

## **Miniemulsion Polymerization: New Products from a New Process'**

F. Joseph Schork  
Professor and Chair,  
Department of Chemical and Biomolecular Engineering  
University of Maryland  
College Park, Maryland, 20742 USA  
fjschork@umd.edu

Miniemulsion polymerization offers some advantages over conventional emulsion (macroemulsion) polymerization systems. Among these are a process that is more robust to contaminants, and a product with a more uniform copolymer composition, narrow particle size distribution, and high shear-stability. In addition, miniemulsion polymerization can be used to produce a whole new range of graft copolymers. Miniemulsion polymerization involves the use of a more effective emulsifying system to produce very small monomer droplets (< 500 nm). Particle nucleation occurs primarily via radical entry into the small monomer droplets. These must be stabilized against coalescence and diffusional degradation. Coalescence may be precluded by the addition of an appropriate surfactant. Diffusional degradation or Ostwald ripening can be eliminated by the addition of a small amount of a water-insoluble, monomer-soluble stabilizer (costabilizer). Polymers, comonomers, and chain transfer agents have been evaluated as costabilizer.

Miniemulsions have some unique and desirable properties that are detailed in this talk. They are far more robust to variations in the recipe or contaminants levels than conventional emulsions. Particle number was found to be less sensitive by at least an order of magnitude, to changes in initiator, water-phase retarder, and oil-phase inhibitor concentrations than macroemulsion polymerizations. Perhaps because of this robustness, it was possible to produce latex with a narrow polydispersity. Hydrophobic comonomers have been used successfully as hydrophobes. It has been found that such systems will give a more uniform copolymer composition since the supply of hydrophobic comonomer is not mass transfer limited as in macroemulsion polymerization. Finally, miniemulsion polymerization has been used to produce alkyd-acrylate graft copolymers that might be the basis for low VOC alkyd coatings. This same technique can be applied to other graft copolymerizations to produce water-borne specialized coatings. Finally, miniemulsion polymerization has been found to be one of the best vehicles for carrying out living free radical polymerization.