Living Free Radical Miniemulsion Polymers

G. Pan, X. Huang, V.L. Dimonie. E.D. Sudol, and M.S. El-Aasser

Emulsion Polymers Institute and Department of Chemical Engineering
Lehigh University, Bethlehem, PA 18015-4732 USA

Controlled/living free radical polymerizations in heterogeneous miniemulsion systems are being pursued to prepare narrow and controlled molecular weight polymers in latex form. Both the SFRP (stable free radical polymerization) and RAFT (reversible addition-fragmentation chain transfer) methods are being investigated. In the former method, narrow and low molecular weight TEMPO-terminated oligomers of polystyrene (TTOPS) were first synthesized by bulk polymerization (1500 g/mol) at 125°C and are being used as macroinitiators to investigate the mechanism of the controlled free radical polymerization in styrene miniemulsions. The TTOPS was characterized by both GPC and MALDI. In miniemulsion polymerizations containing TTOPS, by increasing the stabilizer (Dowfax 8390 and hexadecane) concentration, the particle size of the latexes was decreased as expected, however, the rate of polymerization and resulting molecular weights were largely unaffected. The latter were narrow and varied linearly up to relatively high conversions but deviations from ideal polymerization were apparent by the appearance of low molecular weight dead polymers in the molecular weight distributions. Several means of reducing these deviations are being examined. Analysis of the kinetics of the reactions reveal that a low fraction of the particles have a single growing radical at any given time, a consequence of the equilibrium favoring inactive chains and not radical desorption as would be the case in a conventional emulsion polymerization characterized by a low average number of free radicals per particle.

Normal emulsion polymerization temperatures are one advantage of the RAFT controlled free radical polymerizations. High purity 2-phenylprop-2-yl dithiobenzoate and benzyl dithiobenzoate were synthesized as RAFT agents for use in miniemulsion polymerizations of styrene at 70°C with potassium persulfate as initiator. Sodium lauryl sulfate and hexadecane were used as miniemulsion stabilizer and costabilizer, respectively. Using 2-phenylprop-2-yl dithiobenzoate as the RAFT agent, the average molecular weight follows the theoretical expectation. However, two molecular weight populations were found to move with conversion in styrene miniemulsion systems. The effect of the purity of the RAFT agent and the ratio of the RAFT agent concentration to the initiator concentration are being studied. A third RAFT agent, o-ethyl s-cyanomethyl xanthate, is being used in conventional emulsion and miniemulsion polymerizations of vinyl acetate. As expected, the miniemulsion system showed a better control of the molecular weight than the conventional emulsion system.