

CHAPTER 12

MAJOR ACCOMPLISHMENTS, CONCLUSIONS AND RECOMMENDATIONS

The following are the major accomplishments and findings of the present research:

1. Mixtures of acetone + carbon dioxide are excellent alternative solvents for PCL or PMMA, or their blends in fluid mixtures even with high CO₂ contents.
2. Mixtures of acetone + carbon dioxide are found to be better solvents for PCL than PMMA. This is linked to specific interaction with the C = O groups in the PCL which are more exposed than the C = O groups in the side groups of PMMA.
3. The competition between the CO₂-acetone and CO₂-CO₂ interactions in the fluid mixtures as a function of composition, temperature or pressure alters the volumetric properties and viscosity of the mixtures. The present study has explicitly shown that even though an increase in volume may suggest an increase in free volume, this does not immediately translate to a reduction in viscosity. Viscosity reflects changes in both the free volume and the changes in the size and shape of the molecules due to an association.

4. The present study has shown that combined information on both the density and viscosity of polymer solutions provides insights as to the polymer chains size and extension, the goodness of the solvent, and polymer chain overlap concentrations for entanglements. Assessment of compressibility, expansivity, excess volume and excess viscosity in polymer solutions and in their corresponding solvents as a function of composition, pressure and temperature provide new perspectives for the properties of these systems. It is shown that polymer solutions can display unusual compressibility behavior if the nature of association between the components in the solvent fluid mixtures is altered.
5. The present study has shown that polymers with higher molecular weights require higher pressures for complete miscibility as one would expect. Furthermore, the study has shown that polymer blends require higher pressures to bring about complete miscibility. In mixtures of PCL, PMMA, or their blends in acetone + CO₂, at a given temperature, complete miscibility is achieved by increasing the pressure. At a given pressure, two phase regions are entered by increasing the temperature. The behavior is typical of systems showing lower critical solution temperature.
6. The present study has shown that monitoring the real time viscosity and density and transmitted light intensity during polymerizations provides new insights with respect to recognizing when the phase separations take place due to chain growth, and over which time intervals there are recognizable changes in the rate of polymerizations. The study has shown that kinetics of polymerization can be readily followed by real-

time viscosity measurements. It is shown that viscosity is sensitive to identify the regimes with different polymerization rates.

7. For the first time, MDO has been homopolymerized in carbon dioxide to form PCL with relatively high molecular weights (ca. 25,000). This is in contrast to ambient bulk polymerization of MDO which results in polymers with molecular weights less than 1,200.
8. The study has shown that for the first time that copolymers of MDO with MMA, ST, and AN can be prepared in carbon dioxide forming polymers with molecular weight up to about $M_w = 100,000$.

The following are some recommendations for future research:

1. The potential utility of acetone + carbon dioxide mixtures should be further explored in processing of polymers. Polymers that have different degree of interaction capability should be considered.
2. Blending studies should be continued and evaluated for their properties.

3. Use of viscosity in monitoring progress of polymerization should be extended to other polymerizations including copolymerizations. The systems that show phase separation can be detected by viscosity measurements.
4. Use of viscosity and density measurements in following the kinetics of polymerization should be further explored.
5. Polymerizations and copolymerizations of MDO in acetone + CO₂ mixtures should be carried out with more complete characterizations of the polymers formed.