

POLYMER SOLUTIONS AND MODIFICATIONS IN SUPERCRITICAL OR DENSE FLUIDS

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Polymer solutions are involved in essentially all stages of polymer synthesis and purification, and often in modifications and processing. In this respect, solutions that involve supercritical or dense fluids are especially significant. These fluids allow the pressure (or density)-tuning of properties and modulating the outcomes.

As is well known, polymer solutions may display an upper or lower critical solution temperature or both. With increasing solvent strength, the region of miscibility is enlarged and complete miscibility may eventually be achieved in all proportions. If instead, the solvent quality is reduced; the UCST and LCST may come closer, reducing the homogeneous one phase region and eventually may merge and lead to an hour glass shaped region of immiscibility. These are illustrated in Figure 1 where x represents the polymer fraction in the mixture. At ambient pressure, such changes in the phase behavior are achievable only by changing the solvent. The attractiveness of supercritical or dense fluids is that similar changes can be brought about without

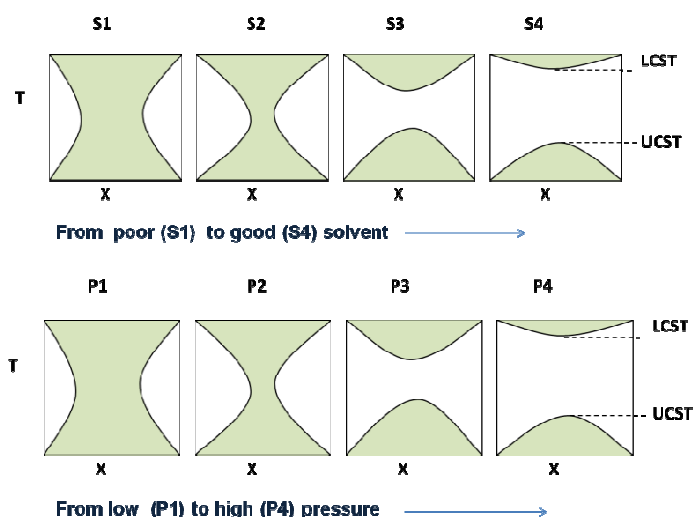


Figure 1. Different phase behavior of polymer solutions that can be achieved by changing the solvent, or by altering the pressure when the solvent is a supercritical fluid.

changing the solvent, but by simply altering the pressure. This flexibility offers unmatched opportunities for fine tuning of the system for targeted outcomes [1].

Additional flexibilities are offered if one were to further consider the effect of solvents on the thermophysical transformations such as the crystallization and vitrification processes that polymers undergo. In the presence of solvents, the glass transition and crystallization temperatures are lowered from their solvent-free values (T_{c^*} and T_{g^*}) as shown by the curves designated as T_c and T_g in Figure 2. The lowering of the glass transition temperature with incorporation of small molecules or liquids into a polymer matrix is well known and is the basis of “plasticization”. When supercritical fluid solvents are involved, the extent of dissolution of the solvent fluid in the polymer can be altered by pressure, and a polymer exposed to supercritical fluid may undergo softening (if glassy) or melting (if semi-crystalline) with increased pressure without changing the temperature.

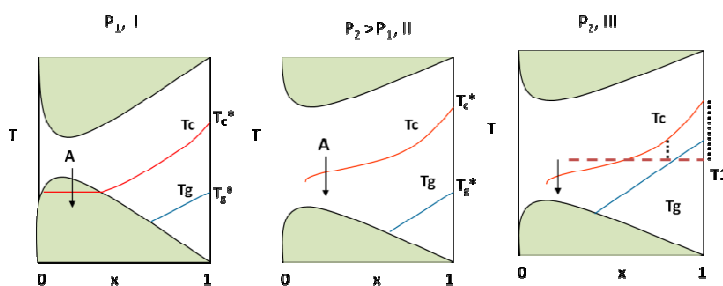


Figure 2. Influence of pressure ($P_2 > P_1$) in the liquid-liquid phase boundary and the change in the crystallization and glass transition temperature of polymers in the presence of a solvent.

Figure 2 illustrates how the liquid-liquid (LL) phase boundaries are shifted with pressure which expands the homogeneous domain, and how the T_c and T_g are altered with solvent incorporation. By altering the pressure and going from a pressure P_1 to a higher pressure P_2 , the relative positions of the LL phase separation and the crystallization curves are altered. At P_1 starting from a homogenous solution conditions such as A, if temperature were to be lowered, the system would first undergo a liquid-liquid phase separation. Crystallization would be possible only after cooling to much lower temperatures and then the outcome is usually a bimodal display of crystal size or morphologies reflecting the consequences of the transformations that occur in the polymer-lean and polymer-rich phases. In contrast, at P_2 , at the same polymer concentration, when temperature is lowered the polymer will undergo crystallization without going through a liquid-liquid phase separation.

In Figure 2, diagram III illustrates the consequences of increasing pressure at a temperature T_1 in the presence of a supercritical fluid. The system follows the path in the direction indicated by dashed arrow. The outcome of increased pressure is an increased level of

fluid dissolution in the polymer. A semi-crystalline polymer may transform from its glassy to rubbery state by crossing the T_g and eventually may undergo its melting transition by crossing T_c , and enter the homogenous solution conditions. Entering the region between T_c and T_g by simply increasing the pressure in the presence of a dense fluid allows easier processing of polymers, such as their impregnation, or their recrystallization or polymorphic transformations without completely dissolving the polymer.

A clear demonstration of the consequences of pressure-induced recrystallization in dense fluid systems is shown in Figures 3 for poly(ϵ -caprolactone) (PCL) + CO₂ system [2]. Here, cylindrical discs of PCL were exposed to carbon dioxide at different temperatures and pressures for 30 min and then depressurized. The samples were then characterized by Differential Scanning Calorimetry (DSC) and freeze-fractured cross sections were examined by a Field Emission Scanning Electron Microscope (FESEM). As illustrated in Figure 3, the DSC scans show that compared to the initial sample, after exposure to CO₂ at 293 and 21 and 45 MPa pressures, melting temperature is increased by about 15 °C. The heat of melting data were found to indicate that about a 40 % greater crystallinity levels were achieved. Similar results are displayed for exposure at 308 K, but with a doublet melting peak, suggestive of heterogeneity of crystal sizes (lamellar thickness). If exposure is carried out at 323 K, the behavior is similar to that of the original polymer, indicating that polymer undergoes complete melting in the presence of carbon dioxide at this temperature and pressure and the crystallization upon pressure reduction proceeds as if it were from melt at ambient pressure. These are substantiated by the FESEM micrographs also shown in Figure 3. At 293 K, the process is recrystallization that is promoted

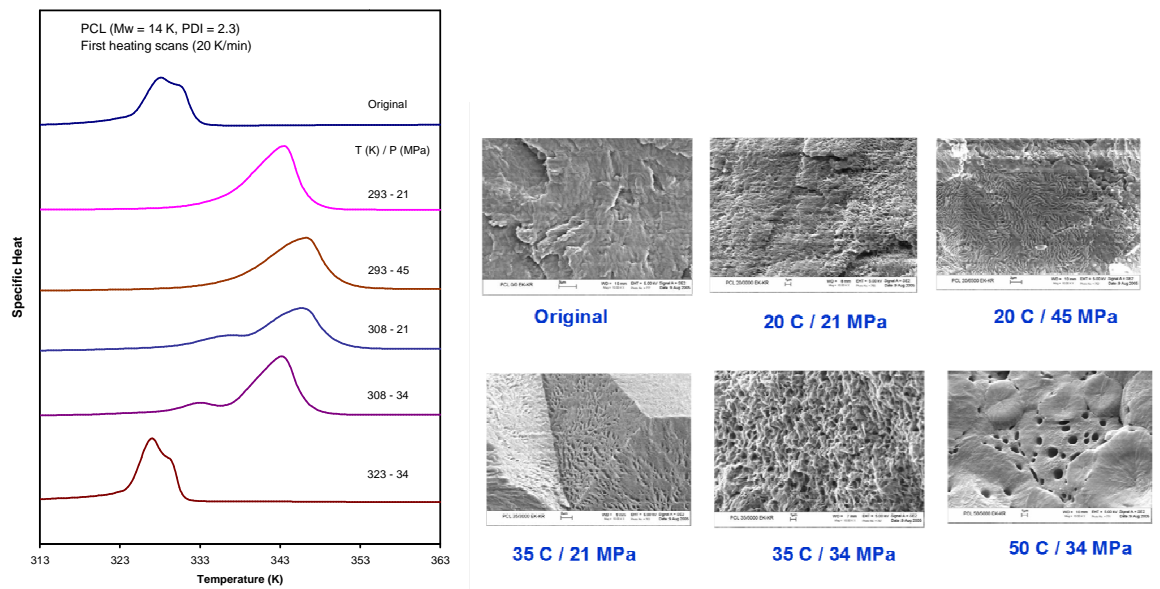


Figure 3. Modifications of poly(ϵ -caprolactone) in carbon dioxide at different T/P conditions as assessed by DSC and FESEM analyses.

by enhanced chain mobility with sorption of CO₂ in the polymer. At the higher temperature 308 K, the recrystallization and lamellar thickening is further facilitated. At 323 K, polymer melts, and upon depressurization the mixture undergoes a liquid-liquid phase separation first leading to a polymer-rich and polymer lean phase that then undergo crystallization, leading to different population of crystals with different lamellar thickness, and thus a doublet melting peak. These notions are illustrated in Figure 4 in diagrams similar to the generalized features of Figure 2 –III. A broader perspective is provided in Figure 5 as to the consequences of shifting the crystallization and glass transition temperatures in dense fluids. Altering the degree of undercooling and chain mobility and promotes changes in the fold thickness, and the degree of crystallinity and melting temperatures. Crystallization does not occur above T_m or below T_g. The closer the crystallization temperature is to melting temperature, the larger are the crystals.

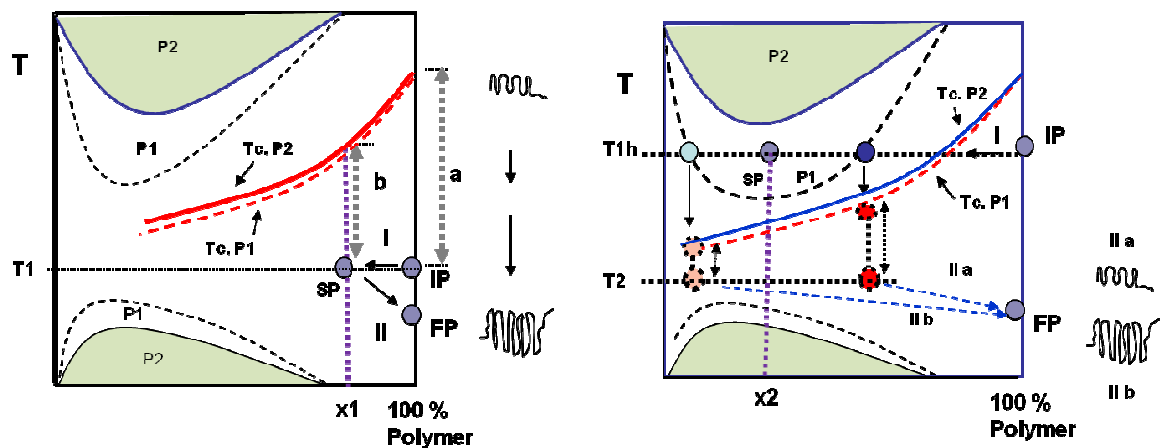


Figure 4. Crystal modification of poly(ϵ -caprolactone) in carbon dioxide: **Left:** Initial polymer (IP) with fluid sorption at high pressure along Path I. Here, the solvent + polymer (SP) system at composition x_1 remains below the equilibrium crystallization curve T_c . Because of the increased chain mobility and the system getting closer to the melting temperature (indicated by arrows a, b), recrystallization with lamellar thickening is promoted. This is locked-in during depressurization along Path II during which temperature is further decreased, and the polymer concentration increases with fluid escaping from the matrix, and the final polymer (FP) displays a higher melting temperature and greater level of crystallinity than the original polymer. **Right:** Fluid sorption is carried out at a higher temperature (T_{1h}) and high pressure (P_2). The initial polymer (IP) melts along Path I and forms a homogeneous one-phase solution of solvent + melt (SP with composition x_2). During depressurization to for example to P_1 , the initially homogeneous system finds itself inside the two-phase region bounded by the dashed curve P_1 , and undergoes a liquid-liquid phase separation forming a polymer-lean and polymer-rich phase. Crystal formation and modifications proceed upon further cooling (for example to T_2) along the solid arrows and along the final depressurization path (Paths IIa and IIb) as the fluid escapes from the polymer-rich and polymer-lean phases. The two-phases lead to different crystalline domains with different lamellar thickness, and as a consequence, the final polymer (FP) displays double melting points.

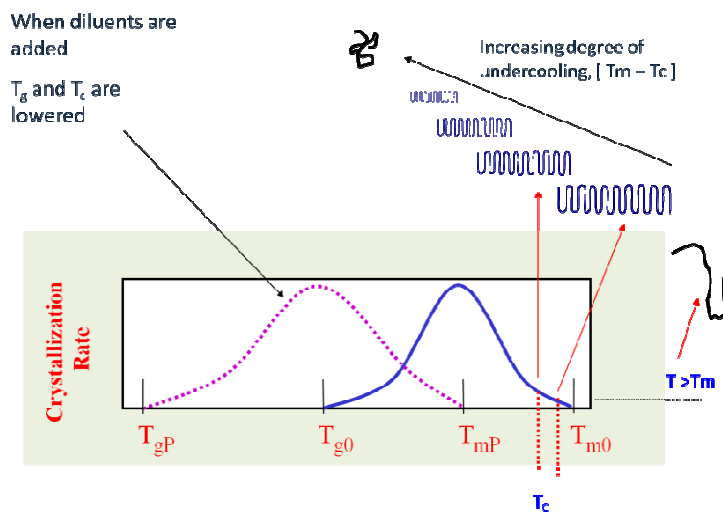


Figure 5. Rate of crystallization as a function of temperature goes through a maximum. In dense fluids under pressure with incorporation of the solvent in the polymer, T_{m0} and T_{g0} are shifted to T_{mP} and T_{gP} . The temperature interval for modifications is shifted to lower temperatures.

Another intriguing example of pressure tuning of miscibility, and the modulation of the phase separation paths for modification of polymers is illustrated in Figures 6-8. Figure 6 shows the phase diagrams displayed by syndiotactic polystyrene (sPS) + toluene at different polymer concentrations and for sPS + toluene + CO₂ mixtures at different CO₂ levels [3]. In toluene the phase boundary is a gelation boundary that arises from coil-to-helix transformation and formation of a “polymer-solvent” compound, which is schematically illustrated in Figure 7. When CO₂ is added to the system, the polymer-solvent compound is destabilized and the system transforms to folded chain crystal domain, and the phase boundary that is observed is a crystallization boundary, which also illustrated in Figure 7. Figure 8 shows the morphological details of crossing the gelation boundary by cooling at high temperature and then reducing the pressure (Path 1) versus crossing the liquid-liquid boundary first to form a polymer-lean and polymer-rich phase and then reducing the temperature (Path 2). In the second case, the path allows the polymer-rich and polymer-lean phases to undergo their solidification/crystallization process. FESEM micrographs show that crossing the gelation boundary leads to a highly porous fibrillar network. The polymer-rich phase on the other hand leads to lamellar morphology while the polymer-lean phase leads to a mixed morphology that displays fibrillar and spherulitic domains. Syndiotactic polystyrene is known to display polymorphism. Further characterizations by X-ray and FTIR shows that when the gelation boundary is crossed, the crystals morphology that develops is delta-form which is the polymorph associated with a polymer-solvent compound in which the solvent molecules are incorporated in such a way that they become part of the crystal structure. The crystal form that is generated from the polymer-rich phase after crossing the liquid-liquid boundary is the beta-form, which is the polymorph with the planar zig-zag structure leading to the folded chain lamellar morphology.

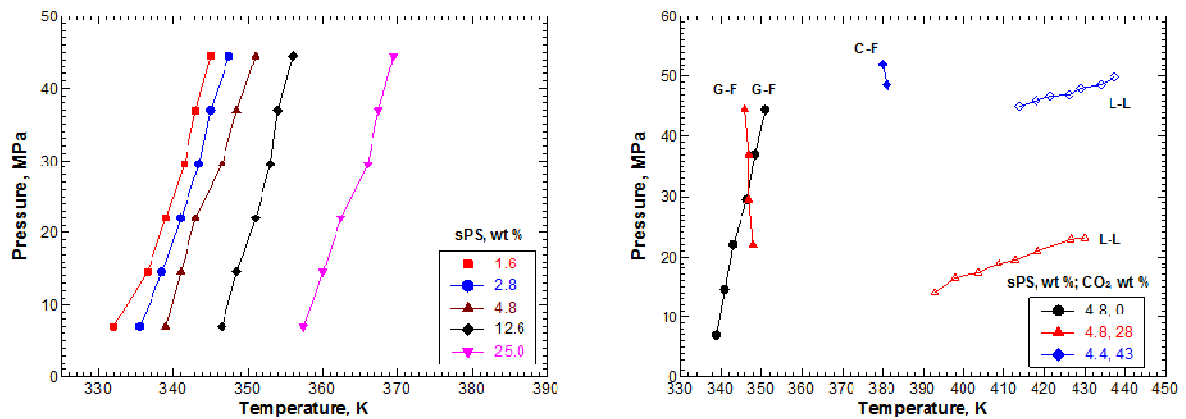


Figure 6. Phase boundaries in syndiotactic polystyrene solutions in toluene (Left) and Toluene + CO₂ mixtures (Right).

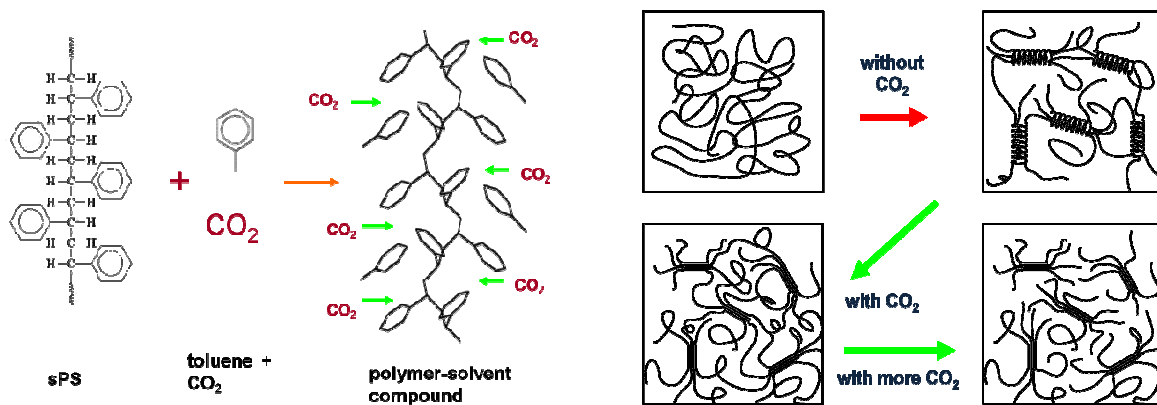


Figure 7. In toluene, sPS forms a polymer-solvent compound in which toluene molecules are held as guest within the cavities of the phenyl side groups. When CO₂ is introduced this polymer-solvent compound is destabilized and eventually the helical structures transform to a folded chain crystal form.

Polymer modifications by tuning the vitrification or crystallization conditions by pressure in a given fluid or fluid mixture is central to essentially all applications that target formation of micro- or nano-structured polymeric matrices ranging from particles to fibers, to foams. Foams and porous polymeric materials have gained an unprecedented attention in the past decade due to the rapid developments that are taking place in tissue engineering and regenerative medicine. Polymeric scaffolds that can promote cell attachment, proliferation and growth are of extreme significance and creation of such scaffolds using supercritical fluids is naturally of growing interest. Some of the target areas such as the vascular or nerve tissue engineering require

forming tubular porous conduits, whereas ligament tissue engineering requires multilayer constructs. A relatively new approach to generate porous constructs of different complexity is the extrusion of polymer solutions generated in dense fluids at high pressures through annular dies into a non-solvent medium [4]. Figure 9 illustrates this approach. The experimental system

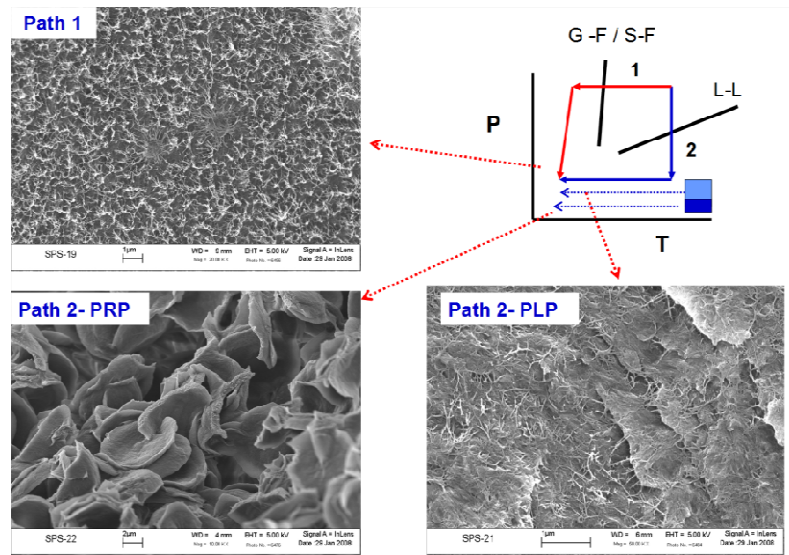


Figure 8. Crystal morphology of sPS depends on the path followed. Crossing the gelation boundary (Path 1) leads to fibrillar morphology with the delta polymorph of the crystals. Crossing the liquid-liquid phase separation first leads to lamellar morphology being generated from the polymer rich phase (Path 2- PRP) with the beta polymorph of the crystal. Polymer lean phase (Path 2- PLP) leads to a mixed morphology with delta- and beta-crystalline forms.

consists of a mixing chamber (VVMC), annular die attachment (D) and an extrusion chamber (EC). Polymer is dissolved in a mixture of organic solvent and carbon dioxide by adjusting the pressure with a movable piston (mp) that is actuated with a pressure generator (PGN). A gear pump (CP) circulates the mixture to achieve homogeneity. Extrusion chamber is filled with carbon dioxide. The pressure and the flow of carbon dioxide are adjusted with a needle valve at the exit. Typically the pressure in the extrusion chamber is maintained to be the same as in the mixing chamber or slightly lower. The solution is extruded by opening the valve between the chambers and gently moving the piston. As the polymer extrudes through the die into the non-solvent carbon dioxide environment, it undergoes phase separation and solidifies as the organic solvent is removed and carried away with the flowing carbon dioxide. The temperature in the extrusion chamber is selected to promote vitrification. The figure shows a tubular segment that was generated by extruding a solution containing 25 wt % of poly(methyl methacrylate), 10 wt % acetone and 65 % carbon dioxide into carbon dioxide at 27 MPa. Mixing chamber was at 80 °C and the extrusion chamber was at 70 °C. A tubular segment with 6mm OD and 1mm wall thickness, with 50-100 μm size pores were generated. By designing different diameter annular dies or dies that allow multiple polymer extrusion lines, multilayer tubular constructs can be generated. Instead of annular dies, one can utilize slit dies and generate flat geometries as well.

The success with these processes requires a broad data base for a rational balance of miscibility, viscosity, mass transfer and heat transfer rates, new phase formation and growth, and the thermophysical transformation processes of vitrification (for glassy polymers like PMMA) and crystallization (for semi-crystalline polymers such as poly(ϵ -caprolactone)). The data base that is of particular interest is for solutions with relatively high polymer concentrations. However, reports and data on the miscibility determinations at high polymer concentrations are not as extensive and present challenges. Rate processes, especially phase separation kinetics are not well documented and present a different level of challenge.

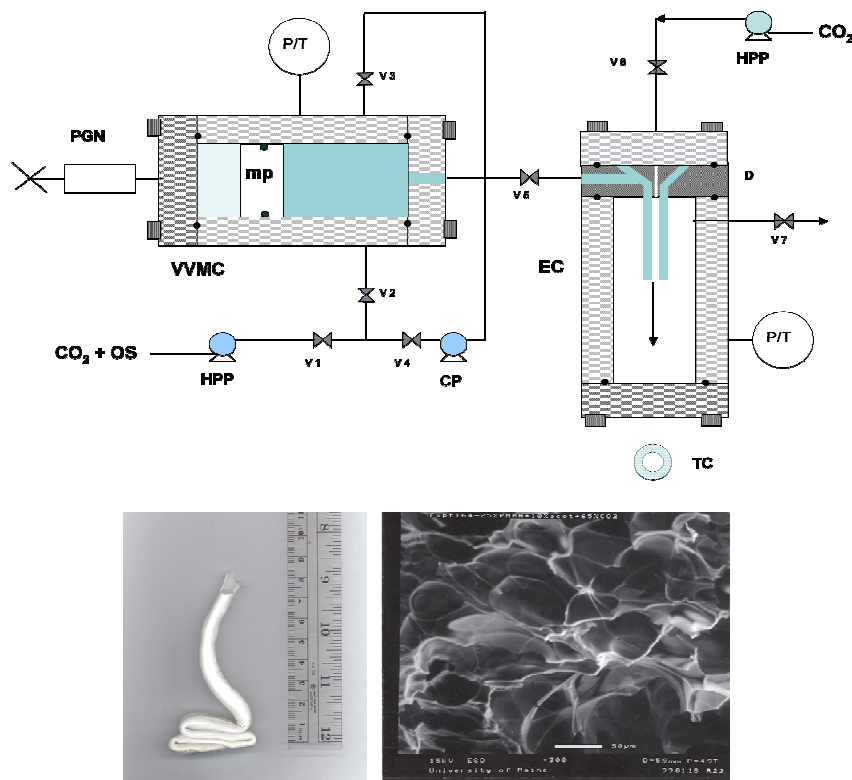


Figure 9. Solution extrusion system and a 6 mm OD tubular construct generated from extrusion of poly (methyl methacrylate) solution in acetone + carbon dioxide into a CO₂ chamber.

Despite the many advances that have been made in understanding polymer solutions in dense fluids over the past couple of decades and the many new application areas that are emerging, there still remain unsolved problems that need further focus and continuing experimental research. Below is a short listing of just a few of the broad-base challenges:

1. *Miscibility- Thermodynamics and Phase Behavior*

Phase compositions that are in equilibrium - polymer concentrations, molecular weights and molecular weight distributions in the respective phases. Heat effects associated with miscibility and phase separation.

2. Phase Separation - Kinetics and Rate Processes

Dynamics of phase separation and differentiation of nucleation and growth and spinodal decompositions processes - the dynamics of early and later stages and phase settlement dynamics. Connectivity to polymer molecular weights, quench depths, viscosity and temperature.

3. Transport Properties – Viscosity, Thermal Conductivity, Diffusivity

Broader documentation of all transport properties of polymer solutions at high pressure – both dilute and concentrated solutions – systems below and above critical entanglement concentrations.

To address some of these challenges a number of new experimental system development activities are in progress in our laboratory. One of these is a continuous density profiler. A variable-volume view-cell system that utilizes a motorized pressure generator and a long-stroke LVDT has been developed for continuous recording of density of fluids and solutions during a pressure scan to fully document conditions where phase changes are occurring if the phase change is accompanied by a detectable change in density. Figure 10 shows the schematic of the experimental system and the density-pressure scans for carbon dioxide at several temperatures along with comparisons with the NIST data base values. The near continuous nature of the density data facilitates with clarity the P/T conditions where vapor-liquid phase transitions occur, and further facilitates fitting the data with equations that are easily manipulated to generate functional descriptions of parameters such as isothermal compressibility, isobaric expansivity, and thermal pressure coefficients [5, 6].

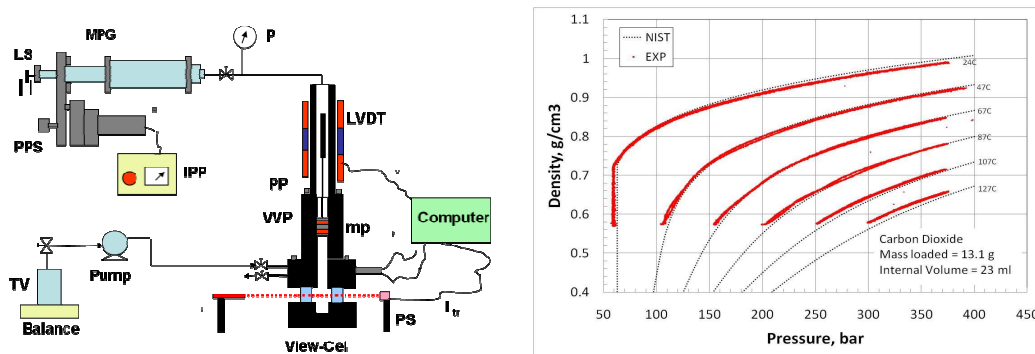


Figure 10. A new experimental system to generate continuous density profiles during pressure scans of fluids and mixtures including polymer solutions; and density profiles for CO₂.

A second system that has been designed permits assessment of the phase-state and the dynamics of phase separation in polymer solutions in the same experimental set up. It involves customized observation windows across which visual and optical assessments (with multiple fiber optic probes) can be conducted as the polymer-lean and polymer- rich phases evolve [Figure 11]. A unique laser light scattering probe has been designed and incorporated to assess

the dynamics of phase separation and to elucidate if the phase separation is proceeding by nucleation and growth or spinodal decomposition in the same instrument, in the same solution for which phase boundaries are determined. A novel mixing arrangement has been incorporated that allows working with high polymer concentrations and/ or solutions with very high viscosities.

A third system that is under development is addressing some of the challenges that pertain to viscosity measurements in both the dilute and concentrated polymer domains.

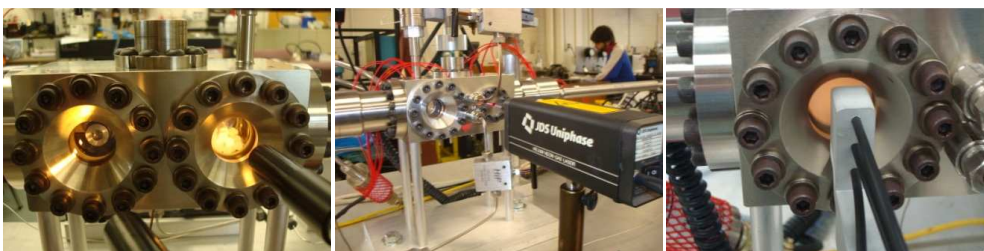


Figure 11. A new experimental system for simultaneous assessment of phase boundaries and phase separation kinetics in polymer solutions.

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