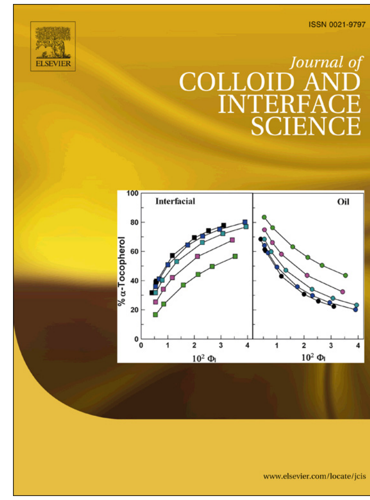
## Accepted Manuscript




# Control of Particle Size by Feed Composition in the Nanolatexes Produced via Monomer-Starved Semicontinuous Emulsion Copolymerization

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PII: S0021-9797(14)00990-4
DOI: http://dx.doi.org/10.1016/j.jcis.2014.12.037
Reference: YJCIS 20080

To appear in: *Journal of Colloid and Interface Science*

Received Date: 12 November 2014
Accepted Date: 12 December 2014

Please cite this article as: S. Sajjadi, Control of Particle Size by Feed Composition in the Nanolatexes Produced via Monomer-Starved Semicontinuous Emulsion Copolymerization, *Journal of Colloid and Interface Science* (2014), doi: http://dx.doi.org/10.1016/j.jcis.2014.12.037

# Control of Particle Size by Feed Composition in the Nanolatexes Produced via Monomer-Starved Semicontinuous Emulsion Copolymerization

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## ABSTRACT

Conventional batch and semicontinuous emulsion copolymerizations often produce large particles whose size cannot be easily correlated with the comonomer feed compositions, and are to some degree susceptible to composition drift. In contrast, we found that copolymer nanolatexes made via semicontinuous monomer-starved emulsion copolymerizations are featured with an average nanoparticle size being controlled by the feed composition, a high conversion achieved, and a high degree of particle composition uniformity. This was achieved because the rate of particle growth, during nucleation, was controlled by the rate of comonomer addition, and the copolymer composition, surfactant parking area on the particles, and nucleation efficiency by the comonomer feed composition. Two model systems, methyl methacrylate/styrene and vinyl acetate/butyl acrylate, with significant differences in water solubility were studied. Monomers were added to the aqueous solution of sodium dodecyl sulfate and potassium persulfate at a low rate to achieve high instantaneous conversions.

*Keywords:* Semicontinuous Emulsion copolymerization, copolymer nanoparticles, copolymer composition, nanolatxes, monomer-starved nucleation.

## INTRODUCTION

Nanolatexes, which are dispersions comprised of particles smaller than 50 nm in diameter, have received extensive attentions in recent years [1-8]. With the advancement of nanotechnology, the demand for hybrid nanolatexes with different compositions is increasing [9-11]**.** Microemulsion polymerization is a well-established technique to produce nanolatexes, but uses a high concentration of surfactant/co-surfactant and produces low solids-content products [12-15]**.** Semicontinuous monomer-starved emulsion polymerization has been found as a powerful technique to produce high-solids content nanolatexes with an improved particle size uniformity [2,16] but using relatively low surfactant concentrations [1,2,4,6,17-23]**.** These nanolatexes have found applications for ultra-thin coatings and as intermediary in producing advanced functional particles and hybrid nanoclusters [7,24]**.**

Several investigators attempted to explain the mechanistic of particle formation in such systems [25,26]. We have shown that for semicontinuous emulsion polymerization reactors of sparingly water-soluble monomers under starved conditions the number of particles ($N_p$) can be given by [23]:

$$N_{\mathrm{p}} = k_1 (a_{\mathrm{s}} N_{\mathrm{A}} [S]) R_i^{2/3} R_{\mathrm{a}}^{-2/3} \quad (1)$$