

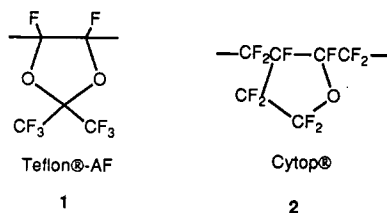
## New Ring-Containing Fluoropolymers†

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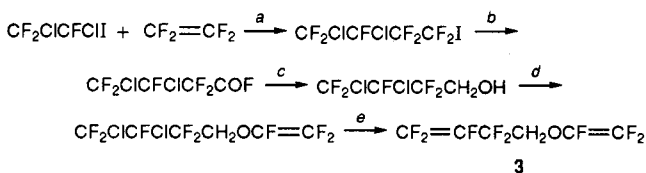
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Perfluoropolymers have excellent thermal and chemical stability, high insulating ability, and low refractive index and dielectric constant, but their limited solubility and high crystallinity necessitate extreme processing conditions.<sup>1</sup> Recently, ring-containing polymers Teflon-AF<sup>2</sup> and Cytop<sup>3</sup> were introduced by DuPont<sup>4</sup> and Asahi Glass,<sup>5</sup> respectively. In contrast to poly-(tetrafluoroethylene), these cyclic fluoropolymers are amorphous but soluble only in selected fluorinated solvents.



We now report that the partially fluorinated diene **3** undergoes a facile cyclopolymerization to afford a novel ring-containing fluoropolymer **4**.<sup>6</sup> The presence of only two hydrogens in the repeat unit of **4** results in remarkable changes in its solubility behavior and morphology as compared to its perfluorinated analog.

Monomer **3**<sup>7</sup> was prepared from 1,2-dichloriodotrifluoroethane by the sequence shown in Scheme 1.

Scheme 1<sup>a</sup>

<sup>a</sup> Reaction conditions: (a) (PhCOO)<sub>2</sub> (initiator), 135 °C, 55%; (b) 30% oleum, HgO (catalyst), 110 °C, 87%; (c) LiAlH<sub>4</sub>, 90%; (d) NaH; CF<sub>2</sub>=CF<sub>2</sub>, 50 °C, 55%; (e) Zn, 90 °C, 65%.

The polymerization of **3** can be carried out neat or in solution. Suitable free-radical initiators include bis(perfluoropropionyl) peroxide (3-P) and bis(4-*tert*-butylcyclohexylperoxy) dicarbonate. For example, when the monomer was mixed with 1 mol % of 3-P, sealed, and kept at 40–45 °C overnight, white solid was observed,

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(1) (a) *Fluoropolymers*; Wall, L. A. Ed.; John Wiley & Sons, Inc.: New York, 1972; Vol. XXV. (b) Carlson, D. P.; Schmiegel, W. *Ullmann's Encyclopedia of Industrial Chemistry*; VCH Publishers: New York, 1988; Vol. A11, p 393.

(2) DuPont registered trademark.

(3) Asahi Glass registered trademark.

(4) Resnick, P. R. *Polym. Prepr., Am. Chem. Chem. Soc. Div. Polym. Chem.* 1990, 31, 312.

(5) Nakamura, N.; Kawasaki, T.; Unoki, M.; Oharu, K.; Sugiyama, N.; Kaneko, I.; Kojima, G. *Preprints of the First Pacific Polymer Conference*, Maui, HI, Dec, 1989; p 369.

(6) Feiring, A. E.; Smart, B. E.; Yang, Z.-Y. U.S. Patent 5,260,492, (1993).

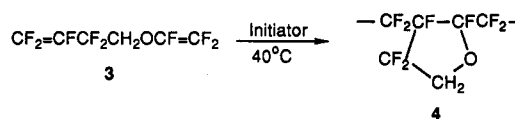
(7) <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.32 (t, J = 11.3 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -91.9 (ddt, J = 57.7 Hz, J = 36.6 Hz, J = 5.4 Hz, 1F), -107.9 (ddt, J = 115.7 Hz, J = 57.8 Hz, J = 31.1 Hz, 1F), -111.3 (m, 2F), -121.5 (dd, J = 99.4 Hz, J = 59.0 Hz, 1F), -127.8 (dd, J = 109.0 Hz, J = 99.5 Hz, 1F), -137.4 (dd, J = 109.0 Hz, J = 59.0 Hz, 1F), -190.2 (ddt, J = 115.5 Hz, J = 36.7 Hz, J = 14.7 Hz, 1F). IR (neat): ν 2980 (w), 1845 (w), 1790 (vs), 1320 (m), 1175 (vs), 1040 (v). Anal. Calcd for C<sub>6</sub>H<sub>2</sub>F<sub>8</sub>O: C, 29.75; H, 0.83. Found: C, 30.15; H, 0.85.

Table 1<sup>a</sup>

comonomer	incorp (%)	M <sub>w</sub>	M <sub>n</sub>	T <sub>g</sub>	T <sub>m</sub>	TGA <sup>b</sup>
none	0	404 000	190 000	126.9	347	485
TFE <sup>c</sup>	52.3	84 300	57 100	85	no	480
CTFE	52	229 000	108 000	105.7	no	440
PPVE <sup>d</sup>	12	71 200	18 100	100.7	301.4	470
PSEPVE <sup>e</sup>	5.6	118 000	19 000	111.2	288.2	440

<sup>a</sup> Polymerizations were carried out neat overnight. <sup>b</sup> 10% weight loss under N<sub>2</sub> when heated at 20 deg/min. <sup>c</sup> Reaction in CF<sub>2</sub>CICFCI<sub>2</sub> at 38 °C for 8 h. <sup>d</sup> PPVE = n-C<sub>3</sub>F<sub>7</sub>OCF=CF<sub>2</sub>. <sup>e</sup> PSEPVE = CF<sub>2</sub>=CFOCF<sub>2</sub>-CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F.

which was dissolved in ethyl acetate and then reprecipitated by addition of methanol. The yield of polymer is greater than 90%.<sup>8</sup>



Unlike any other highly fluorinated polymer, **4** is soluble in polar aprotic solvents such as DMF, THF, glyme, acetone, and acetonitrile. It is insoluble in benzene, chloroform, 1,2,2-trichlorotrifluoroethane, perfluorocarbons, and methanol, however. The high solubility indicates that the polymer is not cross-linked.<sup>9</sup> The inherent viscosity of this polymer in DMF at 25 °C is 0.945 dL/g, and its refractive index is 1.394. GPC analysis (relative to polystyrene as standard) indicates M<sub>w</sub> = 4.04 × 10<sup>5</sup> with M<sub>w</sub>/M<sub>n</sub> = 2.12.

Thermal gravimetric analysis of the homopolymer shows a high degree of thermal stability under nitrogen. Mass loss begins at 420 °C, with a 10% weight loss temperature of 485 °C. However, the stability of **4** significantly decreases in air (10% weight loss at 360 °C), presumably due to oxidation of carbon-hydrogen bonds in the polymer. The polymer has a glass transition temperature of 127 °C by differential scanning calorimetry (DSC) and shows a melting point at 347 °C. The powder X-ray diffraction further confirms that the polymer is semicrystalline,<sup>10</sup> in contrast to its perfluorinated counterpart **2**.

Monomer **3** readily copolymerizes with other fluorinated monomers, such as tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), and perfluorovinyl ethers. The results are summarized in Table 1.

The copolymers, even those containing up to 52 mol % of TFE or CTFE, surprisingly retain good solubility in polar organic solvents, so colorless and transparent thin films can be readily cast from solution. All copolymers show good thermal stability with 10% mass loss above 440 °C in nitrogen. The trifluorovinyl ether copolymers are still partially crystalline, but, as expected, T<sub>g</sub> and T<sub>m</sub> are lower than those of the homopolymer. By contrast, the copolymers containing relatively large amounts of TFE or CTFE are amorphous, with no melting points by DSC. Film X-ray diffraction further confirms that they are amorphous polymers.<sup>11</sup>

(8) Anal. Calcd for (C<sub>6</sub>H<sub>2</sub>F<sub>8</sub>O)<sub>n</sub>: C, 29.75; H, 0.83; F, 62.79. Found: C, 29.14; H, 0.93; F, 61.68.

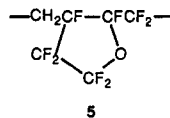
(9) The IR spectrum shows no absorption at around 1790 cm<sup>-1</sup> which could be attributed to residual double bonds. The <sup>19</sup>F NMR spectrum indicated no vinylic fluorines. Peaks for saturated fluorines are shown at -112.5 to -122.0 and at -176.0 to -187.0 ppm in a 7:1 ratio. The latter peaks are assigned to the fluorine on tertiary carbon and can be further considered as two sets of broad peaks at -176.0 to -179.0 and at -183.0 to -187.0 ppm in a 2:1 ratio, suggesting the existence of cis and trans isomers in a ratio of 2:1. This cyclic structure is further confirmed by <sup>13</sup>C{<sup>19</sup>F} NMR analysis. Peaks at 121.05, 114.49, and 112.78 ppm correspond to the carbons of three CF<sub>2</sub>, and two sets of triplets at 73.40 ppm are assigned to CH<sub>2</sub> carbon. Two tertiary carbons are observed at 114.57 and 96.55 ppm, respectively.

(10) X-ray diffraction exhibited two type patterns: one with relative sharp peaks at 2θ = 14.635° (d = 6.050 29 Å) and 17.395° (d = 5.0982 Å) and another with broad peaks at 2θ = 30.142° (d = 2.9649 Å) and 38.202° (d = 2.3559 Å).

(11) X-ray diffraction for CTFE copolymer shows a broad amorphous peak at 2θ = 15.395° (d = 5.7557 Å).

In conclusion, we have synthesized a new hydrofluoroalkenyl vinyl ether which readily homo- or copolymerizes to give ring-containing fluoropolymers. The new polymers show remarkable solubility,<sup>12</sup> high thermal stability, and excellent optical clarity,

(12) The reason for this unprecedented solubility is not entirely clear, although there is accumulating evidence that the hydrogens in a  $-\text{CF}_2\text{CH}_2-\text{OR}_F$  unit have peculiarly strong hydrogen-bonding capabilities. For example, the methylene  $^1\text{H}$  chemical shifts in  $[\text{CF}_2\text{CFHO}\text{CF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CH}_2\text{O}]_n$  polyethers range from 3.77 ppm in  $\text{C}_6\text{D}_6$  to 4.69 ppm in  $\text{DMSO}-d_6$ ,<sup>13</sup> and certain related cyclic ethers actually form stable hydrogen-bonded complexes with fluoride ions.<sup>14</sup> Notably, the solubility character of the isomeric polymer **5** is very similar to that for **2** but entirely different from that for **4**.<sup>15</sup>



which may lead to many potential applications. Further investigation is underway.

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**Supplementary Material Available:** Experimental details and characterization data for monomer **3** and homopolymer (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(13) Hung, M.-H.; Farnham, W. B.; Feiring, A. E.; Rozen, S. *J. Am. Chem. Soc.* **1993**, *115*, 8954.

(14) Farnham, W. B.; Roe, D. C.; Dixon, D. A.; Calabrese, J. C.; Harlow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 7707.

(15) Inukai, H. Japanese Patent 91 JP-234319, 1993.