368a High Pressure Crystallization of Polymers in Dense Fluids

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Understaning polymer crystallization and/or solidification is important for processing of semicrystalline polymers to produce particles, fibers, foams and other microstructured materials. With recent developments in the use of supercritical fluids in polymer processing, there is a greater need in understanding of crystallization processes under pressure in the presence of diluent- or solvent fluids. In the presence of supercritical fluids (and for that matter in any solvent) polymer chain mobilities are altered which significantly influence their thermal transitions, lowering both the glass transition and crystallization temperatures. The changes in the crystallization temperatures are reflected in the shifts in the solid-fluid phase boundary. Liquid-liquid boundaries are also alteerd in the presence of dense fluids. The consequences of bringing about phase separation from a homogeneous solution of a polymer in a fluid then become sensitive to the path followed. Crystallization may be induced by cooling at constant pressure to cross the solid fluid boundary, or by first crossing the liquid-liquid phase boundary(forming thus a polymer-rich and polymer-lean phase)with a pressure reduction, which is then followed by cooling to induce crystallization in the coexisting phases. During these processes the polymer experiences different degrees of undercooling and the resulting crystals are found to display differenet lamellar thicknesses as refelcted by the multiplicity of melting transitions. We have been investigating the crystallization processes in solutions of polyolefins in alkanes and alkane + carbon dioxide mixtures. In this presentation we will discuss the recent results on the effect of crystallization pressure, crystallization time, degree of undercooling and polymer type in terms of the multiple melting transitions as displayed in the DSC scans, and in terms of the crystal morphologies that are generated and characterized by SEM. Specific examples will include polyethylene, polypropylene and poly(4-methyl-1-pentene).