



Review

Fluoropolymer synthesis in supercritical carbon dioxide

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ABSTRACT

Herein we review the environmentally friendly synthesis of fluorinated polymers in supercritical carbon dioxide (scCO₂). Historically, many high-performance fluorinated materials are commercially synthesized in aqueous media using fluorinated surfactants or in non-aqueous conditions using fluorinated solvents. Our group has pioneered both the homogeneous and heterogeneous polymerization of fluorinated monomers in scCO₂. This review includes discussions on the synthesis of main-chain and side-chain fluoropolymers conducted via a chain-growth or continuous process. Specific materials consist of acrylate- and styrene-based systems, poly(vinyl ether)s, tetrafluoroethylene- and vinylidene fluoride-based, as well as novel fluorinated elastomers and thermoplastics.

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1. Introduction

Supercritical (sc) carbon dioxide (CO₂) has been studied extensively for decades as an alternative medium for organic solvents or water in many industrial processes. Currently the most notable application areas include its use in separations in the food industry,

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as the carrier medium for automotive and furniture coatings, for polymer production and processing, as a garment dry cleaning solvent, and for various unit operations in the production of microelectronic devices [1]. Recent progress using CO₂ in polymer production and processing has been dramatic [2]. In the fluoropolymer industry, DuPont has recently commercialized certain grades of Teflon® products based on CO₂ technology [3], which offer superior properties to those materials prepared in conventionally.

Carbon dioxide is particularly suitable for fluoropolymer synthesis due to its inertness to chain transfer reactions, its low viscosity which facilitates diffusion controlled reactions, its effectiveness as a precipitating reaction medium for semicrystalline fluoropolymers and its high solubility for many amorphous fluoropolymers [4–8]. Phase equilibria measurements and high-pressure ¹⁹F-NMR studies have suggested specific interactions between CO₂ and fluoropolymers which may account for the high solubility of many amorphous fluoropolymers in CO₂ [9,10]. In addition, the recent turmoil regarding the use of perfluorooctanoic acid (PFOA) in the fluoropolymer industry has put the more-widely-used aqueous emulsion polymerization processes under scrutiny [12]. As such, the environmentally friendly processes involving the polymerization of fluoroolefins in supercritical CO₂ which does not require the use of PFOA will play an increasingly more important role. Fluoropolymers synthesized in scCO₂ have been reviewed previously [4,13–17] but this review will cover both the fluoropolymers synthesized in the past and those recently under development in our lab.

2. Fluoropolymers synthesized in supercritical carbon dioxide

Fluoropolymers discussed in this review can be categorized into two groups: side-chain and main-chain fluoropolymers. We define the side-chain fluoropolymers as those containing fluorine atoms or fluorinated groups only in the side chains such as polymers derived from a fluorinated alkyl(meth) acrylate monomer and an alkylated styrenic monomer. Main-chain fluoropolymers, on the other hand, contain either perfluorinated or partially fluorinated backbones, and may also have fluorinated side chains. Fluoropolymers of this type are mainly produced from fluoroolefins such as tetrafluoroethylene (TFE) and vinylidene fluoride (VDF) through radical polymerization processes. A special class of main-chain fluoropolymers is perfluoropolyethers (PFPE) [18]. PFPEs generally are amorphous and have extremely low glass transition temperatures and hence are usually used for different applications.

2.1. Side-chain fluoropolymers

Side-chain fluoropolymers are not as commercially important as main-chain fluoropolymers. The polymers derived from fluorinated alkyl (meth)acrylates have utility for use in textile finishes, protective coatings, surface modifiers, and optical materials [19]. Some typical monomers of this type are shown in Fig. 1. Although the synthesis of these polymers can be conducted in bulk, solution, or aqueous emulsion polymerization [20], the acrylates with long fluorinated side chains could be polymerized using solution polymerizations in CFCs [21]. Studies have shown that the polymerizations in scCO₂ of these types of monomers with fluorinated side chains were similar to those conducted in CFCs under similar conditions [5,6].

2.1.1. Acrylate-based polymers

The first synthesis of a high molar-mass fluoropolymer in a homogeneous polymerization in scCO₂ was the homopolymerization of 1,1-dihydroperfluorooctyl acrylate (FOA) at 60 °C and 207 bar

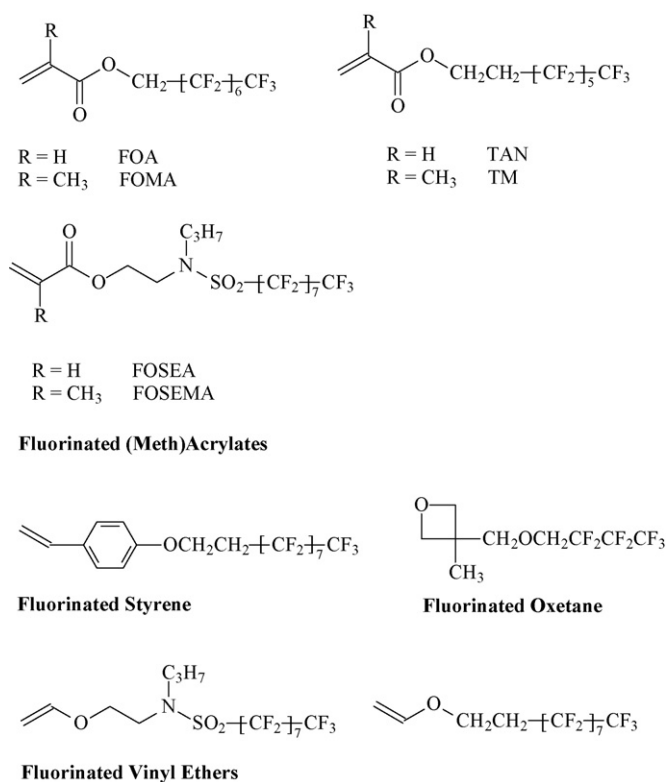


Fig. 1. Typical monomers used to make side-chain fluoropolymers in scCO₂. The length of the fluoroalkyl chains may only be an average number, so the monomers generally represent mixtures of a few homologues.

using AIBN as the free radical initiator [5]. Despite this polymer having a relatively high molar mass of 2.7×10^5 g/mol, it was found to be exceedingly soluble in scCO₂. Such high solubility of fluorinated alkyl(meth)acrylate polymers in scCO₂ is a distinguishing characteristic from other fluoropolymers that are semicrystalline such as poly(chlorotrifluoroethylene) (PCTFE) [22], or polymers derived from TFE and VDF [23,24]. The statistical copolymers of FOA with a few common hydrocarbon comonomers were effectively prepared with the copolymerizations remaining homogeneous even at high comonomer concentrations of over 50 mol% [5]. Previously, the only solvents known to dissolve these high molar-mass fluorinated polymers were CFCs [5]. This study essentially suggested that scCO₂ could be an appropriate replacement solvent for CFCs in fluoropolymer synthesis. A few other fluorinated acrylates and methacrylates were later polymerized in a similar manner as FOA in scCO₂ (see Fig. 1) [25,26].

Before this report, much of the previous work dealt only with heterogeneous polymerizations in supercritical alkanes. Additionally, without proper stabilizers, these polymerizations were mostly precipitation polymerizations, some of which had high yields and high molar masses [7] but most other monomers polymerized in supercritical fluids were often associated with low yields, broad molar-mass distributions, and poorly controlled reactions [27].

The finding of the high solubility of fluorinated alkyl(meth)acrylate polymers in scCO₂ led to their selection the lyophilic segment for the rational design of surfactants for a CO₂-insoluble polymer colloid dispersed in a scCO₂ continuous phase. The successful design of surfactants for CO₂ enabled the first successful dispersion polymerization of methyl methacrylate (MMA) in scCO₂ at 65 °C and 204 bar [28]. In this polymerization, it was postulated that the fluorinated side chains of the alkyl(meth)acrylate polymers behaved as a CO₂-philic moiety while the acrylate backbones functioned as the lipophilic segments

to PMMA. However, the FOA homopolymers showed limitations in the dispersion polymerization of non-acrylate monomers such as styrene due to ineffective anchoring [29]. Later work was focused on the design of molecularly-engineered surfactants for polymerizations in scCO₂-based on the FOA copolymers [30]. Copolymers of different types, including random [5], block [31,32], and graft [33] copolymers were prepared by various polymerization techniques such as iniferter [31,34], ATRP [31,32,35], NMP [35], as well as living anionic [36], and cationic [27] polymerizations. These copolymers, with designed lyophilic CO₂-philic segments and anchoring lyophobic CO₂-phobic segments systems enabled the effective synthesis of a wide variety of commercially important polymers through dispersion polymerization processes [29,37–39].

2.1.2. Styrene-based polymers

Aside from the extensive studies on the homo- and copolymerization of fluorinated alkyl(meth)acrylate in scCO₂, the synthesis of alkylated styrenic fluoropolymers has been much less popular due to the lower availability from commercial sources of these monomers in general. A homogeneous polymerization of a fluorinated alkylated styrenic monomer (Fig. 1) was carried out in scCO₂ at 60 °C and 345 bar [6]. The polymer was characterized to be similar to that prepared in Freon 113. However, the homopolymerization of pentafluorostyrene resulted in a phase separation during the polymerization, and the polymer was insoluble but highly swollen in scCO₂. Two similar alkylated styrenic fluoromonomers with shorter fluorocarbon side chains (–C₄F₉) were prepared and polymerized in scCO₂ in a later study [40]. These polymers were cast into films and were intended to replace the repellents based on perfluorooctyl (–C₈F₁₇) or longer fluoroalkyl chains for surface applications. The aromatic ring could be beneficial for the orientation of the short fluoroalkyl side chain (such as C₄F₉) at interfaces [41]. As many other materials containing long fluoroalkyl chains may also be subject to the PFOA program in the future, more studies are expected in this field.

2.1.3. Poly(vinyl ether)s and poly(oxetane)s

Cationic polymerization is receiving a growing interest in polymer synthesis as many common monomers can be polymerized through cationic routes. However, the polymerizations of this type are usually plagued by various side reactions which mostly lead to chain transfer and termination. After the first living cationic polymerization reported by Higashimura et al. [42], much of the work has been directed to select the proper counter anion, solvent, and temperature conditions to minimize these deleterious side reactions. It was postulated that CO₂, with a widely adjustable solvent strength and low viscosity, could be tuned to stabilize the carbocationic centers of the propagating polymer chains and hence may be beneficial to suppress side reactions.

Previous studies on cationic polymerizations in CO₂ are relatively scarce [43,44]. We have carried out cationic polymerizations of vinyl ethers with both hydrocarbon and fluorocarbon side chains [27,45], as well as the cationic ring-opening polymerization of various oxetanes including some with fluorinated alkyl side chains [45]. The polymerization of isobutyl vinyl ether in CO₂ results in the precipitation of the resulting polymer which stands in contrast to its polymerization in hexane which results in a homogeneous polymerization process. As a result, a broader molecular weight distribution was observed for the polymers prepared in CO₂ [45]. However, polymerizations of the vinyl ethers with fluorocarbon side chains remained homogeneous in CO₂ [45], a phenomenon repeatedly seen in the synthesis of side-chain fluorinated polymers [5,6]. The same trends were observed in the ring-opening polymerizations of the oxetanes [45].

In a later study, a block copolymer of 2-(*N*-propylperfluorooctane sulfonamido) ethylvinyl ether (FVE) and methyl vinyl

ether (MVE) was synthesized, which represented a rare cationic dispersion polymerization in CO₂ (see Scheme 1) [27]. The polymers had very narrow polydispersity, a property less frequently obtained in cationic polymerizations, and were used as effective surfactants in the polymerization of styrene in scCO₂.

2.2. Main-chain fluoropolymers

Main-chain fluoropolymers are a special class of macromolecules, the most notable being PTFE, which contains impressive non-wetting and chemical and thermal stability characteristics. PTFE is most commonly known for its use in cook-ware applications as well as many industrial applications which require stability under harsh conditions. PTFE is the prototypical fluoropolymer and because of its unique and impressive chemical and physical properties it is particularly attractive in a wide range of applications. But fluorolefin polymers in general have a range of properties which include a wide range of molecular weights, high thermal and mechanical stability, low temperature durability, chemical-, ageing-, and weather-resistance, solvent inertness, and oxidative stability, making them suitable for use in aggressive environments. The common fluoroolefins used to make fluoropolymers in scCO₂ are shown in Fig. 2.

2.2.1. TFE-based fluoropolymers

The avid pursuit of alternative technologies for manufacturing fluoropolymers using non-aqueous polymerizations led to the discovery of using scCO₂ as a polymerization medium [5,8]. Early efforts at DuPont discovered that TFE monomer could be handled in a safe manner in mixtures with CO₂ [46]. Previously, TFE was handled as a liquid azeotropic mixture with hydrochloric acid (HCl) (33 mol% TFE and 67% HCl) before polymerization. However, the disposal of the large amount of HCl and the toxicity potential of shipping the acid was a disadvantage. In addition, without any diluent, TFE is very challenging and dangerous to work with as it forms explosive mixtures with air, can disproportionate violently into elemental carbon and carbon tetrafluoride during vaporization from a liquid, and must be kept meticulously free of oxygen to prevent the formation of shock-sensitive polymeric peroxides [46]. Handling TFE in the TFE/CO₂ mixture offers a much safer alternative as it does not form explosive mixtures in air with sufficient CO₂ and forms a “pseudoazeotrope” [23]. Additionally, when using CO₂ as a polymerization medium, the removal of CO₂ from the TFE/CO₂ mixture is not necessary.

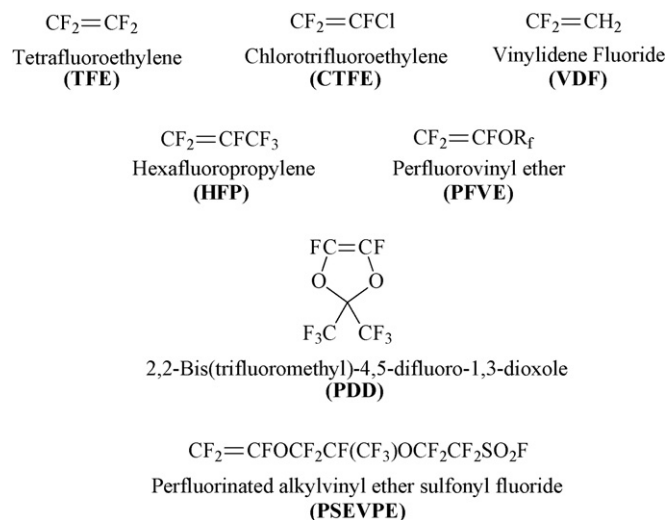
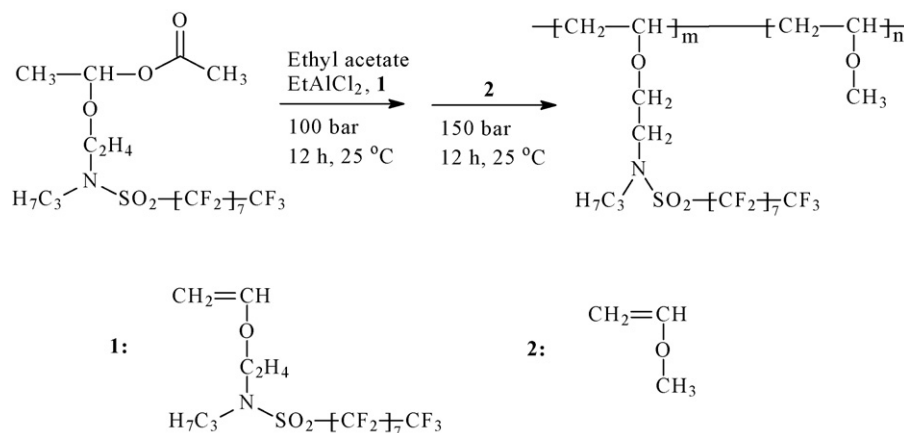


Fig. 2. Typical fluoroolefins used in polymerizations in scCO₂.



Scheme 1. Cationic dispersion copolymerization of FVE and MVE.

Perfluoroalkyl halides which are oligomers of PTFE, were the first TFE-based materials synthesized in scCO_2 . Perfluoroalkyl halides (mainly bromides and iodides) are important intermediates in the manufacture of many commercial fluorinated compounds [51]. Long-chain perfluoroalkyl iodides are generally produced through the telomerization of fluoroolefins using various telogens [51]. Free-radical telomerization of TFE in scCO_2 was carried out by employing perfluorobutyl iodide as a telogen [23]. Products were typically isolated as slightly yellow liquids or waxy yellow solids depending on the monomer to telogen ratio employed. Number-average molecular weights were from 620 to 960 g/mol, while molecular weight distributions (MWDs) were between 1.4 and 1.6. In some cases, reactions proceeded homogeneously throughout the polymerization resulting in products with relatively low molecular weight. When higher molar-mass perfluoroalkyl iodides were yielded, precipitation was observed during the reaction as high molecular weight fractions possess poorer solubility characteristics in CO_2 .

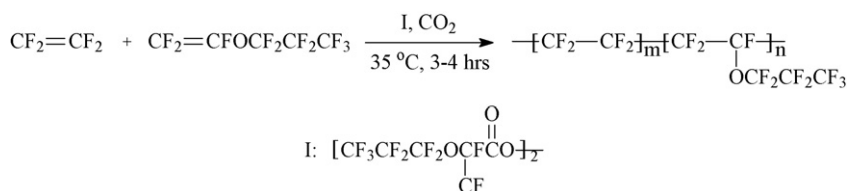
PTFE was readily prepared in scCO_2 using both fluorinated and hydrocarbon initiators at different temperatures and pressures [47]. Scanning electron micrographs showed that the polymers were in the form of fibrils which resembled those prepared via suspension polymerization. However, an interesting study by Filardo's group later showed that more regular colloidal PTFE could be prepared in scCO_2 in a batch reactor by adding PFPE type surfactants [52]. Copolymers of TFE with perfluoro(propylvinyl ether) (PPVE) or hexafluoropropylene (HFP) were prepared in scCO_2 using bis(perfluoro-2-propoxypropionyl) peroxide (BPPP) as a free radical initiator (Scheme 2) [8]. In these polymerizations, PFOA and ionic initiators were not used, so the undesired ionic end groups were greatly reduced. The morphologies of the TFE/PPVE copolymers prepared in scCO_2 were similar to those obtained by conventional solution polymerization in CFCs. Other copolymers of TFE with ethylene (ETFE) or perfluorosulfonyl fluoride perfluorovinyl ether (NafionTM monomers) were prepared in the same manner [47]. These polymerizations demonstrated that scCO_2 is an excellent, environmentally responsible solvent for TFE-based copolymer synthesis, which generally resulted in high molecular weights, good

yields, and less deleterious end groups as typically obtained in aqueous emulsion polymerizations.

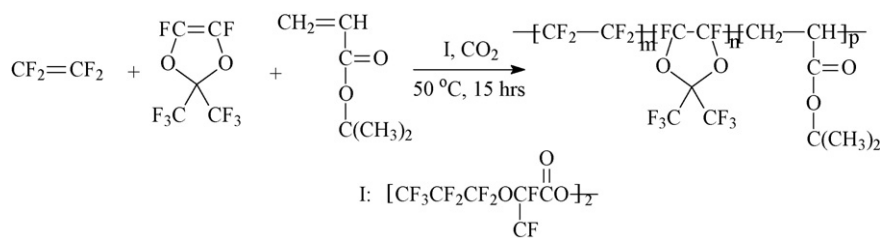
Teflon[®] AF is an amorphous perfluorinated copolymer of TFE and 2,2-bis (trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD) [48]. The material combines attributes of amorphous materials with perfluorinated materials by possessing properties including good optical transparency and good solubility in organic solvents with high thermal stability, excellent chemical stability, and low surface energy [48]. Additionally, these materials possess the lowest refractive index and the lowest dielectric constant of any known solid organic polymer [48]. Copolymerizations of TFE and PDD were carried out in scCO_2 with feed ratios similar to those used in the commercial process [49]. The composition of the copolymers had little drift relative to the feed ratios over the investigated ranges according to ¹⁹F-NMR and IR. A copolymer synthesized in CO_2 at low temperature showed comparable properties to a commercial sample (Teflon[®] AF 1601), indicating that post-treatment may not be needed. As a comparison, commercial samples were usually first treated with ammonia or alkyl amines and then by a high-temperature fluorination with elemental fluorine to remove ionic end groups [48]. Terpolymers of TFE and PDD with a third comonomer were prepared in scCO_2 and were investigated as photoresist material for potential use in 157 nm photolithography studies (see Scheme 3) [50]. The third monomer may be a hydrocarbon or a fluorinated functional monomer, and TFE may also be replaced by other functional monomers. The materials showed excellent transparency in the deep UV region.

2.2.2. VDF-based fluoropolymers

Vinylidene fluoride (VDF) is frequently-used in the production of commercial fluoropolymers including many fluorinated thermoplastics [53–56] and most of the fluoroelastomers [57]. Most of the VDF-based fluoropolymers, like the TFE-based fluoropolymers, are commercially synthesized by free radical emulsion polymerization using PFOA or other fluorinated surfactants or as a suspension polymerization in water [53]. As a more environmentally friendly alternative, scCO_2 can also be used as a polymerization medium to synthesize VDF-based polymers.



Scheme 2. Copolymerization of TFE and PPVE in scCO_2 .



Scheme 3. Synthesis of terpolymers based on PDD.

Poly(vinylidene fluoride) has the second largest production volume among all fluorinated thermoplastics aside from PTFE. Much of its unique properties arise from the alternating arrangement of CH₂ and CF₂ groups in the polymer backbone. A precipitation homopolymerization of VDF and a homogeneous copolymerization with FOA were reported earlier as a comparison to FOA polymerization in scCO₂ [6]. Homogeneous telomerization of VDF using perfluorobutyl iodide as a telogen was carried out in scCO₂ at moderate conditions [24]. A later study on VDF polymerizations compared its precipitation homopolymerizations in scCO₂, CO₂/H₂O, and aqueous systems, and also attempted the dispersion polymerization of VDF in scCO₂ using PMMA-*b*-PFOMA as the surfactant [58]. More recent studies were focused on the development of a continuous process for the synthesis of PVDF [7,59–62]. Substantial work has also been carried out in other groups on precipitation polymerization [63–65], dispersion polymerization using various surfactants [66–68], and homogeneous polymerization [69–71] of VDF in supercritical or dense CO₂. A thorough study and modeling of reaction kinetics of VDF heterogeneous polymerization in scCO₂ was also carried out by Morbidelli's group [72].

VDF-based copolymers are often used in fluoroelastomer compositions [57]. One type of copolymer that has been widely used as fluoroelastomers are the copolymers of VDF and HFP which are sold under different trade names by different companies [57]. The copolymerization of VDF and HFP results in a material with improved flexibility, but without compromised electrical properties. When the content of HFP is lower than 19–20 mol%, the copolymers are thermoplastic and retain a semicrystalline morphology, while for higher HFP contents, the copolymers are elastomeric and possess an amorphous morphology. A study by Howdle's group reportedly showed that the copolymers of VDF and HFP were more soluble than in CO₂ than in either VDF or HFP, and using a stabilizer could lead to higher molecular weights and more regular polymer morphology [73]. Our studies have focused on the copolymerization of VDF and HFP in a continuous stirred reactor in scCO₂ [74–76]. The kinetics of the polymerizations at different pressures with different monomer feed ratios was systematically studied. This part of the research will be discussed in Section 3 of this review in more detail. We have recently initiated the development of new fluoroelastomers based on VDF and HFP which will be discussed in Section 5 of this review.

2.2.3. PFPE synthesis through the photooxidation of fluoroolefins

Perfluoropolyethers represent a class of fluoropolymers having increasingly important applications in many areas [18]. One major type of PFPEs, represented by Fomblin[®], Galden[®] fluids of Solvay, and the like, is manufactured through the photooxidation of fluoroolefins such as TFE and HFP at low temperatures [77]. The raw products contain a high concentration of peroxidic units which needs to be removed through a multi-step post-treatment. When TFE is used as a starting material, an inert diluent, usually CFCs such as dichlorodifluoromethane or other halocarbon solvents, is neces-

sary to prevent TFE homopolymerization. However, a process of this type is not sustainable given the known challenges associated with CFCs [11]. We have conducted the photooxidation of FEP, TFE, and other fluoroolefins in CO₂ at different conditions [23,47,78,79]. The photo-polymerization of HFP or HFP/TFE was carried out in liquid CO₂ at –40 °C and generated crude PFPE polymers containing hexafluoropropylene oxide, difluoromethylene oxide, and fluoro(trifluoro-methyl)methylene oxide repeating units [47,79]. The peroxidic units were reduced significantly due to the viscosity effects in liquid CO₂ when compared to the parallel reactions carried out in bulk HFP and in perfluorocyclobutane. Further studies using a comonomer, an ester-functionalized fluorinated vinyl ether, and produced functionalized PFPEs were also conducted [78]. The average chain functionalities were as high as 7.3 which may be useful in various post-functionalizations.

2.2.4. Fluorinated poly(olefin sulfone)s

A less popular main-chain fluorinated polymer that has been prepared in scCO₂ is fluorinated poly(olefin sulfone) [80]. Due to the remarkable miscibility of sulfur dioxide and carbon dioxide, high concentrations of sulfur dioxide were used and the polymerizations of both hydrocarbon and fluorinated olefins remained homogeneous at moderate temperatures and pressures. Alternating copolymers of sulfur dioxide and 1H, 1H-pentadecafluorooctylallyl were prepared [80], and may potentially be used as a next generation lithographic resist material.

3. Continuous synthesis development

As industrial interests in using CO₂ as an alternative polymerization medium for fluoropolymer synthesis grow, development of a continuous process for precipitation polymerization in scCO₂ has become necessary. Production of large-volume polymers in a batch reactor is often associated with a number of disadvantages, which can be circumvented in a continuous process [7].

A continuous stirred tank reactor (CSTR) was developed for the precipitation polymerization of various fluorinated monomers in scCO₂ [7,59–60,62,74–76]. A detailed description of the set-up was presented in a report using it in PVDF synthesis [7], and a simplified schematic is shown in Fig. 3. The experimental set-up is widely applicable for the precipitation polymerization of various monomers in scCO₂ with and without surfactants. The CSTR system consisted of an intensely mixed tank and was followed by two high-pressure filters in parallel, where the polymer was collected. Carbon dioxide and monomer were pumped continuously by high-pressure syringe pumps in constant flow mode and mixed by an eight-element static mixer before entering the CSTR. The initiator solution was also pumped continuously in by a high-pressure syringe pump in constant flow mode and enters the reactor as a separate stream. All of the feed lines were outfitted with check valves to prevent back flow and rupture disks for safety in case of over pressurization. The system could be modified by adding parallel lines for copolymerizations [76].

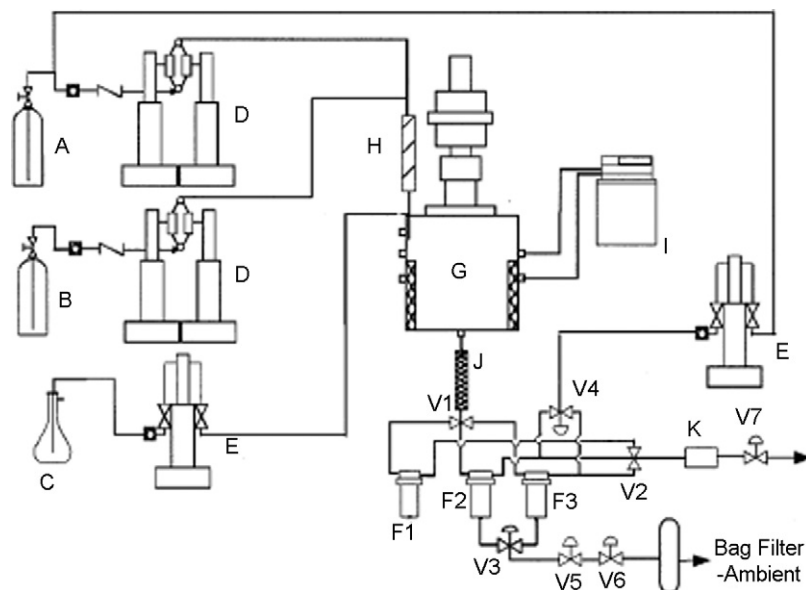


Fig. 3. Continuous polymerization apparatus: (A) CO₂ cylinder; (B) monomer; (C) initiator solution; (D) continuous syringe pumps; (E) syringe pumps; (F1) steady-state filter; (F2, F3) non-steady-state filter; (G) thermostated autoclave; (H) static mixer; (I) chiller/heater unit; (J) effluent cooler; (K) gas chromatograph; (V1, V2) four-way valves; (V3, V4) three-way valves; (V5, V6) two-way valves; (V7) heated control valve (copyright [63]).

The system was first used in the precipitation homopolymerization polymerization of VDF or acrylic acid in absence of surfactant [7]. Significantly higher polymerization rates of VDF in the CSTR were observed than the average rates achievable in batch polymerizations under similar conditions. The kinetics of the homopolymerization of VDF was later investigated [59]. It was found that a kinetics model based on homogeneous chain-growth polymerization could accurately describe the precipitation polymerization of VDF in scCO₂. The observed order of the reaction was 0.5 with respect to initiator and 1.0 with respect to monomer [59]. However, an observed “offset” in the polymerization rate needed to be included as an inhibition step which was likely due to chain transfer to monomer. The PVDF polymers were collected as dry, free-flowing powders with molecular weights up to 150 kg/mol.

Other factors were investigated in a later study [61]. The same homogenous chain polymerization kinetics model was used which predicted the polymerization rates reasonably well. However, the imperfect mixing, rather than a chemical effect, was found more likely to be the reason that caused the apparent inhibition at high monomer concentrations. An extended model was developed by taking into account the chain transfer to polymer and predicted the polydispersity reasonably well and matched the experimental results on a region of inoperability. However, the model could not account for the bimodal distribution of molecular weights of PVDF. Further study considered the decrease in the mobility of polymeric radicals when they grow larger, the modified model could then be used to account for the bimodality [61].

The CSTR system was later modified to be used in the synthesis of copolymers of VDF and HFP [74–76]. The polymerization could proceed either heterogeneously or homogeneously depending on the conditions and feed ratios [75]. Copolymers of different compositions were prepared. At low HFP concentrations (ca. 10 mol%), a precipitation polymerization resulted with dry free-flowing semi-crystalline copolymers being collected [76]. The copolymerization became homogeneous when higher HFP concentrations were used and the polymers became amorphous [74]. Higher monomer concentrations and polymerization pressures always resulted in higher polymer rates and higher molecular weights of the resulting polymers at the investigated conditions. The results suggested the primary polymerization locus was in the CO₂-rich fluid phase.

4. Modification of the carbon dioxide system: hybrid systems

Despite its many advantages as a polymerization medium, pure CO₂ suffers from significant disadvantages such as a lack of reasonable solubility for most high molar-mass polymers, requiring high operating pressures or otherwise having low heat transfer. Much effort has been devoted to the use of hybrid systems to compensate for these disadvantages. Two hybrid systems that have been used in fluoropolymer synthesis are a biphasic mixture of CO₂ with water [81] and a homogeneous mixture of CO₂ with organic solvents [82].

4.1. Hybrid carbon dioxide/aqueous system

The biphasic mixture of CO₂ and water was used in the polymerization of TFE to compare with the conventional aqueous suspension and emulsion polymerization processes [81]. This hybrid process resembles more closely the conventional aqueous polymerization process, but is safer due to the presence of CO₂ as a diluent. Additionally, the versatility of CO₂ aids as the selective compartmentalization of monomer, polymer, and initiator based on their solubility characteristics in the two phases. PTFE with comparable molecular weights and other properties to commercial fluoropolymers were produced. Moreover, development of new materials based on this hybrid systems was anticipated [81]. Our recent study has shown CO₂ may help to emulsify fluoropolymer particles by hydrocarbon surfactants in water [83]. These two studies may point to a solution to the current PFOA problem faced by the fluoropolymer industry where fluorinated surfactants have traditionally been used.

4.2. Carbon dioxide expanded organic solvents

The high pressures commonly associated with CO₂ processes may be lowered using a cosolvent system: CO₂-expanded liquids (CXLs). As many common organic solvents can be expanded by CO₂, CXLs have been used in applications such as separations, nanoparticle formation, enhanced oil recovery, photoresist removal, and various organic reactions, especially in catalysis involving gases and viscous solutions [84]. We recently reported the preparation of

Table 1
Polymerization of TFE in CO₂-expanded acetic acid.

Entry	AA/CO ₂ (v/v)	P (MPa)	Yield (%)	M _n ^a (g/mol)	T ^b (°C)	T _m (°C)
1	4/96	17	68.1	8.5 × 10 ⁴	506.8	328.0
2	8/92	17	60.2	7.6 × 10 ⁴	502.4	328.1
3	20/80	17	53.7	5.7 × 10 ⁴	492.2	328.3
4	40/60	17	22.0	4.6 × 10 ⁴	489.8	327.9
5	4/96	8.5	41.7	6.8 × 10 ⁴	507.7	327.2
6	8/92	8.5	71.1	5.3 × 10 ⁴	508.2	328.0
7	20/80	7.0	76.3	7.6 × 10 ⁴	503.5	328.6
8	40/60	7.0	52.9	4.0 × 10 ⁴	472.8	327.2
9	60/40	5.9	38.1	3.0 × 10 ⁴	483.4	327.4
10	20/80	8.5	N/A	N/A	309.6	N/A

Conditions: Entry 1–9: TFE percent solids: 5 wt%; initiator: bis(perfluoro-2-propoxypropionyl) peroxide; [I]: 0.01 mol%; temperature: 35 °C; time: 4 h; Entry 10: TFE percent solid: 5 wt%; initiator: di(2-ethylhexyl) peroxydicarbonate; [I]: 0.01 mol%; temperature: 50 °C; time: 20 h; 1 wt% of SDS.

T_m: melting temperature.

^a Calculated based on the reported method.

^b Temperatures for 5% weight loss on thermogravimetric profiles.

PTFE in CO₂-expanded organic solvents using both common hydrocarbon and hydrofluorocarbon solvents [82]. Table 1 details the polymerizations of TFE in CO₂-expanded acetic acid at different solvent ratios and pressures. High yields of PTFE could be obtained at fairly low pressures at which pure scCO₂ did not give comparable results [82]. It is also interesting to see that the TFE polymerization could be effective in a medium with a high concentration of a hydrocarbon solvent (up to 60 vol% of acetic acid), which essentially contradicts the conventional wisdom of TFE polymerization being prone to high chain transfer to hydrocarbons resulting in low yields of low molecular weight polymer.

More interestingly, colloidal PTFE could be prepared using a conventional hydrocarbon surfactant, sodium dodecyl sulfate (SDS), in CO₂-expanded acetic acid [82]. The much wider polarity range in CO₂-expanded solvents may have changed the interaction between SDS with both the solvent and the polymer. However, in pure scCO₂, commercial surfactants such as SDS are generally ineffective [85]. This may be an alternative approach to run dispersion polymerizations in CO₂ systems without the need for specially designed surfactants [30].

5. New materials development

Virtually all of the current commercial fluoropolymers may be produced in CO₂. The previous studies have also been heavily focused on realizing the production of these existing fluoropolymers in the CO₂-based media. However, the present industrial uses of CO₂ are still relatively limited, in part due to the challenges associated with introducing new-to-the-world technologies when there are already paid for and developed existing technologies and processes. Alternatively, CO₂ is becoming a tool to develop new materials owing to its long list of unique properties as a reaction media. This has been used in our study to develop new fluoropolymers or composite materials containing fluoropolymers which are difficult to make in conventional solvents.

5.1. Core-shell composite materials

Fluoropolymers and hydrocarbon polymers usually are immiscible in one another and as such have poor compatibility. Therefore, composite materials composed of both types are generally difficult to make but should yield interesting new materials with unique properties. Preparations of composite particles composed of different hydrocarbon polymers in a pure scCO₂ system have been demonstrated elsewhere. Core-shell composite particles of PTFE and PMMA were prepared by us in a CO₂/aqueous system [58,86]. The plasticization of the seed particles by CO₂ was expected to facilitate the infusion of the second stage monomer and the reorien-

tation of the latex particles to a most thermodynamically favorable core-shell arrangement [58]. Moreover, the CO₂/water biphasic system has the benefit of using the compartmentalization in the two phases to better regulate the polymerization rate and location and hence may help prevent the secondary particle nucleation [87]. Because PTFE is more hydrophobic than PMMA, the particles had PMMA shells and PTFE cores in order to minimize the interfacial surface tension [58,86].

5.2. Liquid fluoroelastomers synthesis

Conventional fluoroelastomer synthesis typically includes the synthesis of high molar-mass amorphous prepolymers based on TFE or VDF. These linear or slightly branched polymers are subsequently cured to yield a material with good elastomeric mechanical properties and excellent chemical stability for demanding seal applications. The curing consists of either ionic curing or radical curing steps depending on the composition of the polymer. In general, radical curing, utilizing a free radical initiator and a radical trap, often affords better retention of the physical properties compared to ionic curing [57]. Most conventional fluorinated elastomers are synthesized as high molar-mass copolymers prior to curing. High molecular weight materials and polymers with high TFE content usually make processing difficult, especially in homogeneous mixing of curing reagents with the polymers. A novel approach of using a liquid precursor synthesized in scCO₂ to prepare VDF-based fluoroelastomers has much easier processibility [88].

Co- and ter-polymers of different compositions containing VDF, 2-bromotetrafluoroethyl trifluorovinyl ether (EVEBr) as a cure site monomer, and TFE, were synthesized in scCO₂ (Table 2) and analyzed using NMR, IR, TGA, DSC and GPC [88]. Viscous liquid oligomers, which were colorless and transparent, were obtained in most cases. Glass transition temperatures (T_g) for the copolymers ranged from –63 to –25 °C, while with the glass transition temperatures would range from –30 to –4 °C for the terpolymers. The increase in T_g for the terpolymers relative to the copolymers is likely due to the increase in molecular weight and the presence of TFE in the polymer composition. These functional, fluorinated liquid oligomers could be cross linked with triallylisocyanurate and 2,2-dimethoxy-2-phenylacetophenone under UV irradiation yielding fluoroelastomers with excellent thermal stability (5 wt% loss at a mean temperature of 577 °C) and useful mechanical properties (modulus of 1–13 MPa depending on the composition).

5.3. New functional fluoropolymers

As discussed previously, the synthesis of many commercial fluoropolymers has been realized in scCO₂. In addition, many

Table 2
Summary of physical properties of co- and terpolymer synthesized in scCO₂.

VDF (mol%) ^a	EVEBr (mol%) ^a	TFE (mol%) ^a	M _n (kg/mol) ^b	M _w (kg/mol) ^b	T _g (°C) ^c
34	18	48	33	69	-23
64	9	27	83	145	-13
66	34	0	15	53	-30
71	29	0	31	112	-25
73	7	20	78	137	-19
76	17	7	74	129	-21
76	11	13	50	118	-9
82	10	8	63	120	-18

Conditions: 50 °C; 138 or 345 bar; I: 2-ethylhexyl peroxydicarbonate.

^a Obtained by ¹⁹F-NMR.

^b Obtained by GPS.

^c Obtained by DSC.

monomers which are impossible to use in aqueous medium, or polar functional monomers that do not usually share a common organic solvent with fluoroolefins, are especially suited to polymerize in scCO₂. Here, CO₂ works both as a naturally anhydrous inert medium and a medium able to mix naturally incompatible monomers.

5.3.1. New functional thermoplastics

Fluoropolymers, in general, have relatively low surface energies, which makes the adhesion of fluoropolymers to metals and other polymers such as nylon an often difficult task. This is expected to improve with the appropriate incorporation of monomers with polar or reactive functional groups.

An ongoing study in our lab is to make novel functional fluorinated thermoplastics based on the copolymerization of TFE with functional comonomers in scCO₂. The comonomers used in this study usually contain functional groups that are either reactive or labile in water (see Fig. 4). Their polymerizations, therefore, cannot be carried out in water. There are also very few common solvents that are compatible with both these monomers and fluoroolefins [89]. Our preliminary study for the copolymerizations of these monomers with TFE in scCO₂ has shown some promising results (see Table 3).

Other monomers that may be interesting in this study are vinyl ethers or ketene dialkyl acetals (Fig. 3). These monomers, being electron-rich, are likely to polymerize with fluoroolefins to form alternating polymers like ETFE and others [90–92]. These copolymers likely have different properties from the commercial fluoropolymers and may be hydrolyzed into materials with novel

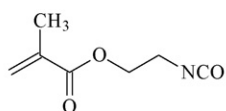
structures. However, a common difficulty faced by these polymerizations may be the chain transfer reaction associated with monomers of this type [93]. Measures have to be taken to suppress this in order to get polymers with reasonable yields and molecular weights. Monomers that do not contain any hydrogen such as tetracyanoethylene (TCNE) may also be interesting in this study as no chain transfer to monomer is expected, however, the radical polymerization of TCNE has not been reported.

5.3.2. New thermal- and UV-curable fluoroelastomers

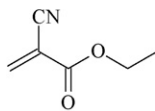
Conventional fluoroelastomers are usually cured ionically with nucleophiles or radically using a radical initiator along with a co-agent called a 'radical trap' [57]. We have recently developed UV-curable PFPE elastomeric polymers for use in a nanoparticle fabrication platform [94,95]. As previously discussed, PFPE polymers are generally expensive due to the often cumbersome synthesis routes [18]. Therefore, there is a need for materials that can be used for the same purpose but at a lesser cost. A possible candidate may be the oligomers based on VDF or other common fluoroolefins with functional groups for easy curing or post-functionalization. The high solubility of a wide range of functional monomers in CO₂ offers a possibility to make new fluoropolymers of this type. These materials may also lead to new facile curing chemistry to formulate elastomers (see Scheme 4).

New types of fluoroelastomers based on copolymers of VDF and maleic anhydride (MAH) have been synthesized (see Scheme 4). Additional monomers may also be used including other fluoroolefins or a functional hydrocarbon monomer. Our preliminary studies have shown that anhydride groups in the polymer chain impart good solubility to the polymers in many common organic solvents versus the limited number of solvents available for PVDF [96]. Additionally, it also provides a new way of curing or cross linking the fluoropolymers through the anhydride groups (see Scheme 4). We have used nucleophiles such as diamines and diols to crosslink the prepolymers in various solvents. The length of the cross linker can be varied to adjust the mechanical properties of the final elastomers. The cross linkers may also contain one primary and one secondary hydroxyl groups or any two functional groups

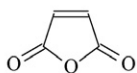
Water-sensitive monomers



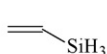
2-Isocyanatoethyl methacrylate (ICMA)



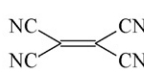
Ethyl 2-cyanoacrylate (ECA)



Maleic anhydride (MAH)

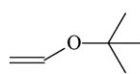


Vinyl silane (VS)

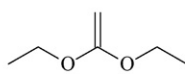


Tetracyanoethylene (TCNE)

Electron-rich monomers



t-Butyl vinyl ether



Ketene diethyl acetal

Fig. 4. Monomers used in copolymerization with TFE in scCO₂.

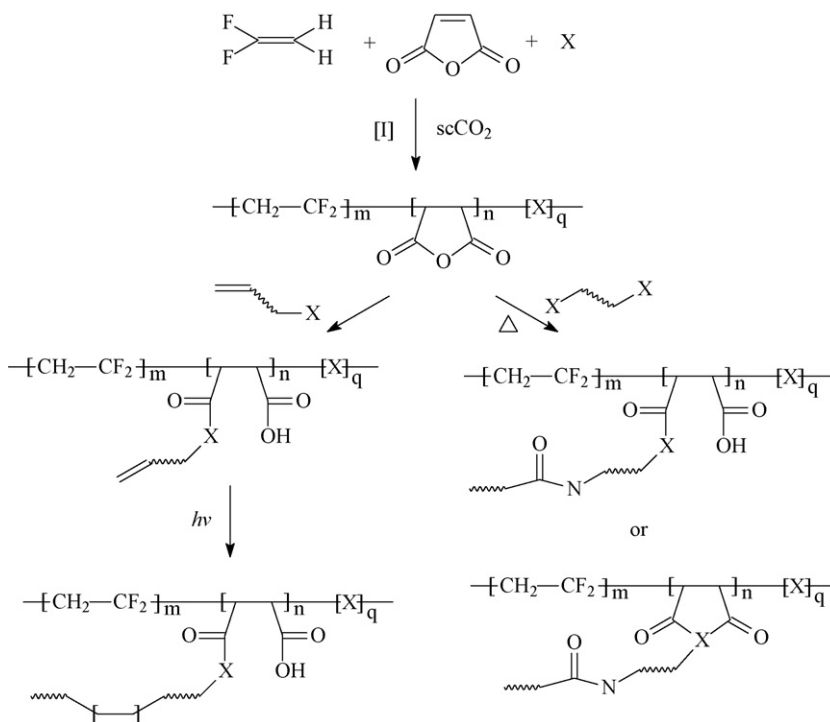
Table 3

Copolymerizations of the reactive monomers with TFE.

M	I	[I] (mol%)	Yield (wt%)	[TFE] ^a (mol%)
MAH	3P	0.01	11.3	94.5
ECA	3P	0.01	N/A	26.8
ICM	AIBN	1	N/A	3.8

MAH: maleic anhydride; ECA: 2-ethyl cyanoacrylate; ICM: 2-isocyanatoethyl methacrylate; 3P: perfluoropropionyl peroxide. Polymerization condition: Monomer percent solids: 8%; TFE/M, 19/1 (mol%); temperature: 35 °C with 3P, 60 °C with AIBN; pressure: 17 MPa.

^a Calculated based on elemental analysis.



Scheme 4. Synthesis of prepolymers for fluoroelastomer formulation.

with different reactivity so that a sequential multistage curing is possible. Currently used liquid fluoroelastomers have many disadvantages and their applications may be limited by the difficulty in handling and the presence of solvents [97]. One-component, liquid (solventless) materials that can be cured into 100% solids materials using facile curing methods should be very useful. A new type of UV-curable liquid prepolymers of fluoroelastomers as such is under development (see Scheme 4).

6. Conclusions

In general, many commercial fluoropolymers have been successfully prepared in $scCO_2$ or CO_2 -based media. These fluoropolymers have superior or comparable properties to the commercial products manufactured in conventional media such as CFCs or water. Carbon Dioxide is becoming an environmentally sensible and industrially viable replacement in many cases. Moreover, its unique properties as a polymerization medium are enabling the development of many new fluorinated polymers or composite materials which are otherwise difficult or impossible to realize. The study in this area is getting more exciting since such laboratory successes may be commercialized more quickly without the competition from existing products or existing conventional equipment and processes.

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