AMPHIPHILIC BLOCK COPOLYMERS AS STABILIZERS IN EMULSION POLYMERIZATION: EFFECTS OF MOLECULAR WEIGHT DISPERSITY AND EVIDENCE OF SELF-FOLDING BEHAVIOUR

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Emulsion polymerizations, used to produce many commodity materials, require stabilizing agents to prevent phase separation. Incorporation of these stabilizers in the final polymer may have negative effects on product properties, so the design of new stabilizers is being actively pursued. Amphiphilic diblock copolymers are a promising type of emulsion polymerization stabilizer and are the focus of this work (Fig. 1). First, the tolerance of an amphiphilic diblock copolymer stabilizer’s performance to high molecular weight dispersity and homopolymer impurity has been investigated. Polystyrene-b-poly(acrylic acid) block copolymers were studied due to their previously demonstrated efficacy as stabilizers in emulsion polymerization, and their similarity to commercially important polystyrene-r-poly(acrylic acid) stabilizers. Neither greater molecular weight dispersity nor homopolymer impurity was found to negatively impact the stabilization performance of these block copolymers, suggesting that the economically unfavorable conditions required to achieve low molecular weight dispersity and homopolymer impurity may be avoided. We then examined novel polystyrene-b-[polystyrene-r-poly(acrylic acid)] block-random copolymers which were shown to stabilize emulsion polymerizations with up to 50 weight percent solids content, exceeding what was possible using the polystyrene-b-poly(acrylic acid) block copolymers. Of even greater significance and scientific value is that the block-random copolymers were also observed to have unusual solution behavior, self-folding rather than self-assembling, to give single chain nanoparticles. Emulsion polymerizations stabilized by these block-random copolymers had a total particle surface area which was directly proportional to the stabilizer concentration and was unaffected by polymerization kinetics. A novel “seeded-coagulative” emulsion polymerization mechanism has been proposed to explain these results, which were unexplainable by any known emulsion polymerization mechanism.

Figure 1. Amphiphilic diblock copolymers, where the block dispersity was systematically varied, were studied as stabilizers in emulsion polymerization.