CHAPTER 1
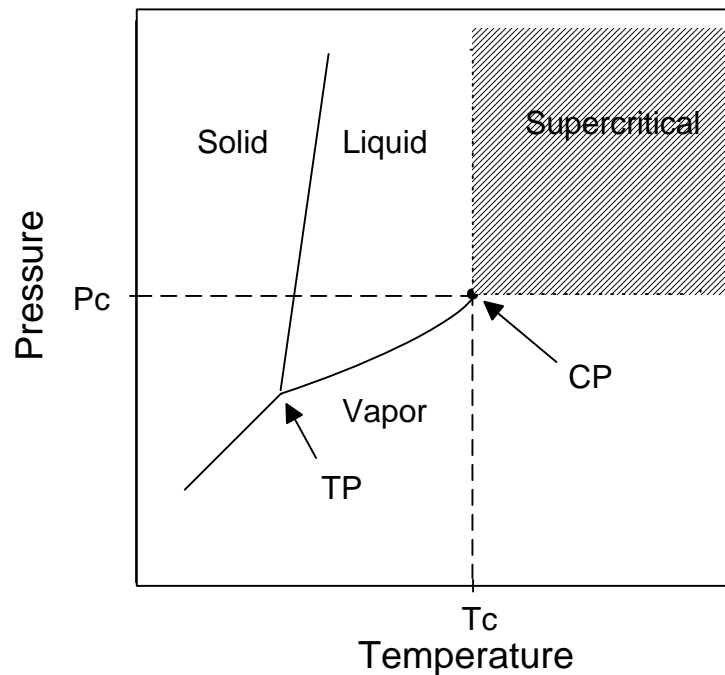
INTRODUCTION

For any pure substance, in the pressure – temperature (P-T) phase diagram, the end point of

the vapor-liquid equilibrium curve is known as the vapor-liquid "critical point" (CP). This is

illustrated in Figure 1.1.

Figure 1.1 Definition of supercritical region for a pure substance. CP: critical point (where

the distinction between liquid and vapor disappears), TP: triple point (where liquid, solid and

vapor coexist), T_c: critical temperature, P_c: critical pressure.

Critical temperatures and pressures for some common substances are listed in Table 1.1 (Brunner, 1994). The region beyond the critical point (i.e., $T > T_c$ and $P > P_c$) is called the supercritical region. For mixtures, the phase behavior is complex and mixture critical points depend on composition and the nature of the components of the mixtures (McHugh and Krukonis, 1994). In the simplest case, the mixture critical points lie on a continuous curve between the critical points of the pure components. This is illustrated in Figure 1.2. Fluids above the critical line are in supercritical state.

Table 1.1 Critical points of some common fluids

|	Tc / K	Pc / MPa
Nitrogen	126.2	3.39
Oxygen	154.6	5.04
Ethylene	282.4	5.04
Carbon dioxide	304.2	7.38
Ammonia	405.6	11.35
n-Pentane	469.7	3.37
Acetone	508.1	4.70
Ethanol	513.9	6.14
Benzene	562.2	4.89
Toluene	591.8	4.10
Water	647.3	22.12

The unique feature of fluids in the supercritical state is the tunability of their properties which are between those of gases and liquids (Schneider, 1978; Kiran et. al., 1994). Generally, they have liquid-like densities and gas-like diffusivities. These and other properties such as the viscosity and the dielectric constant can be continuously adjusted by regulating the temperature or the pressure without entering two-phase regions. Figure 1.3 illustrates two isotherms, one below (T_2) and one above (T_1) the critical temperature,

showing the variation of density with pressure. At $T > T_c$, variation is continuous, and as T_c

is approached small changes in pressure bring about large changes in density. This is one of

the unique attributes of supercritical fluids. By small adjustments in the pressure, liquid-like

behavior is achieved without entering the vapor-liquid two-phase region. This allows

achievement of tunable solvent power for the fluid. This feature of supercritical fluids has led

to a range of applications. Especially attractive are those fluids that are ordinarily gases (such

as carbon dioxide) and are non-toxic.
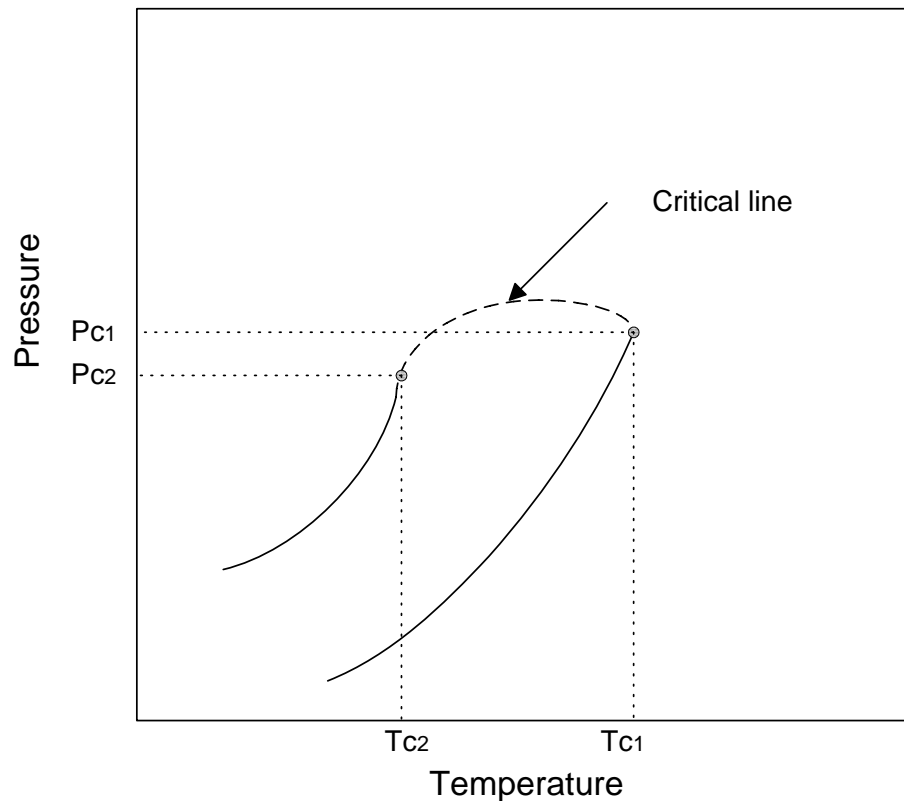
Figure 1.2 Critical line for a simple binary mixture of component 1 and 2. P_{c1}, P_{c2}, T_{c1}, T_{c2}
correspond to pure component critical pressures and critical temperatures.

Among the applications are extractions and separations, reactions, and material synthesis and modifications. Traditional examples of extractions and fractionations are the selective removal of caffeine from coffee or tea or separation of polymers with respect to molecular weight or composition. The adjustability of the solvent power allows the selective extractions of a target molecule from complex networks or mixtures, and the higher diffusivities allow more efficient penetration.
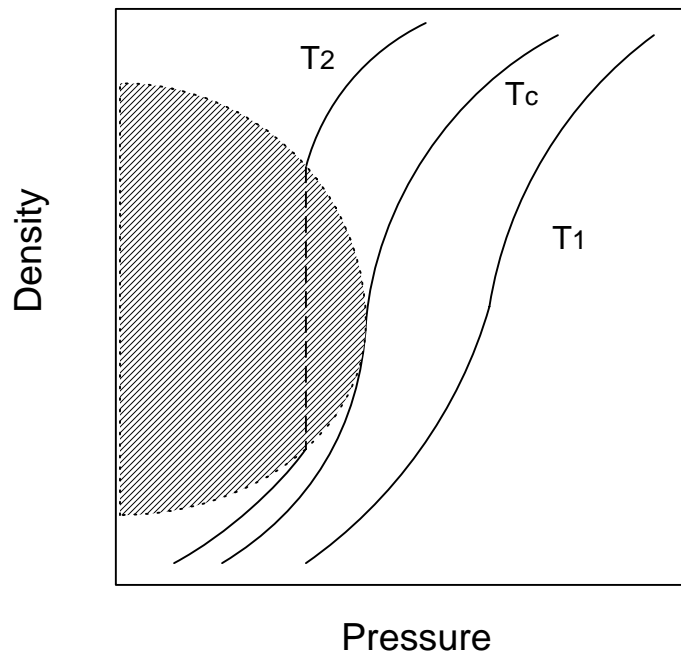
Figure 1.3 Variation of density with pressure for a pure fluid above and below the critical temperature (T_c). $T_1 > T_c > T_2$. The shaded area is the vapor-liquid two-phase region.

In reaction systems, elimination of the inter-phase mass transfer resistances, removal of hot spots, improving the selectivity, prolonging the catalyst lifetime, and even regenerating the deactivated catalyst make use of supercritical fluids attractive. Indeed, numerous reactions

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have been conducted in SCFs (Savage et. al., 1995; Baiker, 1999; Jessop, Ikariya, and Noyori, 1999).

Variety of materials have been processed and modified in supercritical fluids including ceramics, metals, biomaterials, pharmaceuticals, magnetic materials, semiconductors, energetic materials, and polymers. Particle formation, porous material preparation including aerogels, foams, membranes, and composite materials have been reported (Cooper, 2001; 2003; Reverchon et. al., 2003, Tomasko, 2003a; b).

Numerous publications have been reported also on polymerizations including free-radical polymerizations, controlled-radical polymerizations, cationic polymerizations, anionic polymerizations and step-growth polymerizations in supercritical fluids (Jenner, 1978; Ogo, 1984; Cooper and DeSimone, 1996; Kendall et. al., 1999).

Despite its tunability and the non-toxic features, supercritical carbon dioxide has a limitation resulting from the low solubility of most materials, especially the high molecular weight polymers in this fluid. This limitation is partly solved by addition of a co-solvent (Zhang, 2003). Among the co-solvents that have been explored in the literature are ethanol, dimethyl ether, Freons ®, and alkanes such as pentane, or propane. In the present thesis research, our aim is to explore a new set of binary fluid mixtures as solvents for selected polymers, or as solvent medium for polymerizations. The solvent system is acetone + carbon dioxide mixtures. The polymer systems are poly (methyl methacrylate) (PMMA), poly (ε-caprolactone) (PCL), and their blends. The polymerizations are the homopolymerization of

2-methylene-1,3-dioxepane (MDO) and its copolymerizations with MMA, styrene (ST), or

acrylonitrile (AN)). The structures of these polymers, copolymers, and MDO monomer are

shown in Figure 1.4.

PMMA

PCL

Poly (MDO-*co*-MMA)

Poly (MDO-*co*-ST)

Poly (MDO-*co*-AN)

MDO
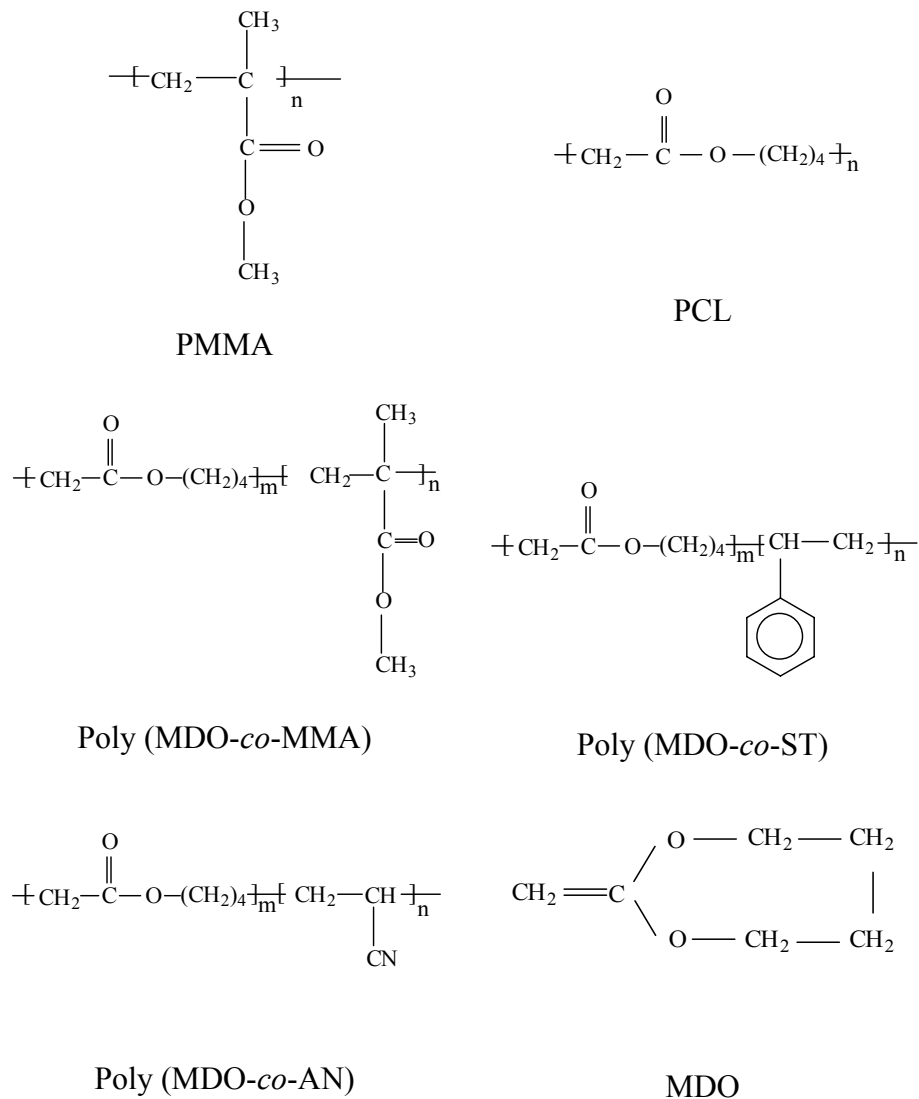
Figure 1.4 Structures for PMMA, PCL, poly (MDO-co-MMA), poly (MDO-co-ST), poly
(MDO-co-AN), and 2-methylene-1,3-dioxepane (MDO).

Acetone-carbon dioxide mixtures are known to display a continuous critical line between the critical points of acetone and carbon dioxide (Pöhler and Kiran, 1997a). At pressures above 12 MPa, the mixtures are all supercritical. This will be the first study in which acetone + carbon dioxide fluid mixtures are extensively evaluated as solvents for polymers. In fact there is no previous data on the miscibilities of PCL in these mixtures. There is no prior published information on the viscosity of acetone and acetone + carbon dioxide mixtures or polymer solutions in these mixtures at high pressures.

Literature reports that PCL has indeed low solubility in carbon dioxide and to achieve miscibility pressures of 3000 bar are needed. To enhance the dissolving power, organic solvents such as dimethyl ether or Freons ® have been previously explored as co-solvents. Our objective is to use acetone as the co-solvent which is a FDA approved chemical.

The literature data on the behaviors of polymers in binary fluid mixtures point to a general trend. In good solvents majority of the high pressure solution behaviors are similar to those solutions that show lower critical solution temperature where phase separation occurs when temperature is increase at a given pressure. When the solvent quality is decreased, the behaviors shift and display features that are more like solutions that display upper critical solution temperature. Then, phase separation occurs when temperature is decreased at a given pressure. In polymer solutions in binary fluid mixtures, with increasing carbon dioxide content, the behavior gradually shifts from LCST to UCST type behavior (Kiran, 1994; Byun et. al., 2006). These are schematically illustrated in Figure 1.5.

Miscibility pressures are also greatly increased as carbon dioxide content is increased. This is also demonstrated in Figure 1.5. The miscibility pressures increase from low (5-10 MPa) to very high (> 100 MPa) pressures. Our aim in this study is to explore if acetone-carbon dioxide mixtures are more efficient in bringing about miscibility of PCL, its blends and copolymers at more moderate pressures compared to other organic solvents that have been used in the literature.
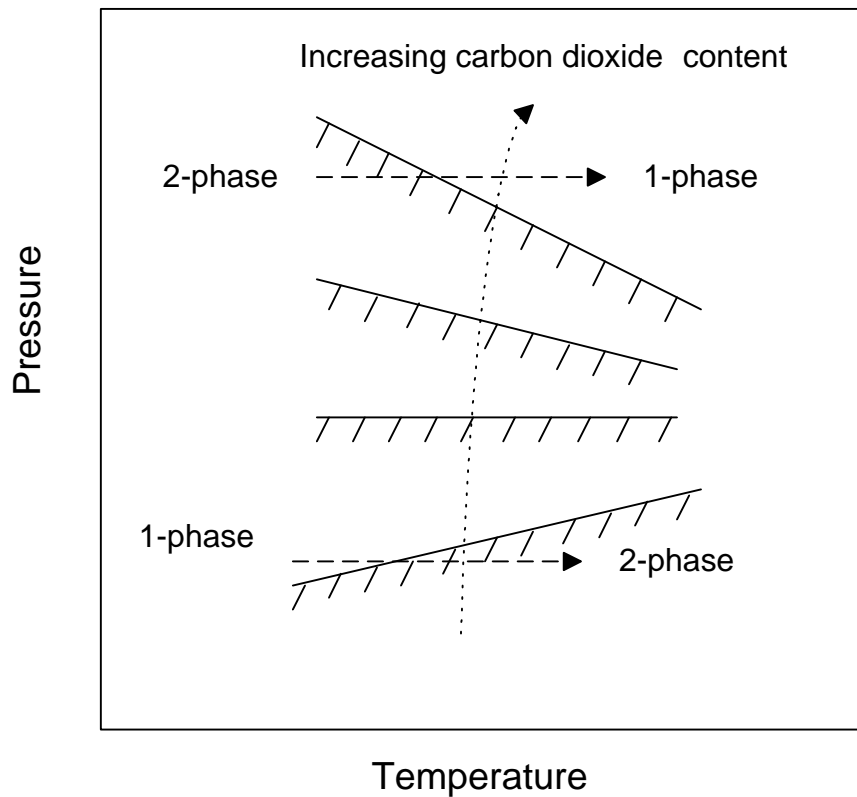

Figure 1.5 The phase behavior in polymer solutions as a function of carbon dioxide content of solvent. The solid lines are the liquid-liquid phase boundaries. Shaded sides depict the two-phase regions.

This investigation is also aimed at using viscosity as a probe of polymerizations at high pressures. In polymerizations, as longer chain molecules are formed, the viscosity of the medium increases, and the rate at which the viscosity increases provides insights as to the progress of polymerization. One other technique that we have explored in these polymerizations is the real time recording of changes in turbidity (as determined from changes in transmitted light intensity) during the entire course of polymerizations. In this way, the onset of phase separation is assessed which is especially useful in precipitation polymerization (Yeo and Kiran, 2004; 2005). In the absence of stabilizers, polymerization systems in dense fluids undergo phase separation with increase in molecular weight. The system which may be initially one phase, enters two-phase regions with progress of polymerization. This is illustrated in Figures 1.6 and 1.7. The Figure 1.6 shows how the LCST may be lowered, or how the UCST may be increased causing phase separation with progress of polymerization. The Figure 1.7 shows the variation of transmitted light intensity with time during homogeneous or heterogeneous polymerizations.

The present study reports for the first time the evolution of viscosity in homogeneous polymerization of MMA in acetone. For the first time homopolymerization of MDO is reported in carbon dioxide. For the first time copolymerizations of MDO with MMA, ST, and AN are reported in carbon dioxide. Use of supercritical fluid mixtures at high pressures is crucial to form high molecular weight polymers in these systems. Information on phase boundaries and conditions for phase separation are crucial in knowing the region where polymerizations are carried out - in the homogeneous one-phase region, or the heterogeneous two-phase conditions.

The thesis thus involves experimental determinations of miscibility conditions, density, and viscosity for these acetone + carbon dioxide mixture solvents and polymer solutions. The homogeneous free-radical polymerization of MMA is conducted in acetone. The changes in density and viscosity with polymerization time are related to the polymerization kinetics. Heterogeneous free-radical ring-opening polymerization of 2-methylene-1,3-dioxepane (MDO) is conducted in carbon dioxide to produce polycaprolactone (PCL) and its copolymers, poly (MDO-co-methyl methacrylate), poly (MDO-co-styrene), and poly (MDO-co-acrylonitrile).
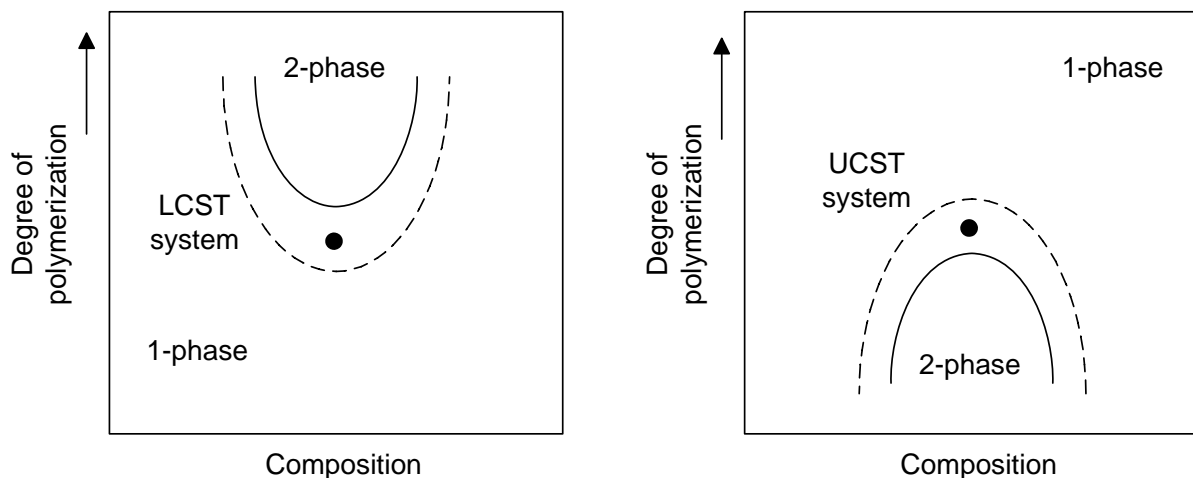
Figure 1.6 Schematic diagrams showing polymerization-induced phase separation (top). With the progress of polymerization, the lower critical solution temperature may be lowered or the upper critical solution temperature may increase, upon which homogeneous system enters two-phase region.
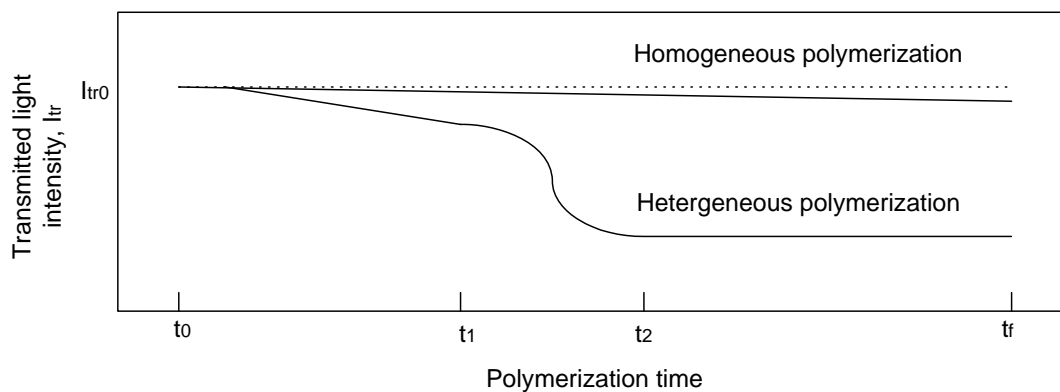
Figure 1.7 Schematic diagram for variation of transmitted light intensity, I_{tr} with polymerization time in homogeneous or heterogeneous polymerizations. In heterogeneous polymerizations, phase separation occurs at time $= t_1$ and thereafter the polymerization proceeds in two phase region.

The specific systems and the nature of the exploration are summarized in Table 1.2. Figure 1.8 illustrates the major elements of the research program and their interrelationships. Our aim has been to first generate a fundamental data base on the density, viscosity, and phase boundaries for the polymers of interest over a wide range of temperatures, pressures, polymer concentrations and CO_2 content. With this data base, in the second stage of the program, the aim has been to explore possibility of polymer blending, and formation of polymers or copolymers in these fluids. The polymers are then characterized by GPC molecular weights and molecular weight distributions, by DSC for thermal transitions (glass transition and melting), by FTIR for changes in crystallinity, or by NMR to assess the structure and evaluate copolymer compositions.

It should be noted that four papers based on the present research results have already been published. These are:

1. Liu, K., and Kiran, E. (2007). Viscosity, density and excess volume of acetone + carbon dioxide mixtures at high pressures. Industrial & Engineering Chemistry Research, 46, 5453-5462.

2. Liu, K., Schuch, F., Kiran, E. (2006). High pressure viscosity and density of poly(methyl methacrylate) + acetone and poly(methyl methacrylate) + acetone + CO_2 systems. Journal of Supercritical Fluids, 39, 89-101.

3. Liu, K., and Kiran, E. (2006). Miscibility, viscosity and density of poly (ε-caprolactone) in acetone + carbon dioxide binary fluid mixtures, Journal of Supercritical Fluids, 39, 192-200.

4. Liu, K, and Kiran, E. (2007). A tunable mixture solvent for poly (ε-caprolactone): Acetone + carbon dioxide, Polymer, 48(19), 5612-5625.

In the following chapters, a general review of polymerization and polymer processing in high-pressure dense fluids and a review of polymer solution viscosity at high pressures are first presented (Chapters 2 and 3). In Chapter 4, the experimental methodology is described. The remaining chapters are devoted to the findings during the course of this thesis research.

Table 1.2 Research Program Outline

Generation of Fundamental Database

Volumetric Properties and Viscosities

Acetone + Carbon Dioxide mixture

PMMA + Acetone

PMMA + Acetone + Carbon Dioxide

PCL + Acetone

PCL + Acetone + Carbon Dioxide

Phase Behaviors and Miscibilities

PMMA + Acetone + Carbon Dioxide

PCL + Acetone + Carbon Dioxide
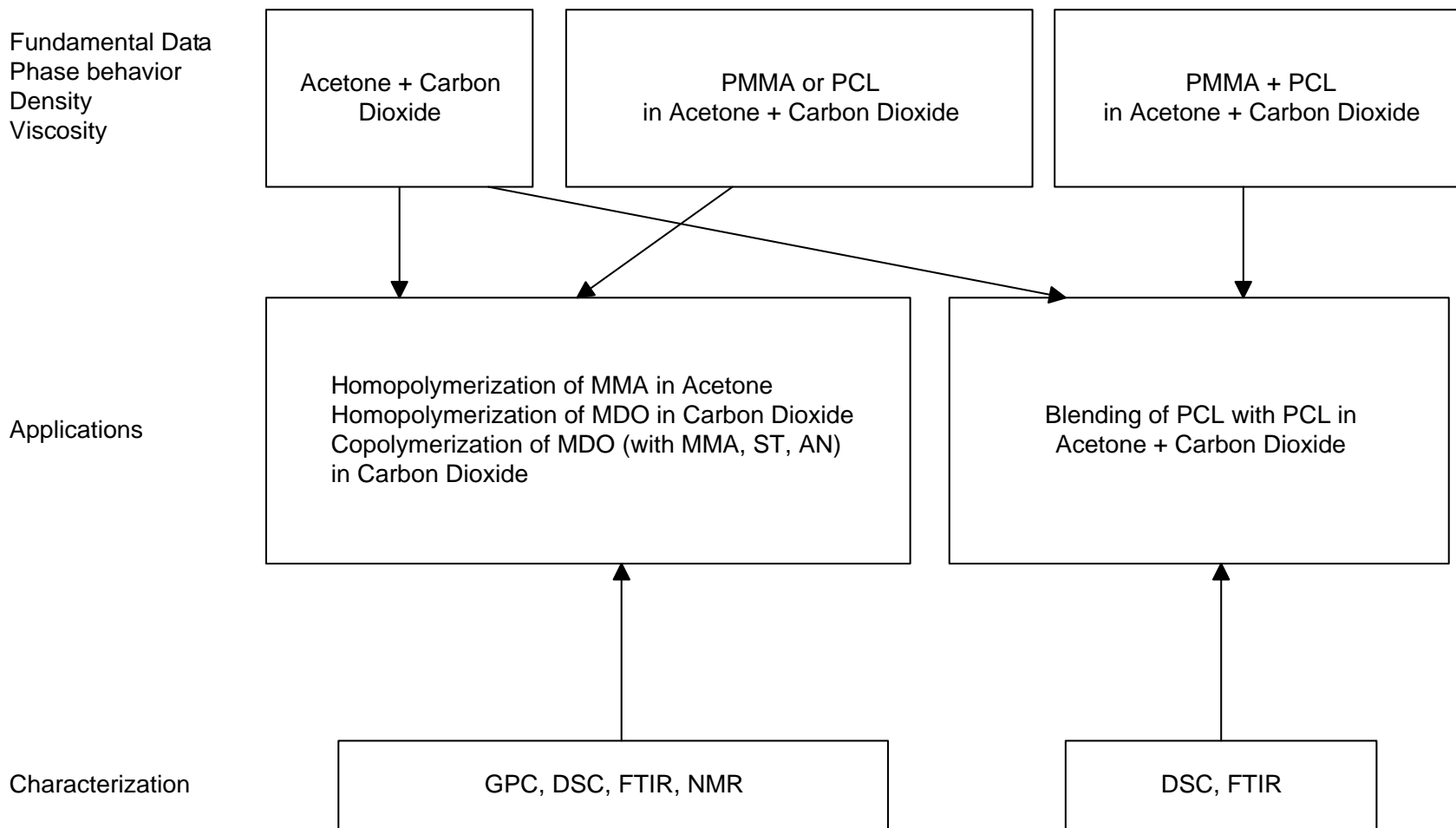
PCL + PMMA + Acetone + Carbon Dioxide

Polymerizations

Free-radical polymerization of MMA in Acetone

Free-radical ring-opening polymerization of MDO in CO_2

Free-radical ring-opening copolymerization of MDO with methyl methacrylate, styrene, and acrylonitrile in CO_2

Processing

High-pressure solution blending of PCL with PMMA in acetone + CO_2 mixtures

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Figure 1.8 Interrelations among different parts of the present program