

Chemical Reactions Utilizing Supercritical Fluids

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The use of supercritical fluids as a reaction media offers the chemical and pharmaceutical industries the opportunity to replace conventional hazardous organic solvents and simultaneously optimize and control more precisely the effect of the solvent on reactions. Supercritical fluids, unlike conventional liquid solvents, can be “pressure tuned” to exhibit gas-like to liquid-like properties. Supercritical fluids have liquid-like local densities and solvent strength, which can be “tuned” by adjusting the pressure in the reactor in allowing for the control of the solubility of the reactants along with density-dependant properties such as dielectric constant, viscosity, and diffusivity. Additionally, solubility control through pressure can allow for easy separation of products and catalysts from the supercritical solvent.

Supercritical fluids are an attractive medium for chemical reactions because of their unique properties. Most of the important physical and transport properties that influence the kinetics of a chemical reaction are intermediate between those of a liquid and a gas in a supercritical fluid medium. The reactants and the supercritical fluid frequently form a single supercritical fluid phase. Supercritical fluids share many of the advantages of gas phase reactions including miscibility with other gases, low viscosities, and high diffusivities, thereby providing enhanced heat transfer and the potential for fast reactions. Supercritical fluids are especially attractive as a reaction medium for diffusion-controlled reactions involving gaseous reagents such as hydrogen or oxygen.

Carbon dioxide has the further advantage of being inexpensive, non-toxic, non-flammable, nonexplosive, and unregulated with regards to air emissions. Carbon dioxide is especially attractive as a reaction media for electro phillic and oxidation catalysis because of its electrophillic unreactive nature. The enhanced

acrylic acid, and vinyl acetate in liquid and supercritical fluid media. These reactions were initiated with either ionizing radiation or common free radical initiators. Because the reactant compounds were soluble in CO₂, but the resulting polymers were insoluble in CO₂, these reactions were precipitation reactions in which the product was recovered as a powder or “sticky liquid.” Also in 1968, Japanese researchers published the free radical precipitation polymerization of ethylene into high molecular weight ($M_n=10^5$ g/mol) polyethylene at 392 bar. In 1986, vinyl C₃ to C₅ carboxylic acids (including acrylic acid) were polymerized to form to form high molecular weight materials.

An important factor when polymerizations occur in a CO₂ media is the plasticization of the resulting polymers by the CO₂. This plasticization affects both the diffusion of the monomer into the polymer and the incorporation of additives into the polymer. Polymers that are significantly to severely plasticized by CO₂ are polystyrene (PS), polymethylmethacrylate (PMMA), polycarbonate (PC), polyvinyl chloride (PVC), polyethyleneterephthalate (PET), and blends of PMMA and polyvinylidene fluoride (PVF₂).

Other collateral advantages of processing polymers in CO₂ media are: 1) the opportunity to extract residual monomer, solvent or catalyst from a solid polymer; 2) the fractionation of a mixture of polymers of different molecular weights by changing the density of the supercritical carbon dioxide, and 3) the polymer morphology can be controlled with supercritical drying or foaming.

Dr. Joseph DeSimone of the University of North Carolina at Chapel Hill has developed a method of performing dispersion polymerizations in carbon dioxide by use of a CO₂-soluble stabilizer and has shown the important of proper selection of stabilizer for these types of reactions in a CO₂ media. He has demonstrated that many step growth polymerizations (e.g. polyesters and polyimides) can be conducted in a CO₂ media. Supercritical fluid methods are capable of driving step growth polymerizations to high polymer molecular weights while reducing the viscosity by swelling of the polymer melt.

Prevention of coagulation or flocculation of colloidal dispersion particles can occur by using electrostatic, electrosteric, and steric stabilization agents. Because CO₂ is a low dielectric reaction medium it requires steric stabilization. The most effective steric stabilizers are amphiphilic molecules that become absorbed or grafted onto the surface of the polymer particle by the anchoring segment. The stabilizer molecules also contain stabilizing segments that are

thermoconductivity of supercritical carbon dioxide relative to organic solvents coupled with its stability towards further oxidation makes it an efficient solvent for buffering heat transfer, even for highly exothermic reactions.

Solubility properties in supercritical fluids are unique because compounds that are largely insoluble in a gas, such as carbon dioxide, can become soluble in the fluid phase at supercritical conditions. Conversely, some compounds, such as salts, that are soluble in water at ambient conditions, can become insoluble at supercritical conditions. Consequently, supercritical fluids provide the opportunity to control the reaction environment by manipulating reaction conditions such as temperature and pressure. Furthermore, the solvent dielectric constant can be influenced, which can lead to changes in the rates of reactions. The density of the supercritical fluid can be manipulated to change the dielectric constant and hence the reaction rates.

Polymerization Reactions in Liquid and Supercritical Carbon Dioxide

Large amounts of volatile organic compounds (VOCs), chlorofluorocarbons (CFCs), and contaminated toxic aqueous wastestreams are released into the environment during synthesis and processing of industrial production of plastics and resins. The use of environmentally benign solvents such as liquid or supercritical carbon dioxide would allow for the production of commodity plastics and resins with the elimination/reduction of toxic wastestreams produced during processing and manufacturing. Furthermore, polymers synthesized in carbon dioxide do not have to undergo costly drying or solvent removal procedures.

It is well known that the dissolving power of carbon dioxide for most natural compounds such as esters, sterols, triglycerides, etc. is similar to hexane (i.e. if a low molecular weight compound is soluble in hexane then it is soluble in carbon dioxide). However for molecules with low vapor pressure and high molecular weight such as most polymers, carbon dioxide's dissolving power is more analogous to a fluorocarbon. Thus many of the industrially important hydrocarbon polymers are insoluble in carbon dioxide and must be polymerized by heterogeneous methods. In contrast, amorphous fluoro carbon and silicone polymers are soluble in carbon dioxide and can be synthesized homogeneously via carbon dioxide as reaction medium.

Carbon dioxide was first shown to be a good solvent for free radical polymerizations in 1968. Sumitomo Chemical filed a patent for the free radical polymerization of vinyl chloride, styrene, methyl methacrylate, acrylonitrile,

soluble in the continuous CO₂ phase. The polymeric stabilizer is a macromolecule which preferentially locates at the polymer-solvent interface and prevents aggregation of particles by coating the surface of each particle and imparting repulsive forces between them. For a stabilizer to be effective, a proper balance must be found between the sections that are soluble and the sections that are insoluble in the carbon dioxide phase.

Flow Reactors

The scale-up of supercritical fluid reactions presents a number of unusual problems. Most substrates (reactants) have critical temperatures far higher than that of CO₂ and so to maintain supercritical condition within a reaction vessel, a high temperature must be maintained or a very dilute solution must be maintained within the vessel. However, dilute solutions would not be cost effective for processing large quantities of large material because the reaction vessel would need to be extremely large. These problems are minimized if not completely resolved by the use of a continuous flow reactor. The gas-like nature of supercritical fluids with respect to low viscosity, good heat transfer, etc. is especially exploited in flow reactors. The principle is simple; the reaction takes place in a sealed vessel but the product is recovered by rapid expansion of the CO₂ following completion of the reaction.

Reactions in Organics with Supercritical Antisolvents (ROSA)

Unfortunately, the flow reactor described above can only be applied to reaction where both reactant and product are soluble in this supercritical fluid. This happens to be the case in a small minority of applications, thus Dr. Martyn Poliakoff of the University of Nottingham invented the ROSA technique specifically for reactions where the products are insoluble in supercritical CO₂. The fact that many substances are insoluble in supercritical fluids has directed much research towards using carbon dioxide as antisolvent to precipitate materials from conventional solvents. The principle is similar to the widespread use of aliphatic hydrocarbons to precipitate materials from more polar organic solvents. The reaction is carried out in an organic solvent that flows through a thermal flow reactor and the product is precipitated by the supercritical antisolvent in a GAS expansion vessel. Solvents and excess reactants are further transported to a separator where they are collected for recycle back to the flow reactor.

Advantages of SF Reaction Medium

- ◆ Density tuning of reactions for rate, yield, selectivity
- ◆ Co-solvent tuning of reactions for rate, yield, selectivity
- ◆ Transforming heterogeneous reactions into homogeneous reactions
- ◆ Improved mass transfer for heterogeneous reactions
- ◆ Improved catalyst life for heterogeneous reactions by mitigating coking by oligomers as byproducts in the catalysts pores
- ◆ Simultaneous separation with reaction
- ◆ Replacement of environmentally desirable solvents with less toxic or nontoxic compressible gases
- ◆ Elimination of drying step to separate solvent from product
- ◆ Supercritical fluid can act as reagent, reactant, or copolymer, as well as solvent
- ◆ High pressures favor many reactions and polymerizations because of a decrease in volume as the reactions proceed
- ◆ Polymerization rates can be fine tuned towards producing polymers of desired properties because the propagation or termination rates can be modulated
- ◆ Precipitation thresholds for specific polymer weights can be chosen by adjusting the dissolving power by adjusting the density sensitive dissolving power of the supercritical fluid
- ◆ Controllable isomer and enantiomer selectivity by pressure tuning (e.g. *cis*-over *trans*- fatty acid in the hydrogenation of vegetable oils)
- ◆ Dielectric constant of the reaction medium can be fine tuned to control ionic reactions and polymerizations
- ◆ Recovery of unreacted monomers, reagents and co-solvents can be easily facilitated by supercritical fluid fractionation methods in multiple stagewise centrifugal separators

- ◆ Micro-structured composites and blends of polymers can be prepared because a polymer can be swollen to allow supercritical fluid infusion or impregnation of another monomer and its in-situ polymerization

Conclusion

Supercritical fluids as a reaction medium offer many advantages over utilizing hazardous liquid organic solvents. Interest in supercritical fluids as a reaction medium has experienced explosive growth, especially since the announcement of a supercritical carbon dioxide reaction medium process that will be commercialized for the production of Teflon by DuPont earlier this year.

References

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