

A STUDY OF THE RADICAL POLYMERIZATION KINETICS OF 2-(DIMETHYLAMINO)ETHYL METHACRYLATE IN AQUEOUS SOLUTION THE INFLUENCE IN THE PRESENCE OF MONOMER IONIZATION AND HYDROLYSIS

Robin A. Hutchinson, Department of Chemical Engineering, Queen's University, Canada
robin.hutchinson@queensu.ca

Opeyemi J. Ajogbeje, Department of Chemical Engineering, Queen's University, Canada

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Amino-functional monomers can be polymerized to form stimuli-responsive polymers with several novel coatings, biomedical, conductive and environmental applications. The synthesis of these polymers, either by conventional free-radical or reversible-deactivation radical polymerization, is impacted by monomer ionization and hydrolysis in aqueous or aqueous-alcohol solutions. Thus, a better understanding of these reactions is needed for efficient polymer synthesis and product development. In this work, solution radical polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) is investigated in organic and aqueous solvents. The pulsed laser polymerization – size exclusion chromatography (PLP-SEC) technique has been employed to determine the propagation rate coefficient, k_p , of DMAEMA in bulk, alcohols, and alcohol/water mixtures. The k_p values of 50 wt% DMAEMA in BuOH and EtOH decrease slightly (~10%) from the bulk values, while the k_p value of 50 wt% DMAEMA in a 75/25 wt% EtOH/H₂O mixture was ~20% higher.

An in-situ nuclear magnetic resonance (NMR) spectroscopy technique is used to examine the aqueous polymerization kinetics of DMAEMA after first quantifying monomer hydrolysis kinetics as a function of pH and temperature. The polymerization of fully ionized monomer at $\text{pH} \leq 6$ proceeds to high conversion without the complication of hydrolysis at a reaction rate more than 5 times faster than that of nonionized DMAEMA in dimethyl sulfoxide. However, when DMAEMA is polymerized at $\text{pH} \geq 8$, a copolymer of methacrylic acid (MAA, a DMAEMA hydrolysis product) and DMAEMA is generated in solution. Therefore, a complete understanding of the system requires knowledge of the (co)polymerization kinetics of protonated and unprotonated DMAEMA in aqueous solution, as well as the terpolymerization of the two forms of DMAEMA with MAA. A mechanistic model of the system is being implemented in PREDICI® to capture kinetic understanding, and to guide reaction conditions for efficient DMAEMA homo- and co-polymers syntheses.

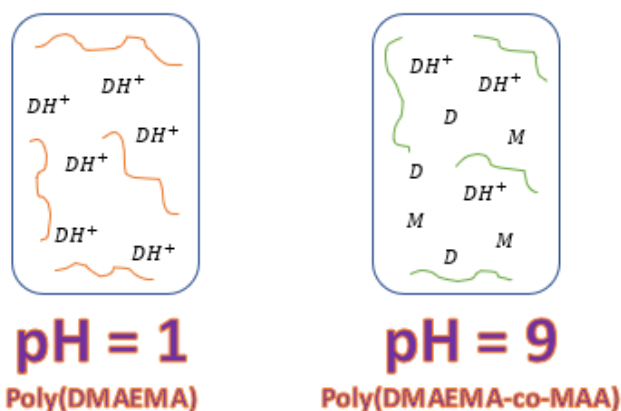


Figure 1 – The aqueous behavior of DMAEMA is studied during polymerization. The cationic monomer (DH^+) forms homopolymer at pH 1. The terpolymerization of unprotonated monomer (D), protonated monomer (DH^+) and deprotonated MAA (M) forms a copolymer at pH 9.