142h Synthesizing Model Block Copolymers Via Atrp: the Utility of Kinetic Modeling in Guiding Experiments

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Nanostructures formed by self-assembly of amphiphilic block copolymers have shown a lot of promise in emerging technologies, including gene delivery, biomedical encapsulation and photonic technologies. However, designing and synthesizing model block copolymers that can yield phase morphologies suitable for specific applications can be a challenging task, especially when the desired morphologies exist within narrow ranges of polymer sizes and compositions. Since the polymer molecular characteristics are fixed at the time of synthesis, it is imperative to use polymerization techniques that afford precise prediction of product characteristics. Traditionally, living anionic polymerization has been the method of choice because it provides complete control over the product molecular weight through the initial monomer to initiator ratio. However, the stringent conditions required for polymerization combined with the limited choice of monomers that can be polymerized restricts the utility of this technique. Recently, a controlled-radical polymerization technique called Atom Transfer Radical Polymerization (ATRP) has been introduced that allows synthesis of a wide variety of polymers with well-defined properties. Unlike living anionic polymerization, however, ATRP is not a truly living polymerization technique, and the degree of control is dependent upon the kinetics of the component reactions. Due to the overwhelming complexity of ATRP mechanism, synthesis of well-defined polymers requires a robust kinetic model to guide the experiments. In this work, we demonstrate the utility of kinetic models in predicting polymer properties and optimizing reaction conditions for the ATRP synthesis of PEO-poly(n-butyl acrylate)(PnBA) diblock copolymers.

We propose a mechanism for homogeneous bulk ATRP of n-BA which includes inhibition steps involving the transfer of the radicals to the N,N,N',N”,N”-pentamethyldiethylenetriamine (PMDETA) ligand species. Based on the polymerization mechanism, we established the kinetic balance equations for the first three moments (i.e., the zeroth, first and second moments) of the molecular weight distributions of all the species participating in the polymerization reaction. These resultant differential equations were numerically solved without any simplifying assumptions. Our model can predict essentially all properties of the polymerization system including the evolution of monomer conversion, polydispersity, and the fraction of chains undergoing degradative chain transfer to the ligand. The proposed mechanism was validated by quantitatively fitting experimental conversion data and the consistency of the kinetic rate constant values extracted from this fitting with the literature.

By fitting the conversions predicted by the kinetic model, we determine the hitherto unknown rate constants for degradative chain transfer to the ligand in the homogeneous ATRP reaction. Our simulation suggests that polymerizations conducted at high ligand/catalyst ratio offer better control over the molecular weight distribution (MWD);thus higher ligand concentrations are desirable for synthesizing model diblock copolymers. Our model predicts, on the other hand, a larger fraction of chains undergoing chain transfer at higher ligand/catalyst ratios. Because the chains undergoing chain transfer lose their halide-end functionality, polymers synthesized at higher ligand concentrations become less suitable, for instance, for sequential addition of another block. This presents a tradeoff between control over MWD and chain end functionality for polymers synthesized by ATRP. The predictive capability of the kinetic model can be utilized to determine a priori the optimal set of conditions to balance such tradeoffs.