Macromolecules **1995,** *28,* 8429−8431 **8429**

Synthesis of Tetrafluoroethylene-Based, Nonaqueous Fluoropolymers in Supercritical Carbon Dioxide

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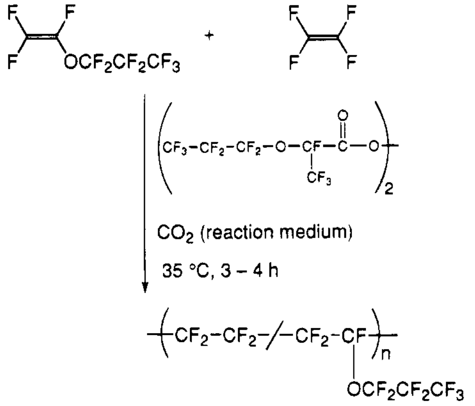
Received June 14, 1995
Revised Manuscript Received September 20, 1995

Nonaqueous fluoropolymers, exemplified by melt processable copolymers of tetrafluoroethylene (TFE) and perfluoro(propyl vinyl ether) (PPVE) or TFE and hexafluoropropylene (HFP) (perfluoroalkoxy, PFA, and fluorinated ethylene propylene, FEP, resins, respectively), are premium products used as wire coatings in high-speed communications, processing baskets for silicon wafers, and for pipe and equipment lining for corrosive chemical service. Many of these materials can withstand long term use at temperatures up to 260 °C, are resistant to chemical attack by all but the harshest of environments (molten alkali metals and elemental fluorine at high temperature are examples), have among the lowest dielectric constants known for solid materials (making them excellent insulators), and possess extremely low surface energies, making them attractive in wide array of applications.[1] In the United States alone, over 7 million kilograms of PPVE/TFE and HFP/TFE copolymers, selling for $15−50/kg, are manufactured each year.[2] Although these materials are often manufactured using aqueous processes, the removal of the resulting unstable carboxylic acid and acid fluoride end groups requires expensive finishing steps such as high temperature hydrolysis or fluorination. Such modifications are necessary since under the extreme conditions which are required to melt process fluoropolymers, these end groups can decompose to form bubbles, discoloration, and erratic molecular weight changes in the final products, as well as cause hydrogen fluoride formation which can damage processing equipment and make the product unsuitable for applications requiring low extractable fluoride ion content. Alternatively, nonaqueous media (historically chlorofluorocarbons (CFCs)) are sometimes employed in the manufacture of these materials to reduce the formation of thermally unstable carboxylic acid and acid fluoride end groups which arise from aqueous initiators. Even for materials currently manufactured using aqueous processes, nonaqueous systems offer significant benefit in terms of product performance.

Prompted by the impending ban on chlorofluorocarbon solvents, there has been an avid pursuit of alternative technologies for use in the manufacture of nonaqueous fluoropolymers. In 1994 alone, no less than 11 patents and patent applications proposing over 25 alternative solvents for nonaqueous polymerizations of fluoroolefins were issued in the United States and Japan. Because the fluorinated free radicals encountered in fluoroolefin polymerizations are highly electrophilic,[3] they readily abstract hydrogen atoms from nearly all hydrocarbons, precluding the synthesis of high molar mass fluoropolymers in most hydrogen-containing solvents. Some exemplary proposed solvent alternatives include perfluorocarbons such as perfluorohexane,[4] hydrofluorocarbons such as 1,1,2,2-tetrafluorocyclobutane,[5] perfluoroalkyl sulfides such as perfluoro-1,4-dithiane,[6] and perfluorinated cyclic amines such as perfluoro-*N*-methylmorpholine.[7] Not only are these fluorinated solvents expensive (prices start at >$150/gal), but many are not even commercially available at present.

Scheme 1. Copolymerization of TFE and PPVE in Carbon Dioxide



Our work[8−14] and the work of others[15−19] has shown that carbon dioxide is an excellent medium in which to conduct free radical polymerizations (a recent review is available).[20] In addition to the obvious environmental advantage offered by CO_2 over CFCs, its use for the preparation of nonaqueous fluoropolymers offers several key advantages over conventional systems: highly toxic initiator residues and decomposition products (typically removed by washing products with chlorofluorocarbons) may be easily extracted employing supercritical fluid extraction techniques (SCFE)[21] and unique new materials and morphologies may be accessible as a result of polymer plasticization by CO_2 or through the addition of appropriately designed amphiphiles, as we have demonstrated for other systems.[9] In addition, for systems involving TFE, the most important and widely employed of the fluoroolefin monomers, carbon dioxide-based processes offer significant benefits in terms of safety.[12,22] To demonstrate the utility of nonaqueous fluoroolefin polymerizations in carbon dioxide, we have investigated copolymerizations of tetrafluoroethylene with perfluoro(propyl vinyl ether) (Scheme 1) and with hexafluoropropylene using bis(perfluoro-2-propoxypropionyl) peroxide as a free radical initiator.

Reactions in our laboratory were carried out in a 25-mL, high-pressure view cell equipped with a full bore rupture disk and housed in a 1/4 in. plate steel enclosure designed to protect personnel and equipment in the event of an explosion. In all cases, bis(perfluoro-2-propoxypropionyl) peroxide, $(CF_3CF_2CF_2OCF(CF_3)C(O)O)_2$, was employed as initiator and was prepared as previously reported.[23,24] Bis(perfluoro-2-propoxypropionyl) peroxide has a half-life of ca. 33 min in 1,1,2-trichlorotrifluoroethane at the commonly used reaction temperature of 35 °C.[25] After evacuation, the cell was placed under a positive argon purge and cooled to well below 0 °C in a dry ice/acetone bath (−78 °C) before initiator solution and liquid monomer(s) were added via syringe. The reactor was then sealed, and gaseous monomer(s) was (were) condensed into the cell in order

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Table 1. Monomer Concentrations Employed, Yield, Percentage PPVE Incorporation, and Melting Point for Copolymerizations of TFE and PPVE

[TFE]	[PPVE]	yield (%)	wt % PPVE	T_m
2.1	0.18	100	0	330
1.9	0.18	99	2.9	321
2.2	0.55	100	8.6	319
2.0	0.55	100	5.2	313
2.2	0.92	100	5.8	314

of increasing vapor pressure (TFE was handled as a 50 wt % mixture with CO_2), followed by additional CO_2, while being cooled. The dry ice bath was then removed, the safety enclosure sealed and bolted down, and the reactor warmed to the desired reaction temperature of 35 °C. The initial reaction formed a homogeneous solution filling the entire reactor volume. Polymer precipitated as it formed. Initial reaction pressures were 90–110 bar for TFE/PPVE copolymerizations. Initial reaction pressures for TFE/HFP copolymerizations ranged from 50 to 100 bar and were a function of the monomer feed ratio (as more HFP was added, less additional CO_2 was added, resulting in lower pressures). After 3–4 h, the reaction vessel was slowly vented into the hood, the cell was opened, and the product was easily recovered as a free-flowing, white powder. Products were washed twice with a 50/50 mixture of methanol/1,1,2-trichlorotrifluoroethane to remove initiator residues and then vacuum dried at elevated temperature prior to analysis by thermogravimetry (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). Selected samples were pressed into thin films and analyzed by Fourier transform infrared spectroscopy (FTIR) to assess comonomer incorporation and end group content. Melt viscosities were determined with an extrusion plastometer according to ASTM D1238 at 372 °C.

Table 1 details monomer concentrations employed, yields (based on TFE), weight percent perfluoro(propyl vinyl ether) incorporated, and crystalline melting point data for selected reactions. Initiator concentrations employed were typically on the order of 5×10^{-5} M, but were varied slightly to accommodate changes in the monomer feed ratio. Because PPVE is significantly less reactive than TFE, an excess of perfluoro(propyl vinyl ether) must be employed to achieve the desired levels of incorporation. For reactions run in carbon dioxide, incorporation of up to 8.6 wt % of PPVE was observed, which is well in excess of the 2–4 wt % desired for most applications.[26] The apparently anomalous melting point of 319 °C for 8.6% PPVE incorporation can be explained by the appearance of broad, low-melting peaks in the DSC plot for this sample, presumably due to the formation of a small amount of copolymer very high in PPVE late in this reaction.

Analysis of end groups by FT-IR showed from 0 to 3 carboxylic acid or acid fluoride end groups per 10^6 carbon atoms, which is on the order of similar copolymers made in CFCs and then subjected to aggressive fluorination.[27] Melt viscosities were too high to measure by conventional methods, indicating that molar masses were in excess of 1×10^6 g/mol for these reactions.[28]

In another reaction not reported in Table 1, perfluoro(propyl vinyl ether) and TFE were copolymerized in carbon dioxide on a 50-g scale in a 500-mL Autoclave Engineers stirred reactor with methanol added as chain transfer agent. The resulting polymer had a melt viscosity of 7.3×10^4 P at 372 °C, which is well within the desired range for commercial products.

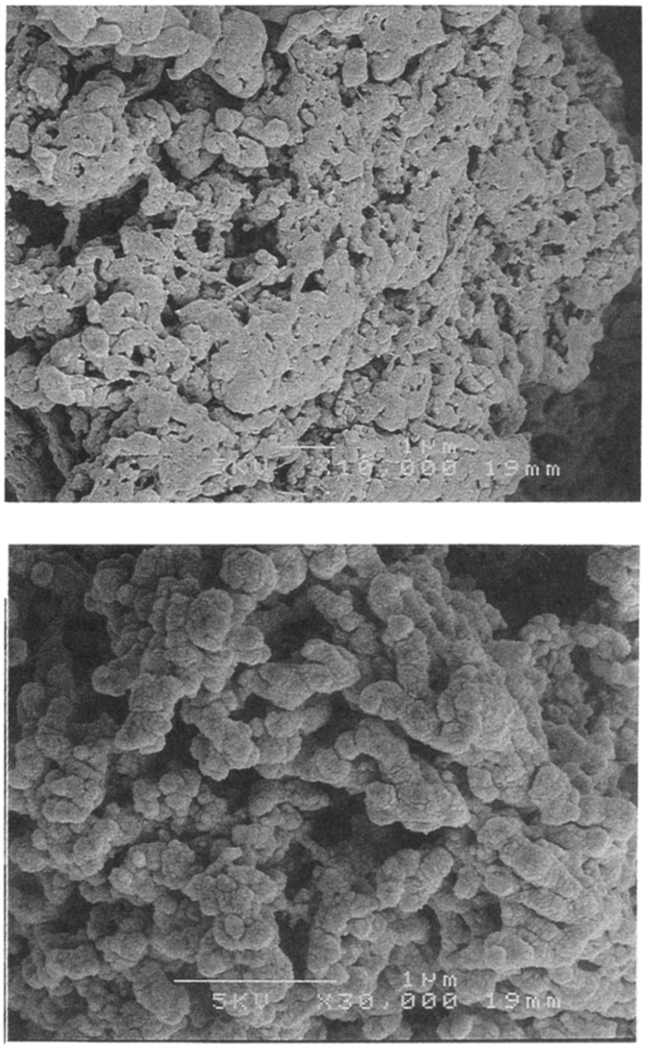

Figure 1. SEMS showing morphology of nonaqueous TFE/PPVE copolymers prepared in (A, top) carbon dioxide and (B, bottom) 1,1,2-trichlorotrifluoroethane.

Table 2. Monomer Concentrations Employed, Yield, Percentage HFP Incorporation, and Melting Point for Copolymerizations of TFE and HFP

[TFE]	[HFP]	yield (%)	wt % HFP	T_m
0.52	3.9	26		267
0.68	5.15	3.1		250
0.88	5.12	82	11.2	266
0.96	5.15	71	13.8	254
0.56	3.4	62	12.2	261

Results for some representative copolymerizations of hexafluoropropylene and tetrafluoroethylene are given in Table 2. Because hexafluoropropylene is even less reactive than perfluoro(propyl vinyl ether), a large excess is required to achieve the incorporation levels necessary for desired properties under batch conditions. Reactions conducted in such an overwhelming excess of hexafluoropropylene were expected to produce lower yields than TFE/perfluoro(propyl vinyl ether) copolymerizations even though high initiator concentrations were employed. Initiator concentrations ranged from 5×10^{-4} to 3×10^{-3} M. As expected, yields were strongly a function of initiator concentration coupled with the monomer feed ratio. Incorporation of 11–14 wt % of HFP achieved under batch conditions seem to be in the appropriate range to yield the desired properties (commercial products are in the range of 10–12 wt %) and clearly indicate that semibatch processes will result in high yields as well as good incorporation.

Apparent anomalies concerning variability in comonomer incorporation can be explained by the formation polymer rich in HFP late in the reaction. Owing to the relatively small amount of sample produced for these reactions, accurate determination of end groups, melt viscosities, and HFP incorporation was not possible for all samples.

Representative scanning electron micrographs (SEMs) of PPVE/TFE copolymers prepared in a conventional liquid CFC solvent (Freon-113) and in carbon dioxide are shown in Figure 1 (parts A and B, respectively). Comparison of the micrographs indicate that although there are some differences, the morphology for the sample made in CO_2 is similar to that made in conventional solvents.

In conclusion, carbon dioxide is an excellent, environmentally responsible alternative to CFCs in which to conduct nonaqueous polymerizations of fluoroolefins. Copolymers of tetrafluoroethylene and perfluoro(propyl vinyl ether), as well as copolymers of tetrafluoroethylene and hexafluoropropylene, were synthesized in high yields employing bis(perfluoro-2-propoxypropionyl) peroxide as a free radical initiator in supercritical carbon dioxide. For TFE/PPVE copolymers, molecular weights achieved were high and FTIR analysis indicated the successful elimination of deleterious end groups. Copolymers of HFP with TFE showed good incorporation and reasonable yields. In light of the impending ban on CFCs and the improved physical attributes afforded by CO_2 based processes, the polymerization of fluoroolefins in such an environmentally responsible medium may well prove to be a viable alternative to conventional solvents for the manufacture of nonaqueous fluoropolymers.

Acknowledgment. The authors are indebted to the National Science Foundation (J.M.D., Presidential Faculty Fellow, 1993–1997), the E. I. Du Pont de Nemours and Company for financial support, and P. R. Resnick, A. E. Feiring, G. F. Leverett, and R. C. Wheland of DuPont for technical support.

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(27) Fluoropolymers containing undesirable end groups can be fluorinated using fluorine gas at high temperature often yielding <5 acid fluoride or carboxylic acid end groups per 10^6 carbon atoms.

(28) For conventional CFC-based systems it is often necessary to add a chain transfer agent such as methanol or ethane to control molecular weight.

MA950832V