

Controlled Radical Polymerization in Batch and Continuous Miniemulsion Reactors

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The advent of controlled radical polymerizations (CRP) has provided a potential means by which polymers of well-defined architecture can be synthesized using more forgiving and robust free-radical chemistry. One of the most versatile of these is Reversible Addition-Fragmentation Transfer (RAFT) polymerization. Moreover, RAFT can be applied using dispersed-phase polymerization techniques, which offer advantages over homogeneous polymerization systems, such as higher production rates and lower organic emissions. Due to the hydrophobicity of most RAFT agents, miniemulsion polymerization has proven to be the most easily applicable dispersed-phase polymerization technique.

Most work in CRP has been in solution polymerization; however, the adaptation of this chemistry to dispersed-phase (emulsion and miniemulsion) systems has been reported. To date, the overwhelming majority of published research of CRP in miniemulsion has been directed at batch systems. Even so, continuous systems offer possibilities for polymer structure control that cannot be realized in batch systems. By combining stirred and tubular reactors in a train, one can in principle dictate the structure of the final copolymer, allowing for the use of process design to carry out molecular design, or “product by process”. In this paper, we will discuss the use of batch, semibatch and continuous (stirred tank and tubular) reactors to create unique molecular and supramolecular architectures from conventional monomers, using miniemulsion polymerization.

Continuous processes yield a consistent product over time, once the process is running at steady-state. RAFT miniemulsion block copolymerization of styrene and n-butyl acrylate in a train of CSTRs was carried out. It was shown that a train of CSTRs can effectively be used to produce unique (multi)block copolymers. Comparison of gel permeation chromatography (GPC) refractive index traces and GPC UV traces revealed that the polymer formed has a very high percentage of living chains. The process variables such as flow rate, temperature and injection point of the second monomer can easily be changed to obtain different block copolymers.

RAFT miniemulsion polymerizations in tubular reactors were also conducted. Batch and tubular reactors behaved in a similar fashion kinetically. Polydispersities of the final product were higher in the tubular reactor, likely owing to a distribution of residence times. A chain extension experiment with the product of the tubular reactor demonstrated the “livingness” of the polymer and the possibility of using the system to make block copolymers.

In both cases of continuous polymerization, it can be shown that the residence time distribution of the reactors is “written in” to the molecular weight distribution.