

MEASUREMENT AND MODELING OF AQUEOUS-PHASE RADICAL POLYMERIZATION

Calista Preusser, Robin A. Hutchinson*
Department of Chemical Engineering, Queen's University
Kingston ON K7L 3N6 CANADA

Abstract

Pulsed-laser experimental techniques have shown that the kinetics of aqueous phase polymerizations is complicated by the influence of monomer concentration and pH on propagation, and thus on resultant monomer conversion profiles and polymer molar masses. The complexities are captured in mechanistic models developed to improve understanding and guide process and product development, with model predictions for the aqueous phase copolymerization of non-ionized acrylic acid and acrylamide compared to data obtained using an in-situ NMR technique at higher monomer contents than previously reported in the literature. The influence of intramolecular chain transfer (backbiting) on polymerization rate is demonstrated.

Keywords

aqueous phase polymerization, polymerization kinetics, simulation

Introduction

Water soluble polymers are used in a variety of applications including cosmetics, pharmaceuticals, water treatment, mining, oil sands, textiles, and paper processing. High molecular weight ($>1 \times 10^6$ Da) polyacrylamide (pAM) and its copolymers with acrylic are commonly used as flocculants for the mining and textile industries due to their ability to bind to various charged particles in aqueous solution. Despite their commercial importance, the kinetics of aqueous phase radical polymerizations are poorly understood relative to their organic counterparts. In this contribution we report on recent experimental investigations and modeling efforts to improve knowledge of these systems.

Kinetic Studies

Although the radical polymerization in aqueous phase has been the subject of scientific study since the 1970s, it is only recently that a more complete understanding of the

kinetic complexities of monomers such as acrylamide has been realized. The application of the Pulsed-Laser Polymerization-Size Exclusion Chromatography (PLP-SEC) technique to acrylic acid and most recently acrylamide (Chovancová et al., 2015) has shown that the propagation rate coefficient (k_p) varies with monomer concentration in aqueous solution, a behavior not seen in typical organic monomer/solvent systems. The value of k_p can increase by an order of magnitude as the monomer concentration of monomer is decreased from bulk to 5 wt% in water. This behavior has been attributed to competitive hydrogen bonding in the transition state between the reacting monomer unit and side groups of the monomer and the solvent, and has a profound influence on batch polymerization rates.

Another PLP technique, in which radical concentration after a pulse is directly measured using electron paramagnetic spin resonance spectroscopy (SP-

* To whom all correspondence should be addressed

PLP-EPR), has been utilized to measure the importance of backbiting, also known as the 1,5 hydrogen transfer reaction, in aqueous-phase polymerization. Known to be important for acrylic acid (AA), the presence of the mid-chain radicals formed by the reaction has recently been observed for acrylamide (AM) by Kattner and Buback (2015), thus confirming for the first time the occurrence of backbiting during acrylamide polymerization.

Model Development and Verification

In addition to the PLP experiments used to estimate the homopolymerization rate coefficients required for kinetic modeling, an in-situ NMR technique has been applied to follow the batch copolymerization of AA and acrylamide AM under near-isothermal conditions at much higher monomer contents than previously reported in the literature (Preusser and Hutchinson, 2013). The composition data obtained over the entire conversion range provides a precise estimate of monomer reactivity ratios not available from low conversion data. It was found that the rate of monomer conversion increases with increasing monomer concentration, a trend contrary to the known decrease in the AA and AM chain-end propagation rate coefficients.

Kinetic models have been developed for AA (Wittenberg et al., 2015) and AM (Preusser et al., 2015) homopolymerizations. The models successfully represent the batch conversion profiles measured over a range of conditions, as well as the associated polymer molar mass distributions. In particular, as demonstrated in Figure 1 for AM, the model captures the decreased rate that occurs at lowered monomer concentrations as a result of the formation of less-active midchain radicals by backbiting. Most recently the model has been extended to consider the copolymerization of these two monomers.

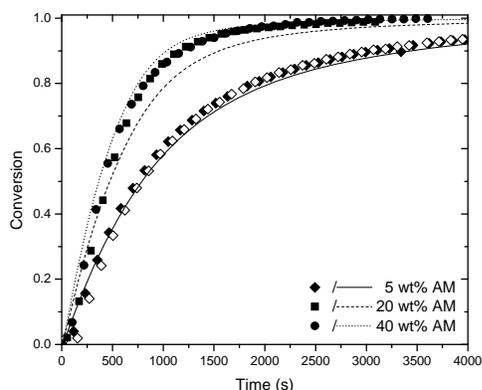


Figure 1. Experimental and predicted batch polymerization conversion profiles at 40 °C, 0.22 wt% V-50 at 5, 20, and 40 wt% AM in aqueous solution.

Conclusions

Kinetic models have been developed to capture the new mechanistic insights developed for AA and AM homo and copolymerization kinetics and the rate coefficients measured by the recent PLP investigations. The predictions of the model were compared to experimental monomer conversion and polymer MW data collected from recent isothermal batch experiments followed in-situ using NMR spectroscopy. The resulting model is shown to capture the observed experimental trends over the complete range of initial monomer concentrations, compositions and temperatures.

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