

## Developments in CO<sub>2</sub> research\*

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*Abstract:* CO<sub>2</sub> can be a good solvent for many compounds when used in its compressed liquid or supercritical fluid state. Above its critical temperature and critical pressure ( $T_c = 31\text{ }^\circ\text{C}$ ,  $P_c = 73.8\text{ bar}$ ), CO<sub>2</sub> has liquid-like densities and gas-like viscosities, which allows for safe commercial and laboratory operating conditions. Many small molecules are readily soluble in CO<sub>2</sub>, whereas most macromolecules are not. This has prompted development of several classes of small molecule and polymeric surfactants that enable emulsion and dispersion polymerizations as well as other technological processes.

### INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is a natural solvent that can be utilized in the replacement of water and common organic solvents for many processes and applications. Several of the advantages in using CO<sub>2</sub> include that it is inexpensive, nonflammable, environmentally benign, and readily separated from products [1]. Most of the CO<sub>2</sub> sold today is a by-product from the production of other chemicals, such as ammonia, ethanol, hydrogen and natural gases [2–4]. As well as being “environmentally friendly”, CO<sub>2</sub>-based processes can be more energy efficient than processes based on water and common organic solvents, owing to its low heat of vaporization. This feature drastically reduces energy costs associated with processing. It is the only solvent we know of that can be used for both pollution prevention as well as energy efficiency.

Recognizing that CO<sub>2</sub> can impart numerous potential benefits to industry, it has been studied extensively for utilization as a solvent replacement in commercial processes. For instance, since the 1970s, CO<sub>2</sub> has been used for the extraction of caffeine from coffee, tea, and spices. More recently, the dry-cleaning industry is witnessing a revolution as the traditional solvent of perchloroethylene is being replaced with CO<sub>2</sub> and molecularly engineered surfactant molecules [4–5]. Another example of CO<sub>2</sub> being brought into industry is the announcement by DuPont of the construction of a \$275 million plant for the manufacturing of Teflon<sup>™</sup> and other fluoropolymers using CO<sub>2</sub> technology. [6]. This review will focus on such developments in the use of CO<sub>2</sub> and, more specifically, surfactant use in CO<sub>2</sub> and polymerization of fluoroolefins and fluoroacrylates.

### FLUOROOLEFIN POLYMERIZATIONS

Fluoropolymers, such as poly(tetrafluoroethylene) (PTFE) and PTFE copolymers of perfluoro(propyl vinyl ether) (PPVE) or hexafluoropropylene (HFP), are melt-processable materials in high demand for premium products used in applications requiring thermal and chemical resistance. A traditional syn-

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thesis for these materials involves aqueous dispersion or emulsion polymerization. However, these methods result in a high degree of carboxylic acid end groups, which interferes with melt processing. The acid end groups are unstable and must be treated by either high-temperature hydrolysis or fluorination before melt processing. Untreated, the acid end groups decompose under the high temperatures, upsetting the molecular weight of the chains as well as produce hydrogen fluoride, which damages equipment. A method to circumvent acid end group formation involves the use of nonaqueous media solvent systems such as chlorofluorocarbons (CFCs). This method is successful in producing higher-performance materials with a lower occurrence of the acid end groups. With the ban on CFCs in effect, alternative solvents have become necessary. For free-radical polymerizations, unfortunately, hydrocarbon solvents are too prone to hydrogen abstraction, and fluorinated solvents are quite expensive and of low availability.

With preliminary results [7,8] indicating that CO<sub>2</sub> was an excellent medium for free-radical polymerizations, investigations into using CO<sub>2</sub> as a replacement for the CFCs began in earnest. It was found that handling tetrafluoroethylene (TFE) was safer in mixtures with CO<sub>2</sub>, overcoming difficulties with disproportionation and autopolymerization. DeSimone *et al.* first reported free-radical telomerizations of 1,1-difluoroethylene [9] and TFE [10], demonstrating the feasibility of these polymerizations in CO<sub>2</sub>. Further studies of TFE examined the polymerization of TFE in a hybrid CO<sub>2</sub>/aqueous medium [11]. A water-soluble persulfate initiated polymerization of TFE, providing PTFE particles of spherical morphology similar to granular PTFE. Spherical particles were obtained both with and without added surfactant. Copolymers of TFE with either HFP or PPVE were also studied since these materials are melt-processable, with lower melting points than PTFE [12]. The morphology of these copolymers is similar to those materials synthesized using CFCs.

## SURFACTANTS

For the most part, macromolecules are not soluble in CO<sub>2</sub>. Therefore, as it was desired to conduct polymerizations and processing in CO<sub>2</sub>, surface-active agents (surfactants) were needed for stabilization of growing particles in the CO<sub>2</sub> continuous phase. Eventually, with the discovery that fluoropolymers and polysiloxanes were indeed soluble in CO<sub>2</sub>, steric stabilizers were envisioned to stabilize emulsion and dispersion polymerizations in a CO<sub>2</sub> continuous phase. These surfactants consist mostly of amphiphilic block copolymers that have “CO<sub>2</sub>-philic” and “CO<sub>2</sub>-phobic” components, comprised of a polysiloxane or fluoropolymer block and a hydrophilic or lipophilic polymer block, respectively [13–15]. Self-assembly leads to the formation of micelles having a core of the CO<sub>2</sub>-phobic blocks adsorbed to the polymer and an outer corona of the CO<sub>2</sub>-philic blocks dispersed in CO<sub>2</sub>. Micelles are formed once the concentration has reached a critical micelle concentration (cmc). It was also discovered that with careful design of the surfactant system, one could design a surfactant that at certain densities exists as micelles but at higher densities breaks up reversibly into unimers.

## Fluoroacrylates

Based on the need for surfactants for CO<sub>2</sub>, fluoroacrylates were identified as a class of highly soluble polymers capable of steric stabilization in CO<sub>2</sub>. Controlled free-radical polymerizations were used to synthesize most of the fluoroacrylates via iniferter [16] and atom-transfer radical polymerization (ATRP) [17] techniques. The CO<sub>2</sub>-phobic block has been synthesized to include polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(*tert*-butyl acrylate) (PTBA), poly(vinyl acetate) (PVAc), and poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) [18–20]. The first generation of CO<sub>2</sub>-philic blocks have included the following fluoroacrylates: poly(1,1-dihydroperfluorooctyl acrylate) (PFOA), poly(1,1-dihydroperfluorooctyl methacrylate) (PFOMA), poly(1,1,2,2-tetrahydroperfluorooctyl acrylate)

(PTAN), poly(2-(*N*-ethylperfluorooctanesulfonamido) ethyl acrylate) (PFOSEA), and poly(2-(*N*-ethylperfluorooctanesulfonamido) ethyl methacrylate) (PFOSEMA) [18–20].

### Dispersion polymerizations

Dispersion polymerizations have been used in industry for controlled particle synthesis, with diameters ranging from 100 nm to 10 μm. This method involves starting with a homogeneous mixture of reagents, which produces insoluble particles stabilized as a latex by steric stabilization from a surfactant. High molecular weights are obtainable, as well as uniform particle size, which is controlled by the concentration of surfactant. DeSimone *et al.* reported the first successful dispersion polymerization in CO<sub>2</sub> [13,21]. Methyl methacrylate (MMA) was polymerized using PFOA as an amphiphilic surfactant in CO<sub>2</sub>. Further examination of this polymerization showed that a stable dispersion could be carried out with a surfactant concentration as low as 0.24 wt %, based on MMA. Due to the success realized with MMA, other lipophilic and hydrophilic monomers were also studied in CO<sub>2</sub> dispersion polymerizations. These monomers included styrene [22,23], vinyl acetate [24], glycidyl methacrylate [25], 2-hydroxyethyl methacrylate [26], 1-vinyl-2-pyrrolidone [27], and sugar-containing amphiphiles [28].

### Spin-coating development and photolithography

In the semiconductor industry, growth of 15% annually has been seen in each of the last 30 years. With industry expansion, improvement of the microchip performance, while lowering the cost of production per chip, is a driving force. Typically, a semiconductor line that fabricates 5000 silicon wafers daily generates approximately 8000 liters of organic solvent waste and 8000 liters of aqueous rinse waste. The cost associated with recovery and disposal, as well as the environmental costs, is by no means trivial. Research in our group is focused on replacing the use of water and organic solvents in the manufacture of integrated circuits (ICs) and microelectromechanical (MEMs) devices with CO<sub>2</sub>. Another benefit to the use of CO<sub>2</sub> in lithography lies in the development of smaller wavelengths of light used for patterning on the silicon wafers. As the images on the wafers get smaller and smaller, image collapse emerges as a problem with the use of water, as a result of its inherently high surface tension. Using CO<sub>2</sub> eliminates this problem as it has gas-like viscosities and low surface tension.

Incorporating CO<sub>2</sub> as the solvent for photolithography involves several challenges. A major challenge lies in the development of CO<sub>2</sub>-compatible resist materials capable of being spin-coated from CO<sub>2</sub>. A spin-coating material needs to be soluble at 20 wt % at 5 °C in liquid and vapor CO<sub>2</sub>. As to this end, Hoggan *et al.* have reported the synthesis of a CO<sub>2</sub>-compatible resist, as well as a high-pressure spin-coating apparatus [29]. The resist is comprised of a random copolymer of FOMA and *tert*-butyl methacrylate (TBMA) that is initiated by 2,2'-azobis(isobutyronitrile) (AIBN) at 60 °C with 340 bar CO<sub>2</sub> for 48 h. The *tert*-butyl groups are acid-sensitive and undergo hydrolysis in the presence of an acid generator. The solubility of the resulting polymer in CO<sub>2</sub> is greatly reduced, enabling this polymer to form negative resists.

### Dry cleaning

With surfactants capable of stabilizing lipophilic and hydrophilic materials in CO<sub>2</sub>, the development of a new garment care process was designed. Traditionally, dry cleaners use hazardous organic solvents, such as perchloroethylene (perc), hydrocarbons, or cyclic siloxanes to clean clothes in the absence of water. In addition, cleaning with these solvents requires an evaporative heating cycle that does not fully remove the solvent, which can expose the consumer to the toxic hazard.

Using CO<sub>2</sub> would prove to be beneficial to both the operator and customer. The process developed by Micell Technologies is capable of recycling up to 98% of the CO<sub>2</sub> and most of the surfactant [5]. When clothes are cleaned using CO<sub>2</sub>, there is no residual solvent. Also, with CO<sub>2</sub> no heat cycle is necessary for solvent removal, which protects clothing from fading or shrinking. With the use of various filters, lint, dirt, and loose fibers are removed while the surfactant lifts and removes oils and stains.

## LOOKING AHEAD

Carbon dioxide has been shown to be useful in the replacement of various solvents in a wide range of applications. It has the potential to have a major impact on industry now at the beginning of the 21<sup>st</sup> century. As research and development progress, applications and possibilities could grow exponentially. With encouraged usage of CO<sub>2</sub>, a cleaner environment is clearly envisioned.

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