Polymer synthesis and characterization in liquid / supercritical carbon dioxide

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The use of carbon dioxide as an inert solvent has emerged recently as an important development in polymer chemistry. The past year has seen major advances in the synthesis of a variety of polymeric materials in carbon dioxide. At the same time complementary studies have successfully elucidated the physical behavior of a range of polymers in carbon dioxide solution. Herein we review both synthetic and physical studies that are defining the scope of this approach.

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Abbreviations

scCO₂ SCF ₽.	supercritical carbon dioxide supercritical fluid critical pressure
PFOA	poly (1,1-dihyroperfluorooctylacrylate)
PMMA	poly (methyl methacrylate)
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering
Tc	critical temperature
TFE	tetrafluoroethylene
VOCs	volatile organic compounds

Introduction

Until recently, most solution polymerizations have been carried out in traditional organic solvents or in aqueous media. Concern over the emission of volatile organic compounds (VOCs) and polluted aqueous waste streams into the environment has prompted many researchers to look for less harmful solvent alternatives. Carbon dioxide has intrinsic environmental advantages; it is nontoxic, nonflammable, and can be easily separated and recycled. Furthermore, CO_2 is widely available and inexpensive which suggests potential for large scale industrial use.

Carbon dioxide only acts as a good solvent under relatively high pressures in the liquid or supercritical state [1]. A supercritical fluid (SCF) is defined as a substance which is above its critical temperature (T_c) and critical pressure (P_c) . Under these conditions the substance does not behave as a typical gas or liquid but exhibits hybrid properties of these two states. Like gases, SCF solvents have low viscosities and are highly compressible. It is therefore possible to tune the density of a SCF isothermally, simply by raising or lowering the pressure. Since the density of CO_2 varies with pressure from vapor-like to liquid-like, one can control solvent properties such as density, viscosity and dielectric constant over a considerable range. From a practical standpoint, CO_2 has rather modest supercritical parameters (T_c =31.1°C, P_c =73.8 bar) and supercritical conditions are therefore quite easily obtained. (For an excellent general introduction to the properties and applications of supercritical fluids, see [1]).

This review deals with the most recent advances in polymer synthesis in CO_2 before focusing on physical studies of the behavior of polymeric materials in $scCO_2$ solution. It should be noted that the use of $scCO_2$ for the processing of polymers is also an important area of research that lies beyond this discussion [1].

Homogeneous polymerizations in carbon dioxide

Whilst CO_2 is a good solvent for many small molecules (e.g. monomers) [1], only two classes of polymer have shown significant solubility in CO_2 under practical conditions; amorphous (and low melting) fluoropolymers and polysiloxanes [1-4]. Polymers with an affinity for CO_2 have been termed ' CO_2 -philic' [5].

The first homogeneous polymerization using scCO₂ as an inert reaction medium was reported by DeSimone, Guan and Eisbernd in 1992 and involved the free-radical polymerization of a semifluorinated acrylate [2]. More recently, the same group has described the free-radical telomerization of tetrafluoroethylene (TFE) in scCO₂ by means of a perfluoroalkyl iodide telogen [6]. At the temperatures used this reaction was homogeneous at low monomer to telogen ratios, but showed precipitation as the ratio (and therefore product molecular weight) was increased. Telomerizations were initiated by both free radical and thermal methods giving high yields of telomers (75-90%). In all cases, the separation of the polymer from homogeneous CO₂ solution was quite simple. Upon venting CO₂ from the reaction vessel, the polymer precipitated from solution leaving a dry, solvent-free product. To date, however, the number of homogeneous polymerization reactions in CO₂ is still relatively small (Table 1).

Heterogeneous polymerizations in carbon dioxide

Lipophilic and hydrophilic polymers tend not to be soluble in CO_2 and these polymers have been described as ' CO_2 -phobic'. Nevertheless, heterogeneous polymerizations of CO_2 -soluble hydrophilic and lipophilic monomers

Table 1

Summary of selected polymerization reactions in liquid / supercritical CO₂

Monomer	Phase*	Temp(*C) 68-180	Press (bar) 165-345	<m<sub>n>(kg/mol) 0.6-900‡</m<sub>	PDI†	Yield (%) 13-90	References [6,7•,23•,24]
CF ₂ =CF ₂ (MMA)							
$CF_2 = CFO(CF_2)_2CF_3$ (PPVE)/TFE	Р	35	90-110	>1000#	n/a	99-100	[10**]
CF2=CF(CF3) (HFP)/TFE	Р	35	50-100	>1000¶	n/a	3-82	[10••]
$CH_{2} = CF_{2} (VF_{2})^{g}$	н	60	280-340	~0.64	1.05	32-35	[26]
$CH_2 = CH - C(O)O - CH_2(CF_2)_6 CF_3$ (FOA)	н	60	207	11-1600**	n/a	65	[2.5.7•]
CH ₂ =CH-Ph (styrene)	D/P ^{††}	65	204-345	3.8-84.3	1.4-5.3	12-98	[9,15•,16]
$CH_2 = CH(CH_3)C(O)O - CH_3$ (MMA)	D/P ^{††}	30-65	69-345	65-390	2.1-5.3	10-98	[7*,13,14**,18**]
(CH ₃) ₃ C=CH ₂ (isobutylene)	Р	32.5-36	75-135	0.5-2.5	1.5-3.4	5-35	[21]
CH ₂ =CH-CO ₂ H (acrylic acid)	Р	62	125-345	2.9-153	1.3-3.9	>90	[8]
CH ₂ =CH-C(O)-NH ₂ (acrylamide)	E	60	340	4900–7000‡‡	n/a	91.4-99.8	[7•,22]
Norbornene	Р	65	68-345	15-511	2.0-4.5	6-75 ^{§§}	[7•,19•]
Cyclic/vinyl ethers	H/P##	-10-60	290-345	7-152	1.2-9.4	43-91	[7•,20•]
2,6-Dimethylphenylene oxide	P/D¶¶	25-40	345	0.9-17.2	1.6-5.8	16-86	[17]

*Phase behavior during polymerization: H=homogeneous, P=precipitation, D=dispersion, E=emulsion. [†]Polydispersity index of molecular weight distribution. [‡]Reaction conducted as both telomerization and polymerization. [§]PDI refers to telomerization reaction [6]. [#]Incorporation of PPVE in copolymer=2.9-8.6 wt. %. [§]Incorporation of HFP in copolymer=11.2-13.8 wt.%. [§]Telomerization reaction. **Molecular weights have been determined by both gel permeation chromatography (GPC) [13**] and small angle neutron scattering (SANS) [43**]. ^{††}A dispersion is only observed in the presence of a stabilizer. ^{†‡}Viscosity average molecular weight (M_v) is reported. ^{§§}Methanol used as a cosolvent in some reactions. ^{##Only} fluorinated systems were found to be homogeneous. [§]Some evidence for dispersion in presence of stabilizer, at least in early stages of reaction.

in liquid or supercritical CO_2 have proved very successful in the past few years [7^{\circ}] (Table 1).

In the absence of a stabilizing or solubilizing agent, CO₂-phobic polymers will precipitate rapidly from CO₂ solution as they are formed. The polymerizations of acrylic acid [8], styrene [9] and the copolymerization of tetrafluoroethylene [10**] in $scCO_2$ are good recent examples. The latter process provides a convenient route to commercially important, melt-processable fluoropolymers. In certain systems such as these, particularly where the polymer is insoluble in its corresponding monomer, precipitation polymerizations can be quite efficient and can give high molar mass products in good to excellent yields [8,10**]. However, for amorphous polymers precipitation often leads to undefined morphologies and, in many cases, low degrees of polymerization [11]. The use of CO₂-soluble amphiphilic stabilizers, as pioneered by DeSimone and coworkers, has proved to be an effective way to overcome these problems and to extend the range of CO₂-based polymerization reactions [12,13**]. Carbon dioxide has been employed for a variety of dispersion polymerizations, in which monomer and initiator are soluble whilst the resulting lipophilic polymer is insoluble in the CO₂ continuous phase. High degrees of polymerization are observed because the insoluble polymer is stabilized sterically as a colloid and does not precipitate (Fig. 1a). Stabilization effects will depend strongly on the precise chemical structure of the polymeric stabilizer (Fig. 1b). The free radical initiated dispersion polymerizations of methyl methacrylate [13,14.] and styrene [15.,16] have demonstrated that it is possible to synthesize polymers in CO₂ with well defined particle morphologies (Fig. 1c). In these cases it is often possible to isolate the polymer as a dry, free flowing powder. It has also been shown that amphiphilic stabilizers increase both yield and molecular weight in the oxidative coupling polymerization

of 2,6-dimethylphenylene oxide, even when the polymer was observed to precipitate from solution [17].

Less expensive siloxane-based alternatives have been used as stabilizers for the dispersion polymerization of methyl methacrylate in CO₂ [18^{••}]. In this case the stabilization mechanism is rather different; small amounts of a CO₂-soluble poly(dimethylsiloxane) macromonomer are grafted chemically onto the growing poly(methyl methacrylate) (PMMA) chains, thus preventing coalescence and precipitation. High molecular weights and yields of PMMA were obtained (120–380 kg mol⁻¹, 50–90%) in the presence of siloxane stabilizer and the resulting polymer existed as well defined spherical particles, with diameters ranging from 1.1–5.8 μ m depending on the reaction conditions. In the absence of stabilizer, a tacky polymer was formed in low yield (24%) and with much lower molecular weight (65 kg mol⁻¹).

Other examples of heterogeneous polymerizations in CO_2 include the ring opening metathesis polymerization of norbornene [19•], the cationic polymerization of cyclic and vinyl ethers [20•] and the carbocationic polymerization of isobutylene [21]. There are fewer examples of the synthesis of hydrophilic polymers in CO_2 . Adamsky and Beckman have reported the inverse emulsion polymerization of acrylamide in $scCO_2$ /water mixtures [22]. It appears that a latex is formed in the presence of fluorinated surfactants, but the precise stabilization mechanism is still somewhat unclear. In fact, very high yields were obtained in all cases, regardless of surfactant concentration.

In the future, the use of CO_2 in conjunction with a second immiscible solvent phase could become very important. The free radical polymerization of TFE has been carried out in hybrid mixtures of CO_2 and water, giving high molecular weight products (Fig. 2) [23•,24].



Mechanism of a dispersion polymerization in $scCO_2$. (a) Schematic representation of a polymer particle stabilized by PFOA in $scCO_2$. The extension of the PFOA chain into the CO_2 continuous phase prevents coalescence and precipitation [7*,13**]. (b) Structure of the stabilizer PFOA. The lipophilic backbone anchors the fluorocarbon steric stabilizing moieties to the growing polymer particle. (Adapted from [7*].) (c) Scanning electron micrograph (SEM) of poly(methyl methacrylate) (PMMA) particles synthesized in $scCO_2$ with PFOA (0.48 wt.%) as a steric stabilizer. Particle diameters=1.5-3 μ m. (Note the 2 μ m scale bar in the SEM.)

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Figure 2



Free radical polymerization of TFE. (a) The polymerization of TFE in a hybrid CO_2 /water mixture [23••]. (b) Scheme illustrating the continuum of possible CO_2 : water compositions. Each composition will give rise to a unique environment for polymerization. The design of effective surfactants/phase transfer catalysts will be vital to tailor these solvent systems to particular needs.

This novel system has the advantage that CO_2 and water have low mutual solubilities and the resulting biphasic solvent system allows compartmentalization of monomer, polymer and initiator based on their respective solubility characteristics. In this case, the use of CO_2 as a continuous phase gives an added safety advantage. TFE forms explosive mixtures with air and can also disproportionate violently under anaerobic conditions, however mixtures of CO_2 and TFE can form a "psuedoazeotrope" which may be handled more safely. Further examples of the homogeneous or heterogeneous polymerization of fluorinated monomers suggest that CO_2 could become an important general solvent for fluoropolymer synthesis $[10^{\circ\circ}, 20^{\circ}, 25, 26]$.

It is well known that CO_2 can plasticize and swell many polymeric materials [1,27–29]. Indeed, this is an intrinsic advantage in the heterogeneous polymerizations mentioned above; CO_2 swells the growing polymer particle and allows diffusion of monomer into the particle interior. Researchers have exploited this effect further by forming novel composite materials, in which a second monomer is polymerized inside a CO_2 -swollen polymer host [30,31•,32] (Fig. 3). In addition to plasticizing the polymer and facilitating diffusion of reactants, CO_2 diffuses rapidly from the polymer matrix upon depressurization thus leaving no solvent residues [33,34,35].

In all cases discussed so far, CO_2 has acted as an inert medium towards polymerization. However, there is much large literature which has showed that CO_2 can be used as a comonomer, particularly with epoxides to form aliphatic polycarbonates. As yet, there are only preliminary reports of the use of $scCO_2$ as both monomer and solvent in a copolymerization process [36•], although this is likely to be an attractive area for future research since CO_2 is a very inexpensive C_1 feedstock.





Schematic illustration of the formation of a polymer blend in a $scCO_2$ -swollen polymer host [30,31,32]. (a) The polymer host (P) is placed in a solution of a second monomer (M) and an initiator (I) in $scCO_2$. (b) Monomer and initiator diffuse into polymer substrate at a temperature where polymerization does not occur. (c) Temperature is raised to polymerize the impregnated monomer, either in the presence or absence of CO_2 as a swelling agent. A phase segregated polymer blend (PB) is formed.

It should be noted that the synthesis of polymers in liquid and supercritical CO_2 has also been reviewed in greater detail elsewhere [37].

Behavior and characterization of polymers in carbon dioxide

Until now, advances in CO₂-based polymer synthesis have tended to outpace discoveries concerning the underlying physical chemistry of these systems. However, this trend appears to be changing as researchers explore new methods to probe the behavior of polymers in supercritical solution.

An understanding of the factors which influence polymer solubility in CO₂ is of key importance for the design of new synthetic methods [3,4]. It has been suggested that the anomalously high solubility of fluoropolymers in CO₂ may result in part from a solute-solvent interaction between the quadrupole moment of CO₂ and multipoles along the CF₂ polymer chain. Fourier transform infrared (FT-IR) studies of fluorinated alcohols in scCO₂ produced no direct evidence for any such specific interaction [38]. More recent work has employed high pressure, high resolution NMR (HPHR-NMR) to investigate the interaction of poly(1,1-dihydroperfluorooctylacrylate) (PFOA) with CO_2 in homogeneous $scCO_2$ solution [39•] (see Fig. 1b for PFOA structure). The ¹H and ¹⁹F chemical shifts for PFOA showed qualitatively different trends when the CO_2 density was varied at constant temperature. The variation in ¹H chemical shift as a function of CO₂ density for a particular proton was determined soley by the bulk magnetic susceptibility of the CO₂ continuous phase and was independent of the position of the proton on the polymer chain. By contrast, the variation in the ¹⁹F chemical shift for a fluorine nucleus showed distinct deviations which depended strongly on the location of the fluorine nucleus. This may suggest a specific solvent-solute interaction for the fluorinated segment which is not uniform along the segment.

Spectroscopic studies of PMMA films subjected to high pressures of CO_2 have provided important evidence for a specific intermolecular Lewis acid-base type interaction between CO_2 and the carbonyl groups of PMMA [40••,41]. Similar interactions were observed in other polymer films with basic functional groups [40••]. Although these particular polymers were not actually soluble in scCO₂, it is reasonable to expect interactions of this type to occur with CO_2 -soluble polymers containing closely related functional groups (e.g. PFOA). If this is true, the development of methods to quantify the energy of these interactions could be of considerable importance in the future.

In order to design more effective surfactants and stabilizers for use in CO₂, it is vital that we can understand and, ideally, predict their behavior in supercritical solution. Recently much progress has stemmed from the use of small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) techniques. In collaboration with the Pacific Northwest Laboratory and Oak Ridge National Laboratory, DeSimone and his coworkers have used SAXS and SANS to investigate the aggregation behavior of amphiphilic molecules in scCO₂. Three types of aggregation behavior were observed from SAXS measurements [42**]. A graft copolymer consisting of a CO₂-philic, fluorinated backbone and CO₂-phobic, poly(ethylene oxide) grafts (PFOA-g-PEO) was found to associate into micellar structures in the presence of water to promote hydrogen bonding in the micelle core (Fig. 4). A commercially available surfactant (F(CF₂)₆₋₁₀CH₂CH₂O(CH₂CH₂O)₃H) formed classic reverse micelle structures with a radius of about 84 Å. By contrast, a semifluorinated diblock molecule $(F(CF_2)_{10}(CH_2)_{10}H)$ showed little tendency to aggregate at the temperatures and pressures studied. SANS studies on the CO₂-soluble polymer PFOA determined both molecular weights and important solution parameters (i.e. radii of gyration and second virial coefficients) [43.]. In particular, it was shown that the second virial coefficient was positive and that there was no evidence for a collapsed chain conformation, confirming that CO_2 is a good solvent for this polymer. Another approach has been developed by Johnston and coworkers who have used tensiometric methods to establish the effect of surfactants (including PFOA) on the interfacial tension between $scCO_2$ and poly(ethylene glycol) [44^o]. This method could prove extremely valuable for the evaluation of candidate surfactants, because the measured interfacial tension can be correlated with the surfactant activity.

The general insolubility of hydrophiles (e.g. biopolymers) in CO₂ is a major constraint on its use as a solvent and there has been considerable effort to develop surfactants which can form water-in-CO2 microemulsions [5,42.,45-47,48.]. Johnston, Harrison, Clarke, Howdle, Heitz et al. have demonstrated recently that an aqueous microemulsion is formed in scCO₂ in the presence of an ammonium carboxylate perfluoropolyether surfactant [49**] (Fig. 5). Several spectroscopic techniques were used to characterize the system and it was shown that the polarity of the water droplets approached those of bulk water. Importantly, the protein bovine serum albumin (MW = 67 kg mol^{-1}) was found to be soluble in the microemulsion. This is a very promising development and could lead to the manipulation of biological molecules in scCO₂, particularly if nontoxic surfactants can be found.

Conclusions and outlook

A growing body of work by various research groups has established that carbon dioxide is an important solvent for polymer chemistry. Environmental aspects aside, it also appears that CO_2 may be uniquely suited for certain applications and could open up new directions in polymer synthesis and processing. Most of the CO_2 -based polymerizations reported so far involve polymers which are already quite well understood; this is a logical place to begin when developing new methods. Also, polymer synthesis in CO_2 has attracted a great deal of industrial interest and the production of high volume commodity plastics is therefore of particular relevance. The discovery of inexpensive surfactants and stabilizers for use in CO_2 could help to promote industrial implementation of these techniques.

As this field of research grows and the understanding of general SCF properties increases, one can expect to see more novel polymeric materials being synthesized in carbon dioxide. We have already seen that the synthesis of polymer blends in CO_2 -swollen substrates can be achieved. An interesting extension of this would be to exploit the plasticization effects of $scCO_2$ in order to synthesize composite polymer materials with more rigidly defined structures. To do this, it would be crucial to have a clear understanding of the relative solubilities (or



Representation of a PFOA-g-PEO micelle in scCO₂ solution (total MW=100 kg mol⁻¹, graft MW=5 kg mol⁻¹). Small angle X-ray scattering measurements showed that the overall radius of these micelles was about 125 Å. A low size polydispersity was observed which suggests very uniform aggregates. Each micelle contained approximately 600 grafts in the aggregate core. Reproduced with permission from [42**].

Figure 5



FT-IR spectra demonstrating the emulsification of D_2O in CO_2 by use of a perfluoropolyether (PFPE) surfactant. (a) Spectrum of monomeric D_2O dissolved in CO_2 (2000 psi, 31°C) in the absence of surfactant; no emulsion is formed. (b) In the presence of the PFPE surfactant, a D_2O -in- CO_2 microemulsion is formed (2300 psi, 31°C, W=15, 1.4wt% PFPE surfactant). The IR spectrum shows a very broad absorption arising from bulk D_2O in the microemulsion. Small features in the spectrum correspond to residual monomeric D_2O (arrowed) and interfacial D_2O (dotted arrow) respectively.

perhaps the relative CO₂-phobicities) of the composite constituents.

It is hoped that this review has demonstrated that there is a strong link between the synthesis of polymers in carbon dioxide and the understanding of the fundamental parameters which describe the SCF solution. As synthetic projects become increasingly ambitious, the need for complementary physical data will remain vitally important.

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References and recommended reading

Papers of particular interest, published within the annual period of review, have been highlighted as:

- of special interest
- •• of outstanding interest
- 1. McHugh MA, Krukonis VJ: *Supercritical fluid extraction*, (edn 2nd), Butterworth-Heinemann, 1994.
- DeSimone JM, Guan Z, Eisbernd CS: Synthesis of fluoropolymers in supercritical carbon dioxide. *Science* 1992, 257:945-947.

- Tuminello WH, Dee GT, McHugh MA: Dissolving perfluoropolymers in supercritical carbon dioxide. Macromolecules 1995, 28:1506–1510.
- Rindfleisch F, DiNoia T, McHugh MA: Solubility of polymers and copolymers in supercritical CO₂: why high pressures and temperatures are needed. *Polym Mater Sci Eng* 1996, 74:178–179.
- Maury EE, Batten HJ, Killian SK, Menceloglu YZ, Combes JR, DeSimone JM: Graft copolymer surfactants for supercritical carbon dioxide applications. ACS Polym Prepr 1993, 34:664-665.
- Romack TJ, Combes JR, DeSimone JM: Free-radical telomerization of tetrafluoroethylene in supercritical carbon dioxide. Macromolecules 1995, 28:1724–1726.

 Shaffer KA, DeSimone JM: Chain polymerizations in inert nearand supercritical fluids. *Trends Polym Sci* 1995, 3:146–153.
 A useful review (47 references) with emphasis on research by DeSimone and coworkers in the period 1992–1995. Provides a good introduction to free radical, cationic and transition metal catalyzed polymerizations in CO₂.

- Romack TJ, Maury EE, DeSimone JM: Precipitation polymerization of acrylic acid in supercritical carbon dioxide. Macromolecules 1995, 28:912–914.
- Odell PG, Hamer GK: Living free radical polymerizations in supercritical carbon dioxide. *Polym Mater Sci Eng* 1996, 74:404-405.
- 10. Romack TJ, DeSimone JM, Treat TA: Synthesis of
- tetrafluoroethylene-based, nonaqueous fluoropolymers in supercritical carbon dioxide. Macromolecules 1995, 28:8429–8431.

This work gives much support to the claim that CO_2 may be a practicable solvent in the polymer industry for certain materials. Commercially important fluoropolymers were synthesized in high yield using scCO₂ as the continuous phase. FT-IR analysis showed that the concentration of undesirable acid fluoride end groups in the polymers was very low.

- Cooper AI, DeSimone JM: Synthesis of polyesters from diacid chlorides in carbon dioxide. *Polym Mater Sci Eng* 1996, 74:262–263.
- Guan Z, DeSimone JM: Fluorocarbon-based heterophase polymeric materials. 1. Block copolymer surfactants for carbon dioxide applications. *Macromolecules* 1994, 27:5527-5532.
- DeSimone JM, Maury EE, Menceloglu YZ, McClain JB, Romack TJ, Combes JR: Dispersion polymerizations in supercritical carbon dioxide. Science 1994, 265:356-359.
- Hsiao Y-L, Maury EE, DeSimone JM, Mawson S, Johnston KP:
 Dispersion polymerization of methyl methacrylate stabilized with poly(1,1-dihydroperfluorooctylacrylate) in supercritical carbon dioxide. *Macromolecules* 1995, 28:8159-8166.

The authors present detailed systematic studies on the effect of stabilizer concentration on the polymerization of methyl methacrylate, giving further insight into the stabilization of polymer dispersions in $scCO_2$. It is also shown that one can remove a significant amount of the polymeric stabilizer after polymerization by SCF extraction. Furthermore, cloud point measurements for the stabilizer in $scCO_2$ prove that lower critical solution temperature (LCST) phase behavior is exhibited. An excellent example of collaborative research in this area.

 Canelas DA, Betts DE, DeSimone JM: Dispersion polymerization of styrene in supercritical carbon dioxide: importance of effective surfactants. *Macromolecules* 1996, 29:2818-2821.

Partially fluorinated diblock copolymers are used as stabilizers for the dispersion polymerization of styrene in CO_2 . Poly(styrene) was formed as small spherical particles and it was found that the particle size distribution was affected by changes in the relative block lengths of the stabilizer. Systematic studies of this type will be invaluable for stabilizer design in the future.

 Canelas DA, Betts DE, DeSimone JM: Dispersion polymerizations stabilized by amphiphilic diblock copolymers in supercritical carbon dioxide. *Polym Mater Sci Eng* 1996, 74:400-401.

- Kappellen KK, Mistele CD, DeSimone JM: Synthesis of poly(2,6dimethylphenylene oxide) in carbon dioxide. Macromolecules 1996, 29:495–496.
- 18. Shaffer KA, Jones TA, Canelas DA, DeSimone JM: Dispersion •• polymerizations in carbon dioxide using siloxane-based

stabilizers. Macromolecules 1996, **29**:2704-2706. A new stabilization mechanism which takes advantage of less expensive siloxane stabilizers. The paper demonstrates the dramatic influence of stabilization on the outcome of the reaction. It is also shown that the dispersion polymerization can be carried out in liquid CO_2 at considerably lower pressures; this is a very important consideration when evaluating potential for industrial applications.

 Mistele CD, Thorp HH, DeSimone JM: Ring-opening metathesis
 polymerizations in carbon dioxide. J Macromol Sci - Pure Appl Chem 1996, A33:953-960.

One of relatively few papers which do not involve free radical polymerization. This work should also prove interesting to those involved with organometallic catalysis in SCFs. The authors report the effect of methanol cosolvent concentration on the microstructure of the resulting polymer.

 Clark MR, DeSimone JM: Cationic polymerization of vinyl

 and cyclic ethers in supercritical and liquid carbon dioxide. Macromolecules 1995, 28:3002–3004.

A good example of the compatibility of CO_2 with cationic polymerization mechanisms. Heterogeneous and homogeneous polymerizations were observed, depending on the nature of the particular monomer. Good polymer yields were reported in both cases.

- Permecker T, Kennedy JP: Carbocationic polymerizations in supercritical carbon dioxide. I. Exploratory experiments with isobutylene. *Polym Bull* 1994, 32:537–543.
- Adamsky FA, Beckman EJ: Inverse emulsion polymerization of acrylamide in supercritical carbon dioxide. Macromolecules 1994, 27:312–314. (See also correction in Macromolecules 1994, 27:5238).
- Romack TJ, Kipp BE, DeSimone JM: Polymerization of
 tetrafluoroethylene in a hybrid carbon dioxide / aqueous medium. Macromolecules 1995, 28:8432–8434.

Demonstrates how the use of $scCO_2$ may be extended to biphasic CO_2 /water systems. This approach could open up a range of new possibilities in polymer synthesis.

- Kipp BE, Romack TJ, DeSimone JM: Polymerizations of tetrafluoroethylene in hybrid CO₂ / aqueous systems. *Polym Mat Sci Eng* 1996, 74:264–265.
- Guan Z, Combes JR, Menceloglu YZ, DeSimone JM: Homogeneous free radical polymerizations in supercritical carbon dioxide: 2. Thermal decomposition of 2,2'azobis(isobutyronitrile). Macromolecules 1993, 26:2663-2669.
- Combes JR, Guan Z, DeSimone JM: Homogeneous freeradical polymerization in carbon dioxide. 3. Telomerization of 1,1-difluoroethylene in supercritical carbon dioxide. *Macromolecules* 1994, 27:865–867.
- Condo PD, Johnston KP: In situ measurement of the glass transition temperature of polymers with compressed diluents. J Polym Sci Part B Polym Phys 1994, 32:523-533.
- Briscoe BJ, Kelly CT: The plasticization of a polyurethane by carbon dioxide at high pneumatic stress. *Polymer* 1995, 36:3099–3102.
- Kwag C, Gerhardt LJ, Khan V, Gulari E, Manke CW: Plasticization of polymer melts with dense or supercritical carbon dioxide. *Polym Mater Sci Eng* 1996, 74:183–185.
- Watkins JJ, McCarthy TJ: Polymerization in supercritical fluid-swollen polymers: a new route to polymer blends. Macromolecules 1994, 27:4845–4847.
- Watkins JJ, McCarthy TJ: Polymerization of styrene in supercritical CO₂-swollen poly(chlorotrifluoroethylene). Macromolecules 1995, 28:4067–4074.

An interesting approach to the formation of polymer blends. This paper studies one system in considerable detail and concludes that styrene can be polymerized in a CO₂-swollen poly(chlorotrifluoroethylene) (PCTFE) host to give high molecular weight poly(styrene) (MW >100 kg/mol⁻¹) in discrete phase-segregated regions through the thickness of the PCTFE sample. The distribution of the blended polymer through the sample depended strongly on the impregnation conditions. There appeared to be little or no grafting onto the host polymer. In the absence of CO₂ as a swelling agent, only surface modifications were observed.

- Watkins JJ, McCarthy TJ: Chemistry in supercritical carbon dioxide – swollen polymers. *Polym Mater Sci Eng* 1996, 74:402-403.
- Howdle SM, Ramsay JM, Cooper Al: Spectroscopic analysis and in situ monitoring of impregnation and extraction of polymer films and powders using supercritical fluids. J Polym Sci Part B Polym Phys 1994, 32:541–549.
- Shieh Y-T, Su J-H, Manivannan G, Lee PHC, Sawan SP, Spall WD: Interaction of supercritical carbon dioxide with polymers. I. Crystalline polymers. J Appl Polym Sci 1996, 59:695-705.
- Shieh Y-T, Su J-H, Manivannan G, Lee PHC, Sawan SP, Spall WD: Interaction of supercritical carbon dioxide with polymers. II. Amorphous polymers. J Appl Polym Sci 1996, 59:707-717.
- 36. Costello CA, Berluche E, Han SJ, Sysyn DA, Super MS, Beckman
 EJ: Supercritical CO₂ as monomer and solvent: polycarbonates from cyclohexene oxide and carbon dioxide. Am Chem Soc Polym Mater Sci Eng 1996, 74:430.

Rather few details are included in this preliminary report but the approach is very appealing: the use of CO₂ as both solvent and reactant could have obvious economic/chemical advantages in polymer chemistry. The insolubility of polycarbonates in CO₂ is a problem which will need to be addressed in order to exploit this idea.

- Canelas DA, DeSimone JM: Polymerization in liquid and supercritical carbon dioxide. Adv Polym Sci 1996, in press.
- Yee GG, Fulton JL, Smith RD: Fourier infrared spectroscopy of molecular interactions of heptafluoro-1-butanol or 1-butanol in supercritical carbon dioxide and supercritical ethane. J Phys Chem 1992, 96:6172–6181.
- Bardin A, DeSimone JM, Samulski ET: High pressure NMR
 studies in liquid and supercritical CO₂. Am Chem Soc Polym Mater Sci Eng 1996, 74:258-259.

Important preliminary results; a promising approach which could help to explain the high solubility of fluorinated species in CO₂. An understanding of the specific contributions of individual fluorinated moieties would be useful in the design of surfactants.

 Kazarian SG, Vincent MF, Bright FV, Liotta CL, Eckert CA: Specific
 interaction of carbon dioxide with polymers. J Am Chem Soc 1996, 118:1729–1736.

The authors use attenuated total reflection IR spectroscopy (ATR) to observe the v_2 bending mode of CO_2 incorporated into various polymer films containing functional groups which can act as Lewis bases. A splitting in the v_2 mode was observed which the authors attributed to a loss of symmetry in CO_2 , arising from a Lewis acid-base interaction with these functional groups. This splitting was not observed in polymers which do not contain basic groups e.g. poly(ethylene), poly(styrene).

- Kazarian SG, Vincent MF, Eckert CA: Infrared cell for supercritical fluid - polymer interactions. *Rev Sci Instrumen* 1996, 67:1586–1589.
- Fulton JL, Pfund DM, McClain JB, Romack TJ, Maury EE, Combes
 JR, Samulski ET, DeSimone JM, Capel M: Aggregation of amphiphilic molecules in supercritical carbon dioxide: A small

angle X-ray scattering study. Langmuir 1995, 11:4241-4249. A very important demonstration of the effect of chemical structure on the aggregation behavior of amphiphiles in scCO₂. The SAXS technique can provide direct measurements of aggregate size and geometry.

- McClain JB, Londono D, Combes JR, Romack TJ, Canelas DA,
 Betts DE, Wignall GD, Samulski ET, DeSimone JM: Solution
- properties of a CO₂-soluble fluoropolymer via small angle neutron scattering. *J Am Chem Soc* 1996, 118:917–918. This paper shows how SANS studies can provide information which is highly

complementary to that given by SAXS [41**]. The scattering light density (SLD) for the fluoropolymer studied is significantly different from the SLD for

 $\rm CO_2$ over a range of densities. This contrast made it possible to 'see' the polymer in solution and to investigate its physical properties as a function of solvent strength in the compressible $\rm CO_2$ medium. SAXS and SANS studies are currently being applied to a variety of $\rm CO_2$ -soluble species and this work should lead to a much better understanding of solution properties and aggregation phenomena.

 Harrison KL, Johnston KP, Sanchez IC: Effect of surfactants on the Interfacial tension between supercritical carbon dioxide and polyethylene glycol. Langmuir 1996, 12:2637–2644.

The authors develop an interesting method which can be used to evaluate the interfacial activity of surfactants for CO_2 -based applications.

- Hoefling TA, Enick RM, Beckman EJ: Microemulsions in near-critical and supercritical CO₂. J Phys Chem 1991, 95:7127-7129.
- 46. Harrison K, Goveas J, Johnston KP, O'Rear EA: Water-in-carbon dioxide microemulsions with a fluorocarbon-hydrocarbon hybrid surfactant. *Langmuir* 1994, 10:3536–3541.

- McFann GJ, Johnston KP, Howdle SM: Solubilization of nonionic reverse micelles in carbon dioxide. AIChE J 1994, 40:543–555.
- 48. Bartscherer KA, Minier M, Renon H: Microemulsions in
- compressible fluids-A review. Fluid Phase Equilibria 1995, 107:93–150.

A comprehensive review (120 references) which describes the formation and characterization of microemulsions in $scCO_2$ and other compressed fluids. The review discusses the fundamental aspects of this topic and also goes into some detail about the potential scientific and industrial applications of the research.

 Johnston KP, Harrison KL, Clarke MJ, Howdle SM, Heitz MP,
 Bright FV, Carlier C, Randolph TW: Water-in-carbon dioxide microemulsions: An environment for hydrophiles including proteins. Science 1996, 271:624–626.

This article breaks new ground in the emulsification of water in CO_2 and demonstrates how it may be necessary to use several techniques to characterize these complex systems. Even greater amounts of emulsified water may be necessary to realise many practical applications and further research in this area will be essential.