

OC 7. Particle Nucleation in High Solids Miniemulsion Polymerization

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Droplet nucleation is the distinctive feature of miniemulsion polymerization¹ that allows incorporating hydrophobic compounds into polymer particles, because mass transfer through the aqueous phase is avoided. This has led to the development of a wide range of useful polymer materials only accessible through this technique². The successful synthesis of many of these materials requires an efficient nucleation of the monomer droplets. This can be illustrated by considering the synthesis of polymer-polymer hybrid dispersions. In this process, a preformed polymer is dissolved in a monomer mixture containing a costabilizer (low molecular weight highly water-insoluble compound) and dispersed in an aqueous solution of surfactants to obtain a miniemulsion. The challenge is to transform most of the droplets into polymer-polymer composite particles maintaining the same polymer/polymer ratio in all particles. This requires a fast nucleation of all the droplets (to avoid monomer mass transfer from droplets to growing particles), and to minimize secondary nucleation, particle-particle coagulation and particle-droplet coagulation. Droplet nucleation has been controversial, although recent results show that nucleation of most of the droplets can be achieved in low solids content batch miniemulsion polymerization³.

However, high solids content is required for commercial applications. In addition, because free radical polymerization is a highly exothermic process, heat removal is critical for large scale operations, and semicontinuous reactors are used to control the heat generation rate. Droplet nucleation in high solids semicontinuous miniemulsion polymerization has not been investigated, although one may anticipate that these conditions are far from the ideal ones required for the nucleation of most of the droplets. The main objective of this work was to study the nucleation mechanisms in high solids content semicontinuous miniemulsion polymerization using as a case study a silicone-acrylic system. High solids batch processes were also considered because frequently the semicontinuous processes start with the batch polymerization of the initial charge of the reactor. Strategies to maximize the extent of droplet nucleation and to minimize the formation of polymer particles by homogeneous nucleation were discussed.

¹ Ugelstad, J.; El-Aasser, M.S.; Vanderhoff, J.W. *J Polym Sci Polym Lett* **1973**, *11*, 503-513

² Asua, J.M. *Prog. Polym. Sci.*, **2002**, *27*, 1283-1346

³ Landfester, K.; Bechthold, N.; Förster, S.; Antonietti, M. *Macromol Rapid Comm* **1999**, *20*, 81-84