

PV-II-4

IMPORTANCE OF DIFFUSION-CONTROLLED EFFECTS ON CONTROLLED RADICAL POLYMERIZATION PROCESSES

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Abstract

Controlled-radical polymerization (CRP) has become a major field in polymer science and engineering. CRP is also known as “pseudo-living” radical polymerization. A polymerization process is considered to be living if the growing chains do not experience permanent termination and/or transfer during the course of polymerization. The conventional routes to synthesize polymer molecules with controlled architecture has been through ionic polymerizations. However, ionic processes are extremely sensitive to impurities, and the type of solvent. The use of free-radical polymerization processes, which are more versatile and robust to impurities, to produce polymers with controlled structure via “pseudo-living” or “controlled” processes, has become a very important alternative.

The first controlled radical polymerization process was introduced by Otsu and Yoshida (1982), using an iniferter (initiator-transfer agent-terminator) molecule, and the concept of reversible deactivation of growing radicals as a means to reduce bimolecular termination. The current most effective and versatile CRP processes are (i) stable free-radical polymerization (SFRP), best represented by nitroxide mediated polymerization (NMP), (ii) metal catalyzed atom transfer radical polymerization (ATRP), and (iii) reversible addition-fragmentation chain transfer (RAFT) polymerization, along with other degenerative transfer processes. The common feature in these processes is the dynamic equilibration between growing free-radicals and various types of dormant species. The difference among them is due to the mechanism and chemistry of the equilibration/exchange process (Matyjaszewski, 2000).

It has been recognized that diffusion-controlled reactions are important in controlled-radical polymerization processes. As mentioned before, Shipp and Matyjaszewski (1999) and Butté et al. (1999) have used empirical models to take into account diffusion-controlled termination in their models for controlled-radical polymerization. Using electron spin resonance (ESR) measurements, Yu et al. (2001) experimentally demonstrated that the deactivation of growing radicals in ATRP of poly(ethylene glycol) dimethacrylate was impeded by the restricted diffusion of the Cu(II)/ligand

complex in polymer networks. The diffusion-controlled deactivation resulted in an increase in radical concentration and the reaction was converted to a conventional free-radical polymerization process. Diffusion-controlled phenomena (auto-acceleration and glass effects) in conventional free-radical polymerization have been studied and modeled for almost four decades, and have been reviewed elsewhere.

Although diffusion-controlled phenomena in controlled-radical polymerization have been addressed using fully empirical models (Shipp and Matyjaszewski, 1999; Butté et al., 1999), the abundant theoretical studies on the topic for conventional free-radical polymerization processes provide a more mechanistic approach for modeling. In a previous paper from our group, the diffusion-controlled reactions present in ATRP (radical termination, monomer propagation, transfer to small molecules, and transfer between chains and catalyst in the forward and backward directions) were modeled using free volume theory, and incorporating some important ideas and concepts in this area (Delgadillo-Velázquez et al., 2002).

In this presentation, a similar modeling approach to the one used by Delgadillo-Velázquez et al. (2002) for ATRP is applied to the controlled/"living" iniferter and RAFT free-radical polymerization situations. Detailed reaction mechanisms are considered in this paper, including thermal initiation, reversible initiation in the case of the iniferter process, transfer to small molecules, dormant termination, degenerative transfer reactions, and reversible transfer reactions for RAFT process, in addition to the propagation and termination reactions present in a conventional free-radical polymerization (FRP) process. Detailed kinetic and moment equations were derived and will be presented. Model performance is compared against experimental data from the literature for styrene and MMA iniferter free-radical homopolymerizations.

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