MISCIBILITY, VISCOSITY, DENSITY, AND FORMATION OF POLYMERS IN HIGH-PRESSURE DENSE FLUIDS

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(Abstract)

This thesis is an experimental investigation of the phase behavior, volumetric properties, and viscosity of poly (ε-caprolactone) (PCL), poly (methyl methacrylate) (PMMA) and their blends. Homopolymerization and copolymerizations of 2-methylene-1,3-dioxepane (MDO) and methyl methacrylate (MMA) in acetone or CO_2 have also been explored.

The viscosities and densities of acetone + CO_2 mixtures were measured in the temperature range 323-398 K at pressures up to 35 MPa. This is the first study in which viscosity of acetone + CO_2 mixtures have been measured and the mixtures have been evaluated as solvents for PCL. It is shown that PCL can be readily dissolved in these fluid mixtures at modest pressures even at high carbon dioxide levels. Investigations have been conducted over a temperature range from 323 to 398 K at pressures up to 50 MPa for polymer concentrations up to 20 wt %, and CO_2 concentrations up to 60 wt %. It is shown that in these mixtures PCL is dissolved at pressures that are much lower than the pressures reported for miscibility in the mixtures of carbon dioxide with other organic solvents. It is shown that PMMA also readily dissolves at modest pressures. Blends of PCL and PMMA require higher pressures than for the individual polymers for complete miscibility.

Free-radical polymerizations of MMA in acetone at 343 K were followed using in-situ measurements of viscosity and density at different pressures from 7- 42 MPa. This is the

first time viscosity has been used as a real-time probe of high pressure polymerizations. Two distinct kinetic regimes were identified. Homopolymerizations of MDO were conducted in carbon dioxide at 323 and 343 K at pressures up to 42 MPa. For the first time it is shown that high molecular weight PCL can be produced from MDO in high pressure CO_2. Ring-opening free-radical copolymerizations of MDO with MMA, styrene and acrylonitrile were conducted for the first time in carbon dioxide and have been shown to lead to polymers with high molecular weights.