

Thermodynamic Aspects of PET Depolymerization by Glycolysis at High Pressures

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Due to its unique solvent properties, supercritical fluids (SCFs) have been used as reaction media in various applications including polymerization and depolymerization. In plastics recycling, supercritical fluids have been utilized in the depolymerization of poly(ethylene terephthalate) by solvolysis. The feasibility of PET glycolysis reaction in supercritical ethylene glycol (EG) has been demonstrated recently. To elucidate the phase behavior, phase equilibrium modeling of the PET-EG system at high pressures was done using the Sanchez-Lacombe equation of state. The PET-EG system studied is predicted to show LCST behavior with critical temperature 608 K at the solvent P_c of 82 bar. Beyond this temperature, the phase stability of the system becomes strongly dependent with pressure. In order to explain the enhanced rates observed when depolymerization is shifted from subcritical to critical state, transition-state analysis is employed. The effect of pressure on the depolymerization rate constant and monomer yields were correlated to solvent effects near critical conditions.