Controlled Radical Polymerization on a Chip

Polymers Division, National Institute of Standards and Technology,

100 Bureau Dr., Gaithersburg, Maryland 20899.

Abstract

Research on chemical reactions in micro-size reactors has attracted wide interests and is a promising field from both academic and industrial perspectives due to potentially better control of reaction conditions, speed, smaller specimen sizes, improved safety, and portability. In our presentation, we demonstrate the successful application of controlled radical polymerization on a chip (CRP chip) to synthesize block copolymers (poly(ethylene oxide-*b*-hydroxylpropyl methacrylate) (PEO-b-PHPMA) through atom transfer radical polymerization (ATRP). The CRP chip design enables control of polymer relative molecular mass and architecture through flow rates, which govern the polymerization time. Thus by conducting a series of well-controlled copolymerizations, carried out at different pumping rates (*i.e.*, reaction times) with a constant concentration ratio of monomer to initiator, we can produce a block copolymer library with a range of relative molecular masses of the second block. A unique advantage of the CRP chip is that it can be used to execute complex designed experiments. For example, we have used the CRP chip to rapidly measure polymerization kinetics in a new way. Based on the well-known ATRP model, we have derived a relationship between molecular weight and concentration ratio of monomer to initiator. Using this relationship, we are able to study the polymerization kinetics by simply measuring the relative molecular mass of polymer products from a series of experiments having the same reaction time but different initiator concentrations. Compared to the difficulty of preparing batch reactions with a wide range of different concentrations, we show that a CRP chip can quickly produce similar results with this so-called stoichiometric design, in which the stoichiometry of the mixture is adjusted by varying the relative flow rates of each input to change reactant concentrations.