(54) Title: METHOD OF MAKING FLUOROPOLYMERS

(57) Abstract

A process for making a fluoropolymer is disclosed. The process comprises solubilizing a fluoromonomer in solvent comprising a carbon dioxide fluid, and then polymerizing the fluoromonomer to produce a fluoropolymer. A preferred solvent for carrying out the process is supercritical carbon dioxide; preferred fluoromonomers for carrying out the process are fluoroacrylate monomers such as 1,1–dihydroperfluorooctyl acrylate. The polymerization step is preferably carried out in the presence of an initiator such as azobisisobutyronitrile.

METHOD OF MAKING FLUOROPOLYMERS

Cross Reference to Related Applications

This application is a continuation-in-part of
copending U.S. Application Serial No. 08/529,873, filed
September 18, 1995, which is a continuation of U.S.
5   Patent application Serial No. 08/302,642 filed
September 27, 1994, which is a continuation under 35
U.S.C. §371 of PCT Application No. PCT/US93/01626 filed
February 26, 1993, which is a continuation-in-part of
U.S. Patent Application Serial No. 07/858,150 filed
10   March 27, 1992, abandoned.

Field of the Invention

The present invention relates to a method of
making fluoropolymers, including copolymers thereof, in
15   a solvent comprising a carbon dioxide fluid such as
supercritical carbon dioxide.

Background of the Invention

Chlorofluorocarbons (CFCs) have been
20   identified as one of the main causes of the depletion
of atmospheric ozone. As a result, extensive effort
has been directed towards discovering alternatives to
CFCs in a variety of applications. In addition to the

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utilization of CFCs as refrigerants and aerosols, CFCs
are commonly used as solvents for the manufacture of
fluoropolymers, which are generally insoluble in
traditional organic solvents but can often be
5   solubilized in CFCs. Hence, there is a need for
alternative methods of manufacturing fluoropolymers.

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A supercritical fluid (SCF) is a substance above its critical temperature and critical pressure (or "critical point"). Compressing a gas normally causes a phase separation and the appearance of a

5   separate liquid phase. However, if the fluid is in a supercritical state, compression will only result in density increases: no liquid phase will be formed. The physical properties of supercritical fluids are highly unpredictable, and the use of supercritical fluids for

10 carrying out polymerization processes has received relatively little attention.

S. Kumar et al., *Polym. Prep.* 27, 224 (1986), describe the free radical precipitation polymerization of polystyrene chains in supercritical ethane. The

15 styrene monomers were dissolved in ethane and polymerized with azobisisobutyronitrile ("AIBN") as an initiator using an apparatus having a high-pressure optical cell.

V. Sarai and E. Kiran, *Polym. Prep.* 31, 687

20 (1990), describe the free radical polymerization of styrene in supercritical ethane, propane, and butane, using AIBN, t-butyl peroxide and t-butyl peroxybenzoate as initiators.

K. Scholsky, *Polym. Prep.* 31, 685 (1990),

25 describe a variety of polymerization reactions using supercritical fluids. The article summarizes publications on the polymerization of fluorinated olefins, such as vinyl fluoride, tetrafluoroethylene, the copolymerization of tetrafluoroethylene and sulfur

30 dioxide, and polyperfluoropropylene. Other fluorinated olefins mentioned include n-tetradecafluoroheptene-1, n-perfluoropentadiene-1,4, vinylidene chlorofluoride, and a variety of vinylic monomers. The polymerization of fluoropolymers in carbon dioxide is not suggested.

35 E. Beckman and R. Smith, *J. Phys. Chem.* 94, 345 (1990) describe the microemulsion polymerization of acrylamide ($CH_2CHCONH_2$) in supercritical fluids, and

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particularly the inverse microemulsion polymerization
of water-soluble acrylamide monomers within near-
critical and supercritical alkane continuous phases.

5   G.S. Varadarajan, *Free Radical Polymerization
in Supercritical Fluid Solvents (November 29, 1990)
(MIT Doctoral Thesis) describes the free radical
polymerization of polymethylmethacrylate
(MMA)$(CH_2=C(CH_3)COOCH_3)$ in supercritical carbon dioxide
using AIBN as an initiator. The polymerization of
10   fluoromethacrylates in supercritical carbon dioxide is
not suggested.

          Canadian Patent No. 1,274,942 is directed to
acrylic acid polymerization by homopolymerizing
carboxylic acids such as acrylic acid and methacrylic
15   in supercritical carbon dioxide. The polymerization of
fluoroacrylate or fluoromethacrylate monomers in
supercritical carbon dioxide is not suggested.

          V. Krukonis and M. McHugh, *Supercritical
Fluid Extraction*, 156-158, describes the fractionation
20   of a perfluoroalkylpolyether oil and a
chlorotrifluoroethylene oligomer in supercritical
carbon dioxide, but does not suggest the polymerization
of fluoromonomers in supercritical carbon dioxide.

                    Summary of the Invention
25   A process for making a fluoropolymer is
disclosed. The process comprises solubilizing a
fluoromonomer in a solvent, the solvent comprising
carbon dioxide fluid; and then polymerizing the
fluoromonomer in said solvent to produce said
30   fluoropolymer. The fluoromonomer may be a
fluoroacrylate monomer, a fluorostyrene monomer, a
fluorinated vinyl ether monomer, or a fluoroalkylene
oxide oligomer. Fluoromonomers of the type which
undergo free radical polymerization are preferred.
35   The polymerization reaction is, in general, carried out
in the presence of an initiator. The carbon dioxide

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fluid may be liquid carbon dioxide or supercritical
carbon dioxide.

In one embodiment of the foregoing, the
process may further comprise solubilizing a comonomer
in the carbon dioxide fluid, with the polymerizing step
comprises copolymerizing the fluoromonomer with the
comonomer.

The fluoropolymers can be used as a
composition for altering surface tension properties,
e.g., to create low energy surfaces such as for stain
resistance properties.

Brief Description of the Drawings

In the drawings which form a part of the
disclosure of the invention:

Figure 1 is a phase equilibria diagram of
poly(chlorotrifluoroethylene) in carbon dioxide at
40°C, wherein the x axis of the diagram represents the
weight fraction of the sample, and the y axis
represents pressure in bars; and

Figure 2 is a phase equilibria diagram of
poly(1,1-dihydroperfluorooctyl acrylate) in carbon
dioxide at 60°C, wherein the x axis of the diagram
represents the weight fraction of the sample, and the y
axis represents pressure in bars.

Detailed Description of the Invention

The term "fluoropolymer," as used herein, has
its conventional meaning in the art. *See generally
Fluoropolymers* (L. Wall, Ed. 1972)(Wiley-Interscience
Division of John Wiley & Sons); *see also Fluorine-
Containing Polymers*, 7 Encyclopedia of Polymer Science
and Engineering 256 (H. Mark et al. Eds., 2d Ed. 1985).
Likewise, the term "fluoromonomer" refers to
fluorinated precursor monomers employed in the
synthesis of fluoropolymers. The term "solubilizing,"
as used herein, is used to indicate that the

fluoromonomers are in the same phase as the carbon
dioxide fluid in the process of the present invention;
hence the polymerization reactions of the present
invention are solution polymerizations, as opposed to
heterogeneous polymerizations or bulk polymerizations,
with these terms having their ordinary meaning in the
industry. *See, e.g.,* G. Odian, *Principles of
Polymerization*, 301-334 (3d Ed. 1991)(Wiley
Interscience).

Any suitable fluoromonomer may be used,
including, but not limited to, fluoroacrylate monomers,
fluoroolefin monomers, fluorostyrene monomers,
fluoroalkylene oxide monomers (e.g., perfluoropropylene
oxide, perfluorocyclohexene oxide), fluorinated vinyl
alkyl ether monomers, and the copolymers thereof with
suitable comonomers, wherein the comonomers are
fluorinated or unfluorinated. Fluoromonomers which are
polymerized by a free radical polymerization process
are preferred.

Fluorostyrenes and fluorinated vinyl alkyl
ether monomers which may be polymerized by the method
of the present invention include, but are not limited
to, α-fluorostyrene; β-fluorostyrene; α,β-
difluorostyrene; β,β-difluorostyrene; α,β,β-
trifluorostyrene; α-trifluoromethylstyrene; 2,4,6-
Tris(trifluoromethyl)styrene; 2,3,4,5,6-
pentafluorostyrene; 2,3,4,5,6-pentafluoro-α-
methylstyrene; and 2,3,4,5,6-pentafluoro-β-
methylstyrene. These monomers are particularly useful
as comonomers in the method of the present invention.

Tetrafluoroethylene copolymers which are
amorphous or have low melting points can be prepared by
the method of the present invention and include, but
are not limited to, tetrafluoroethylene-
hexafluoropropylene copolymers, tetrafluoroethylene-
perfluorovinyl ether copolymers (e.g., copolymers of
tetrafluoroethylene with perfluoropropyl vinyl ether),

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tetrafluoroethylene-ethylene copolymers, and
perfluorinated ionomers (e.g., perfluorosulfonate
ionomers; perfluorocarboxylate ionomers).

Fluorocarbon elastomers (see, e.g., 7
Encyclopedia of Polymer Science & Engineering 257) are
a group of amorphous fluoroolefin polymers which can be
produced by the process of the present invention and
include, but are not limited to, poly(vinylidene
fluoride-co-hexafluoropropylene); poly(vinylidene
fluoride-co-hexafluoropropylene-co-
tetrafluoroethylene); poly[vinylidene fluoride-co-
tetrafluoroethylene-co-perfluoro(methyl vinyl ether)];
poly[tetrafluoroethylene-co-perfluoro(methyl vinyl
ether)]; poly(tetrafluoroethylene-co-propylene; and
poly(vinylidene fluoride-co-chlorotrifluoroethylene).

The term "fluoroacrylate monomer," as used
herein, refers to esters of acrylic acid ($H_2C=CHCOOH$) or
methacrylic acid ($H_2C=CCH_3COOH$), where the esterifying
group is a fluorinated group such as perfluoroalkyl. A
specific group of fluoroacrylate monomers useful in the
method of the invention are compounds represented by
formula (I):

$$H_2C=CR^1COO(CH_2)_nR^2 \hspace{3cm} (I)$$

wherein:

n is 1 or 2;

R^1 is hydrogen or methyl; and

R^2 is a perfluorinated aliphatic or
perfluorinated aromatic group, such as a perfluorinated
linear or branched, saturated or unsaturated C1 to C10
alkyl, phenyl, or naphthyl.

In a particular embodiment of the invention,
R^2 is a C1 to C8 perfluoroalkyl or $-CH_2NR^3SO_2R^4$, wherein
R^3 is C1-C2 alkyl and R^4 is C1 to C8 perfluoroalkyl.

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The term "perfluorinated," as used herein, means that all or essentially all hydrogen atoms on an organic group are replaced with fluorine.

Monomers illustrative of Formula (I) above, and their abbreviations as used herein, include the following:

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("EtFOSEA");

2-(N-ethylperflooctanesulfonamido) ethyl methacrylate ("EtFOSEMA");

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate ("MeFOSEA");

2-(N-methylperflooctanesulfonamido) ethyl methacrylate ("MeFOSEMA");

1,1-Dihydroperfluorooctyl acrylate ("FOA"); and

1,1-Dihydroperfluorooctyl methacrylate ("FOMA").

In the process of the invention, the fluoroacrylate monomers may be polymerized in the presence of a free radical polymerization initiator. Any of the various organic and inorganic initiators which are known for the polymerization of monomers can be used, so long as it is compatible with carbon dioxide. The polymerization is carried out at two different temperatures by first subjecting the monomers to initial polymerization at a lower temperature, and then completing the polymerization at a substantially higher temperature.

Organic free radical initiators are preferred and include, but are not limited to, the following: acetylcyclohexanesulfonyl peroxide; diacetyl peroxydicarbonate; dicyclohexyl peroxydicarbonate; di-2-ethylhexyl peroxydicarbonate; tert-butyl perneodecanoate; 2,2'-azobis (methoxy-2,4-dimethylvaleronitrile; tert-butyl perpivalate; dioctanoyl peroxide; dilauroyl peroxide; 2,2'-

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azobis(2,4-dimethylvaleronitrile); tert-butylazo-2-
cyanobutane; dibenzoyl peroxide; tert-butyl per-2-
ethylhexanoate; tert-butyl permaleate; 2,2-
azobis(isobutyronitrile); bis(tert-
butylperoxy)cyclohexane; tert-butyl
peroxyisopropylcarbonate; tert-butyl peraceatate; 2,2-
bis(tert-butylperoxy)butane; dicumyl peroxide; ditert-
amyl peroxide; di-tert-butyl peroxide; p-menthane
hydroperoxide; pinane hydroperoxide; cumene
hydroperoxide; and tert-butyl hydroperoxide.
Preferably, the initiator is azobisisobutyronitrile
("AIBN").

The process of the invention is carried out
in a carbon dioxide fluid, e.g., carbon dioxide in a
liquid or supercritical state. As will be appreciated
by those skilled in the art, all gases have a critical
temperature above which the gas cannot be liquified by
increasing pressure, and a critical pressure or
pressure which is necessary to liquify the gas at the
critical temperature. For example, carbon dioxide in
its supercritical state exists as a form of matter in
which its liquid and gaseous states are
indistinguishable from one another. For carbon
dioxide, the critical temperature is about 31°C (88°F)
and the critical pressure is about 73 atmospheres or
about 1070 psi. The term "supercritical carbon
dioxide" as used herein refers to carbon dioxide at a
temperature greater than about 31°C and a pressure of
greater than about 1070 psi.

Liquid carbon dioxide may be obtained at
temperatures of from about -15°C to about -55°C and
pressures of from about 77 psi to about 335 psi.

One or more solvents and blends thereof may
optionally be included in the carbon dioxide.
Illustrative solvents include, but are not limited to,
tetrahydrofuran, cyclohexane, and methanol. Such

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solvents are typically included in an amount, by
weight, of up to about 20%.

The polymerization initiators are used in the
amounts conventionally employed for polymerization.
For example, the initiator may be used in an amount of
about 0.01 to 10, preferably about 0.01 to 5, parts by
weight per 100 parts by weight monomer.

The polymerization reaction may be carried
out at a temperature of about -55°C to about 300°C, and
is typically carried out at a temperature of about -30
to 100°C. The reaction may be carried out at a
pressure ranging from about 15 psi to about 45000 psi,
and is typically at a pressure of from about 500 psi to
about 10000 psi.

In alternative embodiments of the present
invention, at least one monomer or comonomer is
solubilized in carbon dioxide and copolymerized with
the fluoromonomer. Any suitable monomers or comonomers
can be employed, including, but not limited to,
acrylate, methacrylate, acrylamide, methacrylamide,
styrenics, ethylene, and vinyl ether monomers. The
copolymerizations of the present invention may be
carried out under temperature and pressure conditions
similar to those given above.

The polymerization can be carried out
batchwise or continuously with thorough mixing of the
reactants in any appropriately designed high pressure
reaction vessel (i.e., capable of withstanding
pressures up to 45000 psi). To remove the heat evolved
during the polymerization, advantageously the pressure
apparatus includes a cooling system. Additional
features of the pressure apparatus used in accordance
with the invention include heating means such as an
electric heating furnace to heat the reaction mixture
to the desired temperature and mixing means, i.e.,
stirrers such as paddle stirrers, impeller stirrers, or

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multistage impulse countercurrent agitators, blades, and the like.

The polymerization can be carried out, for example, by placing the monomer and initiator in the pressure apparatus
5   and introducing carbon dioxide in liquid form. The reaction vessel is closed and the reaction mixture brought to the polymerization temperature and pressure. Alternatively, only a part of the reaction mixture may be introduced into an autoclave and heated to the
10   polymerization temperature and pressure, with additional reaction mixture being pumped in at a rate corresponding to the rate of polymerization. In another possible procedure, some of the monomers are initially taken into the autoclave in the total amount of carbon dioxide and the monomers or
15   comonomers are pumped into the autoclave together with the initiator at the rate at which the polymerization proceeds.

When the polymerization is complete the reaction mixture is cooled (if necessary), the carbon dioxide separated off (e.g., by simply venting to the atmosphere),
20   and the polymer collected. After separation of the carbon dioxide, the polymer can be collected simply by physical isolation, or by dissolution and precipitation, for example, by adding Freom-113™ or α,α,α-trifluorotolune to the polymer to dissolve the polymer and recover it from the
25   reaction vessel and then precipitating the same with methanol.

The solution of polymer and carbon dioxide can be separated by any method known to those in the art used to isolate polymers from solution. Examples of such methods
30   include, but are not limited to, boiling off the carbon

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dioxide and leaving the polymer (e.g., fluropolymer) behind, precipitation of the polymer into a non-solvent either by introducing a non-solvent for the polymer, isolation of the polymer by passing (e.g., spraying, and more particularly, spray-drying) the solution through an orifice to form particles, powders, fibers, a coating, mixtures thereof, and the like on substrates. A wide variety of substrates may be used including, but not limited to, metals, organic polymers, inorganic polymers, textiles, and composites thereof. These isolation methods have been demonstrated for conventional liquid solvent systems, as well as for solutions of polymers present in supercritical or densified gases. Often coatings applications, polymer solutions are used as a method for delivering coatings materials to a substrate. Accordingly, the polymer and carbon dioxide do not necessarily need to be separated until used in the final application.

The following Examples are provided to further illustrate the present invention. In Examples, SCF means supercritical fluid; AIBN means azobisisobutyronitrile; MMA means polymethylmethacrylate; psi means pounds per square inch; g means grams; mg means milligrams; mL means milliliters; min means minutes; M_w means weight average molecular weight; M_n means number average molecular weight; MWD means molecular weight distribution (M_w/M_n); mmol means

millimoles; dL/g means deciliters per gram; cm means
centimeters; THF means tetrahydrofuran; DMF means N,N-
dimethylformamide; DMAc means N,N-dimethylacetamide;
[n] means intrinsic viscosity; NMR means nuclear
magnetic resonance; GPC means gel permeation
chromatography; FTIR means fourier transform infrared;
IR means infrared; and temperatures are given in
degrees celsius. These examples are illustrative of
the invention, and should not be construed as limiting
thereof.

EXAMPLES 1-17

*Solubility, Polymerization and Copolymerization of
Fluoroacrylate Monomers*

EXAMPLE 1

Experimental Procedures

Materials. Five fluoromonomers, illustrated
by Formula (II) and Table 1 and Formula (III) and Table
2, were kindly provided by Minnesota Mining and
Manufacturing Company (3M). MeFOSEA, EtFOSEA and
EtFOSEMA were purified by recrystallization in
methanol. 1,1-Dihydroperfluorooctyl acrylate (FOA) was
purified by running through Al_2O_3 column to remove the
inhibitor. AIBN (Kodak) was recrystallized twice from
methanol. Carbon dioxide (Matheson, 99.99%) was passed
through copper oxide catalyst column to remove trace
amounts of oxygen and then through a molecular
sieve(3A) column to remove trace amounts of moisture.
Freon-113 ($CF_2ClCFCl_2$) was fractionally distilled before
use. Methanol (Mallinckrodt) was used as received.

$$H_2C=C \overset{R}{\underset{\underset{O}{\overset{|}{C=O}}}{|}}$$

$$\overset{|}{O} \qquad \overset{R'}{|}$$

$$CH_2CH_2-N-SO_2-(CF_2)_7CF_3$$

(II)
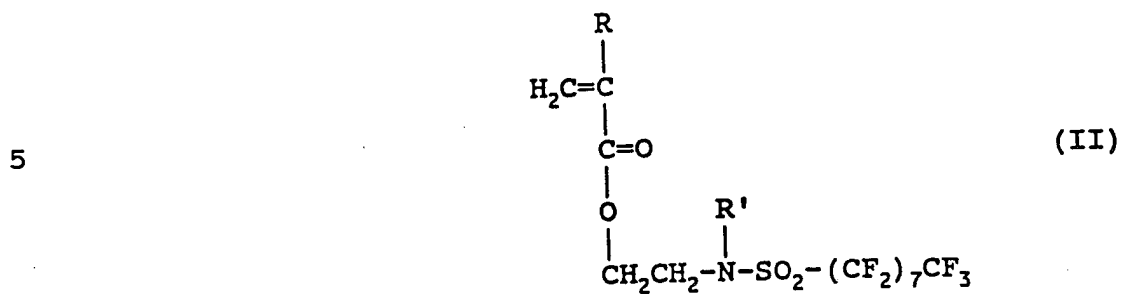
Table 1.
·Fluorinated Monomers of Formula (II)

Name	R	R'
MeFOSEA	H	CH_3
EtFOSEA	H	CH_2CH_3
MeFOSEMA	CH_3	CH_3
EtFOSEMA	CH_3	CH_2CH_3

$$H_2C=C \overset{R}{\underset{\underset{O-CH_2(CF_2)_6CF_3}{\overset{|}{C=O}}}{|}}$$

(III)
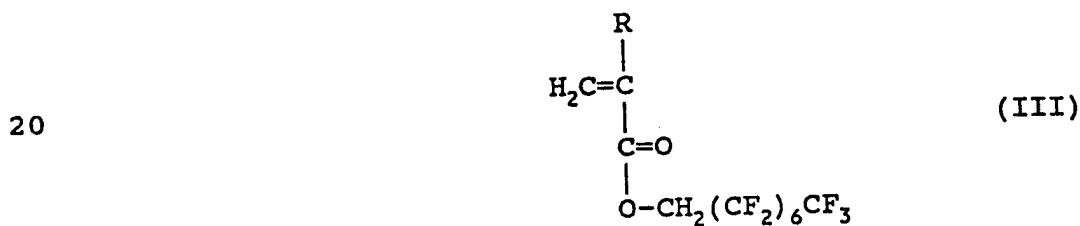
Table 2.
Fluorinated Monomers of Formula (III)

Name	R
FOA	H
FOMA	CH_3

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EXAMPLE 2

Comparative Example: Polymerization in Freon 113

Before running polymerizations in supercritical carbon dioxide, a series of poly(perfluoroalkyl acrylate)s and poly(perfluoroalkyl methacrylate)s were prepared using free radical polymerization methods in Freon-113 and in α,α,α-trifluorotoluene and studied their solubility in both liquid and supercritical carbon dioxide. The fluoromonomers employed for this study are those set forth in Tables 1 and 2 above. The polymerization conditions (feed ratios of monomers, initiator and solvents), intrinsic viscosities and molecular weight data are summarized at **Table 3**.

A typical procedure is described below. EtFOSEA (5 g), azobisisobutyronitrile (AIBN) (10 mg) and 10 mL of Freon-113 were put into a 50 mL test tube. After sealing the tube with a rubber septum, the solution was purged with argon for ca. 15 min, placed in a water bath at 60°C and left to polymerize for ca. 20 hours. The tube was opened next day and ca. 30 mL of Freon-113 was added to dilute the polymer solution, followed by precipitation of polymer into methanol. The polymer was filtered and dried in vacuum oven overnight. All of the monomers were polymerized in Freon-113 at 60°C except MeFOSEA which was polymerized in α,α,α-trifluorotoluene at 70°C due to solubility considerations.

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Table 3

Sample	Feed Ratio			[n]	Mw	Mn	MWD
	monomer (g)	AIBN (mg)	solvent (ml)				
P(EtFOSEA)							
910607-1	2	5	10	0.14	7.68e4	1.13e4	6.79
910607-2	2	10	10	0.11	9.23e4	1.32e4	7.02
910607-3	2	20	10	0.078	7.67e4	2.06e4	3.73
910614-0	3	2+2	2	0.44	1.24e5	5.14e4	2.41
910614-1	5	5	10	0.28	1.14e5	1.39e4	8.20
910614-2	5	10	10	0.28	1.56e5	5.56e4	2.80
910614-3	5	20	10	0.24	1.38e5	5.46e4	2.54
P(EtFOSEMA)							
910710-3	5	5	10	0.13	7.20e4	8.23e3	8.75
P(FOA)							
910710-1	5	5	10	0.21	1.10e6	2.90e5	3.78
P(FOMA)							
910710-2	5	5	10	gel-like			
910711	5	5	20	0.26*	unable to filter		
P(MeFOSEA)**							
910620-1	5	10	20	0.077			
910620-2	5	20	20	0.066			
910620-3	5	30	20	0.010			

All polymerizations are run at 60°C.
* The viscosity of the soluble part.
**Polymerized in , , -trifluorotoluene.

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EXAMPLE 3

Solubility Evaluation in Carbon Dioxide

The solubilities of poly(EtFOSEA) and poly(MeFOSEA) in carbon dioxide were measured using a flow system, the results of which are set forth at **Table 4**. Poly(EtFOSEA) was found to be very soluble in both liquid and supercritical carbon dioxide (about 25 wt.%). Poly(MeFOSEA) dissolved in liquid CO_2 at 3000 psi at room temperature. A view cell study discussed below verified that the polymer was also soluble in supercritical CO_2.

For comparison, the solubility of poly(methyl methacrylate) (PMMA) in both liquid and supercritical CO_2 was also studied. Quite differently, PMMA of even lower molecular weight than the two fluoropolymers discussed above is insoluble in carbon dioxide with the pressure ranging from 2000 to 5000 psi and temperature ranging from room temperature to 160°C.

To ensure that the fluoropolymers form homogeneous solutions with carbon dioxide, the solubility of the five fluoropolymers was also determined using a view cell. The results of the observations are set forth at **Table 5**. We observed that all the polymers dissolved and formed clear solutions in carbon dioxide at moderate pressures. Comparatively, poly(FOA) and poly(FOMA) are easier to dissolve in carbon dioxide than poly-(EtFOSEMA), poly(EtFOSEA) and poly(MeFOSEA), but all of the polymers dissolve.

Table 4

Solubility study of F-polymers by flow system:

Sample	[n]	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	T(°C)	P(psi)	Solubility (wt.%)
P(EtFOSEA)	0.44	1.24	5.14	29	5000	25
P(EtFOSEA)	0.28	1.14	1.39	60	4000	25
P(MeFOSEA)	0.077	—	—	25	3000	15-20
PMMA	—	0.22	1.93	29-160	2000-5000	0

Table 5

Solubility study of F-polymers by view cell:

Sample	[n]	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	T(°C)	P(psi)	Conc. wt.%vol
P(EtFOSEA)	0.44	1.24	5.14	25	7000	9
P(EtFOSEA)	0.24	1.38	5.46	25	3000	5
P(MeFOSEA)	0.077	—	—	60	3700	5
P(FOA)	0.21	11.0	29.0	25	2000	5
P(FOA)	0.21	11.0	29.0	25	3000	10
P(FOMA)	0.26	—	—	25	2000	5
P(EtFOSEMA)	0.13	0.72	0.82	25	4000	5

* Pressure at which the polymer totally dissolve.

EXAMPLE 4

Polymerization of 1,1-dihydroperfluorooctyl Acrylate (FOA) in Carbon Dioxide

FOA (5.0 g, 11.0 mmol, purified by running through Al_2O_3 column) and AIBN (50 mg, 0.30 mmol, recrystallized twice from methanol) were put into a 10 mL high pressure reaction cell with a micromagnetic stir bar inside. The reaction cell was purged with

argon for ca. 10 minutes and then filled with carbon
dioxide to a pressure of less than 1000 psi. Over a
period of one hour, the cell was heated to 60°C and the
pressure was increased to 3000 psi by the addition of
more CO_2. The polymerization was continued at these
conditions for 48 hours, during which the system was
homogeneous and clear.

At the end of the polymerization, carbon
dioxide was vented slowly to leave the polymer in the
cell. The polymer was dissolved with Freon-113 and was
precipitated into a large excess of methanol. The
polymer was isolated by suction filtration, washed
several times with methanol, and dried in vacuo
overnight to give 3.25 g of transparent viscous polymer
(yield: 65%).

Characterizations: ^{1}H NMR spectrum showed the
expected pattern, without vinyl proton peaks of the
monomer and without any indication of incorporation of
carbon dioxide onto the polymer backbone. The intrinsic
viscosity was measured to be 0.19 dL/g in Freon-113 at
30°C. The FTIR spectrum was consistent with the
corresponding homopolymer made in Freon-113, with only
one carbonyl peak at 1758 cm^{-1}.

                              EXAMPLE 5

          Polymerization of FOA in carbon dioxide

          FOA (2.0 g, 4.4 mmol) and AIBN (30 mg, 0.18
mmol) were put into the high pressure cell. Following
the same procedure as described in Example 4,
polymerization was proceeded at 3000 psi and 60°C for
24 hours, and 0.41 g of polymer was obtained (yield:
21%).

          Characterizations: ^{1}H NMR and FTIR spectra
were consistent with those of the homopolymer made in
Freon-113.

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EXAMPLE 6

Polymerization of 1,1-dihydroperfluorooctyl
Methacrylate (FOMA) in Carbon Dioxide

FOMA (3.0 g, 6.41 mmol, purified by running
through Al_2O_3 column) and AIBN (30 mg, 0.18 mmol) were
put into the 10 mL high pressure reaction cell. The
reaction cell was purged with argon for ca. 10 minutes
then filled with carbon dioxide to a pressure of less
than 1000 psi. Over a period of one hour, the cell was
heated to 60°C, and the pressure was increased to 4000
psi by the addition of more CO_2. The polymerization was
continued at these conditions for 48 hours, during
which the system was homogeneous and clear. At the end
of the polymerization, carbon dioxide was vented slowly
to leave the polymer in the cell. The polymer was
dissolved with Freon-113 and was precipitated into a
large excess of methanol. The polymer was isolated by
suction filtration, washed several times with methanol,
and dried in vacuo overnight to give 2.19 g of a white
powder (yield: 73%).

Characterizations: ^1H NMR and FTIR spectra
were consistent with those of the same polymer made in
Freon-113. The intrinsic viscosity was measured to be
0.06 dL/g in Freon-113 at 30°C.

EXAMPLE 7

Polymerization of FOMA in CO2

FOMA (5.0 g, 10.7 mmol) and AIBN (50 mg, 0.3
mmol) was put into the 10 mL high pressure cell.
Following the same procedure described in Example 4,
the polymerization was carried out in CO_2 at 60°C and
5000 psi for 48 hours. During the entire course of the
polymerization, the solution was homogeneous and clear.
The polymer was isolated according to the same
procedure as described above.

Characterizations: ^1H NMR and FTIR spectra
were consistent with those of the same polymer made in

Freon-113. The intrinsic viscosity was measured to be
0.06 dL/g in Freon-113 at 30°C.

EXAMPLE 8

Polymerization of 2-(N-methylperfluorooctane-sulfonamido) ethyl Acrylate (MeFOSEA) in Carbon Dioxide

MeFOSEA (5.0 g, 8.75 mmol, purified by
recrystallization from methanol) and AIBN (50 mg, 0.30
mmol) were put into the 10 mL high pressure reaction
cell. The reaction cell was purged with argon for ca.
10 minutes then filled with carbon dioxide to a
pressure of less than 1000 psi. Over a period of one
hour the cell was heated to 60°C and the pressure was
increased to 5000 psi by the addition of more CO_2. The
polymerization was continued at these conditions for 48
hours, during which the system was homogeneous and
clear. At the end of the polymerization, carbon
dioxide was vented slowly to leave the polymer in the
cell. The polymer was dissolved in
α,α,α-trifluorotoluene and was precipitated into a
large excess of methanol. The polymer was isolated by
suction filtration, washed several times with methanol,
and dried in vacuo overnight to give 3.2 g of white
powder (yield: 64%).

Characterizations: FTIR spectra were
consistent with those of the same polymer made in
Freon-113.

EXAMPLE 9

Polymerization of MeFOSEA in Carbon Dioxide

MeFOSEA (1.0 g, 1.75 mmol) and AIBN (10 mg,
0.06 mmol) were put into the high pressure cell.
Following the same procedure of Example 4, the
polymerization was proceeded under 4000 psi and 60°C
for 8 hours, and 0.19 g of polymer was obtained (yield:
19%).

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Characterizations: FTIR spectrum were
consistent with the same polymer made in Freon-113.
The intrinsic viscosity was measured to be 0.064 in
α,α,α-trifluorotoluene at 70°C.

5   EXAMPLE 10

Polymerization of 2-(N-ethylperfluorooctane-
sulfonamido) Ethyl Acrylate (EtFOSEA) in Carbon Dioxide

EtFOSEA (5.0 g, 8.53 mmol, purified by
recrystallization from methanol) and AIBN (50 mg, 0.30
10   mmol) were put into the 10 mL high pressure view cell.
The reaction cell was purged with argon for ca. 10
minutes then filled with carbon dioxide to a pressure
of less than 1000 psi. Over a period of one hour the
cell was heated to 60°C and the pressure was increased
15   to 5000 psi by the addition of more CO_2. The
polymerization was continued at these conditions for 48
hours, during which the system was homogeneous and
clear. At the end of the polymerization, carbon
dioxide was vented slowly to leave the polymer in the
20   cell. The polymer was dissolved in Freon-113 and was
precipitated into a large excess of methanol. The
polymer was isolated by suction filtration, washed
several times with methanol, and dried in vacuo
overnight to give 3.9 g of a white powder (yield: 78%).
25   Characterizations: ^{1}H NMR and FTIR spectra
were consistent with those of the same polymer made in
Freon-113. The intrinsic viscosity was measured to be
0.20 dL/g in Freon-113 at 30°C. Both the polymers made
in CO_2 and in Freon-113 were purified by dissolving in
30   Freon-113 and reprecipitating into methanol and an
elemental analysis by ORS was performed. The results
are summarized in **Table 6** below.

Table 6

*Elemental Analysis of Poly(EtFOSEA) Made in
Carbon Dioxide and in Freon-113*

Sample	% C	% H	% N	% F	% S
P-Freon	28.69	1.86	2.21	51.47	5.05
P-CO$_2$	28.80	1.91	2.24	50.78	4.81
Calculated	29.01	2.01	2.33	50.64	5.34

EXAMPLE 11

*Polymerization of 2-(N-ethylperfluorooctane-
sulfonamido) Ethyl Methacrylate (EtFOSEMA) in CO$_2$*

EtFOSEMA (5.0 g, 8.33 mmol, purified by
recrystallization from methanol) and AIBN (50 mg, 0.30
mmol) were put into the same reaction vessel. The
reaction vessel was purged with argon for ca. 10
minutes then filled with carbon dioxide to a pressure
of less than 1000 psi. Over a period of one hour the
cell was heated to 60°C, and the pressure was increased
to 5000 psi by the addition of more CO$_2$. The
polymerization was continued at these conditions for 48
hours, during which the system was homogeneous and
clear. At the end of the polymerization, carbon
dioxide was vented slowly to leave the polymer in the
vessel. The polymer was dissolved in Freon-113 and
was precipitated into a large excess of methanol. The
polymer was isolated by suction filtration, washed
several times with methanol, and dried in vacuo
overnight to give 3.2 g of white powder.

Characterizations: ^{1}H NMR and FTIR spectra
were consistent with those of the same polymer made in
Freon-113. The intrinsic viscosity was measured to be
0.10 dL/g in Freon-113 at 30°C.

EXAMPLE 12

Copolymerization of FOA with Methyl Methacrylate (MMA) in CO_2

FOA (4.0 g,   mmol, purified by running
through Al_2O_3 column), MMA (1.0 g, 10.0 mmol, purified
by vacuum distillation over CaH_2) and AIBN (50 mg, 0.30
mmol) were put into the 10 mL high pressure view cell.
The reaction cell was purged with argon for ca. 10
minutes then filled with carbon dioxide to less than
1000 psi. Over a period of one hour the cell was
heated to 60°C and the pressure was increased to 5000
psi by the addition of more CO_2. The polymerization was
continued at these conditions for 48 hours, during
which the system was homogeneous and clear. At the end
of the polymerization, carbon dioxide was vented slowly
to leave the polymer in the cell. The polymer was
dissolved in Freon-113 and was precipitated into a
large excess of methanol. The polymer was isolated by
suction filtration, washed several times with methanol,
and dried in vacuo overnight to give 3.25 g of
copolymer (yield: 65%). The copolymer was extracted
with THF three times to remove any possible PMMA
homopolymer.

Characterizations: Solubility of the
copolymer in normal solvents and Freon-113 was checked
and the results are summarized in **Table 7** below.

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Table 7

Solubility Test of PFOA-co-PMMA-1

Solvent	solubility
Freon-113	soluble, but slightly cloudy
acetone	liquified but insoluble
THF	liquified but insoluble
CH_2Cl_2	swelled
toluene	swelled
DMF	slightly swelled
DMAc	slightly swelled

^1H NMR and FTIR spectra were indicative of a
statistical or random copolymer. Composition of the
copolymer was calculated to be 58 mol% FOA from the ^1H
NMR spectrum. IR spectrum showed two carbonyl peaks at
1758 (carbonyl of FOA segments) and 1734 cm^{-1} (carbonyl
of MMA segments), respectively. The intrinsic
viscosity was measured to be 0.10 dL/g in Freon-113 at
30°C.

EXAMPLE 13

Copolymerization of FOA and MMA in Carbon Dioxide

FOA (3.0 g, 6.6 mmol, purified by running
through Al_2O_3 column), MMA (2.0 g, 20.0 mmol, purified
by vacuum distillation over CaH_2) and AIBN (50 mg, 0.30
mmol) were put into the high pressure cell. The
reaction cell was purged with argon for ca. 10 minutes
then filled with carbon dioxide to less than 1000 psi.
Over a period of one hour the cell was heated to 60°C
and the pressure was increased to 5000 psi by the
addition of more CO_2. The polymerization system became
nonhomogeneous after ca. 12 hours. After 48 hours,
there existed two layers, with the bottom layer
accounting for ca. 1/4 of the total reactor volume and
a cloudy upper layer accounting for ca. 3/4 of the

total volume. At the end of the polymerization, carbon dioxide was vented slowly to leave the polymer in the cell. The polymer was dissolved in Freon-113 and was precipitated into a large excess of methanol. The polymer was isolated by suction filtration, washed several times with methanol, and dried in vacuo overnight to give 3.3 g of copolymer (yield: 66%). The copolymer was extracted with DMF three times.

Characterizations: ^{1}H NMR and FTIR spectra show the expected patterns. Composition of copolymer was calculated from proton NMR spectrum to be 27 mol% in FOA. Two carbonyl peaks appear on the IR spectrum (1758 and 1734 cm^{-1}). The intrinsic viscosity was measured to be 0.12 dL/g in acetone at 30°C. The solubilities of the copolymer in normal solvents are summarized in **Table 8** below.

Table 8

Solubility of PFOA-co-PMMA-2 in Different Solvents

Solvent	Solubility
Freon-113	soluble
acetone	soluble
THF	soluble
CHCl$_3$	soluble
CH$_2$Cl$_2$	soluble (40 Ċ)
toluene	soluble (100 Ċ)
DMF	insoluble
DMAc	insoluble

Since this copolymer is soluble in normal solvents, ^{13}C NMR and ^{19}F NMR spectra was measured in d6-acetone. Only two carbonyl peaks appeared on the spectrum (177, 178 ppm). The ^{19}F NMR spectrum showed six resonances. GPC was run with THF as solvent and polystyrene as standard. The results were Mn = 5.10x10^4, Mw = 7.45x10^4, MWD = 1.46.

EXAMPLE 14

Copolymerization of FOA and MMA
in CO_2 with THF as a Co-Solvent

FOA (3.0 g, 6.6 mmol), MMA (2.0 g, 20 mmol)

5   and AIBN (50 mg, 0.30 mmol) were put into the high
pressure cell.   1.0 mL (10 vol%) THF was added into the
mixture.   The reaction cell was purged with argon for
ca. 10 minutes and then filled with carbon dioxide to
less than 1000 psi.   Over a period of one hour the cell

10   was heated to 60°C, and the pressure was increased to
5000 psi by the addition of more CO_2.   The
polymerization was continued at these conditions for 48
hours.   The system was homogeneous for at least 30
hours at which time it became cloudy.   The solution

15   remained homogenous for a longer time than the
polymerization reaction conducted without the cosolvent
(Example 13).   At the end of the polymerization, carbon
dioxide was vented slowly to leave the polymer in the
cell. The polymer was dissolved in Freon-113 and was

20   precipitated into a large excess of methanol.   The
polymer was isolated by suction filtration, washed
several times with methanol, and dried in vacuo
overnight to give 3.9 g of white polymer (yield: 78%).
Characterizations: GPC was run with THF as

25   solvent.   The results were: Mn = 5.50×10^4, Mw =
8.23×10^4, MWD = 1.50.

EXAMPLE 15

Copolymerization of FOA and n-butyl
Acrylate (BA) in Carbon Dioxide

30   FOA (4.0 g, 6.6 mmol), BA (1.0 g, 7.8 mmol,
purified by running through Al_2O_3 column) and AIBN (50
mg, 0.30 mmol) were put into the high pressure reaction
cell.   The reaction cell was purged with argon for ca.
10 minutes then filled with carbon dioxide to less than

35   1000 psi.   Over a period of one hour the cell was

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heated to 60°C and the pressure was increased to 5000
psi by the addition of more CO_2. The polymerization was
continued at these conditions for 48 hours, during
which the system was homogeneous and clear. At the end
5   of the polymerization, carbon dioxide was vented slowly
to leave the polymer in the cell. The polymer was
dissolved with Freon-113 and was precipitated into a
large excess of methanol. The polymer was isolated by
suction filtration, washed several times with methanol,
10 and dried in vacuo overnight to give a transparent
elastic material which was purified by extracting with
acetone overnight.

   Characterizations: ^1H NMR and FTIR spectra
were indicative of a random or statistical copolymer.
15 Composition of the copolymer was calculated to be 59%
FOA based on ^1H NMR. Two carbonyl resonances appeared
in the IR spectrum (1760 and 1720 cm^{-1}). The intrinsic
viscosity was 0.45 dL/g in Freon-113 at 30°C. The
solubility of the copolymer is summarized in **Table 9**.

20   *Table 9*

  The Solubility of PFOA-co-PBA in Different Solvents

Solvent	Solubility
Freon-113	soluble
acetone	insoluble
THF	insoluble
$CHCl_3$	dispersed but insoluble
toluene	insoluble
DMF	insoluble

EXAMPLE 16

Copolymerization of FOA with Styrene in CO_2

   FOA (4.0 g, 6.6 mmol), styrene (1.0 g, 9.6
35 mmol, purified by vacuum distillation) and AIBN (50 mg,

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0.30 mmol) were put into the high pressure reaction
cell. The reaction cell was purged with argon for ca.
10 minutes then filled with carbon dioxide to less than
1000 psi. Over a period of one hour the cell was
5   heated to 60°C and the pressure was increased to 5000
psi by the addition of more CO_2. The polymerization was
continued at these conditions for 48 hours, during
which the system was homogeneous and clear. At the end
of the polymerization, carbon dioxide was vented slowly
10   to leave the polymer in the cell. The polymer was
dissolved with Freon-113 and was precipitated into a
large excess of methanol. The polymer was isolated by
suction filtration, washed several times with methanol,
and dried in vacuo overnight to give a very tacky
15   material. The polymer was extracted with acetone
overnight to remove any possible styrene homopolymer.
Characterizations: ^1H NMR and FTIR spectra
were indicative of a random or statistical copolymer.
All the peaks of FOA were shifted upfield by ca. 0.4
20   ppm. Also the peak of the methylene proton adjacent to
the perfluoroalkyl chain was broadened. IR spectrum
showed one carbonyl resonance at 1758 cm^{-1} and peaks
appeared in the region between 3000 to 3100 cm^{-1} due to
the stretching vibration of C-H on the phenyl ring of
25   the styrene repeating unit.

EXAMPLE 17

Copolymerization of FOA with Ethylene in CO_2

FOA (4.0 g, 6.6 mmol) and AIBN (50 mg, o.30
mmol) were put into the high pressure cell. Ethylene
30   (0.46 g, 16.4 mmol) was transferred from a small bomb
into the reaction cell. CO_2 was added, and the
temperature was raised to 60°C and the total pressure
was 5000 psi. The polymerization was allowed to
proceed for ca. 48 hours. During this time period, the
35   system remained homogeneous and clear. After venting
CO_2, the product was dissolved with Freon-113 and

precipitated into large excess of methanol to give 2.9
g of viscous polymer (yield: 65%). The copolymer was
extracted with boiling toluene for two hours to remove
any polyethylene homopolymer.

5   Characterization: The copolymer was insoluble
in acetone, toluene, THF, chloroform and DMF. It was
soluble in Freon-113. ^{1}H NMR spectrum showed a new peak
appearing at ca. 1.5 ppm, which is presumably due to
the protons of the ethylene repeat unit. FTIR show

10   similar pattern to PFOA homopolymer. The resonance of
ethylene repeat unit may be buried by the resonance of
the backbone of FOA. Intrinsic viscosity was measured
to be 0.14 dL/g in Freon-113 at 30°C.

EXAMPLE 18

15   *Cationic Polymerization of Vinyl Ethers in CO_2*
          Vinyl ethers with a fluoroalkyl group
according to Formula (IV):

$$R^1R^2C=CR^3O(CH_2)_nR \qquad\qquad (IV)$$

      wherein:

20   n is 0, 1, or 2;
            R^1, R^2, and R^3 are each independently hydrogen
or fluorine; and
            R is perfluorinated aliphatic or
perfluorinated aromatic group,

25   for example, $CH_2=CH-OCH_2CH_2N(n-C_3H_7)SO_2C_8F_{17}$ or $CH_2=CH-$
$OCH_2C_8F_{17}$, are polymerized with an initiator such as
boron trifluoroetherate, hydrogen iodine/iodine, and
hydrogen iodine/zinc iodine in liquid and supercritical
carbon dioxide using the procedure of Example 4 above.

30   It has previously been known that these monomers could
be solvent polymerized in Freon. *See* W. Choi et al.,
Polymer J. **20**, 201 (1988). Thus, this example
indicates that the ability of a monomer to undergo
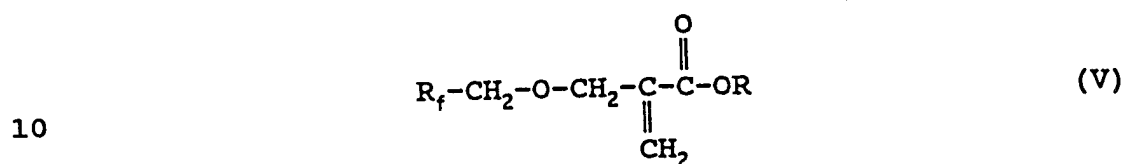solution polymerization in Freon-113 is a good

indicator that the monomer can be polymerized in liquid
or supercritical carbon dioxide.

EXAMPLE 19

Polymerization of 1,1-Disubstituted Monomers

1,1-disubstituted monomers according to
Formula (V):

$$R_f-CH_2-O-CH_2-C\underset{\overset{\|}{CH_2}}{\overset{\overset{O}{\|}}{-C}}-OR \qquad (V)$$

wherein R is C1-C4 alkyl (e.g., ethyl) and R_f is $(CF_2)_nF$
wherein n is 1-10, (e.g., CF_3, $(CF_2)_2F$, $(CF_2)_7F$, or
$(CF_2)_{10}F$), are polymerized in liquid or supercritical
carbon dioxide under conditions using the procedure of
Example 4 above.

EXAMPLE 20

Polymerization with Chain Transfer Agents

Functional fluoropolymers are produced in
liquid or supercritical carbon dioxide by polymerizing
a fluoromonomer such as FOA in carbon dioxide in the
presence of a chain transfer agent such as substituted
allylic sulfides. This results in fluoropolymers
capped with a carboxy, hydroxy, trialkylsilyl, or amino
groups.

EXAMPLE 21

Polymerization of Block Fluoropolymers

Block fluoropolymers are produced in liquid
or supercritical carbon dioxide using the procedure of
Example 4 above, using pseudo-living free radical
polymerization routes. For example, FOA is polymerized
in carbon dioxide with nitroxides similar to that
disclosed in U.S. Patent No. 4,581,429 or with oxygen-

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centered radical species generated from hyponitrite,
arenediazoate, or cyanate anions by reaction with
electron acceptors such as arenediazonium ions or
activated alkyl halides with sequential monomer
additions, similar to Druliner, J.D., *Macromolecules*
1991, 24, 6079.

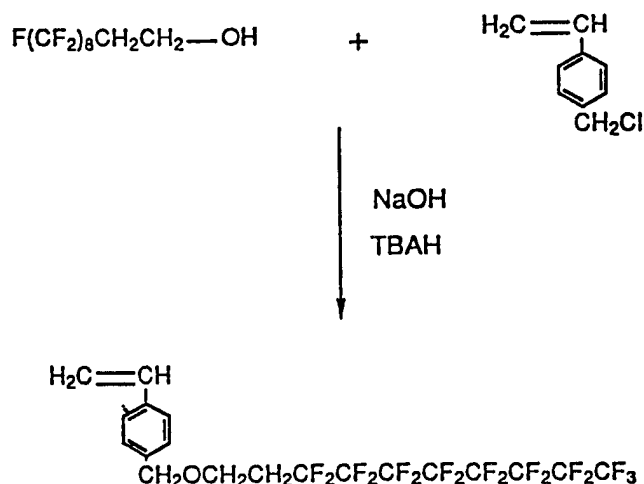## EXAMPLE 22

Poly(perfluoroalkyl ether) Polymerization

Poly(perfluoroalkyl ether)s are made in
liquid or supercritical carbon dioxide using the
procedure of Example 4 above. For example,
perfluoropropylene oxide is polymerized using
initiators derived from alkali metal fluorides and an
acid fluoride such as CF_3CO-F in carbon dioxide to yield
viscous oils.

EXAMPLE 23

Preparation of Monomers

Styrene (Aldrich), methyl methacrylate (MMA)
(Aldrich), acrylic acid (AA) (Aldrich) were purified by
running through an alumina column and deoxygenated
before polymerization. N-Octyl acrylate (OA),
octadecyl methacrylate (ODMA) and all the
perfluoroalkyl acrylates described above in Example 1
were purified in a similar fashion. Vinylidene
fluoride (VF_2) (Aldrich, 99+%) and pentafluorostyrene
(5FSt) (PCR Inc.) were used as received. The styrene-
based monomer carrying a fluorocarbon segment, *p*-
perfluoroalkylethyleneoxymethyl styrene (STF), was
prepared by a phase-transfer-catalyzed etherification
of fluorocarbon-substituted alcohol with *p*-
(chloromethyl) styrene:

F(CF$_2$)$_8$CH$_2$CH$_2$—OH   +   H$_2$C═CH

CH$_2$Cl

NaOH
TBAH

H$_2$C═CH

CH$_2$OCH$_2$CH$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_2$CF$_3$

EXAMPLE 24

Homopolymerization of Fluorostyrene Monomer
p-perfluoroalkylethyleneoxymethyl Styrene (STF)

A typical example of a homopolymerization in
supercritical CO$_2$ was conducted as follows. STF (1.0 g,
1.72 mmol) and AIBN (30 mg, recrystallized twice from
methanol) were put into a 10-mL high pressure view cell
containing a micromagnetic stir bar. The reaction cell
was purged with argon for ca. 10 minutes, and then
filled with CO$_2$ to less than 68 bar. The cell was
heated to 60°C and the pressure was increased to 345
bar by the addition of more CO$_2$. The polymerization was
continued at these conditions for 3 days, during which
time the system remained homogeneous and optically
transparent. At the end of the polymerization, the
cell was cooled to room temperature and CO$_2$ was vented
resulting in the precipitation of the polymer. The
unreacted monomer was extracted with dichloromethane.
The polymer was dried to constant weight and
characterized (65% yield).

The other monomers (VF$_2$, 5FSt, styrene, MMA,
AA) were all homopolymerized in supercritical carbon
dioxide according to a procedure similar to that above;

however, these polymers precipitated during the course
of the reaction in CO_2 under the conditions described.

EXAMPLE 25

Homopolymerization of Fluorostyrene Monomer

Fluorostyrene monomers according to Formula
(VI):

$$R^1R^2C=CR^3$$

(VI)
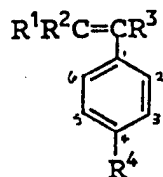
wherein:

R^1 and R^2 are each independently hydrogen,
fluorine, or methyl;

R^3 is hydrogen, fluorine, methyl or
perfluoromethyl;

R^4 is hydrogen, fluorine, or C1-C12
perfluorinated aliphatic group; and

the 2, 3, 5, and 6 positions of the aromatic
styrene ring are each independently hydrogen or
fluorine, are polymerized with an initiator such as
AIBN in liquid and supercritical carbon dioxide using
the concentrations and procedure of Example 24 above.

EXAMPLE 26

*Copolymerization of Fluorinated Monomer (Fluoroacrylate
MeFOSEA) with Non-Fluorinated Comonomer (OA)*

A copolymerization of the fluorinated
monomers with non-fluorinated monomers in supercritical
CO_2 was conducted as follows. 2-(N-Methylperfluoro-
octanesulfonamido) ethyl acrylate (MeFOSEA, 1.3 g, 2.12
mmol), OA (0.70 g, 3.80 mmol) and AIBN (30 mg, 0.18
mmol) were put into the 10-mL high pressure view cell.
Following the procedure as described above in Example
24, the copolymerization was continued at 60°C and 345
bar for 24 hours. The system was homogeneous during
the entire course of the polymerization. After venting

the CO_2, the copolymer was redissolved in Freon-113 and
precipitated into large excess of methanol. The
polymer was filtered and washed with methanol several
times and dried in vacuo overnight to give 1.35 g of
5   copolymer (68% yield).

The other non-fluorinated monomers are also
copolymerized in a similar fashion.

EXAMPLE 27

Copolymerization of Fluorinated Monomer (Fluoroacrylate
10   *FOA) With Fluorinated Comonomer (Vinylidene Fluoride)*

The 10-mL high pressure cell was loaded with
1,1-dihydroperfluorooctyl acrylate (FOA, 3.0 g, 6.6
mmol) and AIBN (50 mg, 0.30 mmol). After purging with
argon thoroughly, the cell was connected to a VF_2
15   cylinder, 3.02 of VF_2 (47.2 mmol) was transferred into
the cell by cooling down the cell in a dry
ice/isopropanol bath. After warming the cell to room
temperature, carbon dioxide was filled to ca. 68 bar.
The heating of the cell was continued and more CO_2 was
20   added until the cell reached 60°C and 345 bar. The
polymerization was continued at these conditions for
ca. 50 hours during which the system was homogeneous
during the entire course of the reaction. The
copolymer was obtained according to the same work-up
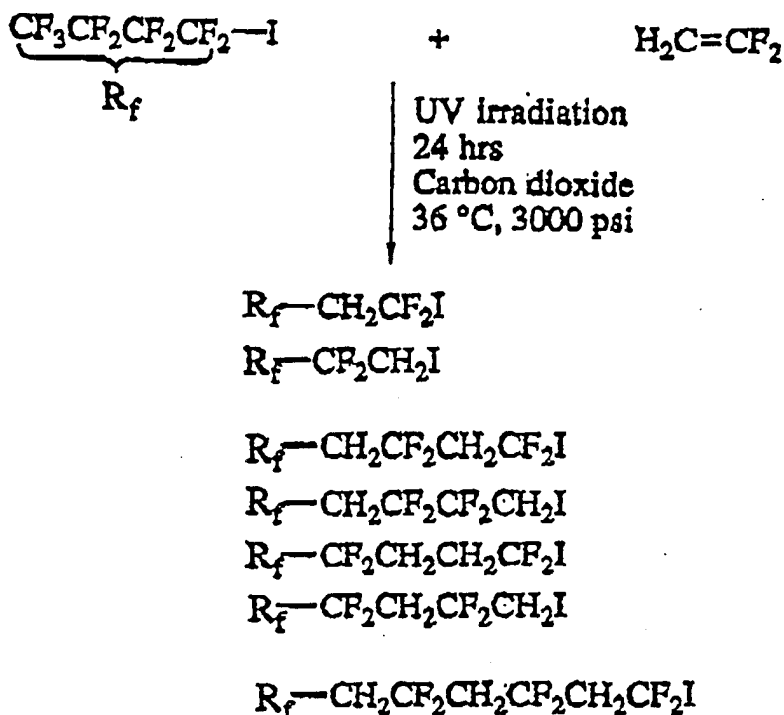25   procedure.

EXAMPLE 28

Polymerization of 1,1-difluoroethylene (VF₂)

A low molecular weight polymer or oligomer
was made in carbon dioxide by polymerizing 1,1-
30   difluoroethylene (VF_2) in the presence of a
perfluoroalkyliodide. 1.0 g of C_4F_9I and 2.0 g of VF_2
was transferred into a 10-mL stainless steel cell
fitted with sapphire windows. The cell was heated to
36°C and filled to 3000 psi with carbon dioxide. The
35   reaction was homogeneous (optically transparent and

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colorless). The cell was irradiated with an
ultraviolet lamp for 24 hours, during which time the
reaction remained homogeneous and turned color from
colorless to light purple or pink.

$$\underbrace{CF_3CF_2CF_2CF_2}_{R_f}-I \qquad + \qquad H_2C=CF_2$$

$$\left\downarrow \begin{array}{l} \text{UV irradiation} \\ \text{24 hrs} \\ \text{Carbon dioxide} \\ \text{36 °C, 3000 psi} \end{array}\right.$$

$$R_f-CH_2CF_2I$$
$$R_f-CF_2CH_2I$$

$$R_f-CH_2CF_2CH_2CF_2I$$
$$R_f-CH_2CF_2CF_2CH_2I$$
$$R_f-CF_2CH_2CH_2CF_2I$$
$$R_f-CF_2CH_2CF_2CH_2I$$

$$R_f-CH_2CF_2CH_2CF_2CH_2CF_2I$$

5   The product distribution was determined by
gas chromatography-mass spectrometry to include the
various products listed above with the various
regioisomers as shown.

EXAMPLE 29

10   A low molecular weight polymer or oligomer is
made in carbon dioxide by polymerizing
tetrafluoroethylene (TFE) using the concentrations and
procedures of Example 28 above, but in the presence of
a chain transfer agent such as trifluoromethyl iodide

15   or IF to yield:

$$CF_3-\left(CF_2CF_2\right)_n-I$$

or

$$F-\left(CF_2CF_2\right)_n-I$$
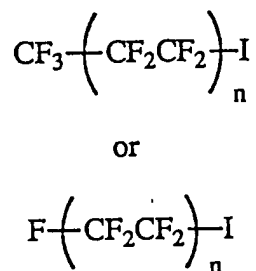
under homogeneous conditions in a stainless steel or Hastalloy reactor/view cell.
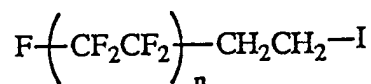
EXAMPLE 30

Following the procedure set forth in Example 28 and 29 above, fluoroolefins, such as tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), perfluoro-2,2-dimethyl-1,3-dioxole or mixtures of these monomers, or with the addition of ethylene monomer, are polymerized under homogeneous conditions in carbon dioxide.

EXAMPLE 31

Low molecular weight polymers or oligomers are made in carbon dioxide using a process essentially as described in Examples 28, 29 and 30 above, but the reaction product is endcapped with ethylene to yield:

$$CF_3 \left(CF_2CF_2 \right)_n CH_2CH_2 - I$$

or

$$F \left(CF_2CF_2 \right)_n CH_2CH_2 - I$$
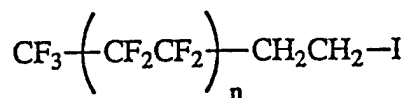
EXAMPLE 32

A dimer, oligomer or low molecular weight polymer of CTFE, HFP, TFE, or VF_2 is obtained by following the procedures of Example 28 above, except that the fluoroolefin or mixtures of the fluoroolefins are treated with I_2 or another Lewis acid (such as $FeCl_3$) in carbon dioxide to form a product soluble in carbon dioxide. Halogenated chain transfer agents or telogens such as Cl_3CBr, $CFCl_3$, $CFCl_3$, CCl_4, $Br-CFCl-CF_2-Br$ are optionally added. The reactions are optionally facilitated by UV irradiation or added peroxide.

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EXAMPLE 33

Terpolymerization of Fluoroolefin Monomers

A fluoropolymer is made by terpolymerizing TFE, CTFE, and ethylene in carbon dioxide using a peroxide initiator and a chain transfer agent such as freon-11 and the following ratios of TFE/CTFE/Ethylene: 20/45/35; 10/55/35; and 30/30/40.

EXAMPLE 34

Polymerization of Fluoroolefin TFE

An oligomer or low molecular weight polymer of TFE is made in carbon dioxide by treating TFE with a nucleophile in carbon dioxide oxide to form a carbon dioxide-soluble product, such as trimer, tetramer, pentamer and hexamer.
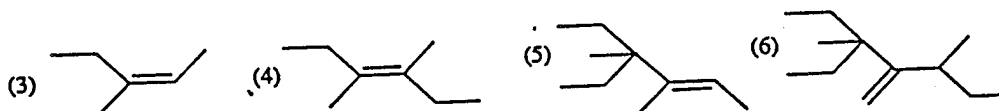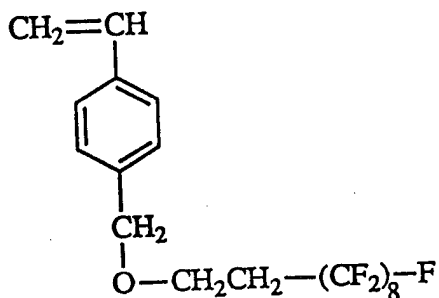

EXAMPLE 35

Polymerization of Fluoroolefin HFP

An oligomer or low molecular weight polymer of hexafluoropropylene (HFP) is obtained by treating HFP with a nucleophile such as CsF in carbon dioxide to form a soluble product in carbon dioxide.
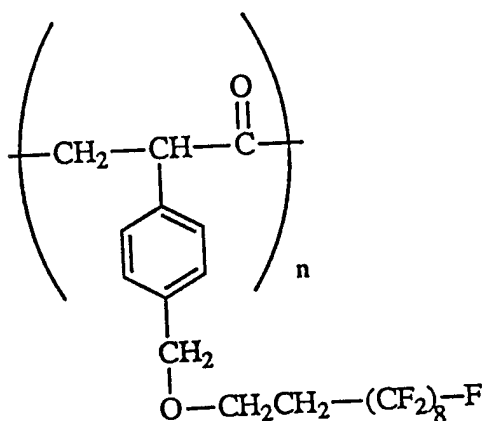
EXAMPLE 36

Polymerization of Fluorostyrene
Monomer STF Using a Palladium Catalyst

A polymer is made in carbon dioxide under the homogeneous conditions by copolymerizing a fluorinated monomer, such as:

$$CH_2{=}CH$$

[structure: styrene derivative with para-substituted benzene ring bearing CH₂–O–CH₂CH₂–(CF₂)₈–F]

$$CH_2$$
$$O{-}CH_2CH_2{-}(CF_2)_8{-}F$$

with carbon monoxide using a palladium catalyst (for
concentrations, see, e.g., M. Brookhart et al., J. Am.
Chem. Soc. 114, pg. 5894 (1992)) to yield:

[polymer structure: repeating unit –CH₂–CH–C(=O)– with pendant benzene ring bearing CH₂–O–CH₂CH₂–(CF₂)₈–F, subscript n]

EXAMPLE 37·

Polymerization Using a Cosolvent

A polymerization is carried out in
essentially the same manner as described above, except
that a cosolvent is added to carbon dioxide, such as
less than about 5% by weight diglyme, to form a product
soluble in carbon dioxide.

EXAMPLE 38

Isolation of Polymer

A process is carried out in essentially the
same manner as described in Examples 23-37 above,
except that the product is isolated either all at once
by continuous reduction of pressure (venting) or is

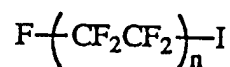-40-

isolated in fractions by controlled release or step-
wise reduction of pressure and subsequent collection
and separation of the product.

EXAMPLE 39

5   *Solubility of Fluoroolefin Polymer TFE*

A low molecular weight polymer or oligomer of
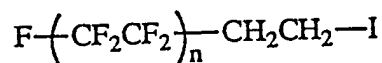tetrafluoroethylene (TFE) with the structure:

$$F-\left(CF_2CF_2\right)_n-I$$

where n = 1-5, was completely dissolved in carbon
dioxide at 5000 psi and 60°C.

10   ## EXAMPLE 40

Solubility of Endcapped Fluoroolefin Polymer TFE

A low molecular weight polymer or oligomer of
TFE which was endcapped with ethylene, having the
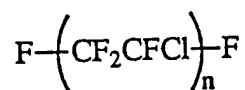structure:

$$F-\left(CF_2CF_2\right)_n-CH_2CH_2-I$$

15   where n = 1-5, was dissolved in carbon dioxide at 2000
psi and 60°C.

EXAMPLE 41

Solubility of Fluoroolefin Polymer CTFE

A low molecular weight polymer or oligomer of
20   chlorotrifluoroethylene (CTFE) with the structure:
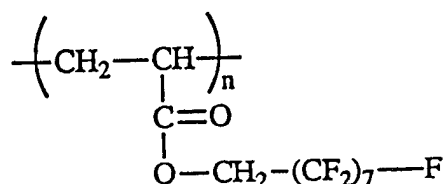
$$F-\left(CF_2CFCl\right)_n-F$$

-41-

was dissolved in carbon dioxide over a wide range of pressures and weight fractions. The phase diagram at 40°C as shown in Figure 1 was determined.

EXAMPLE 42

Solubility of Fluoroacrylate Polymer FOA

A high molecular weight polymer of (1,1-dihydroperfluorooctyl) acrylate with the structure:

$$\left(CH_2-CH\right)_n$$
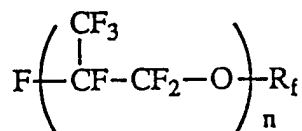$$\begin{array}{c} | \\ C=O \\ | \\ O-CH_2-(CF_2)_7-F \end{array}$$

was dissolved in carbon dioxide over a wide range of pressures and weight fractions. The phase diagram at 60°C as shown in Figure 2 was determined.

EXAMPLE 43

Solubility of Fluoroalkylene Oxide Polymer

A low molecular weight polymer or oligomer of hexafluoropropylene oxide (Krytox) with the structure:
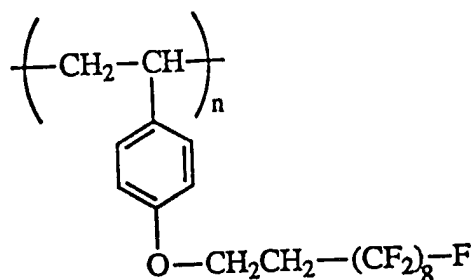
$$F\left(\begin{array}{c} CF_3 \\ | \\ CF-CF_2-O \end{array}\right)_n R_f$$

was dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 44

Solubility of Fluorostyrene Polymer

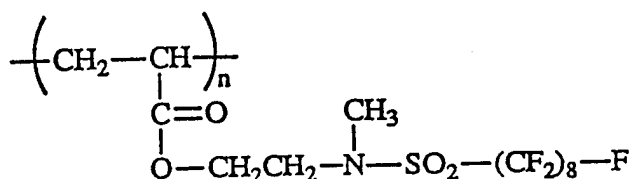A high molecular weight polymer of a fluoroalkysubstituted styrene monomer with the structure:

-42-

$$\left(-CH_2-CH-\right)_n$$

with pendant phenyl group bearing

$$O-CH_2CH_2-(CF_2)_8-F$$

was dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 45

Solubility of Fluoroacrylate Polymer MeFOSEA

A high molecular weight polymer with the

5   structure:

$$\left(-CH_2-CH-\right)_n$$
$$C=O \qquad CH_3$$
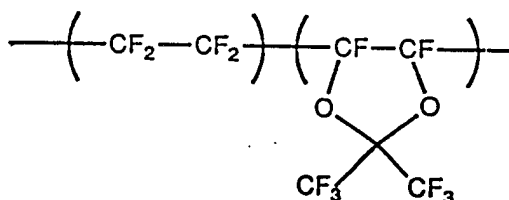$$O-CH_2CH_2-N-SO_2-(CF_2)_8-F$$

was dissolved in carbon dioxide at 5000 psi and 60°C.

EXAMPLE 46

Solubility of Fluoroolefin-Teflon Copolymer

A high molecular weight statistical copolymer

10   of TFE and perfluoro-2,2-dimethyl-1,3-dioxole (Teflon
AF 1600) having the following structure:

$$-\left(-CF_2-CF_2-\right)\left(-CF-CF-\right)-$$
$$O \qquad O$$
$$CF_3 \qquad CF_3$$

was heated to 80°C and pressurized to 6000 psi with
carbon dioxide. At these conditions two liquid phases
formed — a polymer rich phase and a carbon dioxide rich

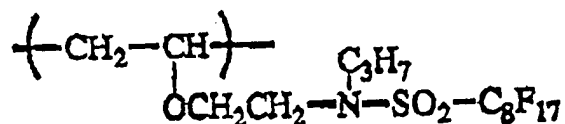15   phase. Upon venting, the carbon dioxide-rich phase

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turned cloudy indicating that some of the polymer dissolved in carbon dioxide.

EXAMPLE 47

Solubility of Fluorinated Vinyl Ether Polymer

5   A high molecular weight polymer with the structure:

$$\left(-CH_2-CH-\right)- \quad C_3H_7$$
$$OCH_2CH_2-N-SO_2-C_8F_{17}$$

was dissolved in carbon dioxide at 3490 psi at 60°C. The polymer also dissolves in freon-113, but is insoluble in common organic solvents such as THF,

10   dichloromethane, and chloroform.

         The foregoing examples are illustrative of the present invention, and are not to be taken as restrictive thereof. The invention is defined by the following claims, with equivalents of the claims to be

15   included therein.

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THAT WHICH IS CLAIMED IS:

1. A process for making a fluoropolymer,
comprising:

solubilizing a fluoromonomer selected from
the group consisting of fluoroacrylate monomers,
fluoroolefin monomers, fluorostyrene monomers,
fluorinated vinyl ether monomers, and fluoroalkylene
oxide monomers in a solvent, the solvent comprising
carbon dioxide fluid; and then

polymerizing the fluoromonomer in said
solvent to produce said fluoropolymer.

2. A process according to claim 1, wherein
said carbon dioxide fluid is liquid carbon dioxide.

3. A process according to claim 1, wherein
said carbon dioxide fluid is supercritical carbon
dioxide.

4. A process according to claim 1, further
comprising the step of separating said fluoropolymer
from said carbon dioxide and collecting said
fluoropolymer.

5. A process according to claim 4, wherein
said separating step is carried out by venting said
carbon dioxide to the atmosphere.

6. A process according to claim 1, further
comprising:

solubilizing a comonomer in said carbon
dioxide fluid,

and wherein said polymerizing step comprises
copolymerizing said fluoromonomer with said comonomer.

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7. A process according to claim 1, wherein said polymerizing step is carried out in the presence of an initiator.

8. A process according to claim 1, wherein said solvent further comprises a cosolvent.

9. A process according to claim 1, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

10. A process for making a fluoroacrylate polymer, comprising:

solubilizing a fluoroacrylate monomer in a solvent, the solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroacrylate monomer in said solvent to produce said fluoroacrylate polymer.

11. A process according to claim 10, wherein said carbon dioxide fluid is liquid carbon dioxide.

12. A process according to claim 10, wherein said carbon dioxide fluid is supercritical carbon dioxide.

13. A process according to claim 10, further comprising the step of separating said fluoropolymer from said carbon dioxide and collecting said fluoropolymer.

14. A process according to claim 13, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

15.   A process according to claim 10, further comprising:

solubilizing a comonomer in said carbon dioxide fluid,

and wherein said polymerizing step comprises copolymerizing said fluoromonomer with said comonomer.

16.   A process according to claim 10, wherein said polymerizing step is carried out in the presence of an initiator.

17.   A process according to claim 10, wherein said solvent further comprises a cosolvent.

18.   A process according to claim 10, wherein said polymerizing step is carried out in the presence of a chain transfer agent.

19.   A process for making a fluoroacrylate polymer, comprising:

solubilizing a fluoroacrylate monomer in a solvent, the solvent comprising carbon dioxide fluid wherein said fluoroacrylate monomer comprises a monomer of formula (I):

$$H_2C=CR^1COO(CH_2)_nR^2 \tag{I}$$

wherein:

n is 1 or 2;

R^1 is hydrogen or methyl; and

R^2 is a perfluorinated aliphatic or perfluorinated aromatic group; and then

polymerizing the fluoroacrylate monomer in said solvent to produce said fluoroacrylate polymer.

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20. A process according to claim 19, wherein R² is a C1 to C8 perfluoroalkyl or $-CH_2NR^3SO_2R^4$, wherein R³ is C1-C2 alkyl and R⁴ is C1 to C8 perfluoroalkyl.

21. A process according to claim 19, wherein said fluoroacrylate monomer is selected from the group consisting of:

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate;

2-(N-ethylperflooctanesulfonamido) ethyl methacrylate;

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate;

2-(N-methylperflooctanesulfonamido) ethyl methacrylate;

1,1-Dihydroperfluorooctyl acrylate; and

1,1-Dihydroperfluorooctyl methacrylate.

22. A process according to claim 19, wherein said carbon dioxide fluid is liquid carbon dioxide.

23. A process according to claim 19, wherein said carbon dioxide fluid is supercritical carbon dioxide.

24. A process according to claim 19, further comprising the step of separating said fluoropolymer from said carbon dioxide and collecting said fluoropolymer.

25. A process according to claim 24, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

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26.   A process according to claim 19, further
comprising:

solubilizing a comonomer in said carbon
dioxide fluid,

and wherein said polymerizing step comprises
copolymerizing said fluoromonomer with said comonomer.

27.   A process according to claim 19, wherein
said polymerizing step is carried out in the presence
of an initiator.

28.   A process according to claim 19, wherein
said solvent further comprises a cosolvent.

29.   A process according to claim 19, wherein
said polymerizing step is carried out in the presence
of a chain transfer agent.

30.   A process for making a fluoroalkylene
oxide polymer, comprising:

solubilizing a fluoroalkylene oxide monomer
in a solvent comprising carbon dioxide fluid; and then

polymerizing the fluoroalkylene oxide monomer
in said solvent to produce said fluoroalkylene oxide
polymer.

31.   A process according to Claim 30 wherein
said fluoroalkylene oxide monomer is selected from the
group consisting of perfluoropropylene oxide and
perfluorocyclohexene oxide.

32.   A process according to claim 30, wherein
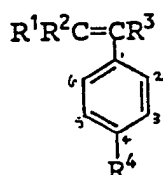said carbon dioxide fluid is liquid carbon dioxide.

33.   A process according to claim 30, wherein
said carbon dioxide fluid is supercritical carbon
dioxide.

34. A process according to claim 30, further comprising the step of separating said fluoroalkylene oxide polymer from said carbon dioxide and collecting said fluoroalkylene oxide polymer.

5   35. A process according to claim 35, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

36. A process for making a fluorostyrene polymer, comprising:
10   solubilizing a fluorostyrene monomer in a solvent comprising carbon dioxide fluid; and then
          polymerizing the fluorostyrene monomer in said solvent to produce said fluorostyrene polymer.

37. A process according to Claim 36, wherein
15   said fluorostyrene monomer comprises a monomer of Formula (VI):

$$R^1R^2C{=}CR^3$$

                                                            (VI)

wherein:
          R^1 and R^2 are each independently hydrogen,
20   fluorine, or methyl;
          R^3 is hydrogen, fluorine, methyl or perfluoromethyl;
          R^4 is hydrogen, fluorine, or C1-C12 perfluorinated aliphatic group; and
25   wherein the 2, 3, 5, and 6 positions of the aromatic styrene ring are each independently hydrogen or fluorine.

38.   A process according to claim 36, wherein said carbon dioxide fluid is liquid carbon dioxide.

39.   A process according to claim 36, wherein said carbon dioxide fluid is supercritical carbon dioxide.

40.   A process according to claim 36, further comprising the step of separating said fluorostyrene polymer from said carbon dioxide and collecting said fluorostyrene polymer.

41.   A process according to claim 40, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

42.   A process for making a fluorinated vinyl ether polymer comprising:
        solubilizing a fluorinated vinyl ether monomer in a solvent comprising carbon dioxide fluid; and then
        polymerizing the fluorinated vinyl ether monomer in said solvent to produce said fluorinated vinyl ether polymer.

43.   A process according to Claim 42, wherein said fluorinated vinyl ether monomer comprises a monomer of Formula (IV):

$$R^1R^2C=CR^3O(CH_2)_nR \qquad (IV)$$

wherein:
        n is 0, 1 or 2;
        R^1, R^2, and R^3 are each independently hydrogen or fluorine; and
        R is perfluorinated aliphatic or perfluorinated aromatic group.

44.   A process according to claim 42, wherein said carbon dioxide fluid is liquid carbon dioxide.

45.   A process according to claim 42, wherein said carbon dioxide fluid is supercritical carbon dioxide.

46.   A process according to claim 42, further comprising the step of separating said fluorinated vinyl ether polymer from said carbon dioxide and collecting said fluorinated vinyl ether polymer.

47.   A process according to claim 46, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

48.   A process for making a fluoroolefin polymer comprising:
        solubilizing a fluoroolefin monomer in a solvent comprising carbon dioxide fluid; and then
        polymerizing the fluoroolefin monomer in said solvent to produce said fluoroolefin polymer.

49.   A process according to Claim 48 wherein said fluoroolefin monomer is selected from the group consisting of difluoroethylene, tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene, perfluoro-2,2-dimethyl-1,3-dioxole and mixtures thereof.

50.   A process according to claim 48, wherein said carbon dioxide fluid is liquid carbon dioxide.

51.   A process according to claim 48, wherein said carbon dioxide fluid is supercritical carbon dioxide.

52. A process according to claim 48, further comprising the step of separating said fluoroolefin polymer from said carbon dioxide and collecting said fluoroolefin polymer.

5   53. A process according to claim 52, wherein said separating step is carried out by venting said carbon dioxide to the atmosphere.

POLY(CHLOROTRIFLUOROETHYLENE) IN
CARBON DIOXIDE AT 40°C

FIG. 1.

PHASE EQUILIBRIA OF P(FOA) IN
CARBON DIOXIDE AT 60°C
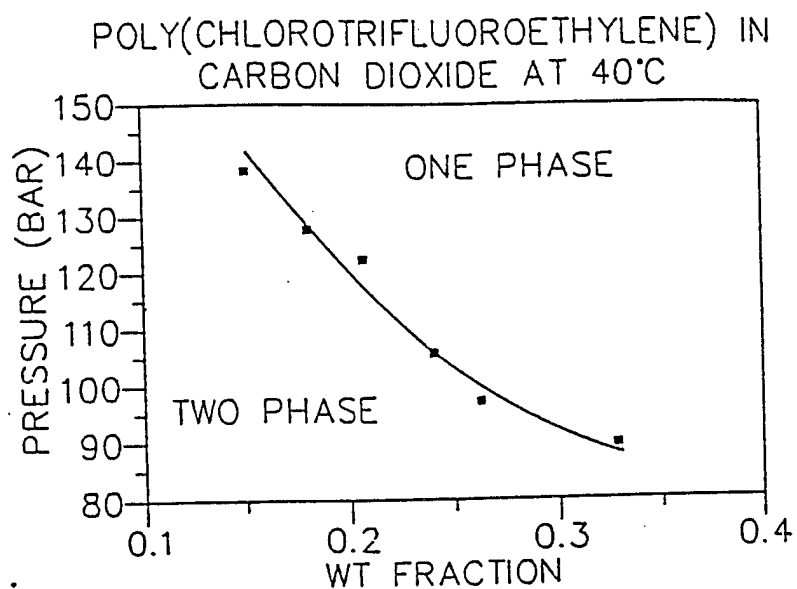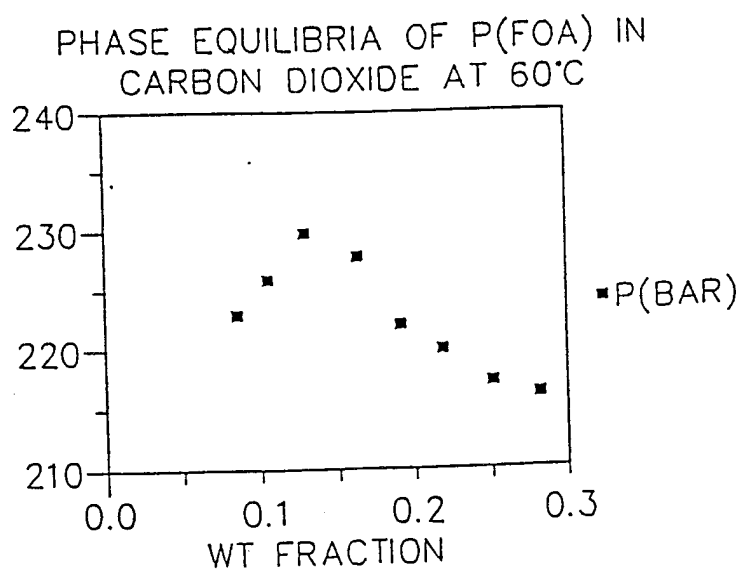
FIG. 2.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F16/24 C08F14/18 C08F20/22 C08F12/20 C08F2/06

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and. where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document. with indication. where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 20116 A (UNIV NORTH CAROLINA ;DESIMONE JOSEPH M (US)) 14 October 1993 cited in the application see the whole document	1-53
X	DATABASE WPI Section Ch, Derwent Publications Ltd., London, GB; Class A15, AN 71-21000S XP002067577 & JP 46 011 031 B (SUMITOMO CHEM CO LTD) see abstract	1,2,48, 50

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| X | Further documents are listed in the continuation of box C. | | X | Patent family members are listed in annex. |

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents. such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 June 1998	19/06/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office. P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Fischer. B

Form PCT ISA 210 (second sheet) (July 1992)

1

page 1 of 2

INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category [*]	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Derwent Publications Ltd., London, GB; Class A15, AN 71-28606S XP002067578 & JP 46 015 511 B (ASAHI GLASS CO LTD) see abstract ---	1,2, 48-50
X	WO 96 28477 A (UNIV NORTH CAROLINA) 19 September 1996 see the whole document -----	1-18,42, 44-53

1

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WO 9320116	A	14-10-1993	AU	3776393 A	08-11-1993
			EP	0638095 A	15-02-1995
			JP	7505429 T	15-06-1995
			US	5496901 A	05-03-1996
			US	5739223 A	14-04-1998
			US	5688879 A	18-11-1997
WO 9628477	A	19-09-1996	US	5618894 A	08-04-1997
			US	5674957 A	07-10-1997
			EP	0813548 A	29-12-1997