

## Did you know? April-June 2024

### Miniemulsion Polymerization

#### Did you know...that miniemulsion polymerization offers an alternative to conventional emulsion polymerization?

Miniemulsion polymerization, pioneered by El-Aasser at Lehigh University, shares many features with conventional emulsion polymerization but has distinct features that offer advantages for some applications. The most striking difference between emulsion polymerization and miniemulsion polymerization lies in the particle nucleation process. In emulsion polymerization, particles are nucleated when radicals from the aqueous phase enter monomer-swollen surfactant micelles (~5-10 nm) and initiate the polymerization of the monomer. These very small particles grow to their final size due to the diffusion of monomer through the aqueous phase into the particles; the monomer can come from monomer droplets (~1-20 microns) for batch emulsion polymerization, or more commonly in industrial practice from monomer that is fed into the reactor.

In contrast, in miniemulsion polymerization the initial water/monomer mixture is subjected to very high shear (e.g. sonication, homogenization) to create a “miniemulsion” of small monomer droplets (~50-300 nm) dispersed in the aqueous phase. These droplets are then directly polymerized to give the final particles, thereby eliminating the need for monomer diffusion through the aqueous phase. A small amount of a “hydrophobe” is added to the monomer to prevent the monomer droplets from undergoing Ostwald ripening. Hexadecane is a commonly used hydrophobe in fundamental studies, but it can be replaced with polymer to avoid increasing the VOC content. Once the miniemulsion is prepared, the polymerization progresses much like a conventional emulsion polymerization; the monomer droplets are nucleated by entry of radicals from the aqueous phase until all the monomer is reacted. The final polymer particle size is the same as the monomer droplet size. If desired, a second monomer (or comonomer mixture) can be fed to give structured morphology such as core-shell particles. Figure 1 below shows a comparison between the sizes of monomer *droplets* in classic emulsion polymerization and miniemulsion polymerization.

Miniemulsion polymerization is well-suited to incorporating highly hydrophobic monomers (less water soluble than 2-ethylhexyl acrylate) that are a challenge for emulsion polymerization due to their very low water solubility and consequent slow diffusion through the aqueous phase to the polymerizing particles. The process is also capable of allowing hydrophobic nano-size additives (e.g. carbon black, pigments, etc.) to be incorporated into latex particles, or to encapsulate pigments. The primary challenge with industrial scale miniemulsion polymerization lies in the miniemulsification of the monomer/water mixture. This can be readily done using homogenizers and even static mixers but it will add cost and time to the overall process. Is miniemulsion polymerization right for you? If you are developing products that use highly hydrophobic monomers or want to incorporate additives into your particles, it may be a viable and attractive alternative to emulsion polymerization.

As always, we invite your questions and comments by going to [info@epced.com](mailto:info@epced.com).

Figure 1. Comparison of emulsion and miniemulsion polymerization.

## Emulsion polymerization

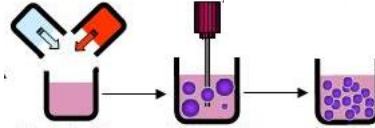


Mix monomer,  
water, surfactant



Monomer droplet  
~1-20 microns

## Miniemulsion polymerization



Mix monomer, water,  
surfactant, hydrophobe



Monomer droplet  
~50-300 nm