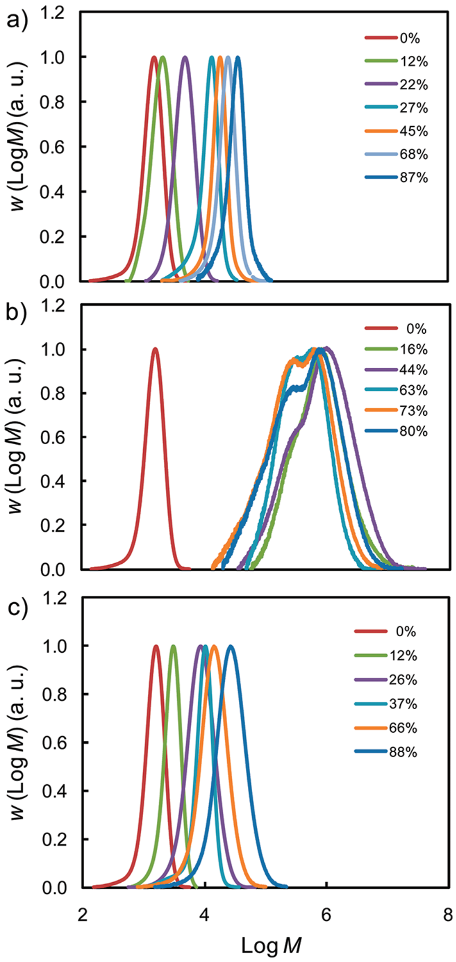

Figure 6. MWDs from NMP of styrene at 90 °C at different conversions as indicated using a PSt-SG1 macroinitiator in solutions comprising (a) 8 wt % oleic acid and 112 wt % toluene relative to styrene, (b) 120 wt % oleic acid relative to styrene, and (c) bulk (details as in Figure 1).

case of SG1, it has been proposed that the confined space effect on deactivation is minor or even nonexistent due to partitioning.[12,14b,c] Qualitatively, one can thus envisage a system where the propagating radicals are segregated (reduced termination), but the nitroxide is able to diffuse throughout the system, leading to an overall effect of reduced termination and thus higher R_p with control/livingness maintained. At present, it is speculated that a combination of effects of compartmentalization (confined space effect on deactivation and segregation effect on termination), nitroxide exit/entry, and a minor rate-enhancing effect of oleic acid creates favorable conditions in these very small particles for the polymerization to proceed very rapidly with good control/livingness. However, extensive modeling and simulations accounting for compartmentalization of both propagating radicals and nitroxide as well as nitroxide partitioning effects are required to fully understand these types of systems. It has recently been shown by modeling and simulations that the exit/entry of nitroxide can lead to a dramatic increase in the polymerization rate for the St/TEMPO system for sufficiently small particles.[22]

In summary, SG1-mediated radical polymerization has been conducted in a miniemulsion with exceptionally small particle diameters generated by ultrasonication combined with in situ formation of a high concentration of potassium oleate, resulting in more than a magnitude increase in polymerization rate and better control/livingness compared to the corresponding bulk system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, molecular weight data, and particle size distributions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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