POLYMERIZATIONS IN SUPERCRITICAL CARBON DIOXIDE

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We are all aware of the manifold problems of using conventional organic solvents such as xylene, acetone, chorofluorocarbons (CFCs) in polymerization processes. Some of these problems are fire hazards, toxicity, high cost, corrosion, environmental pollution (CFCs cause ozone depletion) and handling and storage problems.

Supercritical carbon dioxide (SC CO_2) shows a promising, safe, cheap, noncorrosive and environmentally compatible alternative as a solvent for polymerization processes.

What is Supercritical Carbon dioxide (SC CO_2)?

Carbon dioxide becomes supercritical when compressed above its critical pressure (Pc) and critical temperature (Tc). Critical temperature is the minimum temperature above which the gas cannot be liquefied, however high the applied pressure may be; whereas critical pressure is the pressure needed to liquefy the gas at its critical temperature.

Advantages of Using SC CO_2 as a Solvent in Polymerization Processes

1. SC CO_2 is nontoxic, nonflammable, noncorrosive with an easily accessible critical point with Pc = 73.8 bar and Tc = 31.1°C.
2. It is naturally occurring and abundant hence it is inexpensive.
3. It forms one phase mixture with gaseous reactants, which increases reaction rates by avoiding rate limiting mass transfer steps.
4. By using SC CO_2 as a solvent the final polymer can be readily isolated as a dry product by simple depressurization. Thus energy intensive drying procedures, like evaporation are not needed reducing the processing cost.
5. SC CO_2 exhibits changes in solvent density with small changes in temperature and pressure without changing solvent composition.

Polymerization in SC CO_2.

The solubility of monomers and polymers in SC CO_2 is very important for polymer synthesis in SC CO_2. SC CO_2 is a good solvent for most nonpolar and some low molecular weight compounds, but it is a poor solvent for most of the high molecular weight polymers. For example poly methylacrylate requires 2000 bar pressure at 100 °C for 10^5 g/mol polymer to dissolve in SC CO_2[1], such high pressures are not practical. The only polymers soluble in SC CO_2 under mild conditions are amorphous fluoropolymers and the silicones. Although carbon dioxide is a polar molecule it has no dipole moment, a significant contribution to its solubility parameter is due to its large quadrupole moment. Quadrupole moment is the measure of extent to which the distribution of positive charges deviates from the spherical symmetry [2]. The quadrupole moment of carbon dioxide along with it's Lewis acidity allow it to interact with the polymer functional groups such as sulphones and carbonyl increasing the solubility of the polymer. In silicones the interaction between the silicon backbone of the polymer and CO_2 causes the high solubility of the polymer.

These solubility requirements dictate the type of polymerization technique used for the polymer synthesis, for example the polymers which are highly soluble in SC CO_2 can be made by homogeneous polymerization, but due to the inherent insolubility of most of the polymers in SC CO_2 they are synthesized by heterogeneous polymerization.

Homogeneous polymerization :
Amorphous fluoropolymers which are soluble in SC CO_2 can be synthesized homogeneously either by free radical or ionic polymerization. The synthesis and the processing of these polymers is problematic in conventional solvents due to the poor solubility of the polymer in organic solvents, the only suitable solvents for these polymers are the chlorofluorocarbons (CFCs). Due to environmental concern the use of CFCs is banned. SC CO_2 represents an ideal solvent for these polymers. For example the homogeneous polymerization in SC CO_2 of para-perfluoroethyleneoxymethyl styrene gave a product which was very similar to the product of the solution polymerization in 1, 1, 2-trichloro-1, 2, 2 trifluoroethane (freon-113). Thus SC CO_2 represents a good replacement for the CFCs.

Heterogeneous polymerization : It involves a multiphase system; precipitation and dispersion polymerizations in SC CO_2 are discussed here

Precipitation polymerization : In this process an initially homogenous mixture of monomer, initiator and solvent becomes heterogeneous as the insoluble polymer molecules form a separate polymer phase. The free radical polymerization of ethylene in SC CO_2 carried out by Hagiwara and coworkers [1] showed that there was little effect of CO_2 on the polymer structure. The ethylene monomer was initially soluble in CO_2 and the product polyethylene was obtained as a dry powder, which could be easily recovered with no need for drying off the solvent.

Dispersion polymerization: It is a colloid forming process in which surfactants are a critical component as they control the properties and the morphology of the polymer formed. A dispersion polymerization starts as a initially homogeneous system due to the solubility of all the components in the solvent, as the growing radicals reach a critical molecular weight the polymer chains are no longer soluble and the phase separation starts to begin, at this stage the surfactants adsorb to the polymer colloids preventing coagulation by either steric, electrostatic or electrosteric stabilization. As CO_2 has low dielectric constant, polymeric surfactants are used for steric stabilization. In CO_2 based systems surfactants used for steric stabilization are either CO_2 philic homopolymers, copolymers containing a CO_2 philic component and a CO_2 phobic anchoring component or CO_2 philic reactive macromonomers. Dispersion polymerization of methyl methacrylate in SC CO_2 was reported by De Simone [1] in 1994 in which amphiphilic homopolymer PFOA or poly (1,1 – dihydroperfluorooctyl acrylate) with molecular weight (weight average) of 11,000 or 20,000 gm/mol was used as a surfactant. Polymerization was carried at 65 °C and a pressure of 207 bar with AIBN as an initiator, high conversions (> 90%) with a high degree of polymerization (> 3000) were reported. The spherical polymer particles on scanning by electron microscope showed that the product consisted of spheres in 1-3 micrometer range with a narrow particle size distribution. In contrast the reactions without PFOA resulted in very low conversions (< 40 %) in which the product had unstructured nonspherical morphology. Hence the PFOA surfactant played a vital role of steric stabilization of the growing polymer colloidal particles.

New challenges

As seen above surfactants are very crucial to heterogeneous polymerization in SC CO_2, conventional surfactants, which are designed for aqueous and organic systems cannot be used for the CO_2 based systems. Hence *new surfactants especially for SC CO_2 based systems have to be synthesized.*

Fractionation of Polymers by SC CO_2.

Polymer fractionation involves the separation of an unfractionated polymer sample into several fractions of progressively increasing or decreasing molecular weights. Conventionally polymer fractionation is carried out by tedious processes such as fractional precipitation, partial dissolution, gradient elution etc, which use many solvents and are time consuming. Fractionation by using SC CO_2 is interesting due to its unique properties. The solvating power of the solvent is controlled by its density near the critical point, slight changes in the temperature or the pressure results in a drastic change in the density. Hence separation of the solute from the solvent can be achieved by reduction of the pressure or by changing the temperature or by both. Due to the high diffusivity and low viscosity of SC CO_2, it penetrates into the polymer phase more effectively than a liquid solvent. By this process very selective and efficient fractionation is possible. The feasibility of fractionation by this method is determined by the variation of the solubility of a homologous series of compounds[3]. For example SC CO_2 can be used to fractionate high molecular weight ultra low vapor pressure perfluoroalkylpolyether oil [4] which is difficult to fractionate by conventional methods. All perfluoroalkylpolyether oligomers in the oil are soluble in SC CO_2 but the solubility of a pure oligomer is different than the solubility in a mixture of different oligomers. By appropriate pressure control on the polymer solution in SC CO_2 the polymer can be easily fractionated.
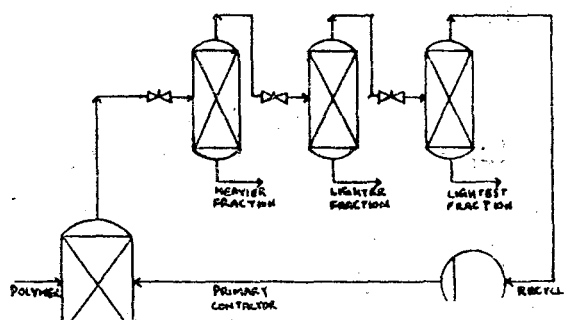

Fig.1 Polymer fractionation by SC CO_2

Process

The polymer is continuously fed to an extraction vessel where it is dissolved in SC CO_2, by careful stepwise pressure reduction of the vapors leaving the vessel the polymer is fractionated into low polydispersity fractions. The number of fractions and the polydispersity of each fraction are functions of the number of the pressure reduction stages and the pressure reduction ratio in each stage. An excellent example of this method is the fractionation of perfluoroalkylplyether (Fomblin Z) of Montedisan Co in which the parent oil with average molecular weight of 60,000 was separated into fractions having average molecular weights ranging from 1200 to 15,000[4].

Plasticisation of Polymers by SC CO_2

In plasiticisation of a polymer the intermolecular forces of attraction between the polymer molecules are reduced resulting in increased flexibility of the polymer, which results in the lowering of the processing temperature of the polymer. Conventional plasticisers such as dioctyl phthalate are toxic hence pose many problems. Polymers are highly plasticised by SC CO_2, which is nontoxic. Plasticisation by SC CO_2 also allows important effects such as –

(1) Removal of residual monomer and side products from the polymer : Due to better transport properties of SC CO_2 such as low viscosity, high diffusivity and the tendency to plasticise polymers it can be used to purify polymers. For example silicone polymers which are produced by the ring opening polymerization of cyclotetrasiloxane monomers which is a equilibrium reaction may have levels of monomer as high as 5% by weight, the polymer may also be contaminated by the high molecular weight side products. As the vapor pressure of the of cyclic siloxane compounds is very low, conventional separation by fractional distillation is very difficult Under the extraction conditions of pressure 80 bar and temperature 100°C SC CO_2 is a good extractant for the cyclic species, but not for the polymer. Thus the cyclic side products can be easily separated using SC CO_2.
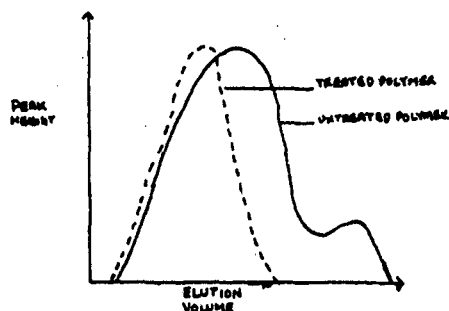

Fig. 2 Gel permeation chromatograph of the treated polymer superposed on the gel permeation chromatograph of the parent (untreated) polymer.

An excellent advantage of this system is that the dissolving power of SC CO_2 can be adjusted specifically to strip the cyclics from the mixture without extracting the linear oligomers, such a condition occurs [4] at pressure of 8 Mpa and temperature of 100°C.

Another example is the treatment of poly (N-vinyl carbazole) by SC CO_2 which results in lower monomer levels from 3.66% to 0.1%, whereas the conventional solvents are unsuitable to remove the monomer residue[1].

(2) **Polymer blend synthesis :** Due to its inherent ability to plasticise polymers SC CO_2 can be used to prepare Interpenetrating Polymer Networks (IPN). A CO_2 insoluble polymer substrate is swelled by SC CO_2 and CO_2 soluble monomers are infused in it. Subsequent polymerization of the monomer gives the polymer blend. Watson and Mc Carthy[1] used SC CO_2 to a swell polymeric substrate containing Poly (chlorotrifluoroethylene), Poly (4 methyl -1 pentene), polyoxymethylene, Nylon 6,6 and Bis phenol A carbonate. The swollen substrate was then infused by the styrene monomer and a free radical initiator. After polymerization of the styrene monomer, mass uptakes of upto 118 % on the original polymer were reported. The diffusion rates in the SC CO_2 were drastically increased over the non-swollen polymer substrates.

Conclusion

The above examples show that SC CO_2 can become a viable solvent for polymerization to the present conventional solvents. Use of SC CO_2 will make the polymerization processes *ecofriendly, safer and inexpensive.*

References

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