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Miniemulsion Polymerization Based on Low Energy Emulsification with Preservation of Initial Droplet Identity

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A miniemulsion (nanoemulsion) is a thermodynamically unstable but kinetically stable dispersion of submicrometer (typically 20 - 500 nm) oil droplets in water. The particle size is usually larger than in microemulsions (thermodynamically stable), but a much lower surfactant content is required in miniemulsions.[1,2] Miniemulsions have a wide range of applications in the pharmaceutical[3] and cosmetics[4] fields and also as polymerization systems.[5,6] Miniemulsion polymerizations are particularly useful for synthesis of hollow particles and organic/inorganic hybrid particles by encapsulation of inorganic materials,[7−9] and for implementation of controlled/living radical polymerization (CLRP) in dispersed systems.[10,11] However, the high energy requirement for preparation of miniemulsions by traditional methods[1,2] (high shear methods such as high pressure homogenization and ultrasonication) has precluded widespread use and commercialization.

Thermodynamically, the generation of very small dispersed oil droplets requires high energy input and/or a large amount of surfactant.[12] However, miniemulsions can also be obtained by low energy emulsification techniques based on catastrophic phase transitions due to a change in the spontaneous curvature of the surfactant[2,13] as a result of the variation in the physicochemical properties (temperature (phase inversion temperature (PIT) method),[14−16] pressure,[17,18] pH,[19] ionic strength[20,21]) and the composition (emulsion inversion point (EIP) method)[22−25] of the system. Recently, Magdassi et al.[26,27] reported miniemulsion polymerization based on sequential use of high energy homogenization and the PIT method. However, the PIT method is of limited use for miniemulsion polymerization because (*i*) it is restricted to nonionic surfactants (most heterogeneous polymerizations rely on ionic surfactants) and (*ii*) it involves increasing the temperature above the cloud point of the nonionic surfactant, which is not practical in connection with a radical polymerization initiated by thermally decomposing initiators.

Herein we report the first synthesis of polymeric nanoparticles employing a low energy miniemulsification procedure. Styrene was polymerized at 70 °C in aqueous miniemulsion initiated by azobis(isobutyronitrile) (AIBN) employing the anionic surfactant Dowfax 8390 (disulfonated alkyl diphenyloxide sodium salt). In addition to the benefits of a low energy process, the system offers excellent control over monomer droplet and particle size, with a hitherto unsurpassed degree of preservation of initial droplet identity. The latter is crucial for synthesis of hollow particles and organic/inorganic hybrid particles as well as advantageous for implementation of controlled/living radical polymerization in miniemulsion.

The oil phase (styrene, hexadecane and AIBN) could not be dispersed in water to form a miniemulsion by gentle mixing using a water content as high as 90 wt % (overall) and 95 wt % (rel. to organic phase) Dowfax 8390. In the low energy EIP method, miniemulsions stabilized by ionic surfactants are obtained by dilution of a bicontinuous or an oil-in-water (O/W) microemulsion with excess water.[21,23] It is a prerequisite that the initial "microemulsion precursor" has the appropriate composition with regards to the equilibrium phase behavior of the initial system. Electrical conductivity is generally employed to locate the phase boundaries of systems comprising an ionic surfactant.[28,29] In the investigated system, the electrical conductivity (Figure 1S) revealed that the initial system evolved gradually with increasing water content from a W/O microemulsion concentrate to an O/W microemulsion concentrate via a bicontinuous concentrate. Only the O/W microemulsion concentrate could be diluted with excess water to form a miniemulsion, although it has been reported that the bicontinuous microemulsion concentrate can also be transformed into a miniemulsion by careful dilution.[21] Three different miniemulsions were prepared by dilution of the O/W microemulsion precursor at the arrow (Figure 1S and Table 1S), corresponding to 57.8 wt % water. All miniemulsions exhibited high stability with no change in visual appearance over 4 weeks; the number-average (d_n) and weight-average droplet diameters (d_w) increased by less than 14% (Figure 2S). The size of the droplets (and subsequent polymer particles) decreased significantly with increasing dilution of the microemulsion precursor (Figure 1) for reasons that remain to be clarified.

The appearances of the miniemulsions did not change after polymerization at 70 °C for 8 h (Figure 1). Dynamic light scattering (DLS; Figure 1) data showed that the particle size and particle size distributions of the polymerized miniemulsions were close to identical to those of the corresponding monomer droplets prior to polymerization. The DLS data were verified by TEM micrographs of the particles obtained (Figure 2). All particle size distributions were monomodal, with polydispersities (d_w/d_n) in the range normal for miniemulsions.[30]

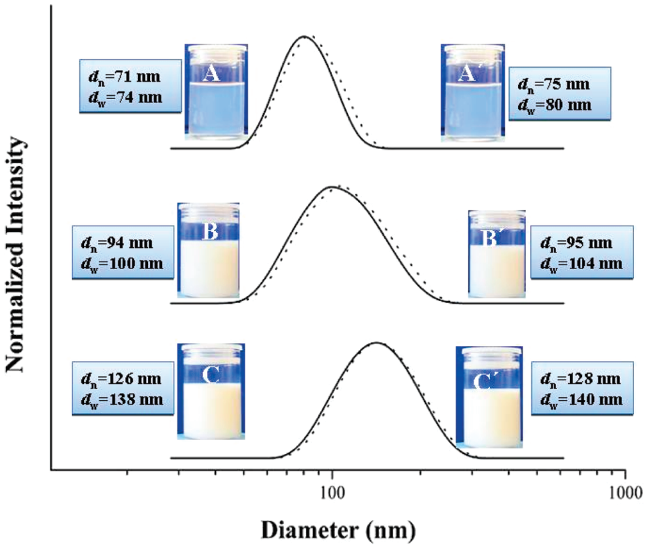

Figure 1. Photographs and DLS data of miniemulsion before (lines) and after (dots) polymerization of styrene initiated by AIBN at 70 °C for 8 h. A, B, C before polymerization correspond to A′, B′, C′ after polymerization, respectively.

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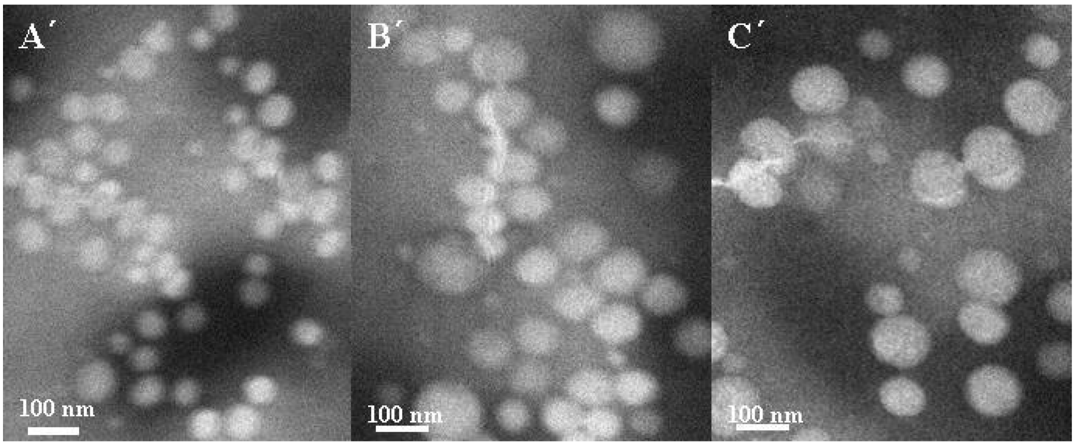

Figure 2. TEM micrographs of polystyrene particles obtained by miniemulsion polymerization of styrene initiated by AIBN at 70 °C for 8 h (A′, B′, and C′ as in Figure 1).

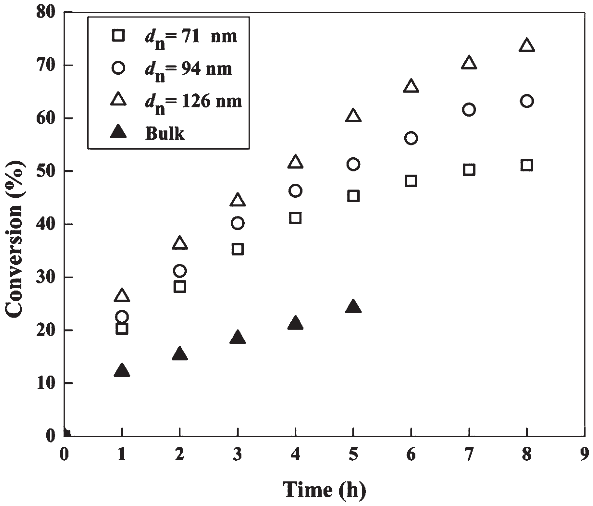

Figure 3. Conversion vs time for miniemulsion and bulk polymerizations of styrene initiated by AIBN at 70 °C.

Before polymerization, (d_n, d_w) of the miniemulsion droplets were (71, 74 nm), (94, 100 nm), (126, 138 nm), respectively, to be compared with (75, 80 nm), (95, 104 nm) and (128, 140 nm) after polymerization. Preservation of droplet identity in miniemulsion polymerization ("one-to-one copy"; ideally, each monomer droplet is converted to a particle with minimal monomer diffusion across the aqueous phase) is of great importance as it offers superior particle size control, and is also a requirement for efficient synthesis of hollow particles and organic/inorganic hybrid particles.[8,9,31] The issue of "one-to-one copy" miniemulsion polymerizations is controversial, and although claimed to be achieved or very close to being achieved,[32−36] strong skepticism has also been raised.[6] The present work arguably constitutes the strongest evidence to date of a true "one-to-one copy" miniemulsion polymerization.

The polymerization rate (R_p) was higher in miniemulsion than in the corresponding bulk polymerization, and R_p(miniemulsion) decreased with decreasing d_n (Figure 3). For sufficiently small particles, segregation of propagating radicals (compartmentalization) leads to a reduction in termination rate,[37] which results in an increase in R_p relative to the corresponding bulk system. The decrease in R_p with decreasing d_n probably originates in increased geminate termination of AIBN radicals, i.e. a lower initiator efficiency for smaller particles.[38−40] In this particular case (i.e., comparing the miniemulsion polymerizations), the effect of the initiator efficiency appears to override the segregation effect of propagating radicals (the latter would cause R_p to increase with decreasing d_n).

The decrease in R_p with decreasing particle size is considerably smaller than what can be predicted based on the termination rate between two radicals generated in the same particle under zero-one conditions. The time taken for termination to occur between two radicals generated in the same particle is given by $N_A v_p / k_t$ (N_A is Avogardro's number, v_p is the particle volume, k_t is the termination rate coefficient; $N_A v_p / k_t$ would be proportional to R_p), i.e. R_p would be proportional to d^3. However, generation of radicals from AIBN located in the aqueous phase (a significant fraction of AIBN would partition to the aqueous phase due to the low solids content), spontaneous radical generation (thermal background radicals),[41−43] as well as exit from particles of one of the pair of AIBN radicals would all lead to particles containing a single radical, thus causing deviation from the simple relationship $R_p \sim d^3$.

The number-average molecular weights (M_n) were in the range $(2-5) \times 10^6$ g mol^{-1} throughout the polymerization (Figures 3S and 4S), which is considerably higher than what is normally observed in conventional radical polymerization in miniemulsion initiated by oil-soluble initiators.[44] Such high M_ns are normally only obtained in emulsion- and microemulsion polymerizations with sufficiently small particles,[43,45,46] where strong segregation of propagating radicals minimizes termination (the termination rate would of course not be zero; termination is still the mechanism responsible for loss of radicals). If the termination rate is low enough, the majority of chains grow until the chain transfer to monomer limit is reached. The main end-forming event is thus chain transfer to monomer, resulting in high M_n and relatively constant M_n with conversion (the chain transfer constant is expected to be independent of conversion[47]). In the bulk system, termination is the only significant end forming event, thus giving much lower M_ns (and R_p). The reduction in initiator efficiency with decreasing d_n would also contribute to the trend of higher M_n for smaller particles (and higher M_n in miniemulsion than bulk; Figures 3S and 4S), although this effect would be minor in a chain transfer dominated system.

In summary, a low energy emulsification technique involving dilution of a microemulsion precursor has been successfully applied to synthesis of polystyrene nanoparticles by miniemulsion polymerization, featuring an exceptionally high degree of preservation of the initial droplet identity, thus offering superior particle size control to conventional high-energy methods. Investigations are currently underway directed at the miniemulsion formation mechanism, as well as application of the technique to other systems (e.g., CLRP).

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Supporting Information Available: Text detailing experimental procedures, a table giving recipes of three different miniemulsions, and figures showing electrical conductivity data, DLS, and molecular weight data. This material is available free of charge via the Internet at http://pubs.acs.org.

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