CONTROLLED FREE-RADICAL POLYMERIZATION: A WAY TO DESIGN POLYMER ARCHITECTURE AND SURFACE PROPERTIES OF LATEX PARTICLES.

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Free-radical polymerization offers the invaluable advantage of being tolerant to water, allowing the reaction to be carried out in aqueous solution or aqueous dispersed systems. With the various types of radical polymerization in aqueous dispersions, it is possible to fine-tune the size, morphology and chemical functionality of the polymer particles. However, because of the features of radical chemistry, the polymer composing the particles is generally ill-defined. With the emergence of controlled free-radical polymerization (CRP), the possibility to control the polymer molecular characteristics was brought about. Whereas CRP has been initially applied to bulk or solution polymerizations, the transfer to aqueous dispersed systems is more recent and was shown to be possible, though not straightforward. Therefore, latexes with well-defined homopolymers and copolymers with complex architecture can be prepared. In this field, the most recent developments in nitroxide-mediated polymerization in aqueous miniemulsion will be presented. The nitroxide used is the N-tert-butyl-N-(1-diethyl phosphono-2,2-dimethyl propyl) also called SG1 and the monomers are styrene and n-butyl acrylate.

Additionally, controlled free-radical polymerization offers the possibility to synthesize amphiphilic copolymers, with controlled structure, predetermined molar mass and narrow molar mass distribution. Such amphiphilic block copolymers can be used as stabilizers in emulsion polymerization, to control both the number of particles and their surface properties. Hairy particles can thus be obtained with tailored hydrophilic shell. The same goal can be achieved by grafting water-soluble polymer chains from the particle surface, owing to the advantage that CRP offers to design well-defined initiators that remain stable in conventional free-radical polymerization and can be activated under selected conditions. In this field, copolymers based on acrylic acid and styrene were synthesized either by ATRP (atom transfer radical polymerization) or by SG1-mediated polymerization. Their application as stabilizers in emulsion polymerization will be presented. Various ways of incorporating a well-defined hydrophilic shell at the latex particle surface will also be discussed.