

## CHAPTER 2

### **LITERATURE REVIEW ON POLYMER SOLUTIONS, POLYMERIZATIONS AND POLYMER PROCESSING AT HIGH PRESSURES IN DENSE FLUIDS**

The high-pressure dense or supercritical fluids have been used in a wide range of reactions and material processing processes. Specifically for polymers, various polymerizations and polymer modifications have been carried out in supercritical fluids (Jenner, 1978; Ogo, 1984; Cooper and DeSimone, 1996; Kendall et. al., 1999; Kiran, 2000; Kikic and Vecchione, 2003; Reverchon et. al., 2003; Tomasko et. al., 2003a,b; Quirk et. al., 2004; Yeo and Kiran, 2005; Nalawade, et. al., 2006). A range of free-radical polymerizations, controlled radical polymerizations, cationic polymerizations, anionic polymerizations, and step-growth polymerizations have been carried out. Polymer processing in SCFs has been focused on polymer impregnation, particle formation, polymer blending, polymer composite preparation, and microporous polymeric material preparation such as foaming and membrane preparation. Many of these processes involve binary fluid mixtures in which carbon dioxide is used as an anti-solvent or a component that reduces miscibility of polymer, or an organic solvent is used as co-solvent to enhance the solvating power of carbon dioxide. In the following section, a brief review of literature on polymer solutions in binary fluid mixtures is presented. This is followed by a review of polymerization and polymer processing.

## 2.1 Polymer solutions in binary fluid mixtures

An excellent recent review article provides summary of polymers and dense fluid systems that have been investigated in the literature (Kirby and McHugh, 1999). Table 2.1 is summary of these systems that have been studied in binary fluid mixtures with additional information from more recent studies.

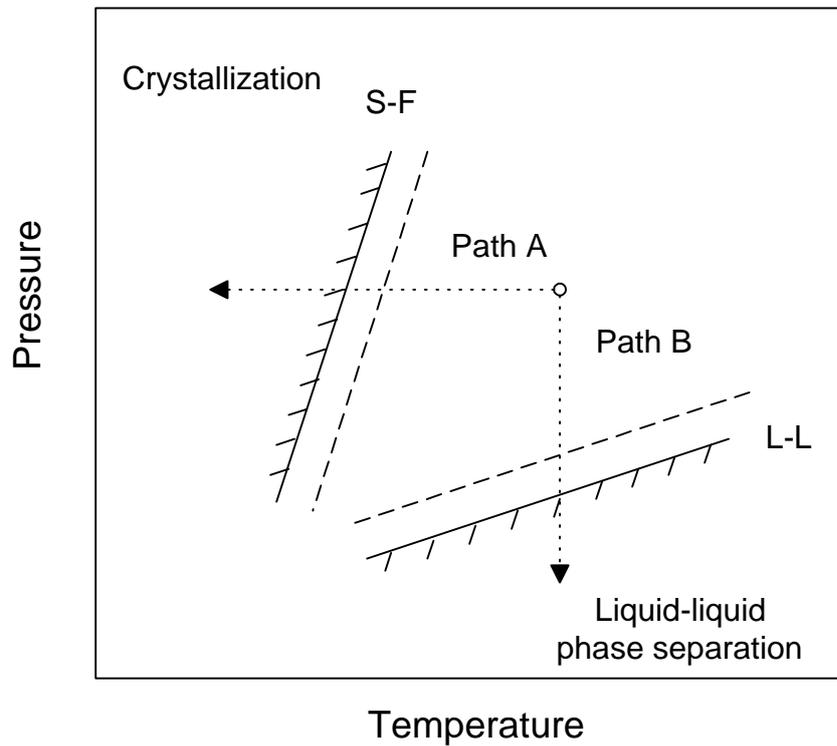
The basic strategy is the selection of co-solvent to bring about miscibility of a given polymer is the introduction of polarity as in the case with solvents like ethanol, methanol, acetone, or non-polar attributes as in the case with alkanes like propane, butane, pentane, and hexane. The extensive data on polymer solutions provide some generalities with regard to polymer molecular weight, polymer concentration, polymer branching, polymer crystallinity, and polymer microstructure. In general, higher molecular weight polymers require high pressures. Branching usually lowers the miscibility pressures. Polymer concentration alters the miscibility pressures, while at a given temperature goes through a maximum, usually at a relatively low polymer concentration ( $< 5$  wt %). The solutions may undergo phase separation by either decrease the pressure (which usually leads to liquid-liquid phase separation) or by decreasing pressure the temperature at a given pressure (which usually leads to fluid-solid phase separation). Figure 2.1 shows the alterations of the liquid-liquid and fluid-solid phase boundaries with the solvent-antisolvent composition in the binary fluid mixtures. As discussed in the introduction, these phase boundaries are altered with the solvent-antisolvent content in fluid mixtures. When carbon dioxide content is increased, L-L phase boundary moves to the higher pressures, and S-F phase boundary moves to higher temperatures. Figure 2.1 is a schematic temperature versus polymer concentration diagram showing the changes in the

liquid-liquid phase boundaries as a function of pressure or solvent composition. When pressure is increased, one phase region is enlarged. Upon pressure reduction, LCST and UCST curve closes and eventually merge forming an hour-glass shaped region of immiscibility. A similar trend is observed, if pressure is held constant but solvent quality is decreased by adding a non-solvent. Polymers that have polar groups are more readily dissolved in polar solvents interact with the solvents. Pressure can be used to alter the extent of these interactions.

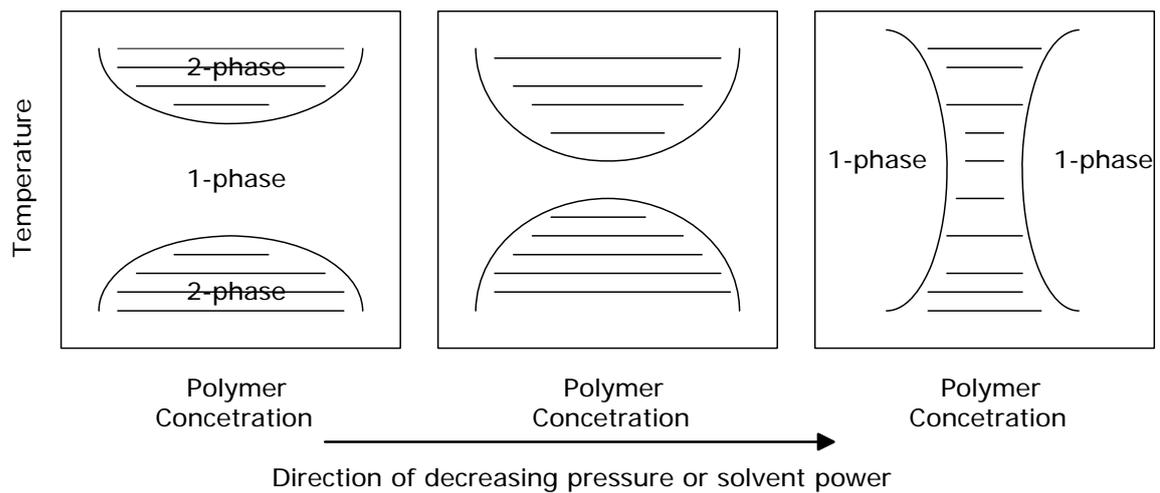
**Table 2.1** Polymer solutions in binary fluid mixtures

<b>Polymer</b>	<b>Solvent</b>	<b>Reference</b>
Polystyrene	Butane + Pentane	Kiran et. al., 1989
Polyethylene	Hexane + Nitrogen	Kennis et. al., 1990
Poly (ethylene-co-propylene)	Butene + Ethylene Hexene + Ethylene	Chen et. al., 1992
Polyethylene	4-Methyl-1-pentene + Ethylene	Wohlfarth et. al., 1992
Poly (ethylene-co-methyl acrylate)	CHClF <sub>2</sub> + Acetone CHClF <sub>2</sub> + Ethanol Propane + Acetone Propane + Ethanol	Hasch et. al., 1993
Poly (methyl acrylate)	CHClF <sub>2</sub> + Acetone CHClF <sub>2</sub> + Ethanol	Hasch et. al., 1993
Polyethylene	Propane + Acetone	Hasch et. al., 1993
Polyethylene	Butane + CO <sub>2</sub>	Xiong and Kiran, 1994
Polystyrene	Toluene + CO <sub>2</sub>	Kiamos and Donohue, 1994
Polystyrene	THF + CO <sub>2</sub>	Kiamos and Donohue, 1994
Poly (ethylene-co-methyl acrylate)	Propane + Hexane Propane + Methanol Propane + 1-Propanol Propane + 1-Butanol	LoStracco et. al., 1994
Poly (ethylene-co-methacrylic acid)	Butane + Dimethyl ether	Lee and McHugh, 1994

Poly (methyl acrylate)	Toluene + CO <sub>2</sub> THF + CO <sub>2</sub>	Kiamos and Donohue, 1994
Poly (vinyl ethyl ether)	Toluene + CO <sub>2</sub> THF + CO <sub>2</sub>	Kiamos and Donohue, 1994
Poly (ethylene-co-acrylic acid)	Butane + Dimethyl ether Butane + Ethanol	Lee et. al., 1996
Polystyrene	Cyclohexane + CO <sub>2</sub>	Bungert et. al., 1997
Poly (ethylene-co-propylene)	Propane + 1-Butanol Propane + 1-Propanol	Whaley et. al., 1997
Poly (butyl acrylate)	Butyl acrylate + CO <sub>2</sub>	McHugh et. al., 1998
Poly (ethylhexyl acrylate)	Ethylhexyl acrylate + CO <sub>2</sub>	McHugh et. al., 1998
Polysulfone	THF + CO <sub>2</sub>	Zhang and Kiran, 2002
Polyethylene	Pentane + CO <sub>2</sub>	Zhang et. al., 2003
Poly (methyl methacrylate)	Acetone + CO <sub>2</sub> Ethanol + CO <sub>2</sub> CH <sub>2</sub> Cl <sub>2</sub> + CO <sub>2</sub>	Domingo et. al., 2003
Poly (dimethylsiloxane)	Methanol + CO <sub>2</sub>	Munson et. al., 2005
Poly (L-lactic acid)	Dichloromethane + CO <sub>2</sub>	Kalogiannis and Panayiotou, 2005
Poly (isobutyl acrylate)	Isobutyl acrylate	Byun and Lee, 2006
Poly (tert-butyl acrylate)	<i>Tert</i> -Butyl acrylate	Byun and Lee, 2006
Poly (isobutyl mathacrylate)	Isobutyl mathacrylate	Byun and Lee, 2006
Poly (tert-butyl mathacrylate)	<i>Tert</i> -Butyl mathacrylate	Byun and Lee, 2006
Poly (L-lactide)	HCFC-22 + CO <sub>2</sub>	Park et. al., 2006
Poly (ε-caprolactone)	HCFC-22 + CO <sub>2</sub> Dimethyl ether + CO <sub>2</sub>	Park et. al., 2006
Poly (ε-caprolactone)	CHClF <sub>2</sub> + CO <sub>2</sub> Propylene + Dimethyl ether Propylene + CHClF <sub>2</sub> 1-Butene + Dimethyl ether 1-Butene + CHClF <sub>2</sub>	Byun et. al., 2006
Polyethylene Glycol	Ethanol + CO <sub>2</sub>	Matsuyama and Mishima, 2006
Poly (4-methyl-1-pentene)	Toluene + CO <sub>2</sub>	Fang and Kiran, 2006



**Figure 2.1** Paths for solid-fluid (S-F) (crystallization) (path A) and liquid-liquid (L-L) (path B) phase separation. The dashed boundaries represent the phase boundaries for solvents with decreased solvent power (higher carbon dioxide content).



**Figure 2.2** Schematic diagram of temperature versus concentration of polymer solutions at different pressures or with different solvent power. The shaded regions in these diagrams represent the immiscible regions.

Information on miscibility and phase separation conditions are crucial for polymerizations and polymer modifications or processing.

## 2.2 Polymerization in high-pressure dense fluids

Polymerization at high pressures has long history beginning with the high-pressure polymerization of ethylene, in which the monomer ethylene functions as both reactant and solvent (Kiran, 1994). It is natural to perform polymerization under high pressures because most polymerizations proceed with a reduction in volume, and pressure favors the polymerization thermodynamically. From the view of polymerization kinetics, there are several effects of pressure on polymerization: the pressure increases the concentration of monomers, especially for polymerizations with gaseous monomers, thereby, increase the polymerization rate. At high pressure, the polymerization rate constant also changes with pressure, according to the equation (Ogo, 1984)

$$(\partial \ln k / \partial P)_T = -\Delta V^\ddagger / RT \quad (\text{Eq.2.1})$$

where  $\Delta V^\ddagger$  is the “volume of activation” representing the change in molar volume from the reactant to the transition state. For most free radical polymerizations, the activation volumes for the overall polymerizations are around  $-20 \text{ cm}^3/\text{mol}$  (Jenner, 1978; Ogo, 1984). The increase in pressure leads to higher overall polymerization rate. For the propagation step, the activation volume is also around  $-20 \text{ cm}^3/\text{mol}$  (Jenner, 1978; Ogo, 1984), the propagation rates increase with increasing pressure. However, for the termination, the activation volume is positive. The increase in pressure results in lower termination rates. This is related to the increase in viscosity of the polymerization

mixtures with increasing pressure, which determines the rate of mass transport in the termination step.

Therefore, higher pressures accelerate the overall polymerization, promote the growth of the polymer chain, and suppress the chain termination, thus produce higher molecular weight polymer (Kiran, 2000). This phenomenon was confirmed by polymerization of styrene in butane at high pressures (Kiran and Saraf, 1990).

### **2.2.1 Chain-growth polymerization in supercritical fluids**

Examples of polymerization that have been carried out in supercritical fluid are numerous and include free or controlled radical polymerizations, ionic polymerizations and coordination polymerizations ((DeSimone et al., 1992; Kiran and Saraf, 1990; Ye and DeSimone, 2005; Pernecker and Kennedy, 1994; Clark et al., 1997; Luft et. al., 1993; Bergemann et. al., 1997). The high-pressure dense fluids can be CO<sub>2</sub>, mixtures of CO<sub>2</sub> with organic solvents, or even other organic solvents such as butane, propane (DeSimone et al., 1992; Romack et al., 1995; Kiran and Saraf, 1990). Due to its easily accessible critical point, stability at high pressures and high temperatures, and low expense, CO<sub>2</sub> is the most-often used solvent.

*A. Radical polymerization* In radical polymerizations, since the polymerization activation center (the radical) is an electrically neutral substance, the polarity of the solvent has little effect on the polymerization. However, high-pressure conditions and the phase behavior of the reaction mixture play an important role. High-pressure conditions enhance the global polymerization rate, promote the chain propagation, suppress the chain termination, and thus produce higher molecular weight polymers. The phase behavior

determines whether the polymerizations proceed in homogeneous one-phase or heterogeneous conditions. For homogeneous polymerizations, monomer, initiator, and polymer formed are all soluble in the high-pressure solvents during the whole polymerization process. However, CO<sub>2</sub> is a poor solvent for most polymers and it is almost impossible to conduct homogeneous polymerizations in neat supercritical CO<sub>2</sub> for most polymers even though there are some exceptions. Fluoro-based polymers and siloxane-based polymers are known to show relatively high solubility in CO<sub>2</sub> (DeSimone et al., 1992), and may be polymerized homogeneously in CO<sub>2</sub> if too high molecular weight are not the target. Various fluoro-based polymers and copolymers have been synthesized via homogeneous free-radical polymerization in supercritical CO<sub>2</sub> (DeSimone et al., 1992; Combes et. al., 1994). In addition, mixtures of CO<sub>2</sub> with a co-solvent or co-solvents are often used to improve the solubility of polymers in SCFs in order to achieve homogeneous polymerization conditions (Romack et al., 1995a; b; Mingotaud et. al., 2001). Other solvents instead of CO<sub>2</sub> can also be used to maintain the homogeneous phase state throughout the polymerization processes (Abbott et al., 2004). Application of extremely high pressure (normally higher than 1000 bar) is another way to perform homogeneous polymerization in CO<sub>2</sub>. Buback and coworkers (Beuermann et. al. 1999) showed the homogeneous polymerization of styrene in supercritical CO<sub>2</sub> at temperature of 200 °C and pressure of 1500 bar.

For polymerizations of most polymers that have limited solubility in CO<sub>2</sub>, precipitation polymerizations have been carried out. In these polymerizations, at the beginning the polymerization mixture is homogeneous but with the process of polymerization, the polymer particles that are formed lead to phase separation and precipitation after passing a threshold condition, which is reflected by the molecular weight. Two phases in

equilibrium, a CO<sub>2</sub> phase and new polymer phase co-exist during polymerization. From the CO<sub>2</sub> phase, polymer particles would continue to be produced and precipitate to the polymer phase. In the polymer phase, the polymerization would continue due to the diffusion of monomer into this phase, which would broaden the molecular weight distribution of the product polymers. Meanwhile, the polymer particle would aggregate in this polymer phase. Therefore, it is hard to collect separate polymer particles with narrow molecular weight distribution from the precipitation polymerization. Various precipitation polymerizations were reported in supercritical CO<sub>2</sub> (Charpentier et. al., 2000; Yeo and Kiran, 2004; Liu et. al., 2005a) or in organic solvents (Kiran and Saraf, 1990; Xu et. al., 2001). A powerful technique is to separate the polymers that formed from the reaction mixtures. It has been shown that the immediate separation of precipitated polymer from the solvent would produce polymer with narrower molecular weight distribution polymers. This was specifically shown in precipitation polymerization of styrene in supercritical n-butane (Kiran and Saraf, 1990). Other researchers adopted this method later as a continuous scheme (Liu et. al., 2005a).

To synthesize polymer particles from polymerizations in supercritical CO<sub>2</sub>, CO<sub>2</sub>-compatible stabilizers were developed. The compounds are designed to have CO<sub>2</sub>-philic and CO<sub>2</sub>-phobic segments. Typically, they are block copolymers that have fluorinated polymer chain or block or siloxane block (e.g., poly (dimethyl siloxane) (PDMS)) as CO<sub>2</sub>-philic arm, and regular polymer block (e.g., PMMA, PS) as CO<sub>2</sub>-phobic arm (O'Neill et. al., 1998; Shiho and DeSimone, 2000; Giles et. al., 2000). By using these stabilizers, the aggregations of polymer particles can be prevented or suppressed. Thus, the polymer particles could be prepared through this polymerization, which provide morphology control on the product polymer over the precipitation polymerization. In

these dispersion polymerizations, the reactant mixtures are homogeneous at the initial stage. With the progress of the polymerization, new polymer particle phase emerges but the polymer particles that are formed are stabilized and aggregations are prevented which tend to formation of uniform polymer particles.

Another type of heterogeneous polymerization that could also be conducted in dense CO<sub>2</sub> is the emulsion polymerization. Starting from the emulsified suspension, emulsion polymerization in high-pressure dense fluid would produce polymer particles by using stabilizer. The research on emulsion polymerization in high-pressure fluid is relative few partly due to the complex in selection of emulsifier and stabilizer. Ye and coworkers (Ye and DeSimone, 2005) used an amphiphilic block copolymer consisting of a D-glucose-containing glycopolymer and a fluorinated block as emulsifier for polymerization of N-ethylacrylamide in CO<sub>2</sub>. Mori et al. and coworkers (Mori et al., 2006) conducted the free-radical emulsion polymerization of tetrafluoroethylene in detergent-free heterogeneous emulsion of supercritical fluoroform/water at temperature of 60 °C and pressure up to 25 MPa. The supercritical fluoroform/water solvent was used as emulsifier and was kept by stirring.

As for the kinetics of free-radical polymerizations in high-pressure dense fluids, by adopting the pulsed-laser-polymerization (PLP) technique coupled with SEC, propagation rate constant of free-radical polymerizations were determined for hydroxypropyl methacrylate (Beuermann and Nelke, 2003), styrene (Beuermann et al., 2002; van Herk et al., 1997), and methyl methacrylate (van Herk et al., 1997) in supercritical CO<sub>2</sub>. Meanwhile, the termination rate constants were measured for the polymerizations of acrylate and methacrylate (Buback et al., 2004), methyl methacrylate and dodecyl

acrylate (Buback et. al., 2002a; b), and butyl acrylate (Beuermann et. al., 1999) in supercritical carbon dioxide. In addition, DeSimone and coworkers studied the thermal decomposition of free-radical polymerization initiator AIBN in supercritical CO<sub>2</sub> (Zhu et. al., 1993).

Recently, some controlled radical polymerizations were carried out in high-pressure dense fluids including catalytic chain transfer (Forster et. al., 1999; Mang et. al., 1999; Wang et. al., 2005), atom transfer radical polymerization (Xia et. al., 1999), and reversible addition fragmentation chain transfer (RAFT) polymerization (Arita et. al., 2004). Meng and coworkers (Mang et. al., 1999) studied the controlled radical polymerization of methyl methacrylate in supercritical CO<sub>2</sub> with porphinatocobalt (II) as catalyst. From the study, PMMA with narrow molecular weight distribution (PDI = 1.2 – 1.9) was prepared and the molecular weight could be regulated by adjust the ration of catalyst to monomer (MMA). It is worth nothing that the fluorinate group was introduced into the catalyst in order to achieve higher solubility in supercritical CO<sub>2</sub>.

Xia and coworkers (Xia et. al., 1999) investigated atom transfer radical polymerization (ATRP) in supercritical CO<sub>2</sub>. They examined the effects of different ligands in the copper-mediated ATRP of FOMA (1,1-dihydroperfluorooctyl methacrylate) in CO<sub>2</sub> by using different ligands. The highest yield and best control of polymer were achieved for ligands with higher solubility in supercritical CO<sub>2</sub>. Precipitation and dispersion ATRP were conducted to prepare well-defined block copolymers including poly (FOMA-b-MMA) and poly (FOMA-b-DMAEMA) where DMAEMA represents 2-(dimethylamino) ethyl methacrylate.

Recently, Arita and coworkers (Arita et. al., 2004) conducted reversible addition fragmentation chain transfer (RAFT) polymerization of cumyl dithiobenzoate-mediated styrene at temperature of 70 °C and at pressure of 2000 bar. They found that the application of high pressure resulted in narrower PDI of the polymer produce.

In the present research we have explored polymerization of MMA, MDO, and copolymerization of MDO with MMA, ST, and AN.

*B. Ionic polymerization* There are some difficulties in conducting ionic polymerizations in supercritical CO<sub>2</sub>. For anionic polymerization, the reactive anions would attack the Lewis acid CO<sub>2</sub>, which makes it somewhat impossible to conduct anionic polymerizations. To overcome this difficulty, organic solvent may be used. However, to our knowledge, there are only reports on anionic polymerization in high-pressure CO<sub>2</sub>. For cationic polymerizations, low polymerization temperatures are needed to suppress side reactions, which would keep the polymerizations in liquid CO<sub>2</sub>. Nevertheless, various ionic polymerizations were carried out in high-pressure dense fluids.

Pernecker and Kennedy (Pernecker and Kennedy, 1994) conducted the cationic polymerizations of isobutylene (IB) in supercritical CO<sub>2</sub> at temperature of 32.5 °C and pressure of 120 bar using 2-chloro-2,4,4-trimethyl-pentane (TMPCL)/SnCl<sub>4</sub> and TMPCL/TiCl<sub>4</sub> as initiator. 30 % convention of IB was achieved with M<sub>w</sub> = 2000, PDI = 2.0 polymer being prepared.

Clark and coworkers (Clark et al., 1997) carried out the cationic polymerization of styrene in liquid carbon dioxide with TiCl<sub>4</sub> as initiator. For this polymerization, the

temperature was 0, 15, or 25 °C, which keep the polymerization in high-pressure liquid CO<sub>2</sub>; a block copolymer - fluorinated alkyl sulfonamide vinyl ether-b-methyl vinyl ether (FVE-b-MVE) synthesized via the living cationic method with sequential monomer addition technique was used as stabilizer for this cationic dispersion polymerization. The 15 °C was found to be the best polymerization temperature with consideration of that low temperature would suppress the side reactions and high temperature would favor the solubility of the stabilizer (FVE-bMVE) in liquid CO<sub>2</sub>. Another stabilizer, poly (dimethylsiloxane-b-styrene), was also used in the polymerizations. However, only low molecular weight ( $M_w < 4000$ ) polymers was prepared, which was attributed to the decomposition of PDMS-b-PS by TiCl<sub>4</sub>.

Recently, ionic polymerization in high-pressure dense fluid has been applied to ring-opening polymerizations of octamethylcyclotetrasiloxane (D<sub>4</sub>), phenyloxazoline (PhOx), ε-caprolactone (Mingotaud et al., 2000; Bergeot et al., 2004), and 2-oxazoline (Hoogenboom et al., 2006) in supercritical CO<sub>2</sub>. The polarity of the supercritical fluids would alter the distance between ionic pairs, thus the polymerization kinetics. It is interesting to control the polarity of the SCFs by manipulating pressure, temperature, and or composition to achieve the desirable ionic polymerization kinetics. However, there is no report on such study so far.

*C. Coordination polymerization* Coordination polymerization is a form of chain-growth polymerization in which monomer adds to a growing macromolecule through an organometallic active center (Odián, 1991). The development of coordination polymerization started in the 1950s with heterogeneous Ziegler-Natta catalysts based on titanium tetrachloride and an aluminium co-catalyst such as methylaluminumoxane.

Coordination polymerization has an important impact on the physical properties of vinyl polymers such as polyethylene and polypropylene compared to the same polymers prepared by other techniques such as free-radical polymerization. The polymers tend to be linear and not branched and have much higher molecular weight. Coordination type polymers are also stereoregular and can be isotactic or syndiotactic instead of atactic.

In many applications, Ziegler-Natta polymerization is succeeded by metallocene catalysis polymerization. This method is based on homogeneous metallocene catalysts such as the Kaminsky catalyst developed in the 1970s. The 1990s brought forward a new range of post-metallocene catalysts.

Application of SCF as solvent for the coordination polymerization would help recovering the catalyst from the polymerization mixture. Luft and coworkers have carried out extensive researches on bulk coordination polymerization of ethylene (Luft et al., 1993a; b), and copolymerization of ethylene with propene (Bergemann et al., 1995), with 1,5-hexadiene (Bergemann et al., 1997), and with 1-butene (Bergemann et al., 1998) using homogeneous metallocene catalyst at pressure of 150 MPa. They draw the conclusion that high-pressure condition enhanced the polymerizations. In addition, olefin bulk polymerizations catalyzed by congested ansa-metallocenes (Suzuki et al., 2000) and Nickel- and Palladium- post-metallocene catalysts (Suzuki et al., 2003) were reported. As for polymerizations in supercritical CO<sub>2</sub>, Vries and coworkers conducted polymerizations of hex-1-ene, ethene and ethylene catalyzed by palladium complex. They found that there was no complex behavior between the active catalyst with CO<sub>2</sub> and the polymer prepared in supercritical CO<sub>2</sub> had identical molecular weight and polydispersity as that from the common solvent such as CH<sub>2</sub>Cl<sub>2</sub>. Furthermore, they designed the process especially for

this polymerization (Kemmere et al., 2001). Additionally, organometallic catalyzed polymerizations of phenylacetylene (Hori et. al., 1999), copolymerization of CO<sub>2</sub> with 1,2-cyclohexane oxide (Mang et. al., 2000), and copolymerization of ethylene with CO (Klauri et. al., 2000) in supercritical CO<sub>2</sub> were also reported.

### **2.1.2 Step-growth polymerization in supercritical fluids**

Many condensation polymerizations are carried out in the melt phase to prepare high molecular weight polymer without organic solvent (O'dian, 1991). A disadvantage of this route is the high viscosity of the high molecular weight polymer melts, which make it difficult to process the polymer products. Addition of supercritical CO<sub>2</sub> has been attractive in that it would lower the melt viscosity significantly by increasing free volume of the polymer melts. Furthermore, CO<sub>2</sub> can lower the glass transition temperature (T<sub>g</sub>) and melting temperature (T<sub>m</sub>) of the product polymer so that lower the temperatures may be used to carry out condensation polymerization. Moreover, CO<sub>2</sub> is a nontoxic swelling agent, which can be readily used in the next foaming process.

In addition to better processability, polymer synthesized in supercritical CO<sub>2</sub> can lead to higher molecular weights. In condensation polymerizations, the reaction is driven by removal of the small molecular condensate. Enhancement of removal of the condensate would result in higher reaction rates and higher molecular weights for the product polymers. In conventional method, the condensate was removed by high vacuum, which requires high capital costs and long preparing time. Since CO<sub>2</sub> can plasticize the polymer and solubilize the small-molecule condensates, addition of supercritical CO<sub>2</sub> would increase free volume in the polymer melts so that provide larger polymer surface area for condensate removal and facilitate carrying the condensate out. Besides, it also leads to

greater mobility of chain ends to allow better reaction kinetics. This strategy has been applied to synthesis of polycarbonate, polyester, and polyamides (Burke et. al., 1997; Givens et. al., 1997; Burke et. al., 1996). Furthermore, using CO<sub>2</sub>-induced crystallization of polycarbonate (Gross et al., 2000), the melt-phase polymerization can be transferred to solid-state polymerization of polycarbonate in supercritical CO<sub>2</sub>. DeSimone and coworkers investigated the solid-state polymerization of poly (bisphenol A carbonate) (BAC) with diphenyl carbonate (DPC) (Gross et al., 1999; Gross et al., 2000, Gross et al., 2001; Shi et. al., 2001a; b; Shi et. al., 2003). Other step-growth polymerizations such as sol-gel polymerization (Cooper, et. al., 2000; Zhang et. al., 2003) and oxidative couple polymerization (Mercangoz et. al., 2004) have been done in high-pressure dense fluids, especially in supercritical CO<sub>2</sub>.

## **2.2 Polymer processing in high-pressure dense fluids**

High-pressure dense fluids, especially supercritical CO<sub>2</sub>, have been widely used in polymer processing for polymer fractionation, polymer particle formation, polymer impregnation, polymer blending preparation, polymer fiber preparation by electro-spinning, polymer membrane preparation, and microporous polymer material preparation (foaming and membrane preparation) (Subramaniam et. al., 1997; Cansell et. al., 2003; Cooper, 2000; 2003; Reverchon et. al., 2003, Tomasko, 2003a, 2003b; Quirk, 2004; Levit and Tepper, 2004). In the polymer processing, SCFs can function as solvent, plasticizer, or foaming agent.

### **2.2.1 Polymer particle formation**

Supercritical fluids can be used not only as solvents but also as antisolvent in preparation of polymer particles. Numerous publications on polymer particle formation using SCFs have appeared (Kim et. al., 1996; Ghaderi et. al., 1999; Elvassore et. al., 2001; Mezirani et. al., 2004). The particle formation techniques follow five general methodologies: rapid expansion of supercritical solutions (RESS), gas antisolvent process (GAS), supercritical antisolvent process (SAS), solution enhanced dispersion by supercritical fluids (SEDS), and particles from gas-saturated solutions (PGSS) (Yeo and Kiran, 2004). In the RESS process, expansions of homogeneous polymer solutions in SCFs through an orifice result in phase separation caused by pressure and or temperature quench, thus particle formation. Some degree of solubility of polymers in SCFs is needed to use this process and an organic solvent as co-solvent is often used to enhance the polymer solubility. In the GAS process, polymer is dissolved in the organic solvent first and then a gas is sprayed into the solution. The addition of the gas as an antisolvent would decrease the polymer solubility in the solution and lead to recrystallization of the polymer, thus the particle precipitation. This process is especially suitable for polymer particle production since most polymers have very limited solubility in supercritical fluids or gases. SAS (also known as aerosol solvent extraction system (ASES) or precipitation with a compressed antisolvent (PCA)) is another antisolvent process, in which the supercritical fluids function as antisolvent. In this process, polymer solutions in organic solvents are sprayed into a chamber filled with SCFs. The sudden contact between the polymer solution and antisolvent (SCFs) causes the high supersaturation of polymer in the new solvent (original solvent + SCFs). Thus, the nucleation and growth would take place to produce the polymer particles. SEDS process is a modified SAS process in which the polymer solution in organic solvent and supercritical fluids (antisolvent) spray

simultaneously through a specially designed coaxial nozzle. Using this nozzle, with different arrangements of fluid flow (either polymer solution in organic solvent or the antisolvent (supercritical fluids) at different channel, polymer particles can be prepared. The SCFs function as antisolvent and dispersion medium for particles produced. In PGSS process, SCFs, especially supercritical CO<sub>2</sub>, are dissolved in molten polymers to form homogeneous solutions, in which the SCFs function as solute. The solutions are expanded through the orifice caused by the pressure difference between inside and outside the chamber to produce polymer particles. The schematic diagrams for all the particle formation processes discussed above are shown in Figure 2.3.

### **2.2.2 Polymer impregnation**

Polymer impregnation is the process in which the solutes are delivered to the desired sites inside the polymer matrix. Supercritical fluids, especially supercritical CO<sub>2</sub>, have been used in the polymer impregnation process (Kikic and Vecchione, 2003). The functions of supercritical CO<sub>2</sub> include swelling the polymer and delivering the solute to the desired sites. Generally, the supercritical CO<sub>2</sub>-assisted polymer impregnation process involves the steps of (1) expose the polymer to supercritical CO<sub>2</sub> for swelling; (2) deliver the solute by CO<sub>2</sub>; (3) release carbon dioxide. Some factors that determine the process such as polymer swelling, solute solubility in supercritical CO<sub>2</sub>, transport rate of solute, compatibility and stability between the solute and the polymer impregnated need to be considered before conducting polymer impregnation. Polymer swelling and solute solubility determine the amount of solute that can be impregnated. Transport rate of solute determines the time for impregnation. Finally, the compatibility and stability between the solute and the polymer determines if the process is worthwhile to develop.

The extent of swelling and the alteration of microstructure of the polymer depends on the chemical nature of the polymer and its interactions with CO<sub>2</sub>. Less swelling means relatively difficult impregnation. Highly crystalline polymers are not suitable for swelling because of the regular structure and slow transport process. Therefore, current studies have been mainly limited to the amorphous polymer or polymer with large amorphous fractions. The polymers include PMMA (Kazarian et. al., 1997; West et. al., 1997), polystyrene (Berens et. al., 1992), and poly (vinyl chloride) (PVC) (Muth et. al., 2000). The solutes studied for impregnation range from dye, to metal complex, to biological molecules, to polymers and even monomers. By impregnate dyes into polymers, the SCF-assisted dyeing can be achieved (Kazarian et. al., 1997; West et. al., 1997; Ngo et. al., 2003). Metallopolymer nanocomposites have been prepared by impregnating metal complex into the polymer matrix (Clarke et. al., 1993; 2000; Popov et. al., 1998; Said-Galiyev et. al., 2000; Yoda et. al., 2004). Impregnation of pharmaceuticals, proteins, and other bioactive molecules into polymer matrix, especially biodegradable polymer matrix has been carried out for preparing drug delivery devices and scaffold in tissue engineering (Kazarian and Martirosyan, 2002; Guney and Akgerman, 2002; Alessi, 2003). The solute can also be polymer to prepare polymer blends using the impregnation process. However, this type of processes is few since most polymers have very poor solubility in supercritical CO<sub>2</sub>. Alternatively, monomers can be impregnated into the polymer matrix together with initiators with aid of supercritical CO<sub>2</sub> first. After releasing CO<sub>2</sub>, the polymerization are initiated by heating, thus polymer blends are prepared. This polymerization in CO<sub>2</sub>-swollen polymer matrix has been conducted to prepare various polymer blends (Li and Han, 2000; Muth et. al., 2000; Xu and Chang, 2004).

### **2.2.3 Polymer blending and polymer composite preparation**

Polymer blends are of great importance for modern industry: they provide exceptional properties with affordable prices that can not be possible for homopolymers. Two or more polymers are mixed to prepare polymer blends. Generally complete miscibility can not be achieved and there are phase separations in most polymer blends. In the simplest cases, the major component-rich phase is continuous (matrix) and the minor component-rich phase is dispersed (droplet). The heterogeneous microstructure of the polymer blends is known as morphology, which determines the properties of the polymer blends. The resulting morphology of an immiscible polymer blend can be viewed as equilibrium between droplet breakup and coalescence (Tomasko et. al., 2003). This equilibrium is formed from the polymer crystallization process (either from melt or from solution). Parameters and properties that determine the crystallization process include temperature, pressure, interfacial tension, viscosity ratio between the polymers, and the shear rate. Additions of SCFs provide a measure to alter the interfacial tension and viscosity ratio by adjusting temperature and/or pressure. Thus, the microstructure of the polymer blends can be adjusted to achieve the desired properties.

With aid of CO<sub>2</sub>, the polymer blends can be prepared either from polymer melts or from polymer solutions. Numerous studies have been conducted to produce polymer blends in supercritical fluids (Domingo et. al., 2003; Thurecht et. al., 2004; Chang et. al., 2004) and to study the effects of supercritical CO<sub>2</sub> on polymers or polymer blends (Walker et. al., 1999; Watkins et. al., 1999; Zhou et. al., 2003). Another method to prepare polymer blends in SCFs is the polymerization after polymer impregnation of monomer. Similarly, polymers can be blended with ceramics (Mathieu et. al., 2006a; b), inorganic compounds

(Wang et. al., 2006), clay (Chang et. al., 2006), or citric acid (Weinstein et. al., 2005) to prepare polymer composites.

In the present research we have explored blending of PCL with PMMA in dense fluids.

#### **2.2.4 Microporous polymer formation**

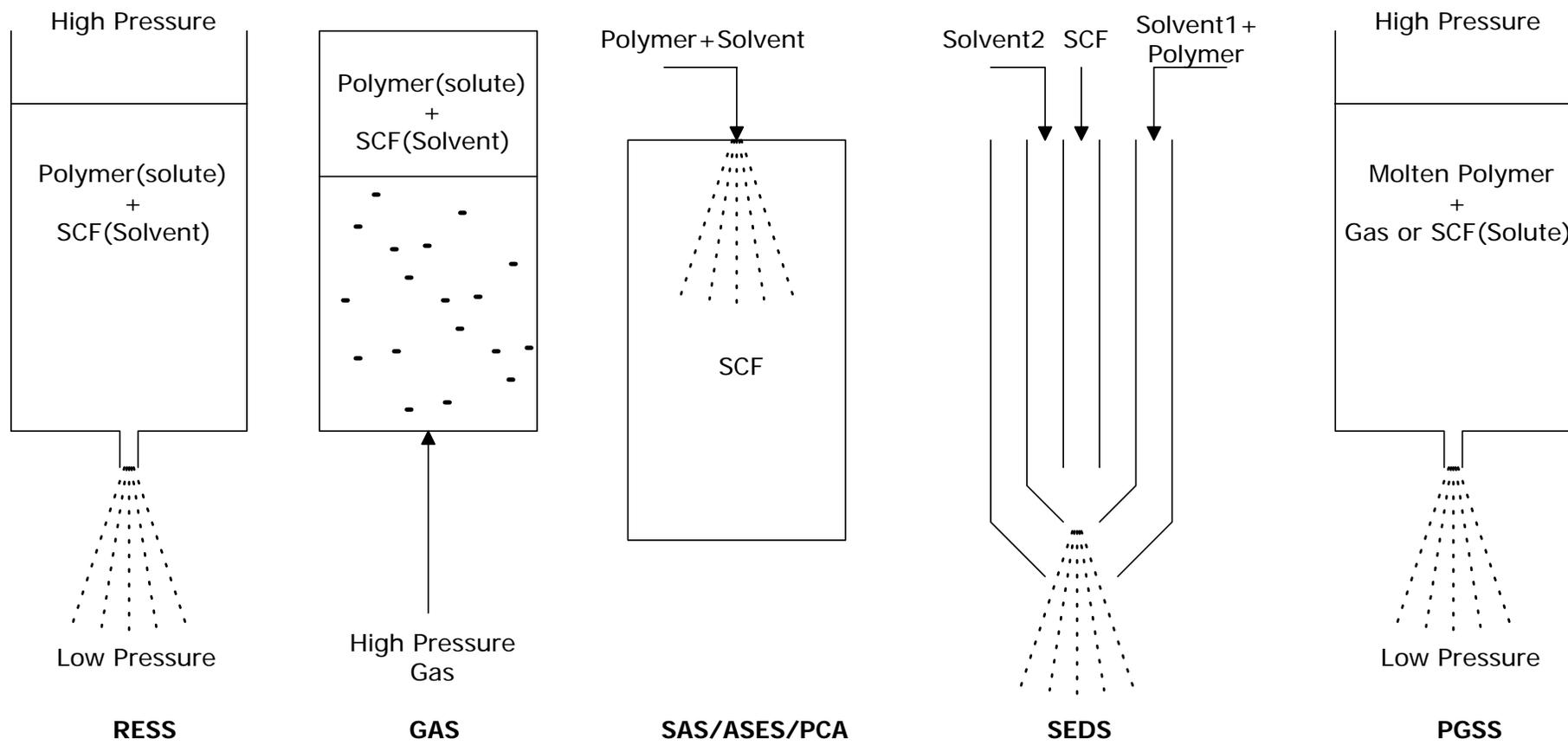
Microporous polymer formation is another active area in which application of SCF is presently investigated. The microporous polymers can be generally divided in foams, in which the porous structure is formed by closed (non-connected) cells, and membrane, in which the microstructure is characterized by open cells.

*A. Foams* Polymer foams are important materials in a variety of applications such as insulation, cushion, absorbents, and weight-bearing structure (Fried, 2003). In addition, biodegradable polymer foams are widely used as scaffolds in tissue engineering (Quirk et. al., 2004). Chlorofluorocarbons (CFC) are the most widely used foaming agent nowadays. However, these foaming agents have been found to cause ozone depletion in the upper atmosphere and will be banned by 2010, according to the Montreal Protocol. Supercritical CO<sub>2</sub>, an environmentally benign fluid, is an attractive alternative for the CFCs as foaming agent for polymer foaming. Additionally, CO<sub>2</sub> is not a good solvent but it is a good plasticizer for most polymers, which makes it a candidate as polymer foaming agent. Generally, the CO<sub>2</sub>-assisted foaming process is basically consists of three steps: 1) mixing, formation of a homogeneous solution composed of polymer melt and foaming agent (CO<sub>2</sub>); 2) cell nucleation, phase separation induced by temperature increase or pressure decrease; 3) cell growth and coalescence, a combination of mass transfer and fluid dynamics (Tomasko et. al., 2003; Kim et. al., 2004; Kichatov and Korshunov,

2005). The foaming process can be conducted in a batch system (Kim et. al., 2004) where the samples are placed in a pressurized autoclave to be saturated with CO<sub>2</sub>. Nucleation and cell growth are controlled by the pressure-release rate and foaming temperature. A continuous extrusion foaming process can also be carried out by using a modified extruder (Lee et. al., 2005a; b; c). In this modified extruder, CO<sub>2</sub> is introduced into the extruder barrel through a CO<sub>2</sub> injection port and the homogeneous solution of CO<sub>2</sub> and polymer melt is achieved with the aid of screw rotation. Rapid and large pressure drop in the die initiates the bubble nucleation.

With the assistance of supercritical CO<sub>2</sub> and by using the batch or continuous process, various polymer foams for homopolymers as PMMA, PS, copolymers as polycarbonate, poly (ethylene-co-vinyl acetate), poly (styrene-co-acrylonitrile), and biodegradable polymers as poly ( $\epsilon$ -caprolactone) (PCL) and poly (lactide-co-glycolide) (PLGA), have been prepared (Lee et. al., 2000a; Xu et. al., 2004; Strauss and D'Souza, 2004; Wong et. al., 2004; Siripurapu et. al., 2004; Jacobs et. al., 2004; Dai et. al., 2005; Siripurapu et. al., 2004; Cotugno et. al., 2005; Lee et. al., 2005a; b; c). Effects of operating parameters such as saturation pressure and foaming temperature have been extensively studied. Generally, increase in saturation pressure results in higher CO<sub>2</sub> solubility in the polymers, thus more nucleation centers and higher pore (cell) density in the resulting polymers. Increase in foaming temperature leads to larger cell size by favoring the bubble growth against the nucleation. Similarly, foams of polymer blends (Wang et. al., 2003; Lee et. al., 2005a; b; c) or polymer composites (Hile and Pishko, 2004; Aydin et. al., 2004; Lee et. al., 2005a; b; c) can be prepared by the batch or continuous CO<sub>2</sub>-assisted foaming processes.

*B. Membranes* The phase separation induced by antisolvent (supercritical CO<sub>2</sub>) for small amount of polymer solution on a surface produces polymer membrane. In this process, supercritical CO<sub>2</sub> functions as not only antisolvent to induce phase separation, but also as clean agent to dry the membrane. The structure collapse in the membrane is avoided since there is no gas-liquid interface in the process. Various polymer membranes such as Nylon 6, polystyrene, cellulose acetate, polylactide, and polysulfone have been prepared with this method (Reverchon and Cardea, 2004, 2005; Xu et. al., 2005).



**Figure 2.3** Schematic diagrams for polymer particle formation.