Recent Advances in Miniemulsion Polymerization

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SUMMARY: Work is presented that explains the phenomenon of 'enhanced droplet nucleation' in miniemulsion polymerization, lists variations of the recipe used in miniemulsion formulation, and contains applications of miniemulsion technology to produce latexes with special characteristics.

Introduction

Miniemulsions are comprised of relatively stable oil droplets, ranging in size from 50 to 500 nm, suspended in an aqueous phase. Ugelstad et al.[1] were the first to show that the predominant mechanism of nucleation in miniemulsions shifts from either micellar or homogeneous nucleation to droplet nucleation. The stability of the small droplets in miniemulsions arises from the use of an ionic surfactant and a low molecular weight, highly water-insoluble costabilizer in the miniemulsification process. Typical costabilizers that have been used are long chain alkanes and fatty alcohols.[1,2] These materials slow molecular diffusion of the monomer from the small droplets to the larger droplets. The rate of degradation of the emulsion has been shown to be governed by the diffusion rate of the least soluble component in the droplets (i.e., the costabilizer). For fatty alcohols, an ordered interfacial complex of ionic surfactant and fatty alcohol has been postulated to reduce the rate of coalescence and retard monomer diffusion providing an additional mechanism to stabilize the initial miniemulsion droplet distribution.[3]

An extensive amount of work on miniemulsions has been conducted since the initial discovery by Ugelstad et al. Review articles by Aizpura et al.[4], Sudol and El-Aasser[5], and Miller and El-Aasser[6] are excellent summaries of the work done in the area up to 1995. This paper will summarize some of the important work accomplished in the area since 1995.

'Enhanced Droplet Nucleation'

Miller et al.[7] studied the polymerization kinetics of miniemulsion systems formed with cetyl alcohol as costabilizer in which the droplets contained a low weight fraction polymer ($\leq$ 2%). The polymer (polystyrene) was predissolved in the monomer (styrene) prior to miniemulsification. They reported a significant enhancement in both the number of droplets nucleated and the rate of polymerization. Furthermore, they were able to show that the final number of particles in the system was equivalent to the initial number of droplets (unlike behavior noted for miniemulsions not containing predissolved polymer where it was estimated only 20% of the droplets become polymer particles). This phenomenon was termed 'enhanced droplet nucleation'. The authors stated that the droplets containing a low weight fraction polymer resemble polymer particles and the cause for the significant enhancement in nucleation is due to particles being more efficient than droplets in capturing aqueous phase radicals.[8] Possible reasons given by the authors for the difference in radical capture abilities of particles and droplets were: 1) polymer chains disrupt the order of the condensed phase of sodium lauryl sulfate and cetyl alcohol residing at the oil-water interface that results in 'openings' that facilitate radical entry; 2) as polymer chains are introduced, the internal viscosity of the droplets increases which, in turn, could provide a longer residence time for entering radicals to propagate rather than desorb from the modified droplet; and 3) the polymer may provide extra stability to the small, uninitiated monomer droplets allowing them to compete for radicals.

To determine which, if any, of the above possibilities could explain 'enhanced droplet nucleation', Blythe et al.[9] carried out a series of experiments in which the properties of the predissolved polymer were varied. A systematic study was undertaken to determine the effects that the molecular weight and the end-group (hydrophyllic or hydrophobic) of the predissolved polymer have on the polymerization kinetics of styrene miniemulsions that use cetyl alcohol as the costabilizer and contain 1% predissolved polystyrene. It was noted that regardless of the molecular weight (39,000 g/mol $\leq M_n \leq$ 206,000 g/mol) or the end-group (H, SO_3^-, or SO_4^-), an identical enhancement in the rate of polymerization and number of droplets nucleated occurred. This was taken as strong indication that a change in the droplet's interior viscosity or surface disruption of the sodium lauryl sulfate/cetyl alcohol condensed phase by predissolving polymer are not the dominant factors determining 'enhanced droplet nucleation'.
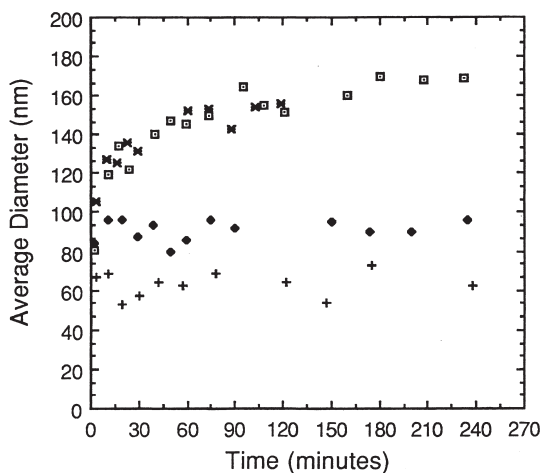
Fig. 1: Average droplet diameter versus time for toluene miniemulsion droplets prepared using either the sonifier (s) or the Microfluidizer (m). Miniemulsions were prepared with 10 mM SLS and either 50 mM cetyl alcohol (□,s;✖,m) or 50 mM hexadecane (◆,s;+,m) (taken from reference 10).

It was noted that predissolving polymer preserves the droplet number available for radical entry during the polymerization. This was ascribed to the swelling of the polymer with monomer coupled with the lack of the ability of the polystyrene to transport through the aqueous phase. As a result, droplets that remain unentered by radicals do not disappear by diffusion to the growing polymer particles, but instead are preserved to approximately 80% conversion of the monomer during the polymerization by the presence of the predissolved polystyrene. Furthermore, it was suggested that the large enhancement in the kinetics resulting from predissolving polystyrene is due to droplet preservation prior to the addition of initiator. The miniemulsion droplet size versus aging time has been measured previously by Miller et al.[10] and is shown in Figure 1. It is evident that the miniemulsion droplets stabilized with cetyl alcohol as the costabilizer are relatively unstable in the droplet sizes produced using the Microfluidizer (the homogenizer used in these experiments). Thus, it was suggested that the polymer can preserve the droplet number not only during the polymerization, but before the polymerization is begun. Since polymer has a high molecular weight, it is unable to superswell with monomer and cannot be thought of as a classical costabilizer. Thus, polymer can preserve the droplet number but not the droplet size.

is constant as a function of time. Therefore, if the preservation of droplet number prior to the addition of initiator is important in determining 'enhanced droplet nucleation', it would be expected that miniemulsion systems that use hexadecane as the costabilizer would not exhibit significant enhancement in the kinetics from the addition of predissolved polymer. Figure 2 compares the effect of predissolving polymer in the three different systems: 1) a miniemulsion using hexadecane as the costabilizer; 2) a miniemulsion using cetyl alcohol as the costabilizer; and 3) a conventional emulsion subjected to homogenization. A significant enhancement in the rate of polymerization resulted only in the miniemulsion using cetyl alcohol as the costabilizer and the emulsion subjected to homogenization. It has been shown that in both of these systems without polymer, the droplet size is relatively unstable. However, as stated earlier, the droplet size in miniemulsions using hexadecane as the costabilizer has been shown to be constant and predissolving polymer in these systems did not result in the same level of enhancement seen in the systems with unstable droplet sizes. Therefore, predissolving polymer in the miniemulsions only created the 'enhanced droplet nucleation' phenomenon when the droplet size was unstable. This is strong evidence that the 'enhanced droplet nucleation' phenomenon is caused by the predissolved polymer stabilizing the droplet number, although not the size, prior to the addition of initiator to the miniemulsion.

Figure 3 shows the effect of varying the level of shear that is used to create miniemulsions that use cetyl alcohol as the costabilizer. The Omni Mixer imparts a much lower level of shear than the Microfluidizer and thus creates a miniemulsion with a larger droplet size. In fact, Blythe et al.[11] postulated that the droplet size formed by the Omni Mixer was likely to be in the stable size regime for miniemulsions that use cetyl alcohol as the costabilizer as indicated by the results in Figure 1 ($D_d > 200$ nm). In Figure 3, it is apparent that the rate of polymerization is significantly reduced in the miniemulsions formed with the Omni Mixer compared to the Microfluidizer. This is due to the much lower number of droplets available for polymerization. However, a much more interesting phenomenon is that the kinetics are not enhanced by predissolving polymer in the miniemulsion system when the Omni Mixer is used for the shear step. Again, Blythe et al. related the lack of enhancement from predissolving polymer to the droplet stability. It was suggested that the 'enhanced droplet nucleation' phenomenon will only occur in systems with unstable droplet size distributions.
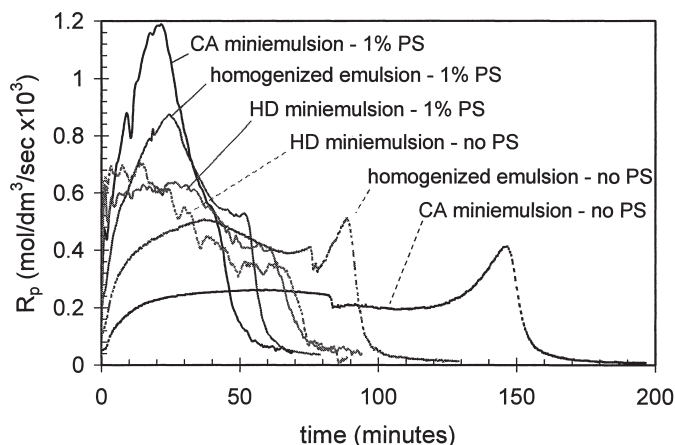
Fig. 2: The effect of predissolving polystyrene into different styrene miniemulsion and homogenized emulsion systems: (a) 10 mM SLS/30 mM CA miniemulsion containing 1% predissolved polystyrene, (b) 10 mM SLS homogenized emulsion containing 1% predissolved polystyrene, (c) 10 mM SLS/40 mM HD miniemulsion containing 1% predissolved polystyrene, (d) 10 mM SLS/40 mM HD miniemulsion, (e) 10mM SLS homogenized emulsion, and (f) 10 mM SLS/30 mM CA miniemulsion; [KPS] = 1.33 mM, T_r = 70°C (taken from reference 12).

Recipe Formulation

Much research has been conducted to eliminate the need for conventional costabilizers (i.e., alkanes and fatty alcohols). The following miniemulsion systems were created and reported to undergo predominantly droplet nucleation: sodium lauryl sulfate (SLS) (surfactant), dodecyl mercaptan (costabilizer and chain transfer agent), and methyl methacrylate (monomer) (Mouran et al.)[13]; SLS (surfactant), dodecyl mercaptan (costabilizer and chain transfer agent), and styrene (monomer) (Wang et al.)[14]; SLS (surfactant), lauryl peroxide (costabilizer and initiator), and methyl methacrylate (monomer) (Reimers and Schork)[15]; and SLS (surfactant), dodecyl methacrylate or stearyl methacrylate (costabilizer and comonomer), and styrene (monomer) (Chern and Chen)[16]. Reimers and Schork[17] used a small amount of polymer as a hydrophobe (somewhat analogous to a costabilizer) and reported a system that exhibited droplet nucleation. The authors did concede that polymer cannot be classified as a true costabilizer since it cannot superswell with monomer. Chern et al.[18] reported using a water-insoluble blue dye as the costabilizer in the polymerization of styrene miniemulsions.

The authors claim to be able to discriminate between particles formed by droplet and homogeneous nucleation by the presence or absence of the dye in the final particles.
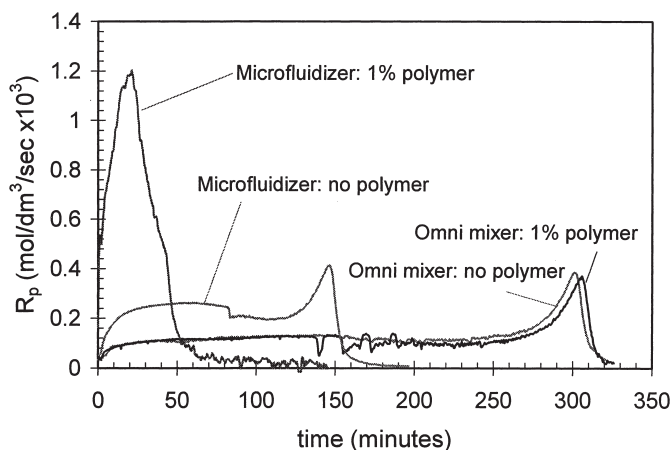

Fig. 3: The effect of predissolving 1% polystyrene on the rate of polymerization in styrene miniemulsions formed from a 10 mM SLS/30 mM CA gel phase and homogenized with: (a) the Omni Mixer or (b) the Microfluidizer; [KPS]= 1.33 mM; T_r = 70 °C (taken from reference 12).

The use of nonionic surfactants in miniemulsion polymerization has also been recently explored. Chern and Chen[19] were able to obtain stable styrene miniemulsions using nonylphenol polyethoxylate (NP40) that underwent significant droplet nucleation. Hexadecane, cetyl alcohol, dodecyl methacrylate, and stearyl methacrylate were used as costabilizers. Successful styrene miniemulsion polymerizations were also conducted with a mixed NP40/SLS surfactant system with the aforementioned methacrylate costabilizer.[20]

Applications

Miniemulsion polymerization has several advantages over conventional emulsion polymerization. Among these are the ease of incorporating water-insoluble components into the particles, strong control over the final particle size, and the ability to adjust the comonomer ratio at the reaction site in copolymerization systems. Recent work in miniemulsions has taken advantage of these unique characteristics. Kukulj et al.[21] were able to incorporate highly water-insoluble cobalt catalytic chain transfer agents in PMMA latex

particles by miniemulsion polymerization without having the catalyst becoming deactivated. Similar reactions run by conventional emulsion polymerization resulted in deactivation of the catalyst by the primary initiator radicals generated in the water phase. Erdem et al.[22] used miniemulsion polymerization to encapsulate hydrophilic and hydrophobic TiO_2 particles in polystyrene latex particles with an efficiency up to 88% TiO_2 encapsulation. Leiza et al.[23] were able to produce butyl acrylate latexes with high solids contents (>50%). Broad particle sizes were produced in a seed stage by semicontinuous miniemulsion polymerization that were deemed critical in the ability to produce latexes with solids contents greater than 60%. Li[24] used miniemulsion polymerization in styrene/butadiene reactions to change the monomer concentration at the reaction site. It was determined that the onset of the gel formation could be slightly delayed by using miniemulsion polymerization as compared to conventional emulsion polymerization. Prodpran et al.[25] were able to successfully apply the living free radical polymerization using the nitroxide radical of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) at 125°C, typically used in bulk polymerizations, to styrene miniemulsions. Thus, stable polystyrene latexes (~20% solids) with relatively narrow molecular weight distributions were prepared.

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