

## WHAT IS GOING ON IN THE AQUEOUS PHASE DURING EMULSION POLYMERIZATION?

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Emulsion polymerization is a multiphase system, where polymerization occurs both in the polymer particles and in the aqueous phase. Most of the polymer is formed in the polymer particles. However, the polymerization in the aqueous phase plays a critical role in both the kinetics of the process and the microstructure of the polymer. In order to produce the high molar masses usually required for the applications, radicals are produced in the aqueous phase, where they react with the monomer dissolved in that phase and if they do not terminate before, when the oligomers become hydrophobic enough, they enter the polymer particles to produce most of the polymer. The importance of the radical entry rate in the polymerization rate and the molar mass of the final polymer has been recognized since the pioneering work of Smith and Ewart. However, more than 75 years later, and in spite of the great effort devoted to understanding this process, the accepted theories are largely based on educated assumptions. The attempts to validate these theories rely on macroscopic measurements such as overall polymerization rate and molar mass distributions of the final polymer, both of them affected by many other processes such as termination in the polymer particles and radical exit.

In the work, we tried to shed light to the processes occurring in the aqueous phase by providing experimental evidence. For that, using methyl methacrylate (MMA) as case study, the polymerization in the aqueous phase was investigated first by decoupling chain growth and entry. A microfluidic reactor system designed to enable the study of the polymerization of MMA in aqueous solution in the absence of particles was used. The molar mass distribution determined by matrix-assisted-laser-desorption/ionization time-of-flight mass-spectroscopy (MALDI-ToF-MS) contained water-soluble chains of up to 45 monomer units that display a Poisson-like distribution. A mathematical model was developed to describe these experimental results, highlighting in particular the importance of chain length dependent propagation and termination reactions in aqueous phase polymerization.

Once the chain growth was understood, the radical entry was studied using miniemulsions of MMA costabilized with hexadecane that contained a hydrophobic radical trap. The rate of radical entry was determined by UV-visible spectroscopy and the molar mass distributions in the aqueous phase and in the monomer droplets were measured by MALDI-ToF-MS. In these experiments, both the rate of entry and the type of radicals that enter in the particles were precisely characterized, which allowed the development of mathematical model for radical entry.

This work offers a unique insight into aqueous phase polymerization kinetics in the context of the relatively hydrophobic monomers used in emulsion polymerization.