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(54) Titre : METHODE DE POLYMERISATION HETEROGENE DE COMPOSANTS DU GAZ CARBONIQUE

(54) Title: HETEROGENEOUS POLYMERISATION IN CARBON DIOXIDE

(57) **Abrégé/Abstract:**

The heterogeneous polymerization of water-insoluble polymer in CO₂ is disclosed. The method comprises providing a heterogeneous reaction mixture comprising CO₂, a monomer, and a surfactant, then polymerizing the monomer to form a water-insoluble polymer.



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HETEROGENEOUS POLYMERIZATION IN CARBON DIOXIDE

Abstract

The heterogeneous polymerization of water-insoluble polymer in CO₂ is disclosed. The method comprises providing a heterogeneous reaction mixture comprising CO₂, a monomer, and a surfactant, then polymerizing the monomer to form a water-insoluble polymer.

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HETEROGENEOUS POLYMERIZATION IN CARBON DIOXIDE

Field of the Invention

This invention relates generally to the polymerization of hydrophobic monomers, and more specifically relates to the heterogeneous
5 polymerization of hydrophobic monomers in a carbon dioxide continuous phase.

Background of the Invention

Emulsion polymerization is a heterogeneous process often used by industry to polymerize a wide
10 variety of monomers using free radical mechanisms. It involves the polymerization of monomers in the form of emulsions or latexes. Polymers commonly formed by emulsion include acrylics, styrenics, polyvinylchloride (PVC), styrene-butadiene rubber, ethylene-propylene-
15 diene terpolymer-based (EPDM), polystyrene, acrylonitrile-butadiene-styrene copolymer (ABS), neoprene rubber, ethyl-vinyl acetate, styrene-maleic anhydride, tetrafluoroethylene, and vinyl fluoride.

Generally, low molar mass ionic surfactants
20 have enjoyed the most use in water-based emulsion polymerizations because they work so efficiently to stabilize the ionic double layer of the emulsion or colloid particles which prevents particle coagulation. In addition, polymeric surfactants have also been
25 utilized to stabilize emulsion polymerizations. See Piirma, Polymeric Surfactants in 42 Surfactant Science Series (Marcel Dekker, New York 1992). This class of surfactants stabilizes colloidal particles by steric, rather than ionic, means. Steric stabilization of
30 emulsions can be advantageous in that (a) steric

-2-

systems are much less sensitive to fluctuations and increases in electrolyte concentrations, (b) they work well at high and low solids contents, and (c) they stabilize aqueous and nonaqueous dispersions equally well. See Napper, Polymeric Stabilization of Colloidal Dispersions (Academic Press, New York 1983). Many nonionic polymeric surfactants are available; the most common of these are basically block copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO)

After polymerization, the polymer must be coagulated and isolated from the aqueous phase for further processing (except for that which is destined for use in water-borne coatings). The large volume of water remaining comprising the continuous phase must be properly handled, as it becomes contaminated with organic compounds—residual monomers, stabilizers, and other materials that are difficult to remove. As a result, it would be desirable to provide a different medium for the continuous phase that can be easily decontaminated.

In view of the foregoing, it is a first object of an aspect of the present invention to provide a heterogeneous polymerization method in which a fluid other than water comprises the continuous phase medium.

It is also an object of an aspect of the present invention to provide surfactants useful for the foregoing methods.

It is a further object of an aspect of the present invention to provide initiators suitable for use with the foregoing methods.

Summary of the Invention

These and other objects of aspects are satisfied by the present invention, which includes as a first aspect a method of carrying out the heterogeneous polymerization of monomers that form a water-insoluble polymer. The method comprises providing a heterogeneous reaction

-3-

mixture comprising carbon dioxide, a monomer, and a surfactant and polymerizing the monomer in the reaction mixture. The method is suitable for both suspension and emulsion polymerizations.

5 The present invention includes as a second aspect a heterogeneous reaction mixture useful for carrying out the heterogeneous polymerization of a monomer that forms a water-insoluble polymer. The reaction mixture comprises a carbon dioxide, the monomer, and a
10 surfactant.

 A third aspect of the present invention is a surfactant useful for carrying out the heterogeneous polymerization of a hydrophobic monomer. The surfactant comprises a first hydrophobic group covalently joined to
15 a second carbon-dioxide soluble group, wherein the carbon-dioxide soluble group comprises a fluorinated siliconated component.

 A fourth aspect of the present invention is a polymerization initiator suitable for use in a
20 heterogeneous polymerization carried out with a carbon dioxide continuous phase. The initiator comprises a first carbon dioxide-soluble group comprising a fluoropolymer covalently joined to a second free-radical forming group.

25 In accordance with one embodiment of the present invention, there is provided a method of carrying out the heterogeneous polymerization of a water-insoluble polymer, the method comprising:

 providing a heterogeneous reaction mixture
30 comprising carbon dioxide, a hydrophobic monomer, and a surfactant that stabilizes the monomer in the carbon dioxide, wherein the surfactant comprises a carbon-dioxide soluble segment; and

 polymerizing the hydrophobic monomer in the reaction
35 mixture to form the water-insoluble polymer.

 In accordance with another embodiment of the present invention, there is provided a heterogeneous reaction mixture useful for carrying out the heterogeneous

-3a-

polymerization of a monomer that forms a water-insoluble polymer, the reaction mixture comprising:

at least one monomer that forms a water-insoluble polymer;

5 a carbon dioxide continuous phase; and

a surfactant that stabilizes the monomer and the polymer in the carbon dioxide, wherein the surfactant comprises a carbon dioxide soluble segment.

10 In accordance with another embodiment of the present invention, there is provided a heterogeneous mixture comprising:

at least one water-insoluble polymer;

a carbon dioxide continuous phase; and

15 a surfactant that stabilizes the polymer in the carbon dioxide, wherein the surfactant comprises a carbon dioxide soluble segment.

In accordance with another embodiment of the present invention, there is provided a mixture comprising carbon dioxide and a surfactant, wherein the surfactant
20 comprises a carbon dioxide soluble segment and a CO₂-phobic group covalently linked to the carbon dioxide soluble segment, wherein the carbon dioxide soluble segment further comprises a fluoropolymer and wherein the surfactant is a copolymer selected from the group
25 consisting of a graft copolymer and a block copolymer.

In accordance with another embodiment of the present invention, there is provided a mixture comprising carbon dioxide and a surfactant, wherein the surfactant
30 comprises a carbon dioxide soluble segment, wherein the surfactant further comprises a CO₂-phobic group covalently linked to the carbon dioxide soluble segment, and wherein the carbon dioxide soluble segment further comprises a siloxane segment.

In accordance with another embodiment of the present invention, there is provided a mixture comprising carbon
35 dioxide and a surfactant, wherein the surfactant

-3b-

comprises a carbon dioxide soluble segment and a CO₂-
phobic group, wherein the carbon dioxide soluble segment
is a fluorine-containing segment, wherein the CO₂-phobic
group is hydrophobic, and wherein the fluorine-containing
5 segment has a terminal perfluorinated group.

In accordance with another embodiment of the present
invention, there is provided a mixture comprising carbon
dioxide and a surfactant, wherein the surfactant
comprises a carbon dioxide soluble segment and a CO₂-
10 phobic group covalently linked to the carbon dioxide
soluble segment, wherein the carbon dioxide soluble
segment further comprises a fluoropolymer; wherein the
surfactant is a copolymer selected from the group
consisting of a graft copolymer and a block copolymer;

15 wherein the carbon dioxide comprises liquid carbon
dioxide;

and wherein the CO₂-phobic group is hydrophobic.

In accordance with another embodiment of the present
invention, there is provided a mixture comprising carbon
20 dioxide and a surfactant, wherein the surfactant
comprises a carbon dioxide soluble segment, wherein the
surfactant further comprises a CO₂-phobic group covalently
linked to the carbon dioxide soluble segment; wherein the
carbon dioxide soluble segment further comprises a
25 siloxane segment;

wherein the carbon dioxide comprises liquid carbon
dioxide;

and wherein the CO₂-phobic group is hydrophobic.

The use of CO₂ as the continuous phase medium rather
30 than water is advantageous for a number of reasons.
First, because water has been replaced as the continuous
phase medium, there is no longer a concern about
contaminating (and thus having to purify) the continuous
phase water. Second, the polymer can be easily isolated
35 from the continuous phase, as the CO₂ can simply be vented
from the reaction vessel. Third, the density and hence

-3c-

the viscosity of CO₂ can be tuned over a large range of conditions due to its compressibility, particularly in the supercritical phase, and thus particle size and morphology of the polymer can be controlled.

-4-

Carbon dioxide (CO₂) has been employed as a polymerization medium. For example, European Patent No. 301532A3, discloses the polymerization of acrylic acid monomer, a comonomer. CO₂, and an initiator. The CO₂ can be used in a supercritical fluid phase. The resulting copolymer is useful as a thickening agent. In addition, Hartmann et al., U.S. Patent No. 4,748,220, disclose a polymerization of monoethylenically unsaturated carboxylic acids, their amides and esters, and aminoalcohols in supercritical CO₂. However, neither of these references disclose a heterogenous polymerization reaction in which CO₂ is the continuous phase medium and in which a surfactant is included to induce micelle formation, nor is a surfactant suitable for use in such a polymerization disclosed. Recently, Consani et al., J. Supercrit. Fl. 3:51 (1990), reported a screening of the solubility of different surfactants in CO₂. Also, it has been shown that a large variety of fluoropolymers and fluorinated copolymers are very soluble in CO₂. See DeSimone et al., Science 257:945 (1992). None of this suggests the use of CO₂ as a continuous phase in a heterogeneous polymerization.

Brief Description of the Figures

Figure 1 is a plot showing the ¹H NMR. spectra for an FOA-styrene-FOA triblock copolymer.

Figure 2 is a plot showing the absorption spectrum for a FOMA-Ethyl hexylacrylate-FOMA copolymer in CO₂.

Detailed Description of the Invention

The present invention is directed to a method of carrying out the heterogeneous polymerization of a hydrophobic monomer. The steps of the method comprise providing a reaction mixture comprising a carbon dioxide (CO₂) continuous phase, and a hydrophobic dispersed phase comprising a surfactant and a

hydrophobic monomer dissolved therein, then polymerizing the monomer in the reaction mixture.

As used herein, a "heterogeneous reaction" is one in which the polymerization is carried out through the use of media that create at least two separate phases. One phase is termed the "continuous phase", which comprises a fluid, and the other is termed the "dispersed phase", comprising the monomer or monomers to be polymerized. The monomer is stabilized in the dispersed phase by a surfactant (also known as an emulsifier, or a stabilizer) that reduces the surface tension between the phases. The term "heterogeneous reaction" is intended to encompass both suspension polymerizations, in which any polymerization initiator is preferentially solubilized in the dispersed phase, and emulsion reactions, in which any polymerization initiator is preferentially solubilized in the continuous phase. As used herein, a compound is "preferentially solubilized" in one phase over another when it is more soluble in that phase.

The present invention is preferably carried out by emulsion polymerization. The generally accepted view of emulsion polymerization is described in Harkins, J. Amer. Chem. Soc. 69:1428 (1947), and further developed in Smith and Ewart, J. Chem. Phys. 16:592 (1948). A classical oil-in-water (O/W) emulsion polymerization generally includes as reagents water, a water-insoluble monomer, a water-soluble initiator, and an emulsifier. As the monomer is insoluble in the continuous phase (water), it is dispersed as droplets, which are stabilized by the surface active emulsifier, and is also solubilized in micelles formed by the emulsifier. The initiator is soluble in the continuous water phase. Upon its decomposition to form radicals, the initiator initiates the polymerization of the trace amount of monomer dissolved in the water-rich phase. As the molecular weight of the macromolecule increases,

it eventually becomes insoluble in water, at which time it precipitates to form a primary particle. These primary particles can coalesce to form larger particles which become stabilized by the surface active emulsifier present in the system.

The overall rate of polymer propagation, R_p , typically follows the so-called Smith-Ewart kinetics described by the following equation:

$$R_p = k_p N \langle n \rangle [M] \quad (\text{I})$$

where k_p is the rate constant for propagation, N is the number of particles that form, $\langle n \rangle$ is the average number of radicals per particle, and $[M]$ is the monomer concentration in the particles. The number average degree of polymerization, $\langle Xn \rangle$, can also be quantified as:

$$\langle Xn \rangle = k_p N [M] R_i^{-1} \quad (\text{II})$$

where R_i is the rate of initiation. It is clear that both the rate of propagation and the overall molar mass of the resulting polymer are both dependant on the number of polymer particles, N . According to Smith-Ewart theory, the number of particles is given by:

$$N \propto [S]^{3/5} \quad (\text{III})$$

where $[S]$ is the total surfactant or emulsifier concentration. This simultaneous dependence of the rate of polymerization and the molar mass of the polymer on the surfactant concentration illustrates the utility of emulsion polymerization processes, as a reaction can simultaneously provide high rates of polymer production and high molar masses; this result

differs markedly from solution polymerizations that transpire in a single phase.

The CO₂ can be employed in a liquid, vapor, or supercritical phase. If liquid CO₂ is used, the
5 temperature of the reaction should be below 31°C. Preferably, the CO₂ in the continuous phase is in a "supercritical" phase. As used herein, "supercritical" means that a fluid medium is at a temperature that is sufficiently high that it cannot be liquified by
10 pressure. The thermodynamic properties of CO₂ are reported in Hyatt, J. Org. Chem. 49:5097-5101 (1984); therein, it is stated that the critical temperature of CO₂ is about 31°C; thus the method of the present invention should be carried out at a temperature above
15 31°C. The reaction temperature should be chosen to provide sufficient heat energy to initiate and propagate the polymerization. Preferably, the reaction temperature will be between 50°C and 200°C, and more preferably will be between 50°C and 100°C.

20 The advantage of conducting the polymerization with supercritical CO₂ inures from the tendency of the solvent strength of a solvent in a supercritical phase to be easily manipulated by varying the pressure of the fluid. As a result of this
25 phenomenon, the use of supercritical CO₂ permits one carrying out the polymerization to significantly influence the particle size, distribution, and other aspects of the final product without varying either the solvent temperature or composition (i.e., including a
30 co-solvent).

The method of the present invention includes a dispersed phase comprising a monomer stabilized by a surfactant. The surfactant provided to the reaction mixture should be one that is surface active in CO₂ and
35 thus partitions itself at the CO₂-monomer/polymer interface. Such a surfactant should cause the formation of micelles in the CO₂ and thus create a

dispersed phase that permits the polymerization to follow the Smith-Ewart kinetics described above. The surfactant is generally present in the reaction mixture in a concentration of between 0.01 and 30 percent by weight. The surfactants can be nonreactive in the polymerization or can react with an thereby be included with the forming polymer. See, e.g., U.S. Patent Nos. 4,592,933 and 4,429,666 for exemplary reactive surfactants.

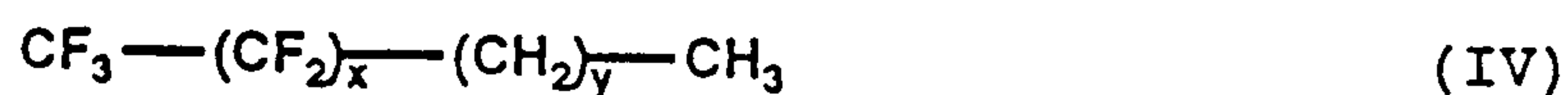
10 The surfactant should contain a segment that is soluble in CO₂ ("CO₂-philic"). Exemplary CO₂-philic segments include a fluorine-containing segment or a siloxane-containing segment. As used herein, a "fluoropolymer" has its conventional meaning in the art. *See generally Fluoropolymers* (L. Wall, Ed. 15 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). Exemplary 20 fluoropolymers are those formed from: fluoroacrylate monomers such as 2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("EtFOSEA"), 2-(N-ethylperfluorooctanesulfonamido) ethyl methacrylate ("EtFOSEMA"), 2-(N-methylperfluorooctanesulfonamido) 25 ethyl acrylate ("MeFOSEA"), 2-(N-methylperfluorooctanesulfonamido) ethyl methacrylate ("MeFOSEMA"), 1,1-Dihydroperfluorooctyl acrylate ("FOA"), and 1,1-Dihydroperfluorooctyl acrylate ("FOMA"); fluoroolefin monomers such as 30 tetrafluoroethylene, fluorostyrene monomers such as α -fluorostyrene, β -fluorostyrene, α,β -difluorostyrenes, β,β -difluorostyrenes, α,β,β -trifluorostyrenes, α -trifluoromethylstyrenes, 2,4,6-Tris(trifluoromethyl)styrene, 2,3,4,5,6-pentafluoro- α -methylstyrene, and 2,3,4,5,6-pentafluoro- β -methylstyrene; fluoroalkylene oxide monomers such as

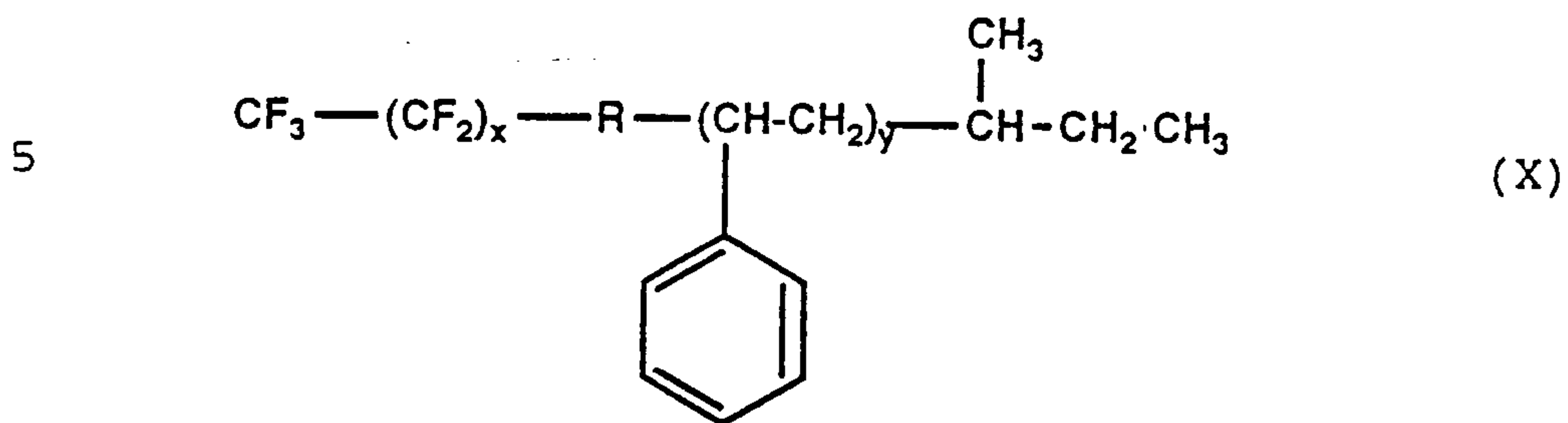
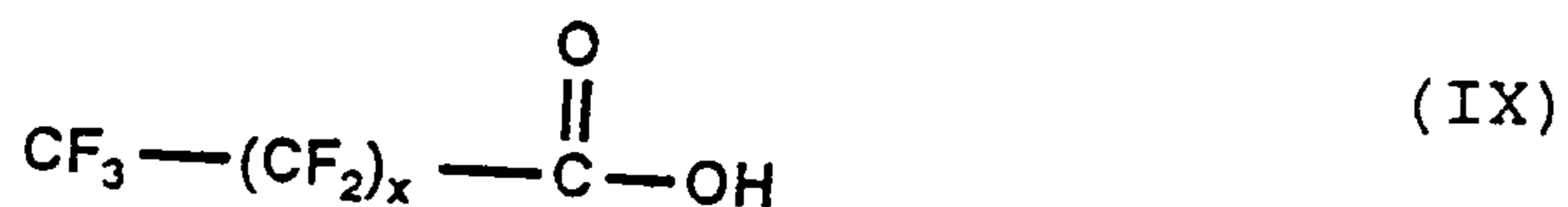
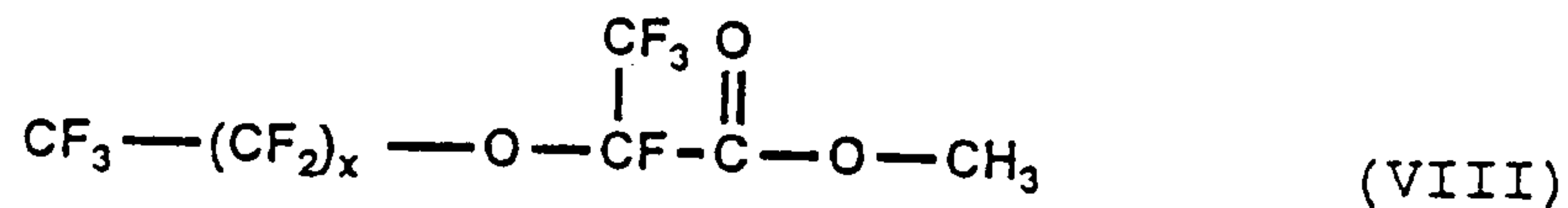
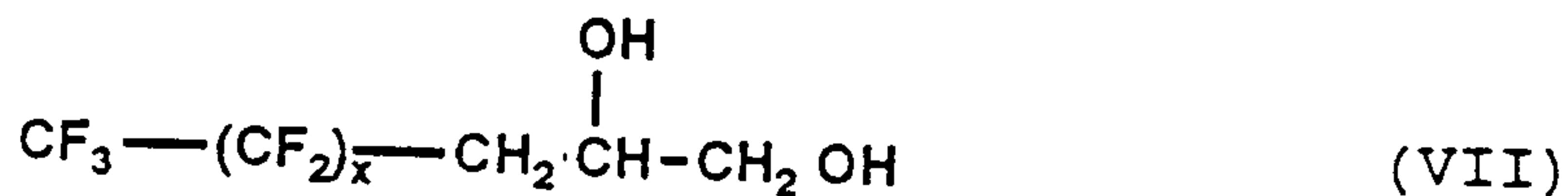
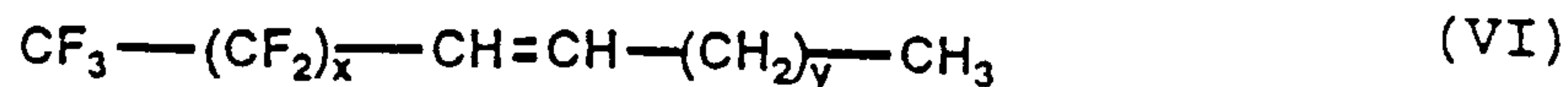
perfluoropropylene oxide and perfluorocyclohexene oxide; fluorinated vinyl alkyl ether monomers; and the copolymers thereof with suitable comonomers, wherein the comonomers are fluorinated or unfluorinated.

5 Exemplary siloxane-containing compounds include alkyl, fluoroalkyl, and chloroalkyl siloxanes.

More preferably, the surfactant comprises a hydrophobic group, such as a polystyrene group, that is "CO₂-phobic," along with a CO₂-soluble group, such as a fluoropolymer. Such copolymers can take many forms; two exemplary forms are graft copolymers having a CO₂-soluble backbone and hydrophobic branches attached thereto and triblock copolymers having a central hydrophobic portion attached at opposite ends to one of a pair of CO₂-soluble portions are preferred. Triblock copolymers often exhibit markedly different properties than their individual constituents, as the individual segments of the copolymers tend to phase separate; the chemical bond between the segments prevents macroscopic phase separation, so microdomains tend to form. When a triblock copolymer as described above is dissolved in CO₂, the CO₂-soluble end portions extend into the CO₂ continuous phase, but the hydrophobic portions can aggregate to form the core of a micelle. It is particularly preferred that the fluoropolymer segment be a perfluoropolymer such as dihydroperfluorooctyl acrylate. A preferred triblock copolymer surfactant comprises poly(1,1-dihydroperfluorooctyl acrylate) end blocks and a polystyrene center block.

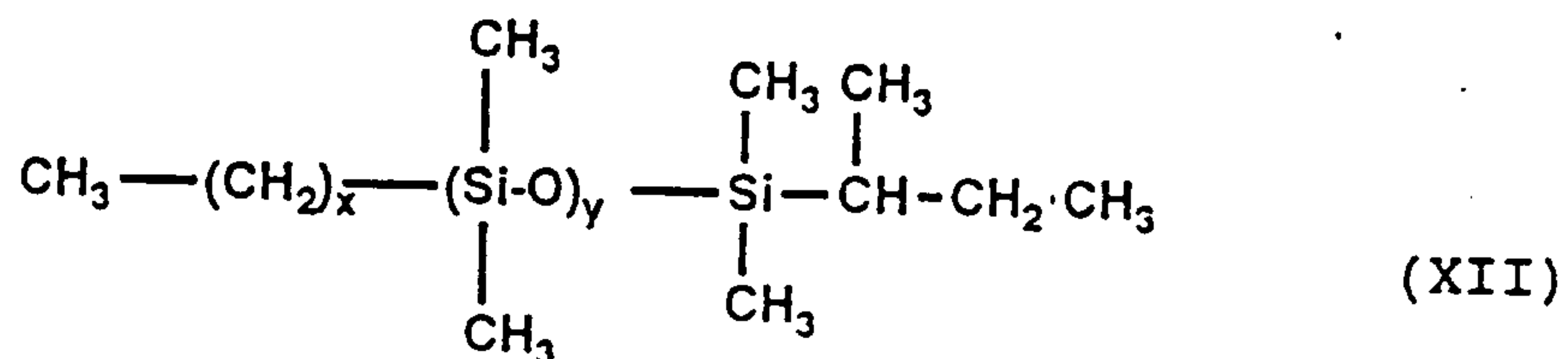
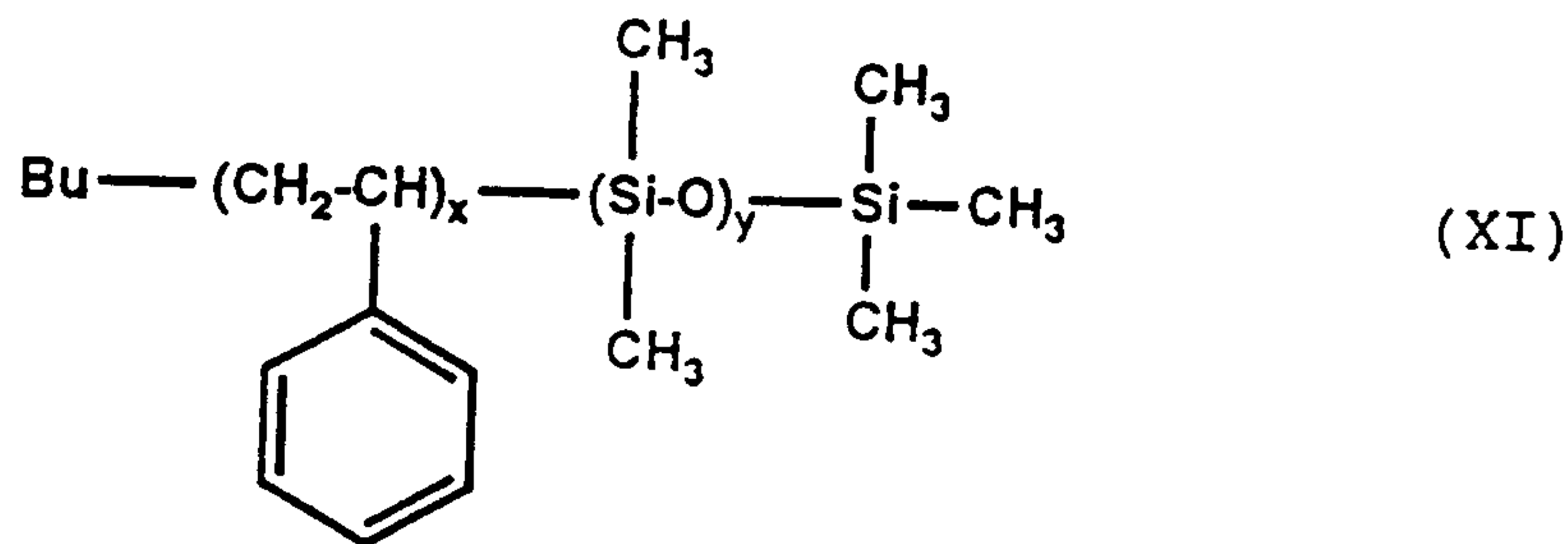
30 Other suitable surfactants that are surface active in carbon dioxide to stabilize the dispersed phase include





where $x=1-30$ and $y=1$ to 30 . The x and y values are chosen to adjust the balance between "CO₂-philic" and "CO₂-phobic" to tailor. The surface activity of the reagents. Exemplary silicone-containing surfactants include

10



wherein x and y are varied to adjust to "CO₂-philic" and "CO₂-phobic" balance.

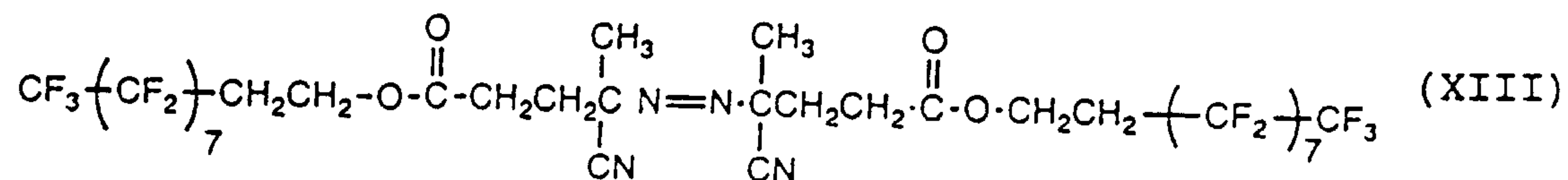
Suitable monomers for use with this invention are those that form water-insoluble polymers. Exemplary monomers forming such polymers include vinyl monomers such as vinyl chloride and vinyl acetate, 5 ethylene, acrylonitrile, dienes such as isoprene and butadiene, styrenics such as styrene and t-butyl styrene, chloroprene, acrylic monomers such as alkylmethyl acrylates, fluromonomers as given above, and maleic anhydride. Particularly suitable 10 hydrophobic monomers can be selected from the group consisting of styrene monomers, acrylic monomers, vinyl chloride monomers, olefinic monomers, fluoroolefinic monomers, fluoroacrylate monomers, fluorostyrenic monomers, and maleic anhydride monomers. The method is 15 suitable for polymerizations of a single monomer or copolymerizations of more than one hydrophobic monomer, and can also be used to copolymerize hydrophobic and hydrophilic monomers. In addition, monomers that provide cross-linking and branching, such as divinyl 20 benzene and di-triacrylates, can also be included. The monomer can be included in the reaction mixture proportions ranging from 1 to 70 percent by weight.

The heterogeneous reaction can optionally include a free radical initiator that accelerates the 25 polymerization. The initiator is chosen based on its solubility characteristics: it should preferentially solubilize in the dispersed phase for a suspension reaction, or in the CO₂ continuous phase for an emulsion reaction. The initiator is included in the solution in 30 a concentration ranging from 0.001 to 20 percent by weight.

Those skilled in this art will be familiar with a number of initiators that can solubilize in hydrophobic media. Organic free radical initiators are 35 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'-azobis
 5 (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
 10 peracetate; 2,2-bis (tert-butylperoxy) butane; dicumyl
 peroxide; ditert-amyl peroxide; di-tert-butyl peroxide;
 p-methane hydroperoxide; pinane hydroperoxide; cumene
 hydroperoxide; and tert-butyl hydroperoxide.
 Preferably, the initiator is azobisisobutyronitrile
 15 ("AIBN").

Initiators that preferentially solubilize in
 CO₂ include a CO₂-philic segment (typically a
 fluorinated or siloxane segment) and a free radical-
 producing segment; thus the attachment of a fluorinated
 20 or siloxane segment to the free radical initiators
 listed above produces initiators that can be used with
 the present invention. A particularly preferred CO₂-
 soluble initiator is that of Formula XIII:



25 The polymerizing step of the present
 invention can be carried out by polymerization methods
 using apparatus and conditions known to those skilled
 in this art. Typically, the reaction begins by heating
 the reaction vessel to a temperature above 31°C
 30 (generally between 50°C and 200°C). The initiator,
 monomer or monomers, surfactant, and CO₂, are added to
 the vessel. Typically the mixture is allowed to
 polymerize for between about 2 and 24 hours, and

preferably is stirred as the reaction proceeds. At the conclusion of the reaction, the polymer can be collected by methods such as venting of the CO₂ or by fractionation. Preferably, the surfactant is
5 fractionated from the CO₂ and polymer by reducing temperature and pressure and thus is able to be reused. After separation, the polymer can be collected by conventional means. In addition, the polymers of the present invention may be retained in the CO₂, dissolved
10 in a separate solvent, and sprayed onto a surface. After the CO₂ and solvent evaporate, the polymer forms a coating on the surface.

The polymer formed by the present invention can also be used to form molded articles, such as
15 valves and bottles, films, fibers, resins, and matrices for composite materials.

The present invention is explained in greater detail in the following examples. As used herein, "M" means molar concentration, "NMR" means nuclear magnetic
20 resonance, "MHz" means megahertz, "GPC" mean gas phase chromatography, "Å" means angstroms, "UV" means ultraviolet, "g" means grams, "mol" means moles, "mL" means milliliters, "°C" means degrees Celsius, "S" means seconds, "h" means hours, "psig" means pounds per
25 square inch (gauge), " M_n " means number merger molecular weight, "MWD" means molecular weight distribution, "f" means functionality, "ppm" means parts per million, "T_g" means glass transition temperature, "nm" means nanometers, "mg" means milligrams, "rpm" means
30 revolution per minute, and "psi" means pounds per square inch. These Examples are illustrative and are not to be taken as limiting of the invention.

EXAMPLE 1

Reagents and Materials

35 The preparation of the reagents and materials used in the subsequent examples is set forth hereinbelow. 4,4'-Azobis-4-cyanopentanoic acid,

potassium *t*-butoxide (1M in THF), and
a,a,a-trifluorotoluene (99+% pure) (Aldrich), sodium
bicarbonate and sodium sulfate (Fisher Scientific),
acetone (EM Science, GR grade), methanol and hexanes
5 (Mallinckrodt, Inc., HPLC grade), 1,1,2-Trifluoro-
trichloroethane (3M) (Freon-113), *sec*-Butyllithium
(1.4 M in cyclohexane - provided courtesy of Lithium
Corporation), chlorosilane perfluorohexylethyl-dimethyl
silylchloride (Petranch), and perfluorinated alcohol
10 (DuPont) were used as received. Pyridine (EM Science)
was purified by vacuum distillation. Tetrahydrofuran
(Fisher Certified Grade) (THF) was refluxed over sodium
and distilled under an argon atmosphere. Acryloyl
chloride (Aldrich) was purified by vacuum distillation.
15 Azobisisobutyro-nitrile (Kodak) (AIBN) was
recrystallized from methanol. 1,1-Dihydroper-
fluorooctyl acrylate (3M) (FOA) was passed through
columns of decolorizing carbon and alumina.
Cyclohexane (Phillips Petroleum Company) was stirred
20 over concentrated sulfuric acid for approximately two
weeks, decanted and distilled from a sodium dispersion
under argon. Styrene (Fisher) was vacuum distilled
from dibutyl magnesium following three freeze-thaw
cycles. *p*-Vinylbenzyl chloride (Kodak) was passed
25 through an alumina column under argon atmosphere.
p-Vinylbenzyl iodide was synthesized from *p*-vinylbenzyl
chloride using the Finkelstein reaction. Carbon
dioxide (Matheson, 99.5%) was purified by passing
through columns of molecular sieves and reduced copper
30 oxide catalyst (BASF R3-11). Tetraethylthiuram
disulfide (TD, Aldrich) was recrystallized twice from
methanol and the purity was checked by ¹H NMR. Toluene
(Fisher, Certified Grade) was distilled under argon
over sodium metal. 1,1-Dihydroperfluorooctyl
35 methacrylate (3M) (FOMA) and 2-ethylhexyl acrylate
(Aldrich) and styrene (Aldrich) were passed through a

column of alumina prior to use. All glassware was rigorously cleaned and flame-dried prior to use.

EXAMPLE 2

Characterization of Polymers

5 ¹H NMR spectra were recorded on a Bruker AMX300 NMR spectrometer or on a Bruker AC-200 at 200 MHz in CDCl₃ or Freon-113/CDCl₃. UV spectra were obtained on a Perkin Elmer Lambda 6 UV/vis spectrometer interfaced to an IBM PS/2 model 50 computer.

10 Differential scanning calorimetry analyses were performed on a Perkin Elmer DSC-7. The molecular data of the telechelic polystyrenes were obtained by running GPC on a Waters 150-CV gel permeation chromatograph with Ultrastyrigel columns of 100, 500, 10³, 10⁴, and

15 10⁵ Å porosities using THF as eluent. Polystyrene standards (Showa Denko) were used to determine the molecular mass and molecular weight distribution. Macromolecular end groups were analyzed by ¹H NMR, UV

20 analyses, and by GPC analyses on another Waters GPC instrument with a Waters 996 photodiode array detector which measures the UV spectrum of each elution of the polymer.

EXAMPLE 3

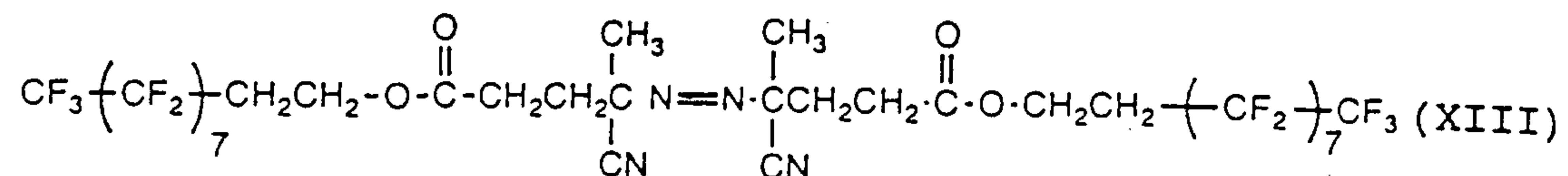
Fluoro-azo Initiator Synthesis

25 4,4'-Azobis-4-cyanopentanoyl chloride was prepared from the acid analog by the method described in Smith, Makromol. Chem. 103:301 (1967). 0.022 mol (7.124 g) of 4,4'-azobis-4-cyanopentanoyl chloride in 160 mL of dry THF was added drop-wise to a solution of

30 0.039 mol (20.302 g) of perfluorinated alcohol and a catalytic amount of pyridine in 60 ml of Freon 113 at room temperature and stirred for 3 hours under inert atmosphere. After the filtering of pyridine hydrochloride, the solution was concentrated and washed

35 with a NaHCO₃ solution and water to remove unreacted 4,4'-azobis-4-cyanopentanoic acid and pyridine. The organic layer was dried over Na₂SO₄ and solvent was

evaporated under reduced pressure to produce a 70 percent yield of a compound of Formula XIII:



EXAMPLE 4

5 Fluoro-Azo Initiator Solubility

The initiator used in an emulsion polymerization should be preferentially soluble in CO₂ and partition itself into the continuous CO₂ phase over the hydrophobic dispersed phase in order to benefit from Smith-Ewart kinetics. The fluorinated azo-initiator synthesized in Example 3 meets this solubility criterion. This molecule is very soluble in CO₂ and decomposes in an analogous fashion to AIBN. The initiator decomposes with a first order rate constant of $k_d = 15.64 \times 10^{-6} \text{ s}^{-1}$ which indicates that it has a 12.3 h half life at 70°C. The highly fluorinated nature of this molecule imparts the desirable solubility/ insolubility profile; it is insoluble in most organic solvents (benzene, toluene, cyclohexane, acetonitrile, carbontetrachloride, dimethylformamide, dimethylacetamide); insoluble in many hydrophobic monomers (styrene, t-butyl styrene, acrylic acid); insoluble in water; and soluble in Freon-113 and CO₂.

EXAMPLE 5

25 Polystyrene Macromonomer Synthesis

A. Anionic Polymerization: The anionic polymerization of styrene was conducted in a one-neck 500 mL round-bottomed flask equipped with a magnetic stir bar and rubber septum under a 5-8 psig argon atmosphere. The polymerization was initiated with sec-butyllithium and stirred overnight at room temperature. The polymerization was functionally terminated by the addition of a two-fold excess of

ethylene oxide followed by the addition of vinylbenzyl iodide. The polymer was precipitated in a ten-fold excess of methanol, dissolved in THF to remove unreacted vinylbenzyl iodide and reprecipitated in methanol. The polymer was then dried *in vacuo* overnight and stored at -8°C .

B. Free Radical Polymerization of Telechelic Polystyrene: Telechelic dithiocarbamate functionalized polystyrenes of different molecular weight were prepared by the so-called "iniferter" technique using TD as the iniferter. See Ostu et al., Makromol. Chem Rapid Commun. 3:127 (1982). Previous studies have shown that TD not only serves as a free radical initiator, but also has high reactivity for chain transfer to initiator and primary radical termination. Id. These features ensure that the polymer will be end-capped with two initiator fragments.

After polymerization, the polymer was recovered by precipitation of the polymerization solution into a large excess of methanol and drying. The resulting polymer was purified twice by dissolution in THF and reprecipitation into methanol.

The telechelic polystyrene produced by this method was then characterized (see Table 1). The molecular weight of the polymer was determined by GPC. The presence of the residual initiator and the functionality of the end groups were determined by ^1H NMR and by UV analyses as described previously. See Turner et al., Macromolecules 23:1856-1859 (1990).

Table 1

Synthesis of Telechelic Polystyrenes

Sample ID	M_n (GPC)	MWD	f (%)
1	3.3K	1.5	1.9
2	5.6K	1.8	1.8
3	8.8K	2.1	2.0

The telechelic polystyrenes were also analyzed by a Waters GPC with a photodiode array detector which can give an elution time-peak intensity-UV absorption spectra 3-dimensional plot. The functionality can also be calculated from the 3-D GPC plot.

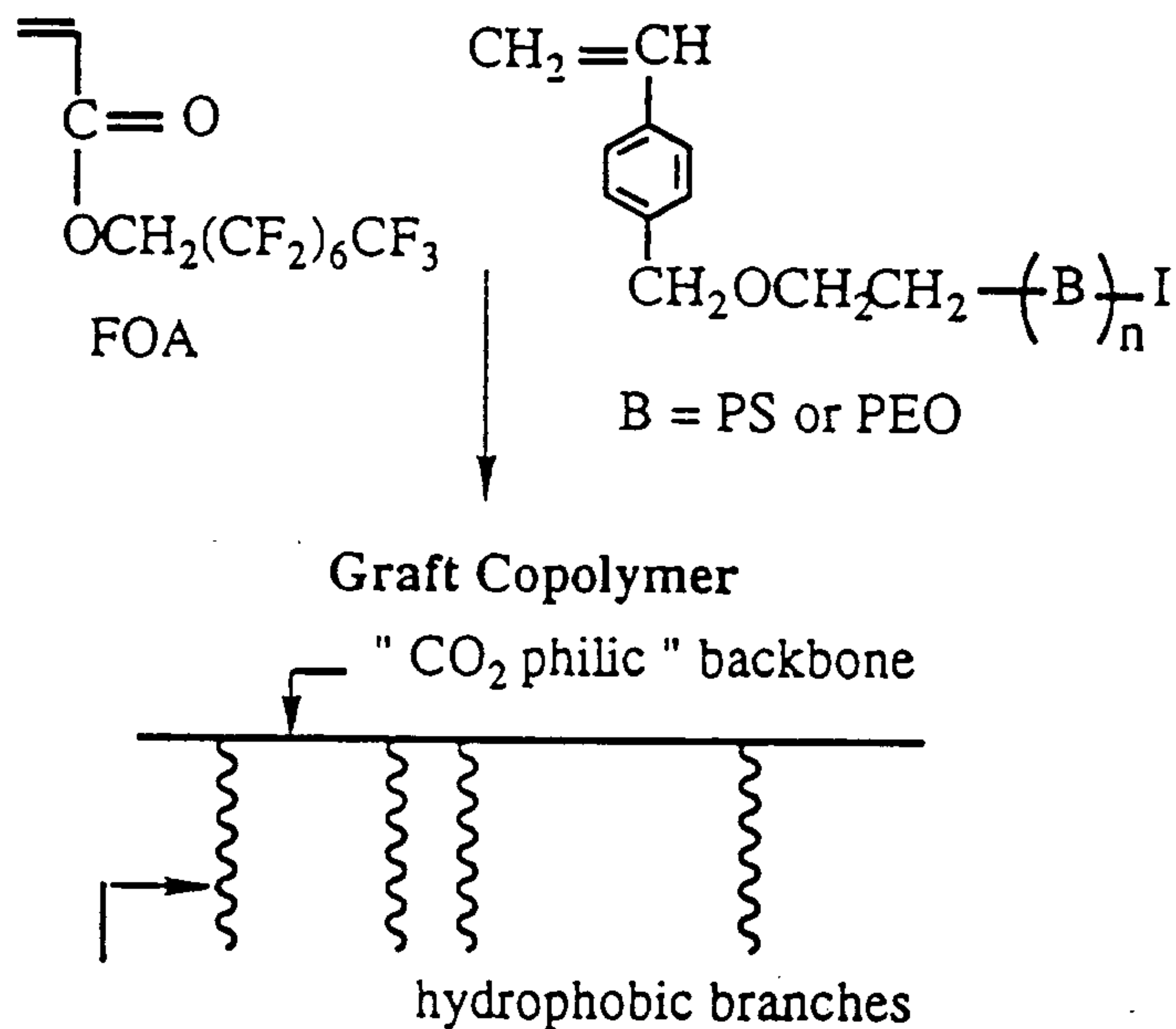
EXAMPLE 6

Synthesis of Graft Polymer Surfactant by Copolymerization of Polystyrene Macromonomer and FOA

A calculated amount of PS macromonomer as synthesized in Example 5.A, FOA and AIBN were added to a round bottom flask and deoxygenated. The synthesis is depicted in Scheme 1 below.

Scheme 1

Scheme 1: Synthesis of CO₂-soluble surfactants



A mixture of Freon-113 and THF were added under argon and the flask was placed in a water bath at 60°C for approximately 48 h. The PFOA-g-PS copolymer was precipitated in methanol, extracted several times with cyclohexane, and dried to constant weight at ambient temperature in vacuo.

The copolymer produced by this method is a graft copolymer having a "CO₂-philic" PFOA backbone with

hydrophobic PS branches. After extraction to remove any unincorporated macromonomer, the poly(FOA-g-PS) copolymer is soluble in CO₂ at 3500 psi, 60°C (10 wt%).

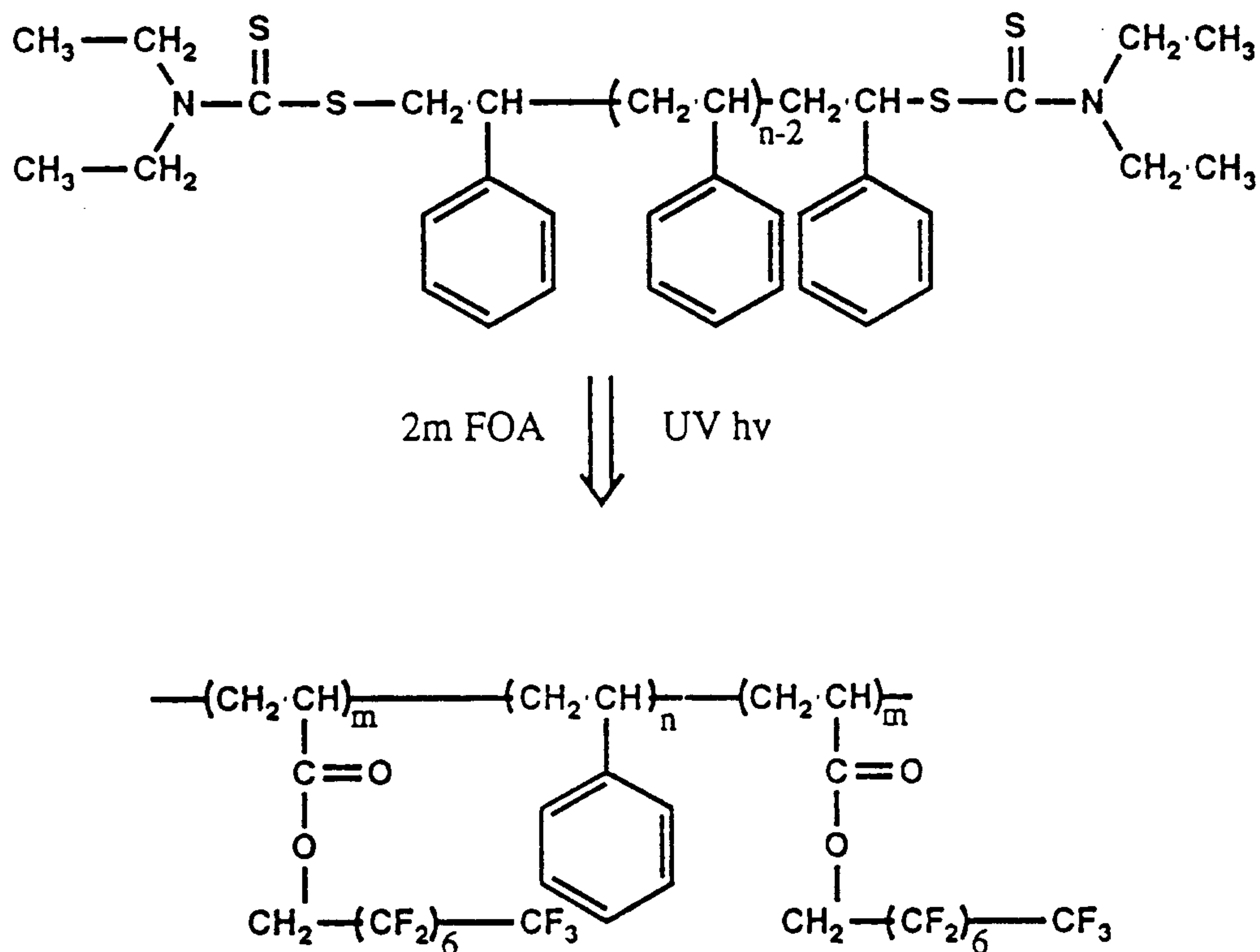
EXAMPLE 7

5 Synthesis of FOA-Styrene-FOA Triblock Copolymer Surfactants

1 g of telechelic polystyrene ($M_n = 5590$, MWD = 1.8) as synthesized in Example 5.B was used as the photoinitiator of FOA monomer (5 g) in
 10 a,a,a-trifluorotoluene solution (20 mL). Three different samples were prepared by Scheme 2 below.

Scheme 2

Photo-Block Copolymerization of TD-PSt with FOA



In Sample 1, $m=25.5$, $n=51$; in Sample 2, $m=79$, $n=51$; in
 15 Sample 3, $m=50.9$, $n=28.7$. Upon UV irradiation of the functionalized polystyrene (Hanovia, 140W), the chain ends dissociate to generate polymeric radicals which in turn initiate the polymerization of FOA. The

dithiocarbamate radical is less reactive and is not effective in initiating the polymerization of acrylate monomers. After 48 h UV irradiation, the polymerization solution was precipitated into methanol to give 4.88 g of polymer (81.3% yield).

EXAMPLE 8

Characterization of FOA-Styrene-FOA Triblock Copolymer

The block copolymers prepared in Example 7 were purified by Soxhlet extraction with cyclohexane to remove any unreacted prepolymer. The copolymer of sample 1, with the short FOA block, is soluble in THF, CHCl₃, and hot cyclohexane. About 5 wt% of the polymer product is soluble in cyclohexane at room temperature which was found to be by ¹H NMR to be mainly unreacted polystyrene. Samples 2 and 3, with longer FOA blocks, were Soxhlet extracted with hot cyclohexane. As determined by ¹H NMR, the hot cyclohexane extract removed not only the unreacted polystyrene, but also some block copolymer that was low in FOA composition. The synthesis data are summarized in Table 2:

Table 2. Synthesis of ABA Triblock Copolymers*

run	TD-PSt			FOA (g)	block copolymer		
	M _n	f	wt(g)		wt(g)	yield(%)	M _n (x10 ⁴)**
1	5.6K	1.8	1.0	5.0	4.88	81	2.87
2	5.6K	1.8	0.5	5.0	4.89	89	7.73
3	3.3K	1.9	0.2	5.0	4.43	85	4.95

* Polymerization run overnight in tribluorotoluene/freon-113 (5/1) mixed solvent with a 140W UV lamp as irradiation source.

** Determined from ¹H NMR and the M_n of the prepolymer.

The purified triblock polymers were characterized with ¹H NMR and DSC. ¹H NMR spectra (Figure 1) show the resonances of both styrene and FOA repeating units. The peak at 4.61 ppm is due to the methylene of the ester group of FOA and the aromatic

resonances (6.3 - 7.3 ppm) are due to the phenyl ring of styrene. From the ratio of the area of the two peaks the chemical composition and the molecular mass was calculated (Table 2).

5 The DSC trace of Sample 1 shows two glass transition temperatures which indicates microphase separation in the bulk. $T_g^1 = -10^\circ\text{C}$ corresponds to the glass transition of FOA microdomains and $T_g^2 = 97^\circ\text{C}$ corresponds to the glass transition of the styrene
10 micro-domains.

As shown in Table 3, the solubility of the block copolymers are quite different from the homopolymers. The FOA homopolymer is soluble in Freon-113 and CO_2 , but insoluble in common organic solvents.
15 However, the sample 1 block copolymer is soluble in THF, CHCl_3 , etc. As the fluorinated block becomes longer (sample 2) or the center block become shorter (sample 3), the copolymer is insoluble in THF or CHCl_3 , but is soluble in Freon-113 and CO_2 .

20 **Table 3.**
Solubility of Triblock Copolymer in Different Solvents

Sample	n	m	Solubility			
			THF	CHCl_3	Freon	CO_2
1	51	25.5	+	+	+	-
2	51	79	-	-	+	+
25 3	28.7	50.9	-	-	+	+

"+" = soluble; "-" insoluble.

EXAMPLE 9

Synthesis of FOMA-2-Ethylhexyl Acrylate-FOMA Triblock Copolymer Surfactant

30 A 450mL Autoclave Engineers o-ring closure, stirred autoclave with a modular furnace and process controller was used as the high pressure polymerization reactor. Pressure was measured with Sensotec Model TJE pressure transducer. Three rupture disks with a burst

pressure of 690 bar are present in the system and all of the components were connected to argon to maintain an inert atmosphere at all times.

The reactor was heated to 60°C and purged with argon for 1-2 hours. 1.35g (1 mol% to monomer) of AIBN dissolved in a minimal amount of THF were injected into the reactor. Following the rapid evaporation of THF, 99.5g of FOMA (50 mol%) and 35.5g of 2-Ethylhexyl acrylate (50 mol%) were introduced under argon atmosphere. The reactor was then rapidly pressurized to 345 bar with CO₂. The reaction was allowed to stir for 24 hours. The reactor was then cooled to room temperature and the polymer was collected into an erlenmeyer flask, washed with methanol and dried in vacuo overnight (yield 75%).

EXAMPLE 10

Solvatochromic Studies of Phenol Blue in CO₂ With and Without FOMA-2-Ethylhexyl Acrylate-FOMA Triblock Copolymers

Solvatochromatic studies were conducted on the copolymer surfactant prepared in Example 9 to investigate micelle formation in CO₂. A dilute solution of phenol blue in cyclohexane (1.5x10⁻⁵ M) was prepared in advance. Ten drops of the solution were syringed into a 2.5mL high pressure UV cell which was loaded with 0.125g of the triblock copolymer (5 wt.%). The solvent was evaporated by purging with argon. The cell was filled with carbon dioxide to 3500 psi at room temperature and UV spectra were recorded after the system became homogeneous. For comparison, UV spectra of phenol blue in pure CO₂ and CO₂/poly(FOA) solution were also measured.

EXAMPLE 11

Results of Solvatochromatic Studies of Phenol Blue in CO₂ With and Without the FC-HC-FC Triblock Copolymers

Since phenol blue itself is soluble in CO₂, in the micelle solution, the dye should partition between the bulk CO₂ phase and the core of the micelle. The

measured λ_{\max} of phenol blue in pure CO₂ at 3500 psi and room temperature was 538 nm, which is consistent with the reported value. No shift of the λ_{\max} of phenol blue was observed in 5 wt.% Poly(FOA)/CO₂ solution at the same temperature and pressure. However, in 5 wt.% triblock copolymer/CO₂ solution, the λ_{\max} of phenol blue shifted from 538nm to 550nm, and the peak was broadened (Figure 2). This suggests the formation of micelles of the triblock copolymer in carbon dioxide, although the broadening of the peak rather than the appearance of an entirely new peak is likely due to the different shapes and sizes of the micelles formed, and probably also due to the dynamic feature of the micelles.

EXAMPLES 12-20

15 Heterogeneous Polymerization of Styrene with AIBN and without Surfactant

Trials attempting to heterogeneously polymerize styrene in CO₂ were carried out. Parameters varied between polymerization trials were the pressure of the reactor (97 or 345 bar), the initiator (either AIBN (155mg - 0.2 wt % to monomer) or the fluoro-azo initiator prepared in Example 3 (2.4 g)), and the presence or absence of the FOMA-styrene-FOMA surfactant prepared in Example 9.

25 The polymerizations commenced by first heating a high pressure reactor to 60°C (with AIBN as the initiator) or 75°C (with the fluoro-azo initiator) and purging with argon for 1-2 hours. The initiator was dissolved in 77.5g (17 wt %) of degassed styrene. 30 The solution was rapidly added to the reactor followed by the addition of CO₂ to the desired pressure. The reaction was stirred for 8 hours at a rate of 500 rpm. Following cooling of the reactor, the polymer was collected, washed with methanol and dried in vacuo 35 overnight.

The results of the polymerization trials are included in Table 4.

Table 4

Sample ID	Pressure (bar)	Surfactant (w/v %)	Initiator	Yield (%)
12	345	none	AIBN	7
13	97	none	AIBN	16
14	345	5	AIBN	22
15	345	none	fluoro-azo	16
16	97	none	fluoro-azo	9
17	345	5	fluoro-azo	20
18	97	1	fluoro-azo	35
19	97	5	fluoro-azo	45
20	97	10	fluoro-azo	60

As shown by the data of **Table 4**, the yield of the polymer increased substantially with the inclusion of the fluoro-azo initiator and a surfactant having a CO₂-philic portion.

EXAMPLE 21

Synthesis of PS-Si(CH₃)₂CH₂CH₂C₆F₁₃

Anionic polymerization was conducted in a one-neck 500 ml, round-bottomed flask equipped with a magnetic stir bar and rubber septa under a 6-8 psig. argon atmosphere. The flask was charged with 2.25 mL of styrene in about 100 mL of dry cyclohexane. The polymerization was then initiated by the addition of 3.63 mL of a 1.38 M solution of sec-butyllithium in cyclohexane. The resulting orange-red solution was then allowed to stir for about two hours after which about 2 mL of dry tetrahydrofuran was added to the solution. To functionally terminate the polymerization, 3.31 mL of perfluorohexylethyldimethylsilylchloride (20% excess) was added via syringe and allowed to stir for ca. 30 minutes. During this time, the solution had become

cloudy due to the precipitation of lithium chloride. The polymer was precipitated in a ten-fold excess of methanol and washed several times with methanol and water. The polymer was then dried under reduced
5 pressure at 40°C for twelve hours.

The resulting polymer was soluble in CO₂ and 60°C and 5000 psi. The precursor polystyrene backing the fluorinated group was less soluble in CO₂.

The foregoing examples are illustrative of
10 the present invention, and are not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

-26-

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of carrying out the heterogeneous
5 polymerization of a water-insoluble polymer, the method comprising:
 providing a heterogeneous reaction mixture comprising carbon dioxide, a hydrophobic monomer, and a surfactant that stabilizes said monomer in said carbon
10 dioxide, wherein said surfactant comprises a carbon-dioxide soluble segment; and
 polymerizing said hydrophobic monomer in said reaction mixture to form said water-insoluble polymer.
- 15 2. A method according to claim 1, wherein said reaction mixture further comprises an initiator.
3. A method according to claim 2, wherein said
initiator is solubilized in said continuous phase so that
20 said polymerization is an emulsion polymerization.
4. A method according to claim 2, wherein said
initiator is solubilized in said dispersed phase so that
said polymerization is a suspension polymerization.
25
5. A method according to claim 1, wherein said hydrophobic monomer is selected from the group consisting of styrene monomers, acrylic monomers, vinyl chloride monomers, olefinic monomers, fluoroolefinic monomers, and
30 maleic anhydride monomers.
6. A method according to claim 1, wherein said carbon dioxide-soluble segment is a fluorine-containing segment or a siloxane-containing segment.

7. A method according to claim 1, wherein said reaction mixture further comprises at least one hydrophilic monomer.

5 8. A method according to claim 1, wherein said surfactant further comprises a hydrophobic segment covalently linked to said carbon dioxide-soluble segment.

9. A method according to claim 1, further comprising separating said polymer from said solution
10 following the polymerizing step.

10. A method according to claim 9, further comprising collecting said polymer from said solution following the separating step.

11. A heterogeneous reaction mixture useful
15 for carrying out the heterogeneous polymerization of a monomer that forms a water-insoluble polymer, said reaction mixture comprising:

at least one monomer that forms a water-insoluble polymer;
20 a carbon dioxide continuous phase; and
a surfactant that stabilizes said monomer and said polymer in said carbon dioxide, wherein said surfactant comprises a carbon dioxide soluble segment.

12. A heterogeneous reaction mixture
25 according to claim 11, further including a hydrophilic monomer.

13. A heterogeneous reaction mixture according to claim 11, further comprising a reaction initiator.

14. A heterogeneous reaction mixture according to claim 11, wherein said carbon dioxide-soluble segment of said surfactant is selected from the group consisting of fluorine-containing groups and siloxane-containing groups.

15. A heterogeneous reaction mixture according to claim 14, wherein said carbon dioxide-soluble segment comprises a fluoropolymer.

10

16. A heterogeneous reaction mixture according to claim 11, wherein said surfactant further comprises a hydrophobic segment covalently linked to said carbon dioxide-soluble segment.

15

17. A heterogeneous reaction mixture according to claim 16, wherein said hydrophobic segment comprises polystyrene.

18. A heterogeneous reaction mixture according to claim 16, further comprising a second carbon dioxide-soluble segment covalently bonded to said hydrophobic segment.

19. A heterogeneous reaction mixture according to claim 13, wherein said initiator comprises a first carbon dioxide-soluble segment and a second free radical-forming group, wherein said carbon dioxide-soluble segment is a fluorine-containing segment or a siloxane-containing segment.

30

20. A heterogeneous reaction mixture according to claim 19, wherein said free radical-forming group of said initiator comprises azobisisobutyronitrile.

21. A heterogeneous reaction mixture according to claim 19, wherein said carbon dioxide-soluble segment of said initiator comprises a fluorine-containing segment or a siloxane-containing segment.
- 5
22. A heterogeneous mixture comprising:
at least one water-insoluble polymer;
a carbon dioxide continuous phase; and
a surfactant that stabilizes said polymer in said
10 carbon dioxide, wherein said surfactant comprises a carbon dioxide soluble segment.
23. A heterogeneous mixture according to claim 22, further including a hydrophilic monomer.
- 15
24. A heterogeneous mixture according to claim 22, further comprising a reaction initiator.
25. A heterogeneous mixture according to claim 22,
20 wherein said carbon dioxide-soluble segment of said surfactant is selected from the group consisting of fluorine-containing groups and siloxane-containing groups.
- 25 26. A heterogeneous mixture according to claim 25, wherein said carbon dioxide-soluble segment comprises a fluoropolymer.
27. A heterogeneous mixture according to claim 22,
30 wherein said surfactant further comprises a hydrophobic segment covalently linked to said carbon dioxide-soluble segment.
28. A heterogeneous mixture according to claim 27,
35 wherein said hydrophobic segment comprises polystyrene.

-30-

29. A heterogeneous mixture according to claim 24,
wherein said initiator comprises a first carbon dioxide-
soluble segment and a second free radical-forming group,
wherein said carbon dioxide-soluble segment is a
5 fluorine-containing segment or a siloxane-containing
segment.

30. A heterogeneous mixture according to claim 29,
wherein said free radical-forming group of said initiator
10 comprises azobisisobutyronitrile.

31. A heterogeneous mixture according to claim 29,
wherein said carbon dioxide-soluble segment of said
initiator comprises a fluorine-containing segment or a
15 siloxane-containing segment.

32. A method of making a water insoluble polymer,
comprising:

20 providing a heterogeneous mixture according to claim
22 in a reaction vessel;
venting CO₂ from the reaction vessel; and
separating said polymer from said mixture.

33. A method according to claim 32, wherein said
25 reaction mixture further comprises an initiator.

34. A method according to claim 33, wherein said
initiator is solubilized in said continuous phase so that
said polymerization is a suspension polymerization.

30

35. A method according to claim 33, wherein said
initiator is solubilized in said dispersed phase so that
said polymerization is a suspension polymerization.

-31-

36. A method according to claim 32, wherein said water insoluble polymer comprises a hydrophobic monomer selected from the group consisting of styrene monomers, acrylic monomers, vinyl chloride monomers, olefinic monomers, fluoroolefinic monomers, and maleic anhydride monomers.

37. A method according to claim 32, wherein said carbon dioxide-soluble segment is a fluorine-containing segment or a siloxane-containing segment.

38. A method according to claim 32, wherein said reaction mixture further comprises at least one hydrophilic monomer.

39. A method according to claim 32, wherein said surfactant further comprises a hydrophobic segment covalently linked to said carbon-dioxide soluble segment.

40. A polymer produced from the method of claim 32, wherein said separating step is carried out by venting.

41. A polymer according to claim 40, wherein said polymer is a film.

42. A polymer according to claim 40, wherein said polymer is a fibre.

43. A polymer according to claim 40, wherein said polymer is a resin.

44. A polymer according to claim 40, wherein said polymer is a molded article.

45. A mixture comprising carbon dioxide and a surfactant, wherein said surfactant comprises a carbon dioxide soluble segment and a CO₂-phobic group covalently linked to said carbon dioxide soluble segment, wherein said carbon dioxide soluble segment further comprises a fluoropolymer and wherein said surfactant is a copolymer selected from the group consisting of a graft copolymer and a block copolymer.
- 10 46. A mixture comprising carbon dioxide and a surfactant, wherein said surfactant comprises a carbon dioxide soluble segment, wherein said surfactant further comprises a CO₂-phobic group covalently linked to said carbon dioxide soluble segment, and wherein said carbon dioxide soluble segment further comprises a siloxane segment.
- 15 47. A mixture comprising carbon dioxide and a surfactant, wherein said surfactant comprises a carbon dioxide soluble segment and a CO₂-phobic group, wherein said carbon dioxide soluble segment is a fluorine-containing segment, wherein said CO₂-phobic group is hydrophobic, and wherein said fluorine-containing segment has a terminal perfluorinated group.
- 20 48. A mixture comprising carbon dioxide and a surfactant, wherein said surfactant comprises a carbon dioxide soluble segment and a CO₂-phobic group covalently linked to said carbon dioxide soluble segment further comprises a fluoropolymer; wherein said surfactant is a copolymer selected from the group consisting of a graft copolymer and a block copolymer;
- 25 wherein said carbon dioxide comprises liquid carbon dioxide;
- 30 and wherein said CO₂-phobic group is hydrophobic.
- 35

49. A mixture comprising carbon dioxide and a surfactant, wherein said surfactant comprises a carbon dioxide soluble segment, wherein said surfactant further comprises a CO₂-phobic group covalently linked to said carbon dioxide
5 soluble segment; wherein said carbon dioxide soluble segment further comprises a siloxane segment;

wherein said carbon dioxide comprises liquid carbon dioxide;

and wherein said CO₂-phobic group is hydrophobic.

10

50. The mixture according to Claim 45, 46, or 47, wherein said carbon dioxide comprises liquid carbon dioxide.

51. The mixture according to Claim 45, 46, or 47, wherein
15 said carbon dioxide comprises supercritical carbon dioxide.

52. The mixture according to Claim 45 or 46, wherein said CO₂-phobic group is hydrophobic.

20

53. The mixture according to Claim 45 or 46, wherein said CO₂-phobic group is hydrophilic.

54. The mixture according to Claim 52, wherein said
25 hydrophobic group aggregates to form micelles in said carbon dioxide.

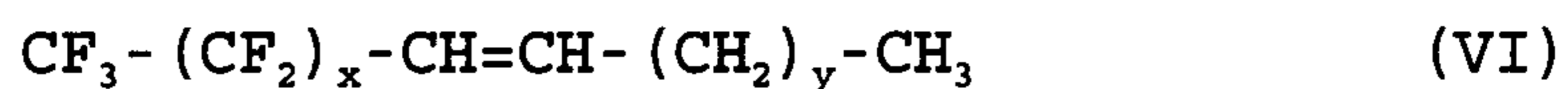
55. The mixture according to Claim 45 or 48, wherein said surfactant comprises a copolymer of a fluoropolymer and
30 polystyrene.

56. The mixture according to Claim 45, 46, 47, 48, or 49, further comprising a cosolvent.

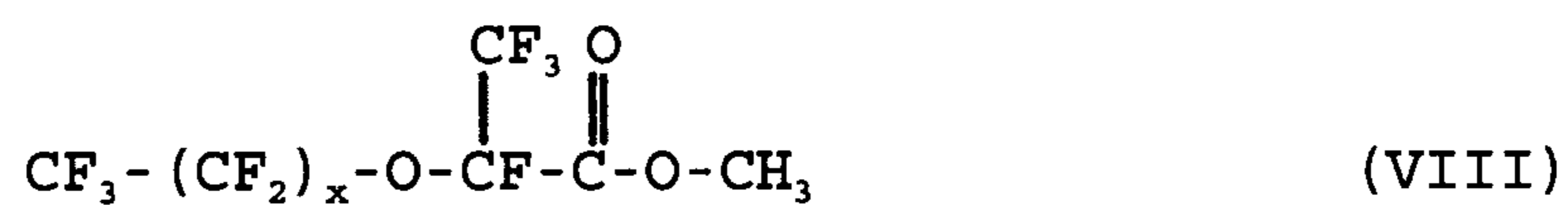
35 57. The mixture according to Claim 45, 46, 47, 48, or 49, further comprising a second surfactant, said second surfactant comprising a carbon dioxide soluble segment.

58. The mixture according to Claim 46 or 49, wherein said surfactant comprises a copolymer comprising a carbon dioxide soluble group and a CO₂-phobic group.

5 59. The mixture according to Claim 47, wherein said surfactant is selected from the group consisting of



10 and

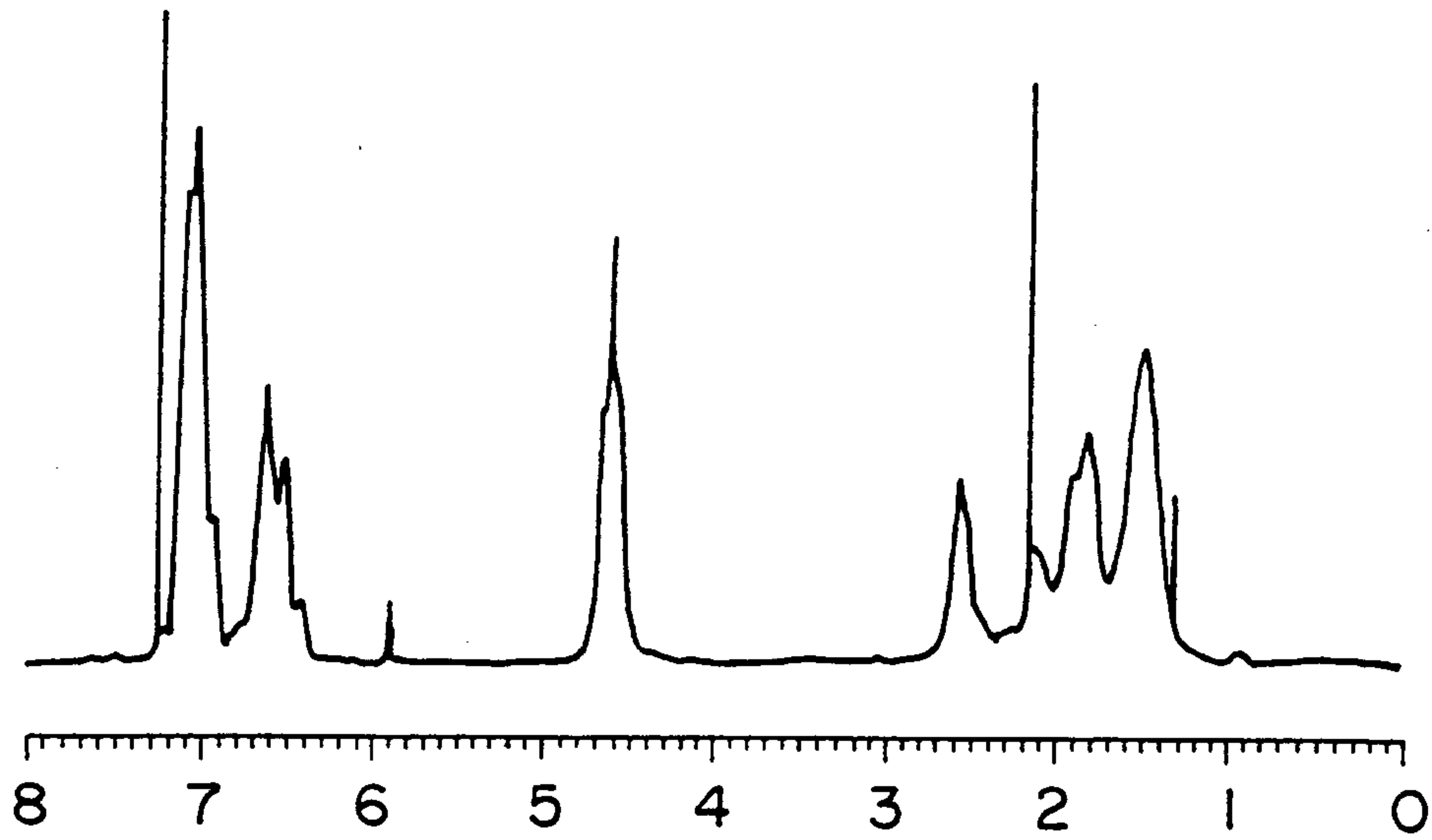


15 wherein x is 1-30 and y is 1-30.

60. The mixture according to Claim 47, 48, or 49, wherein said CO₂-phobic group aggregates to form micelles in said carbon dioxide.

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¹H NMR SPECTRUM OF SAMPLE 1 TRIBLOCK COPOLYMER

FIG. I.

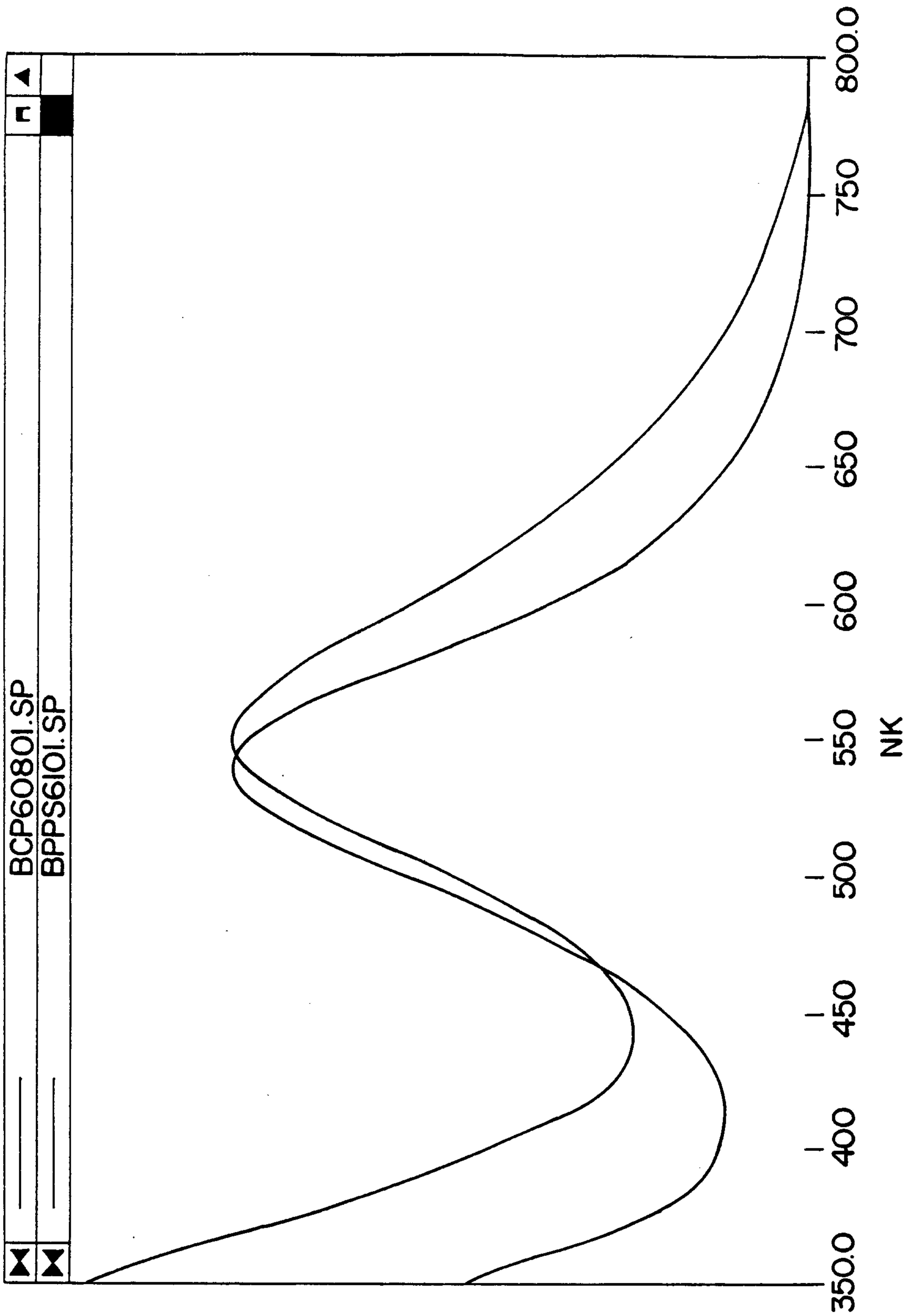


FIG. 2.