ML 01

COMPARTMENTALIZATION IN HETEROGENEOUS LIVING/CONTROLLED RADICAL POLYMERIZATIONS

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Nitroxide-Mediated Radical Polymerizations (NMRP/SFRP) and Atom Transfer Radical Polymerizations (ATRP) were conducted in miniemulsion to investigate the potential role of compartmentalization. While it was previously believed that living/controlled radical polymerizations based on reversible termination mechanisms (SFRP, ATRP) should not exhibit compartmentalization effects, recent theoretical and modelling studies have suggested that such effects could be expected under certain conditions. However, no experimental evidence has yet been presented demonstrating the existence of compartmentalization behaviour in heterogeneous living/controlled radical systems.

In the first part of this study, TEMPO-mediated styeneminiemulsion polymerizations were conducted at varying particle sizes (~50, 90 and 180 nm). Polymerizations were initiated using a TEMPO-terminated polystyrene macroinitiator that also acted as costabilizer for the miniemulsion. Conversion, molecular weight distribution and chain livingness were measured to assess the effects of particle size. A bulk polymerization was also conducted to serve as a control experiment. Smaller particle size yielded lower rates of polymerization.Furthermore, large differences in the chain livingness were observed, with smaller particles exhibiting higher livingness at equivalent conversions.

Compartmentalization effects were also observed in ATRPminiemulsions when the number of chains per particle was low. With n-butyl methacrylate (n-BMA) miniemulsions mediated by $CuBr_2$-tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine(EHA_6TREN), compartmentalization effects reduced the polymerization rate, and also improved control over the polymerization as reflected by lower polydispersity index (PDI).