

Enhanced Stabilization of Water/scCO₂ Interface by Block-Like Spontaneous Gradient Copolymers

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The replacement of conventional organic solvents has been identified as a key step in reducing the environmental cost of chemical synthesis, processing and separations. Supercritical carbon dioxide (scCO₂) is a promising environmentally-benign solvent however for most compounds, scCO₂ is a poor solvent. This drawback can be overcome by the use of water-in-scCO₂ or scCO₂-in-water emulsions or microemulsions, which allow high concentrations of polar, ionic and nonpolar molecules to be solubilized within the dispersed and/or continuous phases. Surfactants are necessary to stabilize these emulsions. For this application, amphiphilic copolymers are of interest as they offer better anchoring and steric stabilization at interfaces than low molar mass surfactants.

In this work we shed light on **how microstructural control in amphiphilic copolymers can give access to a new range of macromolecular emulsifiers for CO₂ media with improved phase behavior and interfacial properties at the water-CO₂ interface**. It is observed that spontaneous amphiphilic block-like gradient copolymers made of hydrophilic monomers (N,N-dimethylacrylamide or acrylic acid) and CO₂-philic monomers like vinyl pivalate and vinyl acetate exhibit slightly lower cloud point pressures in supercritical carbon dioxide (scCO₂) than the corresponding diblock copolymers (Figure 1). Much more pronounced differences are established at the water/scCO₂ interface, with larger critical aggregation concentration (CAC), much faster adsorption kinetics and equilibration, and lower surface tension for gradient copolymers. In the frame of this work we also developed **an improved method for the measurement of cloud point pressures** based on image analysis.

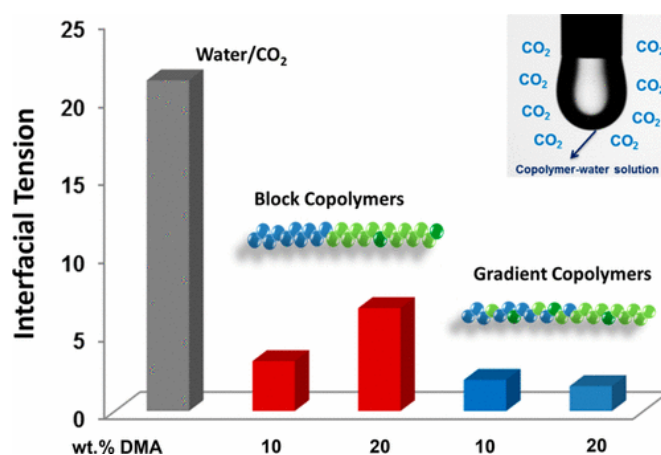


Figure 1: Fluorine-free gradient copolymers cause rapid and significant reductions in the interfacial tension of CO₂/water interfaces

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