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Nitroxide-Mediated Radical Polymerization in Miniemulsion On the Basis of in Situ Surfactant Formation without Use of Homogenization Device

Yi Guo, Jingquan Liu, and Per B. Zetterlund*

*Centre for Advanced Macromolecular Design (CAMD),
School of Chemical Engineering, The University of
New South Wales, Sydney, NSW 2052, Australia*

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Miniemulsion polymerization is an attractive technique for synthesis of polymeric nanoparticles in the particle diameter range 50−1000 nm.[1] The process is based on conversion of monomer droplets into polymer particles (monomer droplet nucleation), and as such it is advantageous for synthesis of hybrid nanoparticles containing encapsulated hydrophobic solids as well as hollow nanoparticles containing hydrophobic liquid.[2] Unlike emulsion polymerization, diffusion across the aqueous phase from monomer droplets to polymer particles is not required, and miniemulsion polymerization is thus ideally suited for implementation of controlled/living radical polymerization (CLRP)[3] in aqueous dispersed systems.[4−12] Miniemulsions are normally prepared by use of a high shear device (e.g., ultrasonication) in an energy intensive process that has been an impediment to commercialization and industrial use.[13] It is thus of great interest to develop low-energy methods for miniemulsion polymerization.[14]

It has been reported by Prokopov and Gritskova[15] and Parker et al.[16] that a miniemulsion can be generated without relying on high energy shear devices by use of in situ formation of surfactant. The method relies on the formation of a fine aqueous miniemulsion on gentle mixing of the organic phase and the aqueous phase as a result of in situ formation of a surfactant at the oil−water interface. Compared to simply adding the surfactant to the aqueous phase prior to mixing, this technique results in dramatically lower interfacial tensions, and has also been reported to generate narrower particle size distributions under appropriate conditions.[15] It has been demonstrated that when employing mechanical homogenization devices, surfactant generation at the interface results in more rapid production of a given droplet diameter than when using a preformed surfactant.[17,18] However, El-Aasser and coworkers reported that the in situ technique (without use of homogenization device) did not result in emulsion stability comparable to normal miniemulsions, and claimed that the polymerization mechanism is similar to that of an emulsion polymerization.[19]

We here report that both conventional (nonliving) radical polymerization and nitroxide-mediated radical polymerization (NMP)[20,21] of styrene can be successfully performed in miniemulsion based on in situ formation of the surfactant potassium oleate without the use of high energy-consuming shear devices.

Conventional radical polymerizations of styrene initiated by azobis(isobutyronitrile) (AIBN) at 70 °C were carried out using oleic acid/potassium hydroxide as the in situ surfactant system (Table 1). On the basis of all oleic acid being converted to the surfactant potassium oleate, the surfactant content would be 22 wt % relative to styrene. The organic phase (containing oleic acid) was added dropwise over approximately 15 min to the aqueous phase (containing potassium hydroxide) under magnetic stirring, resulting in the formation of a whitish/translucent mixture. The subsequent polymerization reached 83% conversion in 4 h (Figure 1S), with a monomodal particle size distribution based on particle number (Figure 3S; d_n = 77 nm; d_w/d_n = 2.21). The monomer droplet and particle size distributions based on volume were bimodal, comprising a small number of larger droplets/particles in the micrometer-size range (Figure 4S) amounting to approximately 6 wt % of the total organic phase at 83% conversion (Table 1S). The overall particle (droplet at 0% conversion) size increased from d_n = 35 nm at 0% conversion to d_n = 77 nm at 83% conversion, thus suggesting the absence of significant secondary nucleation (which would cause a decrease in particle size as new particles are generated). The number of particles decreased with increasing conversion (Figure 5S) consistent with a miniemulsion polymerization mechanism where some Ostwald ripening and coalescence occur.[1] The polymerized emulsion remained stable with no visual phase separation/coagulation for at least 1 month. This result may seem to be in conflict with the report of El-Aasser and co-workers;[19] however, the surfactant (oleic acid) concentration was markedly higher in the present study (22 vs 4.2 wt % relative to styrene).

Table 1. Recipes for Miniemulsion Polymerization of Styrene Based on *in Situ* Surfactant Formation

	conventional (g)	NMP (g)
St	1.05	2.1
oleic acid	0.237	0.6452
PSt-SG1[a]		0.2832
SG1		0.0042
hexadecane	0.074	0.15
AIBN	0.100	
KOH	0.0737[b]	0.208[c]
H_2O	10.2	20.1

[a] M_n = 2370 g/mol; M_w/M_n = 1.12. [b] $n_{KOH}/n_{oleic\ acid}$ = 1.5. [c] $n_{KOH}/n_{oleic\ acid}$ = 2.

NMP of styrene using a polystyrene macroinitiator (PSt-SG1) based on the nitroxide *N*-*tert*-butyl-*N*-[1-diethylphosphono(2,2-dimethylpropyl)]oxy (SG1) was carried out at 100 °C using oleic acid/KOH that would generate 31 wt % potassium oleate relative to styrene assuming full conversion of oleic acid. The miniemulsion exhibited satisfactory colloidal stability throughout the polymerization (16 and 22 wt % oleic acid at the same oleic acid/KOH ratio resulted in significant coagulation) and reached 87% conversion in 10 h (Figure 6S). The amount of surfactant generated in situ is higher than the level normally employed in a miniemulsion (5−15 wt % relative to monomer), but remains much lower than in a microemulsion[22] (which is thermodynamically stable and forms spontaneously in the absence of high energy emulsification). Figure 1 shows the molecular weight distributions (MWDs) at various conversions, revealing narrow MWDs shifting to higher molecular weight with increasing conversion. The number-average molecular weights (M_n) remained close to the theoretical values ($M_{n,th} = (\alpha[\mathrm{St}]_0 M_{\mathrm{St}}/[\mathrm{PSt\text{-}TEMPO}]_0) + M_{n,\mathrm{PSt\text{-}SG1}}$, where α denotes fractional conversion, $[\mathrm{St}]_0$ is the initial St concentration, M_{St} is the molar mass of St, and $M_{n,\mathrm{PSt\text{-}SG1}}$ is the M_n of PSt-SG1), except in the highest conversion range (>80%) where $M_n > M_{n,th}$, possibly due to bimolecular termination by combination (Figure 2). The polydispersities (M_w/M_n) remained below 1.22 throughout the polymerization. These results are consistent with very good control/livingness. The monomer droplet and particle size distributions by droplet/particle number

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*Corresponding author. Telephone: +61 2 9385 4331. Fax: +61 2 9385 6250. E-mail: p.zetterlund@unsw.edu.au.

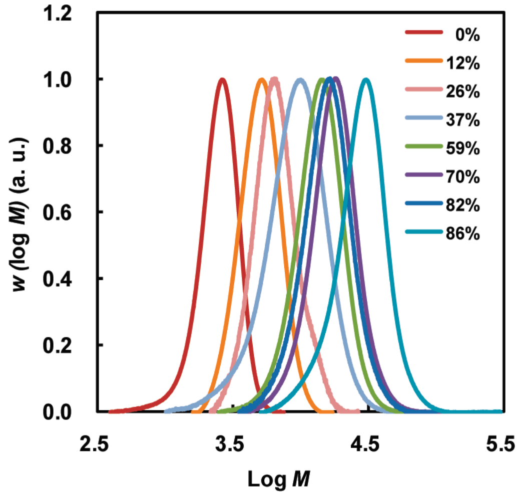

Figure 1. MWDs at various conversions as indicated for miniemulsion NMP of styrene using the nitroxide SG1 employing in situ surfactant formation of potassium oleate at 100 °C (recipe in Table 1).

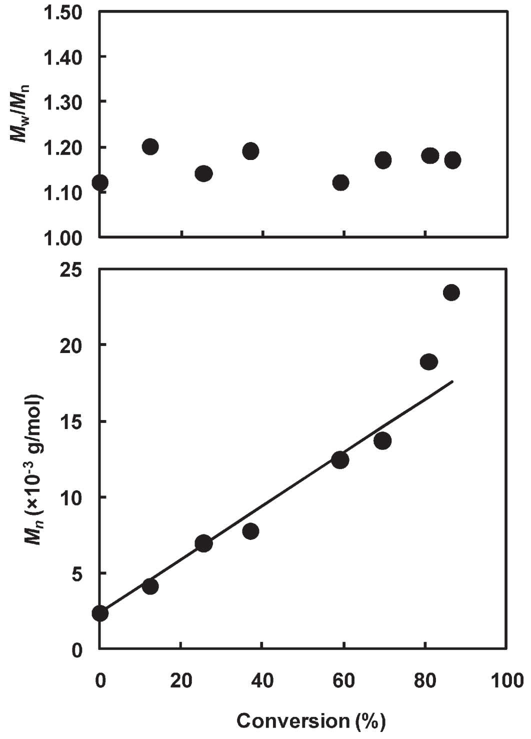

Figure 2. M_n and M_w/M_n vs conversion for miniemulsion NMP of styrene using the nitroxide SG1 employing in situ surfactant formation of potassium oleate at 100 °C (recipe in Table 1). The line depicts the theoretical M_n ($M_{n,th}$).

were monomodal (Figure 7S), but the distributions by droplet/particle volume revealed a significant population of larger droplets/particles with diameters ≈500−3500 nm (Figure 8S). Therefore, even though d_n < 100 nm (Figure 7S), the vast majority of the polymerization (Table 2S) would occur in particles with diameters in the micrometer-scale, and as such particle size effects such as compartmentalization[23] and interface effects[7,24] would not play significant roles on the polymerization kinetics. The DLS data were consistent with TEM images of the particles (Figure 3; note that micrometer-sized particles, although present, are not depicted in the TEM).

The fact that the polymerization exhibited both good control and livingness is consistent with the polymerization proceeding as a miniemulsion polymerization, with minimal secondary nucleation. If the polymerization were to proceed with a mechanism similar to that of an emulsion polymerization (i.e., micellar and/or homogeneous nucleation accompanied by monomer diffusion from monomer droplets to the thus generated particles), as has been argued by El-Aasser and co-workers[19] for the conventional (nonliving) polymerization of styrene using the in situ surfactant approach, it is extremely unlikely that control/livingness would have been maintained, because the macroinitiator is unable to diffuse across the aqueous phase (although SG1 is). As for the conventional (nonliving) polymerization described above, the number of particles (droplets at 0% conversion) decreased with increasing conversion (Figure 5S), consistent with a miniemulsion polymerization mechanism with some Ostwald ripening and coalescence.[1]

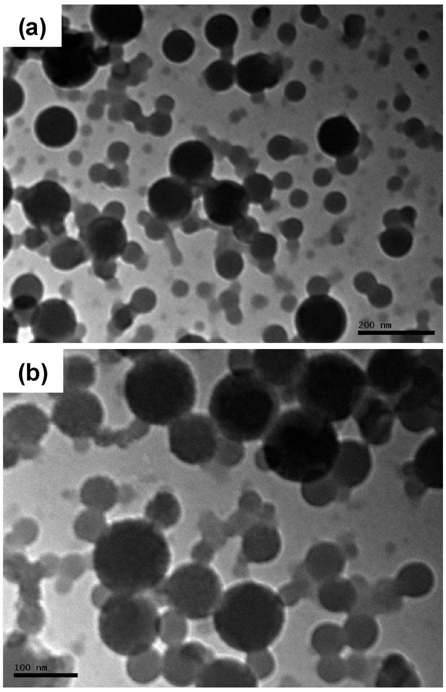

Figure 3. TEM micrographs of polystyrene particles obtained by miniemulsion NMP of styrene using the nitroxide SG1 employing in situ surfactant formation of potassium oleate at 100 °C (recipe in Table 1). Scale bars are (a) 200 nm and (b) 100 nm.

In summary, miniemulsion CLRP, more specifically NMP based on the nitroxide SG1 and styrene, has been carried out successfully for the first time without use of the high energy shear devices normally employed in miniemulsification procedures. The system exhibited good control/livingness and high colloidal stability throughout the polymerization. The present results represent a significant step forward with regards to development of industrially viable miniemulsion CLRP systems, which has to date been an impediment for commercialization of CLRP.

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Supporting Information Available: Text giving experimental procedures, tables of experimental data for the conventional (nonliving) miniemulsion system, and figures showing DLS and conversion−time data for the miniemulsion NMP system and a TEM micrograph. This material is available free of charge via the Internet at http://pubs.acs.org.

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