Frontiers in green chemistry utilizing carbon dioxide for polymer synthesis and applications*

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Abstract: In the last ten years, there has been incredible growth in research involving the use of carbon dioxide as an environmentally benign solvent. This article will highlight polymer synthesis, characterization, and applications in CO_2 and place this research in the context of both green chemistry and the latest developments in CO_2 technology.

INTRODUCTION

In recent years, the use of liquid and supercritical CO_2 as a green, environmentally benign solvent for chemical reactions and polymerizations has become a widespread, growing reality, both in academia and in industry [1–5]. CO_2 is a nontoxic, nonflammable, and inexpensive solvent. Although CO_2 is a "greenhouse gas", CO_2 can be acquired from natural reservoirs or recovered as a by-product of industrial chemical processes, so no new production of CO_2 is necessary and there will be no additional contribution to the greenhouse gases. While CO_2 is a gas at ambient conditions, its liquid and supercritical states are easily attained by compression and heat. The critical conditions of 31.1 °C and 73.8 bar are relatively low. Liquid CO_2 is a compressible fluid, while supercritical CO_2 has relatively high liquid-like densities and low gas-like viscosities. Both liquid and supercritical CO_2 have a tuneable density (and dielectric constant) that increases with increasing pressure or decreasing temperature [6]. The solvency of supercritical CO_2 is often compared to that of fluorocarbon solvents. Many small molecules are soluble in CO_2 [7], including high vapor pressure solvents like methanol, acetone, and tetrahydrofuran, many vinyl monomers, and azo- and peroxy-initiators. Water and ionic compounds are insoluble [8,9], as are most polymers. Only two classes of polymers are soluble in CO_2 at relatively mild conditions (T < 100 °C, P < 350 bar), amorphous or low-melting fluoropolymers and silicone-based polymers [10]. Herein, polymer synthesis, characterization, and applications in CO_2 will be described, highlighting the environmental benefits of using CO_2.

POLYMER SYNTHESIS

In CO_2, few polymers, typically amorphous fluoropolymers, can be synthesized by a homogeneous, solution polymerization. Many insoluble polymers can be synthesized by a heterogeneous chain-growth process, such as precipitation, emulsion, dispersion, or suspension. Due to the solubility of many vinyl monomers and free-radical initiators in CO_2 and the ability to design appropriate CO_2-soluble polymeric surfactants, dispersion polymerization is a common heterogeneous polymerization method in CO_2. Step-growth polymerizations can also be conducted in CO_2 with advantages over other processes. Most of the polymers synthesized in CO_2 to date can be classified into three categories: fluoropolymers, dispersion polymers, and step-growth polymers.

Fluoropolymers

Fluoropolymer synthesis in CO_2, which is the subject of a recent chapter review [11], will now be discussed in the context of green chemistry. The synthesis of fluoropolymers in CO_2 is environmentally advantageous since these polymers are typically prepared in chlorofluorocarbons (CFCs) and other fluorinated solvents as well as in water. The association of CFCs with ozone layer destruction and the environmentally harmful nature and expense of fluorinated solvents necessitate the search for replacement solvents. Many fluoropolymerizations cannot be conducted in hydrocarbon solvents because of the detrimental side reactions arising from radical abstraction of hydrogen atoms from the solvent. Since CO_2 has no hydrogens to abstract, there is no chain transfer to CO_2. Amorphous fluoropolymers, such as highly fluorinated (meth)acrylates and perfluoropolyethers, are highly soluble in CO_2 and have been synthesized by solution polymerizations in supercritical CO_2 [12,13]. Low-molecular-weight oligomers of poly(tetrafluoroethylene) (PTFE) and poly(1,1-difluoroethylene) (PVDF), which remain soluble in CO_2 below a limiting molecular weight, have been synthesized by telomerizations in CO_2 [14,15]. Semi-crystalline, high-melting-temperature fluoropolymers, such as PTFE and PVDF, are insoluble in CO_2 due to their crystallinity and are polymerized by various heterogeneous methods in CO_2 [16–18].

Fluorinated acrylate polymers have been synthesized by homogeneous, solution polymerizations in CO_2 [12]. Using azobis(isobutyronitrile) (AIBN) as the thermal free-radical initiator, 1,1-dihydroperfluorooctyl acrylate (FOA) was polymerized at 60 °C, 207 bar. The high-molecular-weight polymer, PFOA, remained soluble in supercritical CO_2 and was identical to that polymerized in a CFC. It was also shown that statistical copolymers containing FOA and either methyl methacrylate, styrene, butyl acrylate, or ethylene, could be polymerized under homogeneous, solution polymerization conditions in CO_2. PFOA and CO_2-soluble copolymers containing PFOA are useful polymeric surfactants for applications including dispersion polymerizations and extractions, as will be shown later in this review.

Perfluoropolyethers, which find applications as high-performance lubricants and heat-transfer fluids, constitute another class of fluoropolymers that have been synthesized in CO_2 [13]. The photooxidation of hexafluoropropylene (HFP) was performed in liquid CO_2 at –40 °C to yield perfluoropolyethers soluble in CO_2. This study showed that CO_2 is a viable solvent replacement for the dichlorodifluoromethane currently used in some commercial fluoroolefin photooxidations.

Tetrafluoroethylene (TFE) polymerizations in CO_2 are sensible because this dangerous, potentially explosive monomer is safely stored and handled as a pseudo-azeotrope with CO_2 [19,20]. Copolymerizations of TFE with perfluoro(propyl vinyl ether) (PPVE) or HFP in CO_2 have produced polymers with levels of comonomer incorporation similar to commercial polymers [16]. The TFE-PPVE copolymers also contained an unprecedented 0–3 acid endgroups per 10^6 carbon atoms, which are comparable to copolymers synthesized in CFCs and treated with a harsh fluorination process. TFE was also polymerized to high molecular weights in a biphasic mixture of CO_2 and water by heterogeneous methods similar to the industrial suspension and dispersion processes [17]. Using a persulfate initiator in the absence of a surfactant, aggregates with diameters of 0.5–3 μm were produced and resemble the granular PTFE formed commercially by suspension polymerization in water. In the presence of a CO_2-soluble surfactant, particles with diameters of 100–200 nm were produced and are similar to those made commercially by conventional aqueous dispersion polymerization.

In the first continuous polymerizations in CO_2 reported recently [18], PVDF and poly(acrylic acid) were produced by continuous precipitation polymerization. A continuous polymerization process is much more commercially and environmentally viable than a batch polymerization, producing a larger amount of polymer in a given amount of time. The PVDF was formed at 75 °C, 275 bar and collected in a filter after polymerization residence times of between 15 and 40 min in the continuous stirred tank reactor.

Dispersion polymers

CO_2 is well suited as a reaction medium for dispersion polymerizations because many vinyl monomers and polymerization initiators are soluble in CO_2 while the polymers formed are insoluble [1,21]. Surfactants for steric stabilization of the colloidal polymer particles in CO_2 must be soluble and must adsorb or chemically graft to the polymer particles and can consist of homopolymers, block, graft, and random copolymers, and reactive macromonomers. Polymer latexes produced in CO_2 eliminate volatile organic compound (VOC) emissions and can significantly reduce the energy-intensive drying process since CO_2 has a heat of vaporization which is low in the liquid state and zero in the supercritical state. Furthermore, polymer can be shipped dry as 100% solids and later be redispersed to save energy and money in shipping rather than shipping a heavy water latex.

Initial studies illustrated the dispersion polymerization of methyl methacrylate (MMA) using PFOA as the stabilizer [22,23]. The next study of MMA dispersion polymerizations focused on the use of another class of surfactants, based on poly(dimethyl siloxane) (PDMS), which are less expensive than fluoropolymer-based surfactants [24]. Initial attempts of styrene dispersion polymerizations in CO_2 with PFOA and PDMS homopolymer stabilizers gave low yields and latex instability, but the block copolymers PS-*b*-PFOA and PS-*b*-PDMS produced submicron-sized PS particles [25,26]. Block copolymer surfactants containing poly(vinyl acetate) (PVAc), PVAc-*b*-PDMS and PVAc-*b*-PFOA, were effective stabilizers for dispersion polymerizations of vinyl acetate and copolymerizations of vinyl acetate and ethylene [27]. These dispersion polymerizations are summarized more extensively in a recent review with other examples [1].

Recently, PFOA and its methacrylate analog PFOMA were found to be effective stabilizers for PS at higher CO_2 pressures (370 bar) [28] while PFOA was ineffective at lower pressures of 204 bar [25]. Random copolymers, PS-*co*-PFOMA and PS-*co*-TMSOSPMA (3-[tris(trimethylsilyloxy)silyl]propyl methacrylate), are also effective stabilizers, producing micron-sized PS particles [29]. Such random copolymer surfactants, which can be prepared by a free-radical polymerization, are easier to synthesize than block copolymer surfactants, which must be prepared by "controlled" radical polymerization or living anionic polymerization. Recently, several other monomers have been polymerized by dispersion polymerizations, including 1-vinyl-2-pyrrolidone [30], acrylonitrile [31], hydroxyethyl methacrylate [32], and glycidyl methacrylate [33]. These examples extend the dispersion polymerizations into water-soluble, polar polymers and functionalized polymers.

A new concept for the preparation of water-dispersible polymer particles in CO_2 has been developed by Johnston [34]. PMMA was synthesized in CO_2 using an "ambidextrous" surfactant. The surfactant contains a water-soluble polymer block that anchors to the particle in CO_2 but becomes the electrostatic stabilizer in water and a PDMS block that is the steric stabilizer in CO_2 but collapses and anchors to the particle in water. The PDMS-*b*-poly(methacrylic acid) surfactant was less effective during the dispersion polymerization of MMA in CO_2, but up to 10 wt% of the PMMA particles formed could be redispersed in water at pH 8 or 11. The other surfactant, PDMS-*g*-poly(pyrrolidonecarboxylic acid) was more effective during the dispersion polymerization, but the PMMA particles formed could not be redispersed in water.

A recent report demonstrates the synthesis of highly cross-linked polymer particles in supercritical CO_2 [35]. Even in the absence of a stabilizer, the polymerization of divinylbenzene and ethylvinylbenzene produced polymer particles 1–5 μm in diameter. Addition of a block copolymer containing PMMA and a fluorinated polymethacrylate produced submicron-sized, monodisperse particles. Two other cross-linking monomers, ethylene glycol dimethacrylate (EGDM) and trimethylolpropane trimethacrylate (TRM) formed agglomerates of particles when polymerized in the absence of a stabilizer. At higher EGDM and TRM monomer concentrations (40–60%), continuous macroporous polymer monoliths were produced and pore diameters could be varied from 7880 to 20 nm by varying the monomer concentration and CO_2 pressure [36].

The chain-growth polymerizations discussed so far in this paper have been free-radical polymerizations, typically initiated by AIBN. Using "controlled" free-radical polymerization techniques, such as atom transfer radical polymerization (ATRP), it is possible to obtain polymer chains with a very narrow molecular weight distribution and to synthesize block copolymers. Using Cu(0), CuCl, a functionalized bipyridine ligand, and an alkyl halide initiator, the block copolymers containing PMMA or PDMAEMA (DMAEMA = 2-(dimethylamino)ethyl methacrylate) were synthesized in CO_2 [37]. Also in this report the dispersion polymerization in CO_2 of MMA with PFOA as the stabilizer was conducted by ATRP. The resulting PMMA had a relatively narrow molecular weight distribution ($M_w/M_n = 1.4$) in comparison to the same dispersion polymerization initiated by AIBN ($M_w/M_n = 2$-3) [23].

Step-growth polymers

The recent advances in step-growth polymerizations in CO_2 have focused on poly(bisphenol A carbonate). One of the two primary industrial methods for polycarbonate synthesis uses methylene chloride, which is environmentally unfriendly, and phosgene, which is highly toxic. The other method, melt-phase polymerization, uses no solvent, but is limited by the high polymer melt viscosities and the high temperatures necessary for polymerization and processing. The presence of CO_2 in a melt polymerization plasticizes the polymer and reduces the viscosity, so the condensate can be removed more easily and higher molecular weight polymer can be achieved. The condensate, phenol, is soluble in sc CO_2 and can be efficiently extracted from the polymer by supercritical fluid extraction. Low-molecular-weight polycarbonate was shown to swell up to 55% at 235 °C, 350 bar [38]. Also, in this study, bisphenol A and diphenyl carbonate were polymerized to produce molecular weights up to 13 kg/mol. Under each reaction conditions, higher molecular weights were achieved by sc CO_2 extraction as opposed to phenol removal by argon.

Solid-state polymerization of polycarbonate has also been studied using sc CO_2 to crystallize the polymer and to remove the phenol condensate [39,40]. In a solid-state polymerization, low-molecular-weight, semi-crystalline step-growth polymer beads are heated between the polymer Tg and Tm to allow for condensate and chain mobility for further chain extension reactions. Following the crystallization of beads of low-molecular-weight polycarbonate prepolymer by sc CO_2, solid-state polymerizations were conducted. The polymerization rates in the solid state were found to be always greater with condensate removal facilitated by sc CO_2 as opposed to nitrogen under comparable conditions. Also, since the Tg of polycarbonate is decreased by over 70 °C in the presence of sc CO_2, the polymerization can be run at much lower temperatures, saving energy and suppressing the side reactions that lead to unwanted polymer discoloration.

CHARACTERIZATION

In order to study polymers and polymerization mechanisms in sc CO_2, analytical techniques have been modified for high pressure. Methods including IR, UV-vis, and NMR spectroscopies and scattering techniques are now possible at high pressures. This paper will focus on scattering techniques, including small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), and light scattering.

Both SANS and SAXS are powerful tools for determining the polymer radius of gyration, the second virial coefficient, A_2, which indicates the solvent quality for the polymer, and block copolymer micelle formation. SANS studies have shown that CO_2 is a good solvent for PFOA, a theta solvent for poly(hexafluoropropylene oxide), and a poor solvent for PDMS [41,42]. More recently, SANS research has shown a temperature- and pressure-induced theta point for PDMS in CO_2 [43]. At conditions above the theta point, CO_2 becomes a good solvent for PDMS. The aggregation behavior of three different amphiphiles in CO_2 was studied by SAXS [44]. The graft copolymer with a PFOA backbone and poly(ethylene oxide) (PEO) grafts formed micelles which stabilized water in CO_2, while the PTFE-*b*-PEO copolymer formed reverse micelles, and $F(CF_2)_{10}(CH_2)_{10}H$ formed small aggregates of at most

four chains. The block copolymer PS-*b*-PFOA forms micelles in CO_2 with a PS core and a PFOA shell and the data fits a polydisperse spherical core-shell model [45,46]. With an increase in CO_2 density, the change in polydispersity suggests the existence of a critical micelle density, or a density of CO_2 above which the micelles are broken up into soluble unimers.

High pressure static and dynamic light scattering were used to confirm the existence of a critical micelle density for block copolymers of PVAc and poly(1,1,2,2-tetrahydroperfluoroalkyl acrylate) (PTAN) [47]. The block copolymer is insoluble at low CO_2 densities, forms spherical micelles at intermediate densities, and exists as unimers, or free polymer chains in solution, at high CO_2 densities. The transition of micelles-to-unimers was found to be very sharp, with the aggregation number decreasing from 120 to 1 with an increase in density.

The *in situ* analysis of dispersion polymerizations in CO_2 has provided insight into the mechanism of the polymerizations. Turbidimetry, tensiometry, and dynamic light scattering confirmed that the critical flocculation density occurred at the theta point of the surfactant for poly(2-ethylhexyl acrylate) dispersed and sterically stabilized in CO_2 [48,49]. Turbidimetry was also used to study the dispersion polymerizations of vinyl acetate [27]. This *in situ* technique for measuring the polymer particle size is particularly useful since the PVAc particle shape is lost during the removal of CO_2 due to the low Tg of the polymer. The dispersion polymerization of MMA stabilized by PDMS-monomethacrylate has also been the subject of mechanistic investigations [50,51]. The particle formation mechanism, studied by turbidimetry, involved coagulative nucleation and controlled coagulation [51]. The results obtained during the particle formation and particle growth stages agreed with the previous experimental study of Shaffer *et al*. [24].

APPLICATIONS AND OUTLOOK

With the design of specific polymers as surfactants for CO_2, numerous environmentally benign applications for this clean, green solvent can be realized, of which extractions, cleaning, and coatings are just a few examples. For extractions and cleaning, the surfactant acts as a detergent to bring the insoluble species or contaminant into the CO_2 phase. Depressurization of the CO_2 or changing the CO_2 density will cause the contaminant to be released from the surfactant. For example, a block copolymer was used to extract deuterated oligomers into CO_2 [45], and a dendrimer was used to extract a water soluble, CO_2-insoluble dye from the water phase into the CO_2 phase [52]. Detergents for CO_2 can be used for cleaning applications, such as "dry cleaning" using liquid CO_2 as the solvent instead of the common perchloroethylene, a probable human carcinogen [53]. In coating, the polymer to be delivered from the CO_2 can be soluble, such as a fluoropolymer, or an insoluble dispersed species. The application of coatings from CO_2 has been demonstrated by three different methods, including spray, spin, and free-meniscus coating, and extends CO_2 into areas such as microlithography, hard disk lubrication, and protective coatings [54]. Clearly, CO_2 can be used widely as an environmentally benign solvent for polymer synthesis and for numerous polymer-based applications.

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