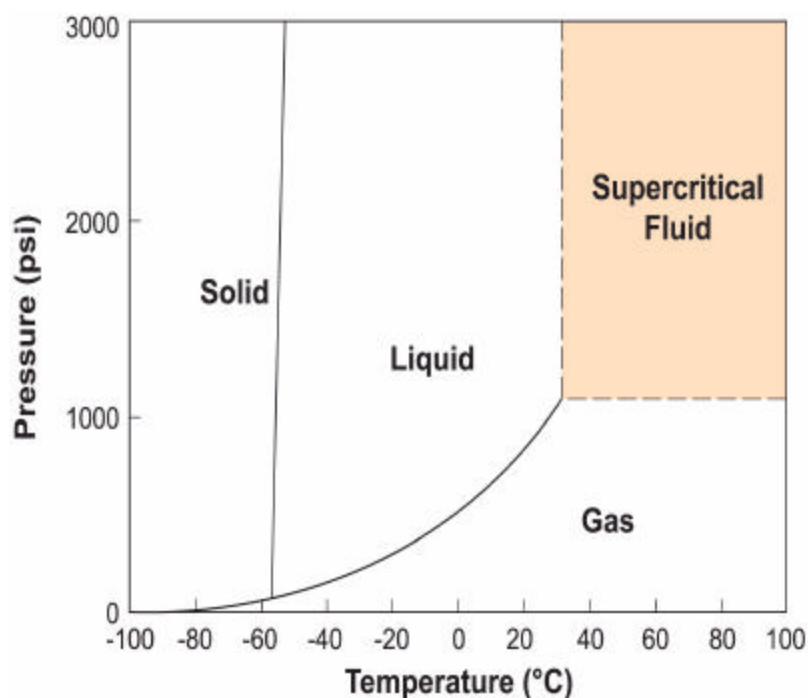


## 2 Polymer/CO<sub>2</sub> Interactions

### 2.1 Supercritical fluids

Supercritical fluids are fluids (a generic term encompassing liquids and gases) that are at a temperature and pressure greater than, or equal to, the critical temperature ( $T_c$ ) and pressure ( $P_c$ ) of that fluid. Figure 2-1 is a temperature-pressure phase diagram showing the phase transitions for a pure substance such as carbon dioxide. In the region  $T \geq T_c$  and  $P \geq P_c$ , shown by the shaded region, the liquid and vapor regions merge into single, homogeneous fluid, a SCF.



**Figure 2-1.** Schematic pressure-temperature diagram showing the solid, liquid, gas, and supercritical fluid phases for a pure, one component system.

While the existence of supercritical fluids has been known since 1822<sup>4</sup> it has only been in the last two decades that the value of SCFs as a medium for extraction, cleaning, and synthesis has been recognized. The attractiveness of SCFs as process solvents stems from their unique combination of liquid-like and gas-like properties. SCFs exhibit gas-like transport properties of diffusivity and viscosity yet possess liquid-like mechanical properties, such as density. Table 2-1 gives a comparison of the diffusivity, viscosity and density of a typical organic fluid in the liquid, gas, and supercritical fluid states.<sup>5</sup>

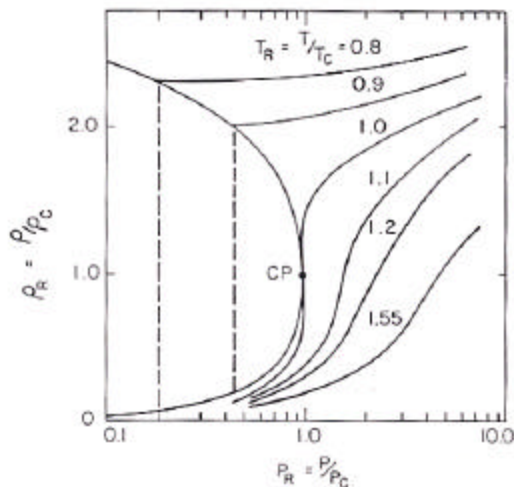
**Table 2-1.** Comparison of physico-chemical properties of a typical organic fluid in the liquid, gas, and supercritical fluid states.

|                     | Diffusivity<br>(cm <sup>2</sup> /s) | Viscosity<br>(mN·s/m <sup>2</sup> ) | Density<br>(g/cm <sup>3</sup> ) |
|---------------------|-------------------------------------|-------------------------------------|---------------------------------|
| Liquid              | 10 <sup>-5</sup>                    | 10 <sup>0</sup>                     | 1                               |
| Supercritical fluid | 10 <sup>-3</sup> - 10 <sup>-4</sup> | 10 <sup>-1</sup> - 10 <sup>-2</sup> | 0.5 - 1.1                       |
| Gas                 | 10 <sup>-1</sup>                    | 10 <sup>-2</sup>                    | 0.001                           |

To a first approximation, the ability of a solvent to solubilize other compounds is related to its density<sup>6,7,8,9</sup> (the reason for this will be discussed in Chapter 3). As seen in Table 2-1 high liquid-like densities, > 1 g/cm<sup>3</sup>, are achievable in SCFs, allowing for substantial solubilities. The combination of properties illustrated in Table 2-1 shows why SCFs are ideal for cleaning substrates having porous, intricate, or rough surfaces, and for confined work areas. The solvent is able to penetrate into otherwise inaccessible regions due to the gas-like viscosity, and is then able to solubilize and remove contaminants, due to its liquid-like dissolving power.

Table 2-1 might suggest that the density of supercritical fluids is always liquid-like. However, it is also the ability to *continuously* vary the density of a SCF from liquid-

like to gas-like by altering the temperature and/or pressure that is their true hallmark. Figure 2-2 illustrates how relatively small changes in temperature and pressure near the critical point result in large changes in density and therefore the solubilizing power of the fluid. It is this “tunability” of solubilizing power that makes SCFs such attractive solvent for manufacturing processes. In terms of developing predictive models for solvent/polymer interactions, however, it is this ability to assume liquid-like or gas-like properties, over such a wide range of temperatures and pressures, that presents the most difficulty.

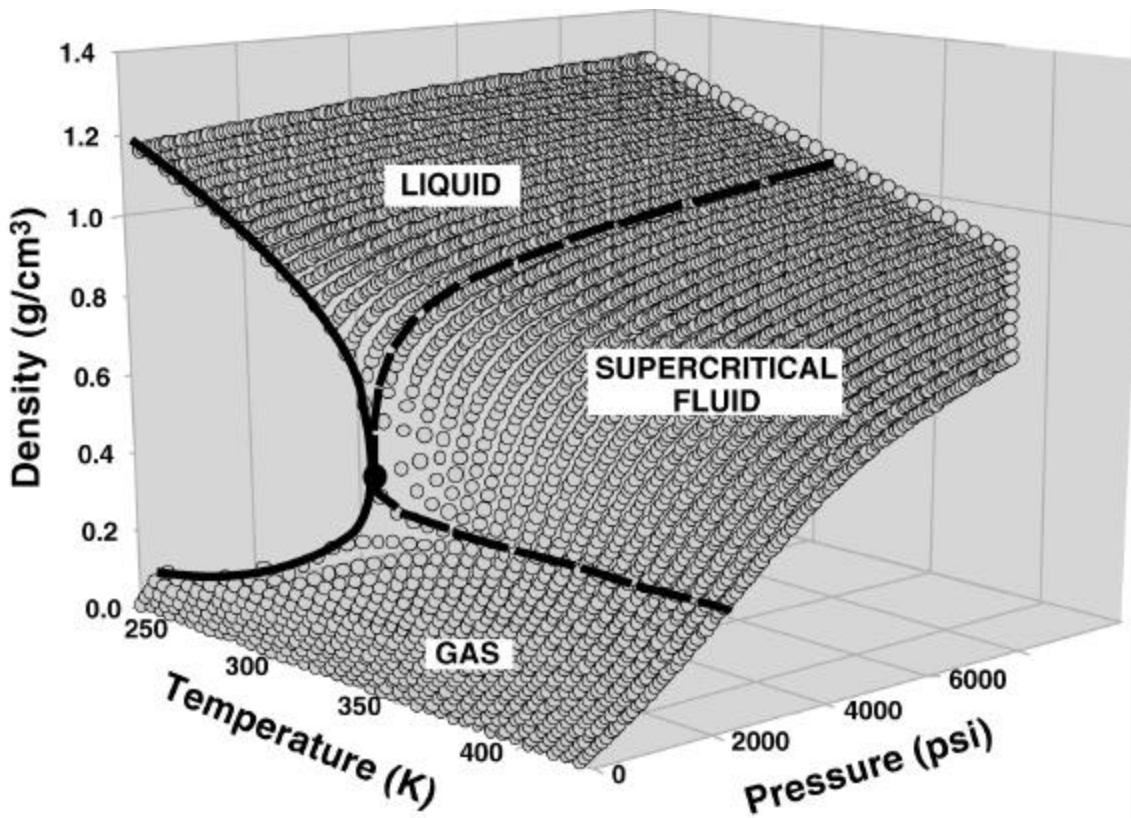


**Figure 2-2.** Variation of the reduced density in the vicinity of its critical point.<sup>10</sup>

### 2.1.1 Supercritical CO<sub>2</sub>

The critical values of temperature and pressure are unique for every compound. The critical temperature of CO<sub>2</sub> is 31.1°C and the critical pressure is 73.8 bar. Figure 2-3 shows the pressure-temperature-density surface of pure CO<sub>2</sub>, with the critical point shown by a large solid circle. As can be seen in Figure 2-3 the density of supercritical

CO<sub>2</sub> can vary over a wide range from gas-like values of 0.0018 g/cm<sup>3</sup> (STP), to liquid-like values of over 1.0 g/cm<sup>3</sup>. This reflects a density change of several orders of magnitude by relatively modest variations of temperature and pressure

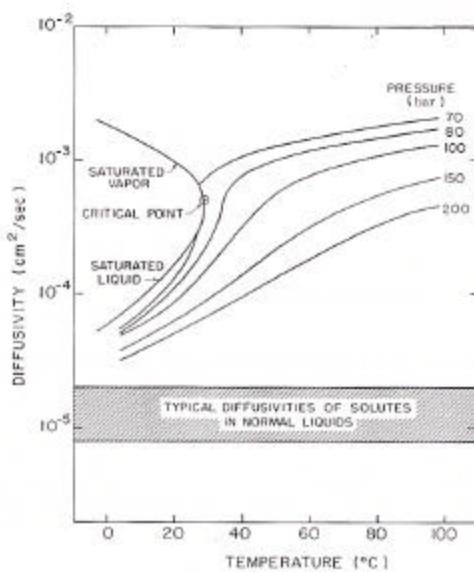


*Figure 2-3. Pressure-temperature-density surface of pure CO<sub>2</sub>.*

In addition to the high liquid-like densities achievable in supercritical CO<sub>2</sub>, it also possesses gas-like diffusivity, shown in Figure 2.4.

Use of SCFs, especially supercritical CO<sub>2</sub>, as an alternative coating removal technology, offers many potential advantages over conventional organic solvents. CO<sub>2</sub> is generally chemical inert with respect to inorganic materials and is therefore compatible with a variety of substrates. CO<sub>2</sub> is noncombustible, readily available in high purity,

environmentally friendly (not ozone depleting), and has a low human toxicity. Supercritical CO<sub>2</sub> is also attractive from the viewpoint of waste minimization. After the cleaning step, carbon dioxide is easily separated from the extracted/dissolved polymers, resulting in streams of concentrated polymer (or polymer residue) and pure, reusable CO<sub>2</sub>. Also, since supercritical CO<sub>2</sub> evaporates completely when depressurized, leaving no residue, supplemental aqueous rinsing and drying steps are also not required.



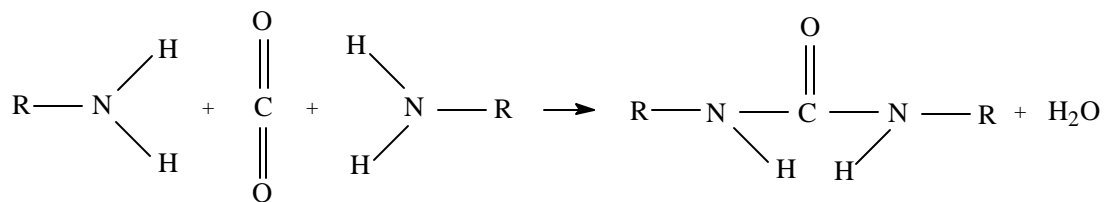
*Figure 2-4. Diffusivity behavior of supercritical CO<sub>2</sub>.*

## 2.2 Polymer/CO<sub>2</sub> Interactions

To further exploit the use of SCFs as a cleaning/polymer coating removal technology it is essential to understand their properties and how SCFs interact with materials. In general, because of their high crystallinity, high density, and resulting impermeability to gases, most metal and glass materials will have little interaction with CO<sub>2</sub>.<sup>11</sup> On the other hand, polymeric materials, which are most often amorphous or semi-crystalline, exhibiting lower than theoretical densities, are known to interact with a

variety of gases and may be expected to show a wide range of behaviors in the presence of a SCF, varying from no effect to very pronounced effects.

Mixtures of polymers and supercritical fluids (SCFs) have many features in common with mixtures of polymers and conventional organic liquid solvents.<sup>12</sup> As a result, a variety of operations, such as swelling, plasticization, crystallization, extraction of impurities, polymerization, and fractionation can be carried out on polymers using SCFs. The following discussion of CO<sub>2</sub>/polymer interactions will be limited to interactions where (a) the supercritical fluid is inert with respect to the overall composition of the polymer, or (b) where changes produced in the polymer composition are the result of polymerization and depolymerization, and not by chemical incorporation of CO<sub>2</sub>. This means that certain types of polymer/SCF interactions will not be considered, such as the chemical reaction of the SCF with the polymer, forming a new compound. One example of such a reaction is that between a primary aliphatic amine and CO<sub>2</sub>, forming a carbamic acid.<sup>13</sup>

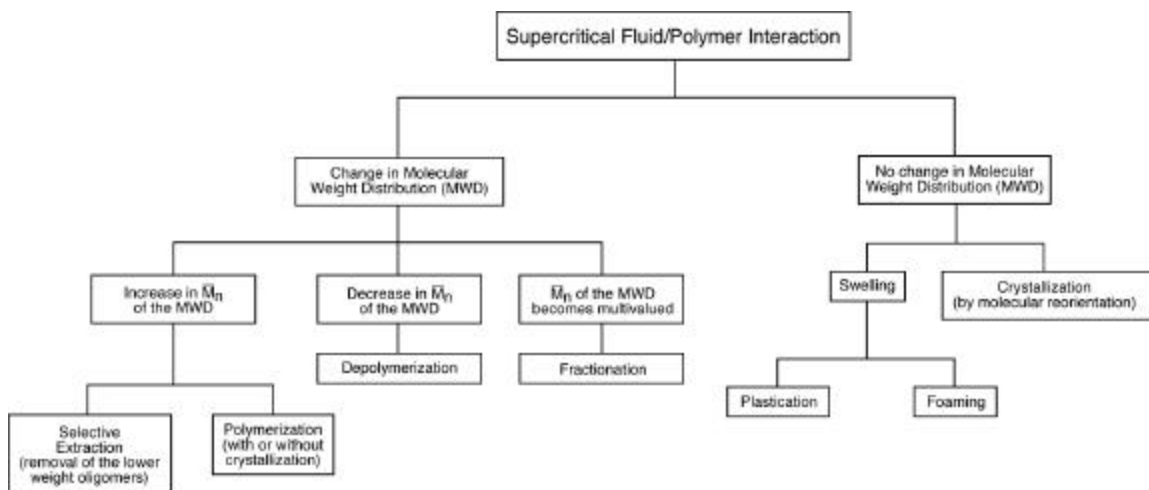


**Figure 2-5.** The chemical reaction of CO<sub>2</sub> with a primary amine to produce a carbamic acid.

All CO<sub>2</sub>/polymer interactions require either some amount of polymer solubility in the SCF, or SCF solubility in the polymer. With the notable exception of some siloxane and fluorinated polymers, few polymers are soluble in supercritical CO<sub>2</sub>. CO<sub>2</sub> is, however, readily absorbed into a wide variety of polymers at elevated pressures,

especially carbonyl-containing polymers, frequently plasticizing the polymer and lowering its glass transition temperature significantly below that observed at atmospheric pressure.<sup>14</sup> The ability of a polymer to solublize CO<sub>2</sub> depends on its chemical structure. Particularly, because CO<sub>2</sub> is a potential electron acceptor compound (Lewis acid),<sup>15,16,17</sup> the presence of a basic site in the polymer's structure is favorable for the sorption of CO<sub>2</sub>. However, the presence of crystallinity in the polymer will inhibit the sorption of CO<sub>2</sub>, since CO<sub>2</sub> sorption is believed to occur only in the amorphous regions.<sup>18</sup> Also, highly crosslinked polymers will expand less freely than those with less crosslinking.<sup>19</sup>

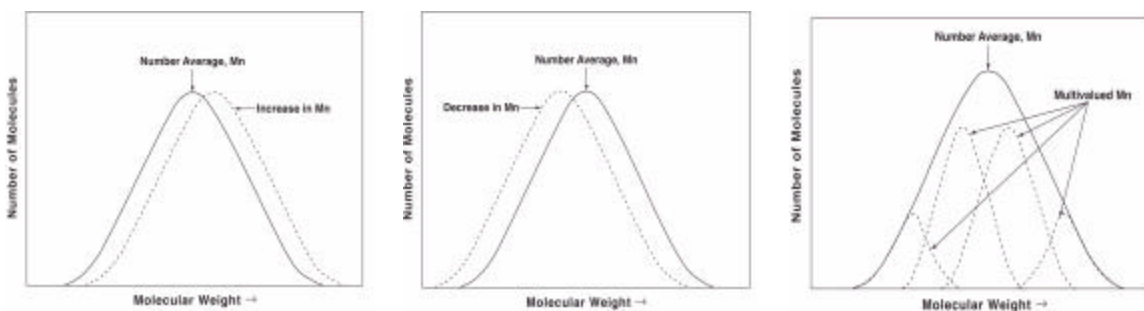
The interaction between a supercritical fluid and a polymer can have pronounced effects on the polymer. Many of these effects are, or can be, the basis of commercial processes. Figure 2-6 illustrates the types of macroscopic interactions that can be achieved by processing a polymer in a supercritical fluid environment. These known and observed interactions between supercritical CO<sub>2</sub> and polymers are here classified according to the effect of the interaction on the molecular weight distribution (MWD) of the polymer. Figure 2-6 is intended to highlight *end-processes* that are, or could be, commercially viable, and there will nearly always be some overlap between the general end-processes shown. For example, fractionation involves both permeation of the supercritical fluid into the polymer, and therefore, swelling, followed by solubilization of the polymer, and therefore, selective extraction.



**Figure 2-6.** *Supercritical CO<sub>2</sub>-polymer interactions.*

By classifying the various CO<sub>2</sub>/polymer interactions by their effect on the MWD, we immediately separate those interactions which rely on the solubility of the polymer in the supercritical fluid from those which rely on the solubility of the supercritical fluid in the polymer. A change in the MWD can be either an increase, a decrease, or the development of a multimodal number average molecular weight,  $M_n$ , distribution. All of the end-processes in Figure 2-6 that involve a change in the MWD depend on having the *polymer soluble in the supercritical fluid*. Interactions where an increase in the  $M_n$  of the MWD is expected include selective extraction and polymerization. While a decrease in  $M_n$  of the MWD is assumed to be the result of depolymerization, and the creation of a multivalued  $M_n$  distribution is characterized as polymer fractionation. Simple illustrations of these changes are shown in Figure 2-7.





**Figure 2-7.** Variations in the number average molecular weight,  $M_n$ .

The simplest interactions between a supercritical fluid and a polymer, from a physical point of view, are those that do not change the MWD. From Figure 2-6, these end-processes are swelling and recrystallization,<sup>20,21,22,23,24,25,26,27,28</sup> and these interactions are characterized by *solubility of the supercritical fluid in the polymer*.

### 2.2.1 Selective Extraction

Selective extraction<sup>29,30,31,32,33</sup> is a process of selective or sequential removal of components from within a polymer matrix, including unreacted monomers, initiators, catalysts, and low molecular weight oligomers. Traditional SCF extraction falls into this category if the matrix is a natural polymer. Current methods for selective extraction include distillation, precipitation, filtration, or liquid solvent extraction. However, many specialty monomers and polymers are difficult to process and purify by these techniques. CO<sub>2</sub>, however, because it can act as a Lewis acid, interacts favorably with many basic polymers. Combined with its small molecular diameter, CO<sub>2</sub> can then diffuse into polymers more quickly than conventional liquid solvents accelerating swelling.<sup>34</sup>

Solubility of the targeted component(s) in supercritical CO<sub>2</sub> is essential for this application. In addition, the lack of solubility of the "parent" polymer matrix in CO<sub>2</sub> is,

in this case, a benefit. As an example, it has been shown that by suitable tuning of processing conditions (temperature and pressure), CO<sub>2</sub> can effectively extract selected components or liquid solvents while leaving 100% of the parent polymer intact.<sup>35</sup> Current commercial applications include the removal of impurities that are coproduced with monomer synthesis and which interfere with polymerization (e.g., diacetone acrylamide, BisGMA, and monomers synthesized with dimethylsiloxane backbones), and the removal of low molecular weight oligomers from polyphenylmethylsiloxane (designated OV-17).<sup>36</sup>

Selective extraction can also result in detrimental effects if CO<sub>2</sub> polymer interactions are not considered. An example is the extraction of plasticizers, such as esters of the benzenedicarboxylic acid terephthalic acid, whose removal from the parent polymer can affect its mechanical properties.

### **2.2.2 Polymerization**

Polymerization is the process of joining together small structural repeat units to produce a compound of higher molecular weight. The prospect of using supercritical CO<sub>2</sub> as an alternative to traditional volatile organic solvents and chlorofluorocarbons, is promising and has been reviewed in several publications.<sup>37,38,39,40,41,42</sup> This approach has been somewhat limited, however, because the polymers which dissolve in supercritical or near-critical CO<sub>2</sub> are limited,<sup>43,44</sup> and in some cases the pressures required for dissolution are extremely high.

Polymers that have been demonstrated to dissolve in CO<sub>2</sub> include hydrocarbon polymers containing fluorinated octyl acrylates. Hydrocarbon-fluorocarbon block and graft copolymers also exhibit a high degree of solubility. Krukonis<sup>45</sup> has shown that CO<sub>2</sub> at or near room temperature and at pressures typically below 600 bar also dissolves many poly(dimethyl)- and poly(phenylmethyl) silicones, perfluoroalkylpolyethers, and chloro- and bromotrifluoroethylene polymers. Beckman and coworkers<sup>46</sup> found poly(perfluoropropylene oxide) and also poly(dimethyl siloxane) to exhibit solubility in CO<sub>2</sub> as well. CO<sub>2</sub> can also dissolve very low molecular weight, slightly polar polymers, such as polystyrene, or telechelic polyisobutylene if the molecular weight is below 1000.<sup>47</sup> The high solubilities of siloxane and fluorinated based polymers<sup>48,49,50,51,52</sup> has resulted in the synthesis polymerization of amorphous fluoropolymers in supercritical CO<sub>2</sub>.<sup>53,54,55</sup>

To enhance solubility of additional polymers, there is considerable research focusing on new monomer and polymer chemistries that achieve enhanced solubilities in CO<sub>2</sub>, and in designing new surfactants that can disperse many polymers, as emulsions, in CO<sub>2</sub>.<sup>56,57</sup> Other polymerization operations in supercritical CO<sub>2</sub> that have been demonstrated include chain-growth free-radical polymerization of styrenics, acrylates, and methacrylates, and cationic polymerization of isobutylene, vinyl ethers, and styrene. Also, step-growth reactions in CO<sub>2</sub> have produced polycarbonates, polyamides, polyesters, polypryrrole, polyphenoxides, and silica gels.<sup>58</sup>

### 2.2.3 Depolymerization

Depolymerization is the "reverse" of reactions that occur during polymerization, resulting in smaller chain lengths and therefore a decrease in the number average molecular weight.<sup>59,60,61,62</sup> This can potentially, lead to extraction of the lower molecular weight components, partial fractionation of the polymer, and/or scission of a polymer's intermolecular interactions.<sup>63,64,65,66</sup> Depolymerization reactions of polymers in supercritical fluids would be of great value for environmental remediation and recycling of mixed polymer wastes. One application that is currently receiving attention is the conversion or breakdown of tires into lower molecular weight components that could be recovered as a chemical feedstock.<sup>67</sup>

This reaction may also have tremendous potential for the use of supercritical CO<sub>2</sub> in the removal of polymer coatings. In this application, however, complete depolymerization or polymer/polymer chain scission is not anticipated. However, some deformation of the polymer matrix will occur as a result of the supercritical CO<sub>2</sub> sorption. This deformation, as swelling, has the potential to disrupt the polymer/polymer bonds, degrading and weakening the polymer, promoting its removal.

### 2.2.4 Fractionation

Many synthetic polymers are produced with a distribution of chain lengths, and therefore molecular weights. Since the solubility of a given polymer fraction in a given solvent is related to the solvent's density, and since the density of supercritical CO<sub>2</sub> can be varied over a wide range, supercritical CO<sub>2</sub> could be used to fractionate polymers

according to molecular weight. This has, in fact, been demonstrated,<sup>68,69,70,71,72,73</sup> and, in addition, it has been found that fractionation into molecular weight ranges more narrow than is generally achievable by traditional distillation or separation techniques is possible. Supercritical fluid fractionation of a polymer is typically carried out in multiple, sequential pressure reduction steps. The number of fractions obtained is dependent on the number of pressure reduction stages, and the molecular weight range of each fraction is related to the ratio of pressure reduction per stage.<sup>74</sup> The heaviest fraction leaving the system is the fraction with the highest molecular weight that has not been dissolved, based upon the extraction pressure and temperature.

Choosing an appropriate supercritical solvent is one of the most important considerations in polymer fractionation. The specific choice of a supercritical fluid solvent for a given polymer is highly dependent on intermolecular forces, such as hydrogen bonding and dipole-dipole interactions between the solvent-solvent, solvent-polymer, and polymer-polymer molecule pairs in solution. This, of course, applies to all the end-processes which rely on the polymer being soluble in the supercritical fluid. Chapter 3 will discuss these forces in further detail.

### **2.2.5 Swelling**

As noted previously, the number of polymers that dissolve in supercritical CO<sub>2</sub> is quite limited. However, CO<sub>2</sub> is readily absorbed into a wide variety of polymers that frequently results in polymer swelling. Polymer swelling can be further characterized as temporary (in-situ or reversible), known as plasticization, and permanent (ex-situ or irreversible), often referred to as foaming.<sup>75,76,77,78,79</sup> Foaming of polymers is achieved by

the injection of high-pressure gas into the molten polymer, followed by rapid depressurization and expansion of the gas. The production of foam using supercritical CO<sub>2</sub> is, in fact, a commercialized process for the manufacture of ultra-low density materials (primarily for use as packing materials, etc.) and ultra-low dielectric constant materials (for use in antennas, etc.).

Reversible, or in-situ, swelling is commercially exploited in the impregnation of polymers with additives. The reversible swelling of polymers in supercritical CO<sub>2</sub> is well known, and has often been reported to plasticize the polymer. Plasticization is a very important commercial operation and is typically achieved by the incorporation of low molecular weight diluents into polymer materials during their manufacture to improve workability and increase flexibility.

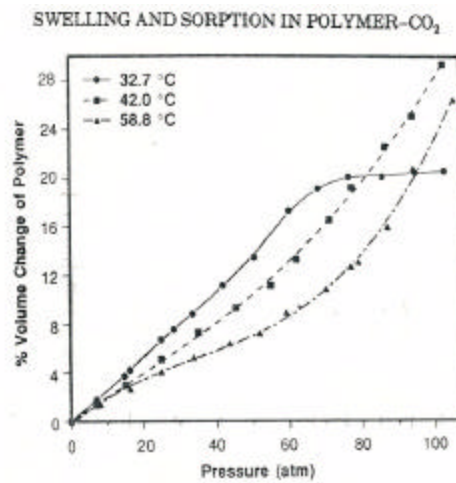
Plasticization by supercritical CO<sub>2</sub> processing increases polymer flexibility essentially through a decrease in the polymer's glass transition temperature,  $T_g$ .<sup>80</sup> The temperatures at which polymers soften, represented by  $T_g$ , and melt are important for their processing, end-use, and potentially for their removal as coatings.  $T_g$  reflects the onset of long-range motions of polymer chains and is intimately related to free volume. According to the "free volume" theory,<sup>81</sup> molecular mobility is controlled by that part of the excess volume which can be randomly redistributed with no or little energy requirement. The glass transition is the result of the temperature-dependent decrease of this free volume of the amorphous phase below some small characteristic value, which limits further molecular rearrangement. Consequently, below the glass transition temperature, further molecular rearrangements of the polymer become energy intensive, so mobility of the polymer is "frozen in".<sup>82</sup> Above the glass transition temperature,

amorphous polymers enter the rubbery state where polymer segments are free to move. Many of the physical properties of an amorphous material change when the material is heated above its glass-transition temperature since above  $T_g$  the amorphous phase can be considered to be an undercooled liquid.

In the absence of any solvent, the free-volume of a polymer decreases with applied pressure and the  $T_g$  therefore increases. However, the  $T_g$  of a polymer exposed to a (pressurized) supercritical fluid, although affected by a decrease in free-volume due to hydrostatic pressure, is more significantly influenced by the pressure dependence of the sorption of the supercritical fluid. The softening of the polymer by lowering of its  $T_g$  enhances penetration and impregnation of polymer materials with additives at much lower temperatures. The advantage to using supercritical fluids over vapors or liquid for polymer impregnation is the ability to tune the solvent strength by changing temperature and pressure, thus allowing the degree of polymer swelling and portioning of penetrants to be adjusted.

Two distinct types of reversible swelling and sorption isotherms have been identified for polymers in the presence of  $\text{CO}_2$  at elevated pressures. One isotherm is characterized by swelling and sorption that begin to level off and reach limiting values at elevated pressures. The other isotherm is characterized by sorption and swelling that continue to increase with pressure.<sup>83</sup> The sorption isotherm behavior is found to depend on the glass transition of the amorphous or semi-crystalline polymer in the presence of compressed  $\text{CO}_2$ . In the absence of a glass transition, the equilibrium solubility of  $\text{CO}_2$  in a polymer will exhibit a maximum with increasing pressure owing to free volume effects. Therefore, at a given temperature, if the pressure corresponding to the maximum

gas solubility is reached before the glass transition, the first type of isotherm described above characterizes the sorption and swelling. However, if the glass transition occurs below the pressure corresponding to maximum CO<sub>2</sub> solubility, the second type of isotherm characterizes sorption and swelling. It is expected that these isotherms will also eventually level off at some high pressure due to free volume effects in the polymer melt.<sup>84</sup>



**Figure 2-8.** Isotherms characterizing polymer sorption and swelling behavior with CO<sub>2</sub>. Isotherms at  $T = 42.0^{\circ}\text{C}$  and  $T = 58.8^{\circ}\text{C}$ , are characterized by swelling and sorption which increase with pressure. Isotherms at  $T = 32.7^{\circ}\text{C}$ , are characterized by swelling and sorption that levels off with increasing pressure.

The use of high-pressure liquid and supercritical CO<sub>2</sub> to lower the glass transition temperature of various polymers has been extensively studied, and a compilation of reported results is presented in Table 2-2

**Table 2-2.** Index of polymers and related studies on  $T_g$  depression.

| Polymer                         | Reference                                      |
|---------------------------------|--|
| Poly(methyl methacrylate), PMMA | 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96 |
| Poly(urethane)s                 | 97, 98   |



|  |  |
|--|--|
| Polycarbonate, PC                                  | 99, 100, 101, 102, 103, 104, 105, 106, 107 |
| Tetramethyl polycarbonate, TMPC                    | 108  |
|  | 109  |
| Tetrachloro polycarbonate, TCPC                    | 110  |
| Tetrabromo polycarbonate, TBPC                     |  |
| Polystyrene, PS                                    | 111, 112, 113, 114, 115, 116, 117, 118     |
| High Impact Polystyrene, HIPS                      | 119  |
| Poly(ethyl methacrylate), PEMA                     | 120, 121, 122                              |
| Poly(2,6-dimethyl phenylene oxide), PPO            | 123, 124, 125                              |
| Poly(vinyl chloride), PVC                          | 126, 127                                   |
| Poly(vinylidene fluoride)                          | 128, 129                                   |
| Poly(amic acid)                                    | 130, 131                                   |
| Polyimide  | 132, 133                                   |
| Poly(p-phenylene sulfide)                          | 134  |
| Poly(vinyl benzoate)                               | 135, 136                                   |
| Poly(vinyl butyral)                                | 137, 138                                   |
| Poly(4-methyl-1-pentene)                           | 139, 140                                   |
| Poly(ethylene terephthalate), PET                  | 141, 142, 143, 144, 145                    |
| Poly(ethylene terephthalate) glycol modified, PETG | 146  |
| Poly(dimethyl siloxane), PDMS                      | 147, 148, 149                              |
| Poly(methyl methacrylate-co-styrene), SMMA60       | 150  |
| Acrylonitrile butadiene styrene, Royalite          | 151  |
| Cellulose acetate butyrate, Uvex                   | 152  |
| Poly(vinyl acetate), PVA                           | 153  |
| Poly(p-methoxystyrene)                             | 154  |
| Nitrile Rubber                                     | 155  |
| Poly(vinyl alcohol), PVOH                          | 156  |
| Polyhydroxybutyrate, PHB                           | 157  |
| Chitosane  | 158  |
| Hydroxypropylcellulose, HPCL                       | 159  |

Plasticization with supercritical CO<sub>2</sub>, as a replacement for conventional vapor or liquid solvents, can be used to facilitate the incorporation of additives into polymers.<sup>160,161,162,163,164,165,166,167</sup> The principle is to swell the polymer with the SCF, allowing the additive, dissolved in the SCF, to migrate into the polymer matrix. The pressure is then released, forcing the CO<sub>2</sub> out of the polymer matrix, while trapping the additive within the bulk of the polymer.<sup>168</sup> The impregnation of colorants or dyes for

textiles and other synthetic polymers with supercritical CO<sub>2</sub> is currently commercialized in Germany.<sup>169</sup> For successful impregnation of a polymer, it must be amenable to swelling by and the additive species soluble in supercritical CO<sub>2</sub>. (It is also possible to use supercritical CO<sub>2</sub> to reversibly swell a polymer for in-situ molding, without the need for incorporated plasticizers.)

### 2.2.6 Crystallization

The second type of polymer/CO<sub>2</sub> interaction which does not produce a change in MWD is crystallization. The degree of crystallinity in polymers influences many of its properties and end-use characteristics.<sup>170,171,172,173,174,175</sup> Crystallinity in polymers, requiring the cooperative movement of polymer chains throughout the matrix, develops in the range between T<sub>g</sub> and the melting temperature, T<sub>m</sub>.<sup>176</sup> Crystallization can therefore be induced either by raising the temperature of the polymer into the range between T<sub>g</sub> and T<sub>m</sub> (known as thermal crystallization), or by the sorption of liquid solvents to swell the polymer and lower T<sub>g</sub> to below the ambient (known as solvent crystallization). As discussed earlier, supercritical fluids can swell polymers leading to a depression in T<sub>g</sub>. Polymer crystallization accomplished through a controlled cycle of pressurization and depressurization using supercritical fluid solvents is an area that is receiving recent attention. Numerous studies of crystallization kinetics of polymers in high pressure CO<sub>2</sub> has been reported.<sup>177,178,179,180,181,182,183,184</sup> It has been observed that with increasing CO<sub>2</sub> pressure, a polymer's characteristic time for crystallization can decrease by an order of magnitude for each MPa increase in pressure, leading to

significantly increased crystallization rates.<sup>185</sup> (The characteristic time for crystallization is defined as the time required for the crystallinity to reach one-half its maximum value.) The advantage of using supercritical CO<sub>2</sub> is that the sorption can be controlled by changing the pressure, providing a highly tunable technique for changing the crystallinity in a controlled manner. Also, after bringing about the desired crystallinity change, the supercritical CO<sub>2</sub> is easily removed from the polymer by simply depressurizing the system, whereas sorbed liquids cannot be desorbed easily. It is possible to completely eliminate the need for liquid solvents in some instances.

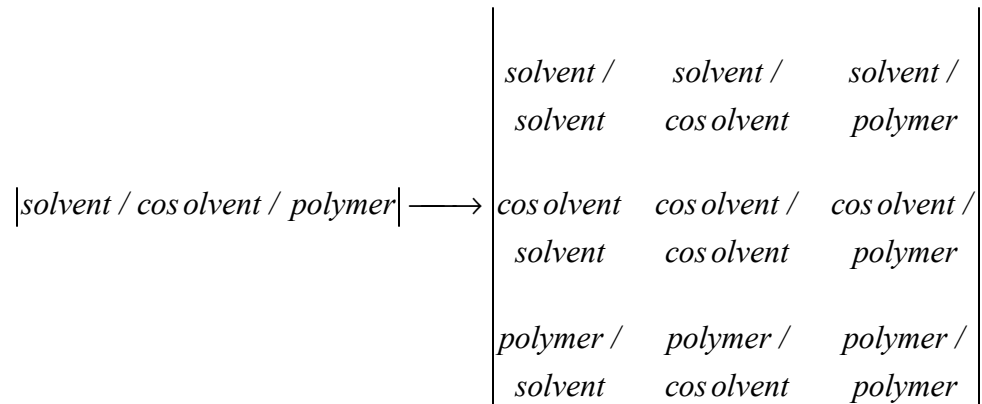
### **2.3 Polymer/CO<sub>2</sub>/Cosolvent Interactions**

Given the broad range of possible supercritical fluid applications in polymer processing, combined with the almost unlimited varieties of polymers used, it cannot be expected that a single SCF will possess all the characteristics necessary for favorable interactions in all cases. To enhance the characteristics of a SCF for a particular application, additional compounds, or modifiers, may be dissolved in the SCF as cosolvents. The addition of a small amount of cosolvent can have dramatic effects on SCF behavior, especially in the presence of specific molecular interactions between the cosolvent and the solute, or in the case of this research, the cosolvent and the polymer.

Because the focus of this research is to utilize supercritical CO<sub>2</sub> as the solvent in coating removal applications, and because of the wide differences in the types of polymers used, it is assumed that cosolvents will be necessary. In addition, if the result

of this work is to be of general applicability, the methodology must be as nearly as possible independent of the nature of the solvent, cosolvent, and polymer.

The most accurate description of the interactions between a given set of components (solvent, cosolvent, and polymer) would be one which considers those components in isolation, that is, the evaluation of molecular interactions between those three specific components taken three at a time. Such an evaluation is clearly possible, but would involve a large number of individual experimental trials, and the results of the evaluation would be applicable to that specific ternary system only. The next most general treatment would be a method which could evaluate any given set of three components. This would require not only the evaluation of a complex ternary interaction parameter, but a theoretical framework in which to use the data. Such a framework does not appear to exist. An alternative approach is to evaluate the interactions between three components, taken two components at a time. This is equivalent to evaluating the ternary system as a set of nine binary systems, Figure 2-9. The analysis to follow will further assume that the interaction between two components is symmetric, so that, for example, the solvent/cosolvent interaction is equivalent to the cosolvent/solvent interaction, etc. This reduces the number of binary pairs from nine to six. The results of these binary system evaluations would then be combined according to "mixing rules". The immediate advantage of this approach is the ability to easily exchange any one component (solvent, cosolvent, or polymer) without having to re-evaluate the interactions between the two remaining components. Further, methods for evaluating unlike binary interactions have been considered by various authors for various solvent/cosolvent, solvent/polymer, and cosolvent/polymer systems.



**Figure 2-9.** A Ternary solvent/cosolvent/polymer system described as a set of binary systems.

Evaluation of the binary pair interactions must necessarily involve an understanding of the intermolecular interactions within the pure components and between unlike component pairs, as well as the ability to optimize the characteristics of the components to predict an ultimately favorable result: the removal of a polymer coating.