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Synthesis and Design of Amphiphilic Diblock Copolymers using Atom Transfer Radical Polymerization and Their Use as a Surfactant and a Macroinitiator in Miniemulsion and Emulsion Polymerizations

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Atom Transfer Radical Polymerization (ATRP) is one of the foremost controlled living radical polymerization methods used in the polymerization of a wide range of monomers. It is also considered one of the more convenient methods for co-polymerization, because extension of homopolymers synthesized by ATRP is easily accomplished due to the end-functionalized state of these polymers. In recent years, ATRP has been applied to emulsion and miniemulsion systems.

Emulsion and miniemulsion polymerizations are extremely applicable processes and are used to make a plethora of industrial products. Polymers produced from these methods are dispersed in water and thus do not require the use of environmentally detrimental volatile organic compounds as solvents. Manufactured goods synthesized using emulsion processes range from paints, adhesives, and paper to electronic and optoelectronic devices, and biomedical and cosmetic products.

One logical and creative application of ATRP in emulsion polymerization would be to develop diblock copolymers that would be able to function as both a surfactant *and* a macroinitiator in miniemulsion and emulsion polymerizations, therefore eliminating the need for one of these key components. In order to achieve this goal, the synthesis of an amphiphilic diblock copolymer is needed. This amphiphilic copolymer must first act as a surfactant in order to form micelles in emulsion by spontaneously self-assembling into a supramolecular shell around the monomer. Additionally, the synthesized copolymer must retain its end-functionality and thus its ability to act as an initiator in miniemulsion and emulsion polymerizations. This system should ideally result in stable latex particles (see Figure 1).

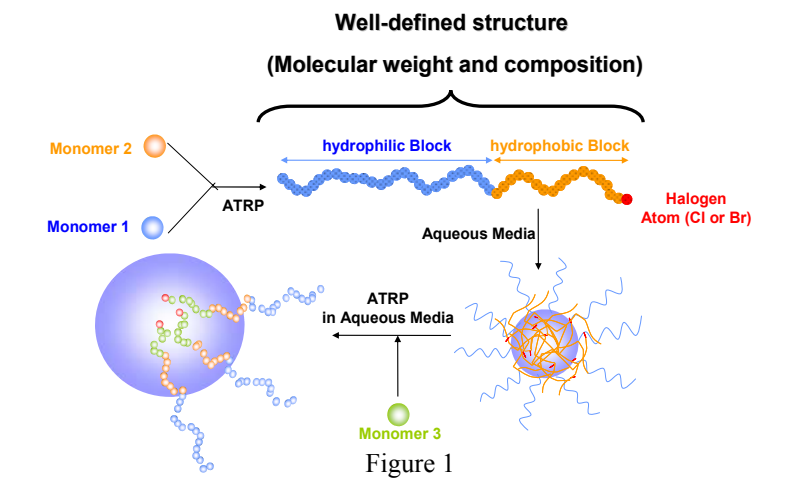

Figure 1

Activator Generated by Electron Transfer (AGET) ATRP. A well-defined poly(ethylene oxide)-b-polystyrene diblock copolymer: M_n = 10,443, M_n/M_w = 1.04, was synthesized using ATRP from a halogen-functionalized poly(ethylene oxide) macroinitiator. This copolymer was then utilized as a surfactant and a macroinitiator in the miniemulsion AGET ATRP polymerization of n-butyl methacrylate: M_n = 52,026, M_n/M_w = 1.47. A kinetic study and comparative analysis with several experimental conditions varied will also be presented.

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