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Synthesis of Fluoropolymers in Liquid and Supercritical Carbon Dioxide Solvent Systems

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13.1. INTRODUCTION

13.1.1. Alternative Solvent Technologies

Prompted by public and regulatory demand to reduce the emission of toxic compounds into the environment, solvent-intensive industries are actively seeking alternatives to traditionally employed organic and chlorinated solvents. Many sectors of industry have turned to aqueous systems, only to discover that the drawbacks associated with mixed aqueous waste disposal and energy-intensive drying offer little improvement over solvent-based systems. Carbon dioxide in liquid or supercritical form is a potential alternative for many of the industrial segments under fire. It is not regulated, it is nontoxic, inexpensive, readily available, and has the potential to be easily separated from other components in a waste stream, reducing the volume of mixed waste produced. As a result, carbon dioxide is actively being pursued as an alternative technology by many solvent- and waste-intensive industries—from precision and textile cleaning to chemical manufacture and polymer synthesis and processing. A detailed discussion of many of the important areas of interest is beyond the scope of this manuscript, but several reviews are available.¹⁻⁴

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13.1.2. Solvent Properties of Carbon Dioxide

A complete understanding of the solvent properties of dense CO₂ has been essential as an increasing emphasis has been placed on its use in a variety of manufacturing and processing applications, but to date these parameters are still somewhat undefined. A traditional view of solubility parameters ascribed to CO₂ based on widely held thermodynamic data would suggest that dense CO₂ has a solvent strength similar to that of toluene or hexane. However, a large contribution to the CO₂ solubility parameter emanates from its large quadrupole moment, similar to that of benzene.^{5,6} Although the large quadrupole moment plays an important role in the physical properties of CO₂ and perhaps in the solubility of many small molecules, its role in the solvation of nonvolatile materials such as siloxanes and amorphous fluoropolymers is not completely clear. Work is ongoing to clarify the role of the strong quadrupole moment in the dissolution of polymeric materials.⁷ It can generally be said that the solvent strength of dense CO₂ is a debatable issue and perhaps best determined through experimentation.⁸

Carbon dioxide in both its liquid and supercritical states is of interest in the synthesis and processing of polymeric materials. Historically, CO₂ has received much attention as a supercritical fluid, owing to its readily accessible critical point ($T_c = 31.8^\circ\text{C}$; $P_c = 73.8$ bars, ca. 1100 psi). By adjusting the pressure above the critical temperature, a range of physiochemical properties (e.g., density, dielectric constant, and viscosity) are achievable (Figure 13.1). Liquid CO₂ can be accessed below the critical temperature and is of great interest for many applications, including the manufacture of polymers, because it has most of the advantages of supercritical CO₂ (e.g., low viscosity and ease of separation from waste components) and can be accessed at greatly reduced pressures. The vapor

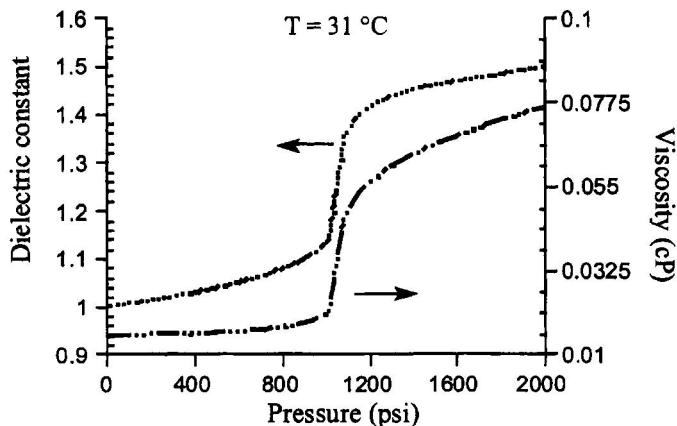


Figure 13.1. Solvent “tunability,” viscosity/dielectric versus CO₂ pressure.

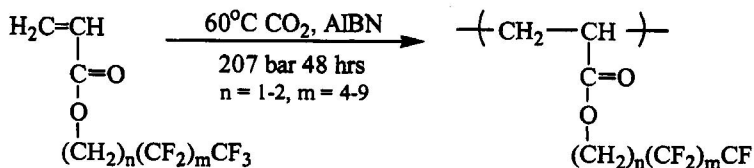
pressure of CO₂ at 0°C is less than 40 bars (\approx 600 psi), only five to ten times the pressure in an ordinary bicycle tire. To put this in context, low-density polyethylene is commonly manufactured on a commercial scale at pressures of over 2000 bars (ca. 30,000 psi).⁹ For liquid and supercritical CO₂ the dielectric constant is from 1.2 to 1.5, consistent with CO₂'s extremely nonpolar nature, and its viscosity ranges from gaslike to approaching that of a liquid solvent.¹⁰ Liquid and supercritical CO₂, under reasonable conditions (pressure \leq 500 bars, temperature \leq 100°C), are good media for low-molecular-weight, nonionic compounds, but poor solvents for most macromolecules.¹¹ The only high-molecular-weight materials that dissolve to a significant degree in CO₂ under readily accessible conditions are siloxanes and some amorphous fluoropolymers, as discussed below.

13.2. FLUOROALKYL ACRYLATE POLYMERIZATION IN CARBON DIOXIDE

13.2.1. Homopolymers

Historically the widespread use of liquid and supercritical CO₂ has been limited by the low solubility of most nonvolatile materials at reasonably low pressures. However, studies carried out over a decade ago established the solubility of oligometric perfluoropolyethers and poly(chlorotrifluoroethylene) in liquid CO₂,¹² and a few years later it was discovered that other highly fluorinated polymers such as fluorinated acrylates were also quite soluble in liquefied CO₂ at relatively low pressures.¹³

The first synthesis of amorphous fluoroacrylate polymers using supercritical CO₂ as an inert reaction medium was reported by DeSimone *et al.* in 1992 and involved the free-radical polymerization of 1,1-dihydroperfluorooctyl acrylate using AIBN initiator¹⁴ (Scheme 1). These studies showed that conditions commensurate with conventional solvent-based systems can be used to produce high conversions of high-molecular-weight materials in CO₂. It has been noted that for traditional types of homogeneous and heterogeneous polymerizations the elevation of pressure can affect free-radical polymerizations by: (1) increasing the concentration of gaseous monomers; (2) modifying rate constants for initiation, propagation, termination, and chain transfer; (3) changing the equilibrium constant for polymerization. The cumulative effect of higher pressure is generally increased reaction rates and larger molar masses.¹⁵ However, owing to the highly compressible nature of supercritical fluids, and the variation in solvent strength that occurs, particularly in the case of supercritical CO₂, the effect of pressure on reaction rate in these media is more complicated than in traditional liquid solvents.



Scheme 1. Free radical polymerization of fluorocarbon acrylates in supercritical CO₂.

Initiator decomposition studies of AIBN in supercritical CO₂ carried out by DeSimone *et al.* showed that there is kinetic deviation from the traditionally studied solvent systems.¹⁶ These studies indicated a measurable decrease in the thermal decomposition of AIBN in supercritical CO₂ over decomposition rates measured in benzene. Kirkwood correlation plots indicate that the slower rates in supercritical CO₂ emanate from the overall lower dielectric constant (ϵ) of CO₂ relative to that of benzene. Similar studies have shown an analogous trend in the decomposition kinetics of perfluoroalkyl acyl peroxides in liquid and supercritical CO₂.¹⁷ Rate decreases of as much as 30% have been seen compared to decomposition measured in 1,1,2-trichlorotrifluoroethane. These studies also served to show that while initiator decomposition is in general slower in supercritical CO₂, overall initiation is more efficient. UV–visual studies incorporating radical scavengers concluded that primary geminate radicals formed during thermal decomposition in supercritical CO₂ are not hindered to the same extent by “cage effects” as are those in traditional solvents such as benzene. This effect noted in AIBN decomposition in CO₂ is ascribed to the substantially lower viscosity of supercritical CO₂ compared to that of benzene.¹⁸

13.2.2. Random Copolymers

Statistical copolymers of fluorinated acrylic monomers with conventional hydrocarbon monomers such as butyl acrylate, methyl methacrylate, styrene, and ethylene, among others, have also been synthesized under homogeneous conditions in supercritical CO₂.¹⁹ The hydrocarbon homopolymers from these monomers, being completely insoluble in supercritical CO₂, differ from these copolymers as homogeneous conditions can be maintained even at high hydrocarbon incorporation levels and relatively low pressures (330 bars at 65°C). In some cases, depending on the hydrocarbon monomer, these conditions can be maintained at molar incorporations greater than 50%. The synthesis of amorphous fluoropolymers in CO₂ also offers the unique benefit associated with an inherently low-viscosity solvent, and thus avoids autoacceleration at high polymer conversions. Moreover, typical polydispersities of 1.5 indicate that termination by radical combination is predominant in these systems, as may be expected with a completely inert solvent. Integrated reaction and separation processes resulting

from the variable density and solvent strength of supercritical CO₂, not available with traditional solvent systems, provide an added benefit in these systems.

13.2.3. Applications of Amphiphilic Copolymers

The insolubility of hydrocarbon polymers in CO₂ has been a limiting factor for the application of CO₂ technologies in the production and processing of many polymeric materials. Heterogeneous polymerizations utilizing CO₂ without the use of efficient dispersants generally result in low yields of unsatisfactory materials having low molecular weight and high polydispersities. However, the development of amphiphilic copolymers, designed for CO₂ applications and predicated on the discovery that CO₂ is a good solvent for fluoroacrylate synthesis, has opened numerous doors for the use of this alternative technology in the production of a broad range of hydrocarbon polymers.²⁰⁻²² These materials, generally containing a “CO₂-philic” segment and a lyophobic segment, self-assemble in CO₂ into well-defined structures providing stable polymeric colloidal dispersions. A detailed discussion of this work is beyond the scope of this paper.

13.3. FLUOROOLEFIN POLYMERIZATION IN CARBON DIOXIDE

13.3.1. Overview

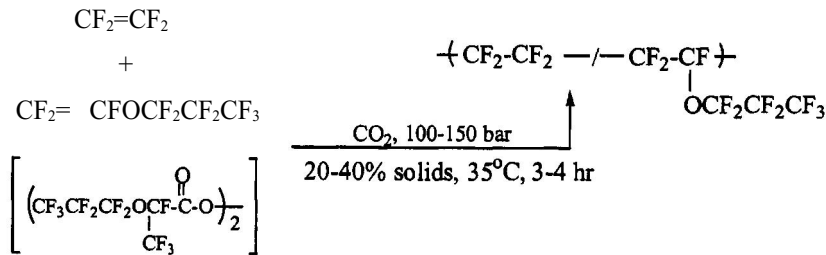
Tetrafluoroethylene (TFE)-based copolymers have become premium high-performance materials for a broad range of applications requiring superior chemical and thermal resistance, and melt-processing capability.²³ Materials embodied by copolymers of TFE with hexafluoropropylene (HFP), perfluoro(propyl vinyl ether) (PPVE), or sulfonyl fluoride functionalized perfluoro(alkyl vinyl ether) monomer (PSEVPE) have often been synthesized in nonaqueous solvent systems to avoid problems associated with traditional aqueous dispersion or emulsion polymerizations. Aqueous suspension or dispersion methods result in increased occurrence of carboxylic acid end groups that are deleterious to the products during melt-processing steps and to the function of the polymer. This is particularly true of the copolymers with perfluorovinyl ether comonomers that are generally used to modify the crystallinity of the fluoroplastic. Fluoropolymer materials containing significant levels of these acid end groups may require finishing steps such as high-temperature hydrolysis or fluorination. Processing without these steps can result in product decomposition, discoloration erratic changes in molecular weight, and the emission of hazardous and damaging hydrogen fluoride. To minimize the occurrence of these acid end groups as much as possible, copolymerizations employing perfluorinated vinyl ether mono-

mers have generally been carried out in chlorofluorocarbons (CFCs). Owing to the highly electrophilic nature of fluoroolefin radicals,²⁴ hydrocarbon solvents must be avoided in the polymerization process to obtain high-molar-mass materials. Otherwise, chain-transfer to the solvent becomes prevalent, limiting the molecular weight of the final polymer. Perfluorocarbon and hydrofluorocarbon solvents have been proposed as suitable alternatives for these polymerization²⁵⁻²⁷; however, these solvents are generally quite expensive.

At the forefront of the development of this technology has been the need to replace detrimental halogenated solvents with viable alternative technologies. Aside from the many advantages afforded by CO₂ over many traditional solvent systems, further advantages may exist in the storage of TFE with CO₂. Many associated dangers of working with TFE, such as disproportionation and auto-polymerization, can be avoided by storage with CO₂.²⁸ Currently to avoid these hazards, TFE is often stored as an azeotrope with hydrogen chloride.

13.3.2. Melt-Processable Fluoropolymers

The first reactions of fluorinated olefins in CO₂ reported by DeSimone *et al.* involved the free-radical telomerization of 1,1-difluoroethylene²⁹ and tetrafluoroethylene.³⁰ This work demonstrated the feasibility of carrying out free-radical reactions of highly electrophilic species in solvents other than expensive fluorocarbons and environmentally detrimental chlorofluorocarbons. The work has since been more broadly applied to the synthesis of tetrafluoroethylene-based, nonaqueous grades of fluoropolymers,^{31,32} such as poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) (Scheme 2). These reactions were typically carried out at between 20 and 40% solids in CO₂ at initial pressures of between 100 and 150 bars, and 30–35°C (Table 10.1).



Scheme 2. Copolymerization of TFE with PPVE in CO₂.

Several observations could be made from these copolymerizations. High yields of high-molecular-weight copolymer can readily be formed at incorporation levels well in excess of the 2–4wt% PPVE desired in commercial products. For reactions done in the CO₂ system, even at high vinyl ether incorporations, melt-

Table 13.1. Selected Data for TFE/PPVE Copolymerization in CO₂

TFE	PPVE	Yield (%)	PPVE (incorporation)	MV ^a (poise)	T _m
1.9	0.18	99	2.9%	*	321.5
2.2	0.55	100	8.9%	*	318.6
2.0	0.55	100	5.2%	*	312.7
2.2	0.92	100	5.8%	*	313.7
1.2	0.35	70	7.8%	**7.3(10 ⁴)	297.1

^a* too high to measure; **methanol added as chain-transfer agent.

flow properties are suppressed, suggesting that chain-transfer reactions and β -scission of the propagating vinyl ether-containing chains are substantially minimized in CO₂, leading to very high-molecular-weight materials. In fact, the addition of small amounts of chain-transfer agents was needed to produce lower-molecular-weight materials having the desired melt-flow properties. Quantitative IR analysis confirmed the substantially reduced occurrence of acid end groups. The extremely low number of unstable acid end groups observed in most samples prepared in CO₂ is unprecedented, detecting only zero to three end groups per 10⁶ carbon atoms. This an order of magnitude or so lower than for materials prepared in traditional solvents and comparable to materials that have been prepared in conventional nonaqueous systems and then subjected to high-temperature aggressive fluorination with F₂ or an alternative posttreatment process to remove unstable end groups. Scanning electron micrographs (SEM) (Figure 13.2) show little differentiation at 30,000 x magnification between resin synthesized in CO₂ versus that made in chlorofluorocarbon solvent.

13.3.3. Ion-Exchange Resins

Perfluorinated ion-exchange resins such as NafionTM, used in chloro alkali cells²³ and as solid acid catalyst^{33,34} are often manufactured in nonaqueous media to avoid loss of the expensive vinyl ether monomers from partitioning into the water phase and the susceptibility of these monomers to hydrolysis, as well as to aid in the avoidance of acid end group formation. The resulting copolymers are then fluorinated with F₂ and fabricated into membranes using melt-extrusion techniques. Membrane production is accomplished by lamination with polytetrafluoroethylene cloth for increased strength followed by conversion of the polymer to the acid or ionic form. The limiting synthetic parameter in the preparation of high-molecular-weight copolymers at high vinyl ether incorporation is chain-transfer stemming from β -scission of the vinyl ether macroradical. If undesirable side reactions are somehow suppressed through the implementation of a CO₂-

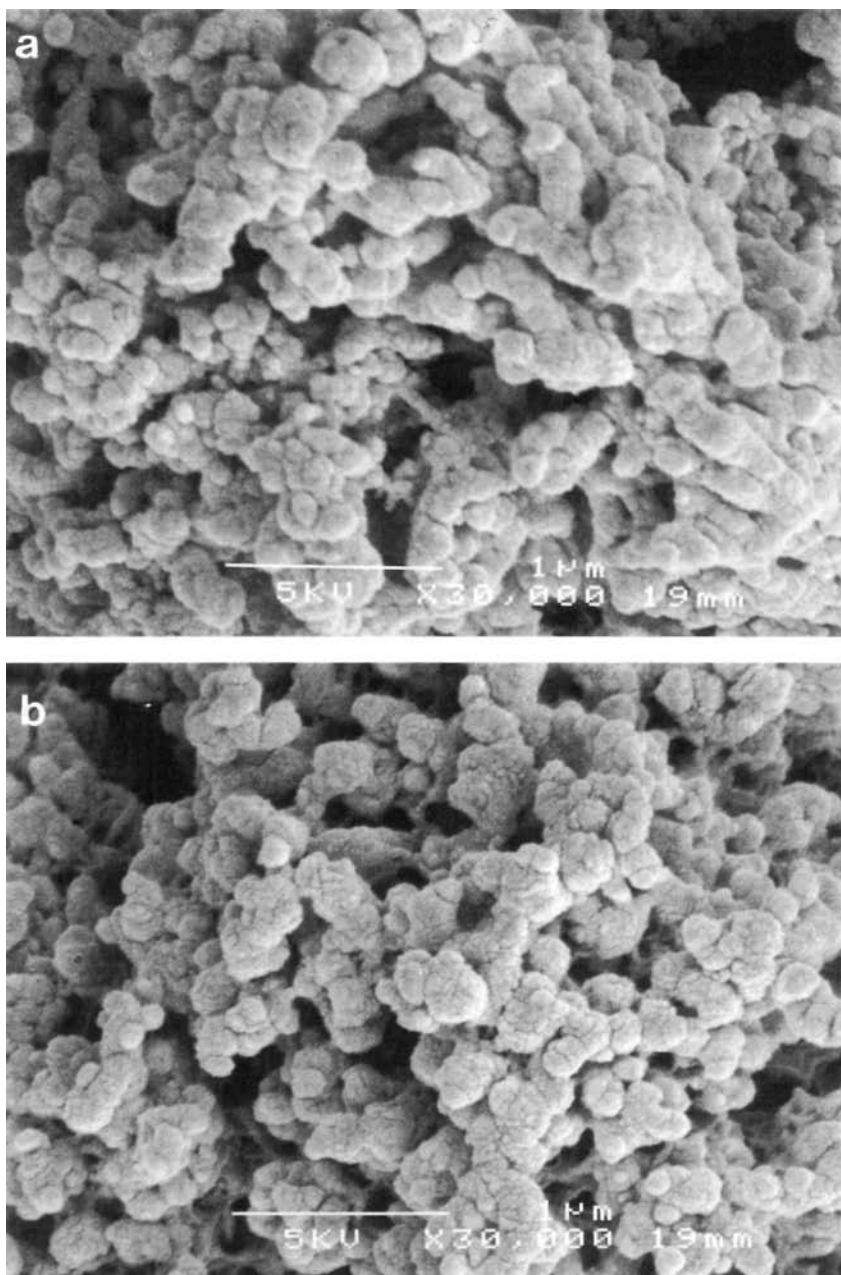


Figure 13.2. SEM of TFE/PPVE copolymer synthesized in (A) CO₂, and (B) chlorofluorocarbon.

based polymerization process, this process could open the door to a new generation of high-performance perfluorinated ion exchange membranes.

Carbon dioxide has also proven to be an exemplary medium for the polymerization of TFE with perfluorinated alkylvinyl ether monomers containing sulfonyl fluoride such as CF₂=CFOCF₂CF(CF₃)OCF₂CF₂SO₂F (PSEVPE). As seen in Table 13.2, the dramatic difference in the number of acid end groups between the commercial sample and those made in CO₂ indicates that chain-transfer processes stemming from vinyl ether radical arrangement are not nearly as prevalent in CO₂ as in conventional systems.

Another series of PSEPVE/TFE copolymerizations was carried out on a larger scale to allow assessment of relative molecular weights through melt-flow analysis and to allow screening of properties important in commercial applications. Reagent concentrations for these reactions are given in Table 13.3 along with equivalent weights, wt% comonomer incorporation, glass transition temperature (*T_g*), melt index, and end group analysis for each sample and for a commercially prepared example. A melt-flow index corresponds to how quickly the polymer flows under a constant pressure at high temperature (270°C). Typical commercial products exhibit a melt-flow index of 10–15. PSEPVE/TFE copolymers that were prepared in CO₂ had melt-flow indexes near the range of commercial products, as well as values corresponding to substantially higher molecular weight than commercial varieties (melt-flow index of 2.4). Samples 1, 2, and 3 in Table 13.4 were prepared targeting increasing molecular weight at similar levels of PSEPVE incorporation and conversion. This was accomplished by moving to higher percent solids (monomer) and lower initiator concentrations. The fact that a significant number of acid end groups are evidenced for two of the copolymers made in CO₂ (Samples 2 and 3) may be due to some oxygen contamination introduced while the reagents were being added. Reactions such as these run on a larger scale required the use of more than one TFE/CO₂ cylinder, necessitating the changing of cylinders during the monomer-charging step. The increasing numbers of acid end groups in the later series could also be

Table 13.2. Copolymerization of (SO₂F)-Functional Perfluorinated Alkyl Vinyl Ether Monomer with TFE

Equivalent weight	Incorporation (Wt%)	Acid end groups ^a
2280 g/eq	21%	1
1120 g/eq	40%	0
1070 g/eq	42%	0
975 g/eq	46%	0
975 g/eq ^b	46%	365

^aDetermined by high-resolution IR, parts per 10⁶ carbon atoms.

^bRepresentative high-incorporation commercial sample.

Table 13.3. Results and Product Analysis for TFE/PSEVPE Copolymerizations in CO₂

	Sample			
	1	2	3	Control
TFE	0.72	0.85	1.0	—
PSEPVE	1.3	1.5	1.8	—
Initiator	4.3 x 10 ⁻⁴	3.0 x 10 ⁻⁴	1.5 x 10 ⁻⁴	—
EN	975	930	999	975
T _g (°C) ^a	0.90	3.6	5.7	-2.8
wt% PSEPVE	46	48	45	46
Melt flow	20.7	16.8	2.4	10–15
End groups/10 ⁶ Carbons	0	177	145	365

^aAs determined by dynamic mechanical analysis (DMA).

due to the change in solvent characteristics brought on by the inclusion of larger amounts of PSEPVE and TFE monomers in the higher-solids runs. PSEPVE monomer comprised the bulk of the monomer charge and is a nonpolar fluorocarbon liquid that could act in a way similar to conventional solvents.

The plasticizing and dissolution characteristic^{5,6} of CO₂ toward fluoropolymers is further demonstrated by the swelling effect that it has on sulfonic acid derivatives of these perfluoroalkyl vinyl ether-containing polymers. The highly insoluble nature of these materials in most common organic solvents substantially inhibits the efficacy of these materials as solid acid catalysts. With small surface area, most potentially active catalytic sites remain buried in the resin, incapable of catalyzing reactions. However, the extremely acidic nature of these materials and their efficacy as solid acid catalysts has been demonstrated by Sun *et al.* in the application of the resins as sol gel products.³⁴ More recent work has demonstrated that the catalytic efficacy of perfluorinated resins containing sulfonic acid can also be improved through the use of supercritical CO₂ in catalytic reaction.³⁷ Kinetic

Table 13.4. Results for the Photooxidation of Hexafluoropropylene in Liquid CO₂^a

HFP (g)	Solvent (volume ml)	PFPE yield (%)	C ₃ F ₆ O/CF ₂ O ^b	M _n ^c (g/mol)
10	CO ₂ (8.9)	31	1.4	590
11	CO ₂ (6.9)	34	2	800
20	CO ₂ (6.8)	16	5.3	1300
17	None	29	10	2700

^aReactions in CO₂ carried out at -40°C.

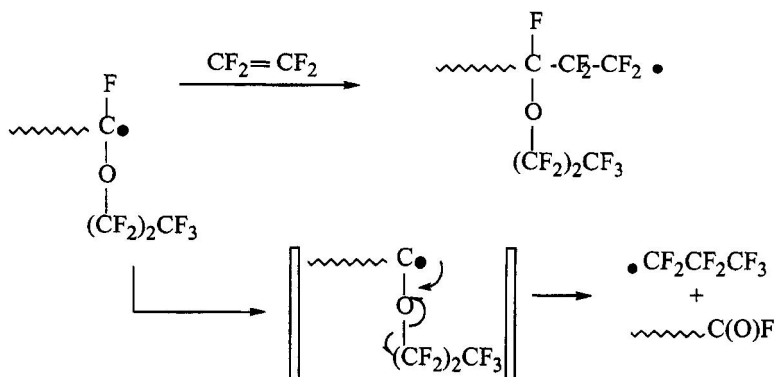
^bMolar ratio of hexafluoropropylene oxide repeat units to difluoromethylene repeat units determined from ¹⁹F-NMR.

^cEstimated from ¹⁹F-NMR

rate constants for the dimerization of α -methyl styrene have proven to be as much as an order of magnitude higher than rates measured in traditional solvents.

13.3.4. β -Scission and Acid End Groups

During polymerization, a polymeric radical with a perfluoro(alkyl vinyl ether)-derived active center can have one of two fates: it can cross-propagate to tetrafluoroethylene or it can undergo β -scission to yield an acid-fluoride-terminated polymer chain and generate a perfluoroalkyl radical capable of initiating further polymerization (i.e., chain transfer to monomer). These scenarios are illustrated in Scheme 3.



Scheme 3. Fate of the vinyl ether macroradical during copolymerizations.

The large reduction in the level of acid end groups occurring in copolymers of TFE and perfluoroalkyl vinyl ether monomers synthesized in CO₂ implies that propagation of terminal vinyl ether-containing radicals is overwhelmingly favored over β -scission, more so than in traditional solvent systems. There are a couple of possible explanations that could account for the difference between the two systems. The ability of CO₂ to plasticize polymeric materials and its excellent transport properties make it a very efficient tool for the conveyance of small molecules into even highly crystalline materials.^{38,39} It is therefore quite likely that the presence of CO₂ facilitates diffusion of TFE monomer into the precipitated polymer phase, increasing the effective bimolecular rates for cross-propagation. It is also plausible to assume that a completely nonpolar solvent such as CO₂, with a dielectric constant between 1.3 and 1.5, would be less able to stabilize the intermediate transition state leading to β -scission than would 1,1,2-trichlorotrifluoroethane. The fact that samples of PPVE/TFE copolymer made in perfluoro-*N*-methyl morpholine, a very nonpolar liquid solvent ($\epsilon \approx 2$), do not exhibit a

substantially reduced number of acid end groups makes this explanation less likely.

13.3.5. Other Fluoropolymers

The polymerization of other fluoroolefins such as TFE with hexafluoropropylene (HFP), TFE with ethylene, and vinylidene difluoride^{31,40} further demonstrates the broad applicability of liquid and supercritical CO₂ in the production and processing of fluorinated polymers. Many of the aforementioned advantages associated with CO₂, including tunable solvent properties, integrated synthesis, separation and purification processes, negligible chain transfer in the presence of highly electrophilic species, and relative ease of recycling, make it an ideal solvent for fluoroolefin polymerization.

13.4. OTHER SYSTEMS OF INTEREST

13.4.1. Photooxidation of Fluoroolefins in Liquid Carbon Dioxide

Perfluoropolyethers (PFPEs) like many other fluoropolymers exhibit exceptional thermal and oxidative stability. However, unlike fluoropolymers synthesized from most fluoroolefins, their properties are modified by a backbone of ether linkages, providing a high degree of chain flexibility. The cumulative result of these properties is manifested in materials that can be functional in a broad range of chemically demanding environments, as well as at very high and very low temperatures.⁴¹ This versatility has presented opportunities for the use of PFPEs in applications ranging from high-performance lubrication for magnetic recording media, to aerospace and electronic devices and equipment, to cosmetics and monument protection.⁴²

Photooxidation reactions of fluoroolefins in the presence of oxygen is one commercial method used in the production of PFPEs, generally employing either TFE or HFP. Fluoroolefin concentration, oxygen level, light intensity, and temperature are all variables that have substantial impact on reaction rates, product distributions, polymer microstructure, peroxide content, and molecular weight. While HFP photooxidations are often carried out in bulk at low temperatures, TFE photooxidation must be carried out in an inert solvent, historically chlorofluorocarbons.

Carbon dioxide, shown to be an ideal medium for reactions involving very electrophilic radicals,^{31,43} has also been shown to be useful in the photooxidation of fluorinated olefins in the synthesis of PFPEs.⁴ Table 13.4 shows some representative results of the photooxidation of HFP in liquid CO₂. Overall, the resulting products of photooxidations in liquid CO₂ are similar to those

emanating from reactions carried out in bulk, with lower C₃F₆O/CF₂O ratios and lower molecular weights seen in the former. This trend is likely a result of the lower HFP concentration in reactions in CO₂ leading to an increased occurrence of β-scission, which competes with propagation in these free-radical reactions involving perfluoroalkoxy radicals. Since TFE is substantially more reactive than HFP and photooxidations must be carried out diluted in an inert medium, CO₂ represents an inexpensive and environmentally benign alternative to chlorofluorocarbons. The easily varied solvent strength and density of CO₂ may also provide unique separation and purification opportunities that are not possible in commercial photooxidation processes.

13.4.2. Hybrid Carbon Dioxide/Aqueous Systems

Poly(tetrafluoroethylene) (PTFE) is manufactured primarily by free-radical methods in aqueous media. These heterogeneous processes, which may or may not involve the use of dispersing agents, result in either coagulated granular resins or fine PTFE resin particles.⁴¹ Recently, DeSimone has shown that a CO₂/aqueous hybrid system is a useful medium for the production of granular and spherical high-molecular-weight PTFE resins.⁴⁵ This system represents a substantial deviation from traditional systems as CO₂ and water exhibit low mutual solubilities allowing for the compartmentalization of monomer, polymer, and initiator based on their solubility characteristics. Storage of TFE with CO₂ forming a pseudo-azeotrope, reducing potential disproportionation hazards,⁴⁶ clearly lends itself well to the use of this technology.

13.5. CONCLUSIONS

Unlike a large portion of the many billions of pounds of organic and halogenated solvents used in industry every year, CO₂ is inexpensive, of low toxicity, and environmentally and chemically benign. The prime factors inhibiting the widespread use of this attractive solvent replacement have been the disappointingly low solubility of most materials in CO₂ in both liquid and supercritical states, and a less than complete understanding of its physical properties. Discoveries made over the past decade identifying the solubility of siloxanes and many amorphous fluoropolymers in CO₂ have facilitated a greater understanding of the solvency properties of this uniquely “tunable” solvent. The subsequent development of amphiphilic surfactants incorporating lyophilic fluorocarbon or siloxane segments with lipophilic or hydrophilic moieties opens the door for the synthesis of a broad range of hydrocarbons. Carbon dioxide technology is of particular significance with respect to the manufacture of many fluoropolymers that require nonaqueous synthesis. Reduction of unwanted side

reactions such as β -scission and opportunities for unique separation and purification processes demonstrate that CO₂ is not only an adequate replacement for chlorofluorocarbons, but in many cases a superior one.

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