Supplementary Material For "An Extraordinarily Rapid Polymerization of Vinylpentafluorocyclopropane: Highly Stereo- and Regio-selective Synthesis of Unsaturated Fluoropolymers"

Zhen-Yu Yang
DuPont Central Research and Development, Experimental Station, P.O. Box 80328, Wilmington, DE 19880-0328
Zhenyu.yang-1@usa.dupont.com

Materials:

CF_2=$CFCH_2CH_2Br$ was obtained from Lancaster, bis(4-t-butylcyclohexylperoxy)-dicarbonate (percadox 16) was obtained from Akzo Nobel Chemical Inc. and bis(perfluoropropionyl) peroxide is DuPont product.

Preparation of 2-bromo-1-(pentafluorocyclopropyl)ethane

A 1L autoclave was charged with 283 g of CF_2=$CFCH_2CH_2Br$ and 415 g of hexafluoropropylene oxide and heated at 190 °C for 6 hrs. Crude product (360.5 g) was distilled to give 7.3 g of bp 87 - 106 °C materials and 329.8 g (92%) of pure 2-bromo-1-(pentafluorocyclopropyl)ethane, bp 111 to 112°C. ^{19}F NMR: -152.5 (dt, J = 197 Hz, J = 7.2 Hz, 2F), -157.1 (dm, J = 197 Hz, 2H), -212.3 (tt, J = 21.5 Hz, J = 7.1 Hz, 1F). ^1H NMR: 3.53 (t, J = 7.1 Hz, 2H), 2.55 (dm, J = 21.5 Hz, 2H). HRMS(Methane CI): Calcd for $C_7H_9F_5Br$ ($M+C_2H_5$): 266.9808, Found: 266.9810.

Preparation of vinylpentafluoropropane **1**

To a stirred solution of 18.0 g of KOH, 15 mL of ethanol and 20 mL of water was slowly added 24.0 g of 2-bromo-1-(pentafluorocyclopropyl)ethane at 70 °C. During the addition, volatile was collected in a -78 °C trap. After the addition was complete, the reaction mixture was stirred at 70 °C for an additional two hours until collection of volatile, which was distilled to give 9.1 g of **1**, bp 30 °C. ^{19}F NMR: -152.3 (dt, J = 195.4 Hz, J = 9.8 Hz, 2F), -156.0 (dm, J = 195.6 Hz, 2F), -210.7 (t, J = 7.7 Hz, 1F). ^1H NMR: 5.86-5.73 (m, 2H), 5.70-5.65 (m, 1H). IR (gas): 3110 (w), 1650 (w), 1515 (m), 1291 (s), 1189 (s), 933 (s). HRMS: Calcd for $C_5H_3F_5$: 158.0155. Found: 158.0152.

Isomerization of Vinylpentafluoropropane

A 5-mL tube was charged with 0.16 g of c-C_3F_5CH=CH_2 and then the tube was evacuated in liquid N_2. The content of the tube was stirred at 120 °C for 3 hrs and then liquid product (0.14 g), 1,2,2,3,3-pentafluorocyclopentene **2**, was transferred to a -78 °C trap at 50 mmHg. ^{19}F NMR: -114.7 (t, J = 11.3 Hz,

2F), -121.7 (d, J = 14.3 Hz, 2F), -137.8 (m, 1F). ^{1}H NMR: 5.72 (m, 1H), 2.87 (m, 2H). HRMS: calcd for $C_5H_3F_5$: 158.0155. Found: 158.0114.

Homopolymerization of vinylpentafluoropropane with bis(perfluoropropionyl) peroxide

A 50 mL glass ampul fitted with a Teflon® coated stir bar was charged with 1.3 mL of 4% bis(perfluoropropionyl) peroxide in 1,1,2-trichlorotrifluoroethane, 10 mL of 1,1,2-trichlorotrifluoroethane and 5.0 g of the title compound. The ampul was sealed and cooled in a liquid nitrogen bath. After being evacuated and purged with N_2 alternately six times, contents of the sealed ampoule were stirred at 40°C for 6.5 hours. The white solids were washed with acetone and dried under vacuum at 100°C to give 4.9 g of polymer. Anal: calcd for $C_5H_3F_5$: C, 37.99; H, 1.91. Found: C, 36.78; H, 1.90. High temperature ^{19}F NMR: -123.0 (m, 1F), -117.0 (m, 2F), -111. 8 (s, 2F). ^{1}HNMR: 5.84 (dt, J = 31.2 Hz, J = 9.4 Hz, 1H), 6.05 (m, 1/14.5 H) 3.22 (m, 2H). The molecular weight was 65000 based on ^{19}F NMR analysis of end groups. The IR spectrum of this polymer showed an absorption at 1719 cm^{-1} which could be attributed to double bonds in the polymer.

This polymer was insoluble in acetone, ethyl acetate, tetrahydrofuran, acetonitrile, DMSO, DMF, hexafluorobenzene and FC-75. The polymer had a melting point of 130°C by DSC (second heat). By TGA the polymer showed 10% weight loss temperatures of about 400°C in nitrogen and 375°C in air, respectively, when heated at 20°C/minute.

Homopolymerization of vinylpentafluoropropane with percadox 16 N initiator

A 50 mL glass ampul fitted with a Teflon® coated stir bar was charged with 87 mg of percadox 16N, 10 ml of in 1,1,2-trichlorotrifluoroethane and 5.0 g of the title compound. The ampoule was sealed and cooled in a liquid nitrogen bath. After being evacuated and purged with N_2 alternately six times, contents of the sealed ampoule were stirred at 56°C for 6.5 hours. The white solids were washed with acetone and dried under vacuum at 100°C to give 4.7 g of polymer. High temperature ^{19}F NMR: -123.0 (m, 1F), -117.0 (m, 2F), -111. 8 (s, 2F). ^{1}HNMR: 5.84 (dt, J = 31.2 Hz, J = 9.4 Hz, 1H) 3.22 (m, 2H). The molecular weight was 76000 based on ^{1}H NMR analysis of end groups. This polymer was insoluble in acetone, ethyl acetate, tetrahydrofuran, acetonitrile, DMSO, DMF, hexafluorobenzene and FC-75. The polymer had a melting point of 131°C by DSC (second heat). By TGA the polymer showed 10% weight loss temperatures of about 400°C in nitrogen and 375°C in air, respectively, when heated at 20°C/minute.

Copolymerization of vinylpentafluoropropane perfluoro-2,2-dimethyl-1,3-dioxole (PDD)

A 25 mL glass ampoule fitted with a Teflon® coated stir bar was charged with 0.3 mL of 5% of bis(perfluoropropionyl) peroxide in 1,1,2-trichlorotrifluoroethane and 1.0 g of the title compound and 1.0 g of PDD. The ampoule was sealed and cooled in a liquid nitrogen bath. After being evacuated and purged with N_2 alternately six times, contents of the sealed ampoule were stirred at 40°C for 18 hours. The white solids were washed with CFC113 and dried under vacuum at 125°C to give 0.9 g of polymer.

This polymer was insoluble in acetone, ethyl acetate, tetrahydrofuran, acetonitrile, DMSO, DMF, hexafluorobenzene and FC-75. The polymer had a melting point of 127.5°C by DSC (second heat). By TGA the polymer showed 10% weight loss temperatures of about 395°C in nitrogen and 355°C in air, respectively, when heated at 20°C/minute.

Copolymerization of vinylpentafluoropropane with chlorotrifluoroethylene (CTFE)

A 25 mL glass ampoule fitted with a Teflon® coated stir bar was charged with 0.3 mL of 5% of bis(perfluoropropionyl) peroxide in 1,1,2-trichlorotrifluoroethane (CFC113), 1.0 g of the title compound, 1.0 g of CTFE and 2 ml of CFC113. The ampoule was sealed and cooled in a liquid nitrogen bath. After being evacuated and purged with N_2 alternately six times, contents of the sealed ampoule were stirred at 40°C for 72 hours. The white solids were filtered, washed with CFC113 and dried under vacuum at 125°C to give 0.15 g of polymer.

This polymer was insoluble in acetone, ethyl acetate, tetrahydrofuran, acetonitrile, DMSO, DMF, hexafluorobenzene and FC-75. The polymer had a melting point of 127°C by DSC (second heat). By TGA the polymer showed 10% weight loss temperatures of about 400°C in nitrogen and 355°C in air, respectively, when heated at 20°C/minute.

Reaction of Vinylpentafluorocyclopropane with iodine

A mixture of 5.1 g (20 mmol) of I_2, 10 mL of CH_2Cl_2 and 3.4 g (21.5 mmol) of vinylpentafluorocyclopropane **1** was stirred in a sealed tube at 50 °C for 3 hours. After removal of solvent, 7.7 g of crude product was distilled to give 7.5 g of Z-$ICF_2CF_2CF{=}CHCH_2I$, **4**, bp 85-86 °C/6.5 mmHg. ^{19}F NMR: -60.5 (m, 2F), -112.9 (m, 2F), -126.6 (m, 1F). ^1H NMR: 5.97 (dt, J = 30.1 Hz, J = 9.0 Hz, 1H), 3.92 (ddt, J = 9.0 Hz, J = 1.6 Hz, J = 1.6 Hz, 2H). HRMS: calcd for $C_5H_3F_5I_2$: 411.8244. Found: 411.8246. Anal: calcd for $C_5H_3F_5I_2$: C, 14.58; H, 0.73; F, 23.06; I, 61.62. Found: C, 14.50; H, 0.79; F, 21.41; I, 61.34.