

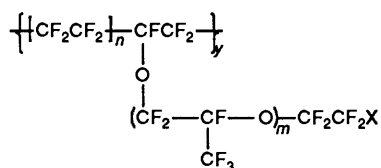
## Synthesis of Functional Perfluorinated Resins, Branched Perfluorinated Ethers and Perfluoroalkanoyl Fluorides

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Functional-group-containing perfluorinated resins have been prepared by carefully controlled direct fluorination of poly-(3-methyloxetane-3-methanol). Branched perfluorinated ethers such as bis(perfluoroneopentyl) ether and perfluoro-(2,2-dimethylbutyl methyl ether) have also been synthesized by direct fluorination of alkanols. The by-products, perfluoroalkanoyl fluorides, are useful intermediates.

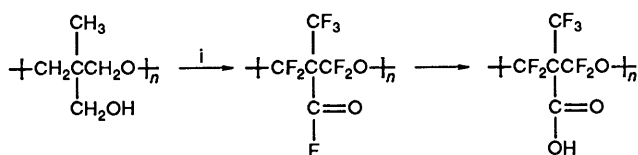
Sulphonic or carboxylic acid containing perfluorinated polymers such as NAFION® or FLEMION®, are useful in very aggressive environments: *e.g.*, chlor-alkali cells, fuel cells, batteries, *etc.*<sup>1</sup>† In addition, the presence of 'superacid' ionic functional groups and the unusual ion-clustered morphology of NAFION® has extended its use as a catalyst for organic reactions,<sup>2</sup> and as a chromatographic stationary phase.<sup>3</sup> The syntheses of these perfluorinated ion-exchange resins involve many steps which are both technically difficult to control and of high cost such as the preparation of unsaturated fluorinated monomers containing sulphonyl fluoride or carboxylate groups followed by polymerizations with tetrafluoroethylene.<sup>4</sup>



X = SO<sub>2</sub>OH for NAFION® and CO<sub>2</sub>H for FLEMION®

Previously in our laboratory we have produced carboxylic acids containing perhalogenated polymer chains by 'oxy-fluorination' of branched hydrocarbon starting materials or by direct fluorination of polyacrylic acid-vinyl chloride copolymers.<sup>5</sup>

We report here a new synthetic method which will open synthetic routes to structurally different perfluoropolymers containing carboxylic acid groups. This synthetic technique involves the conversion of hydrocarbon precursors containing hydroxy groups into branched perfluoropolyethers with pendant acid fluoride groups by direct fluorination. The following hydrolysis produced perfluorinated ion-exchange resins as illustrated in Scheme 1.



Scheme 1 Reagents and conditions: i, F<sub>2</sub>-He, room temp. to 60 °C

It was found that functionalization also occurred, with the generation of some unexpected perfluorinated acyclic ethers. These interesting by-products may have industrial or

biomedical applications. It is impossible to obtain these perfluorinated products easily by any other conventional synthetic method such as electrochemical or cobalt trifluoride fluorination processes. Direct fluorination of aliphatic alcohols usually results in the production of degradation products.<sup>6</sup> In order for us to understand the functionalization which occurred during our reaction, the fluorination of molecularly small alkyl alcohols was studied (Scheme 2).

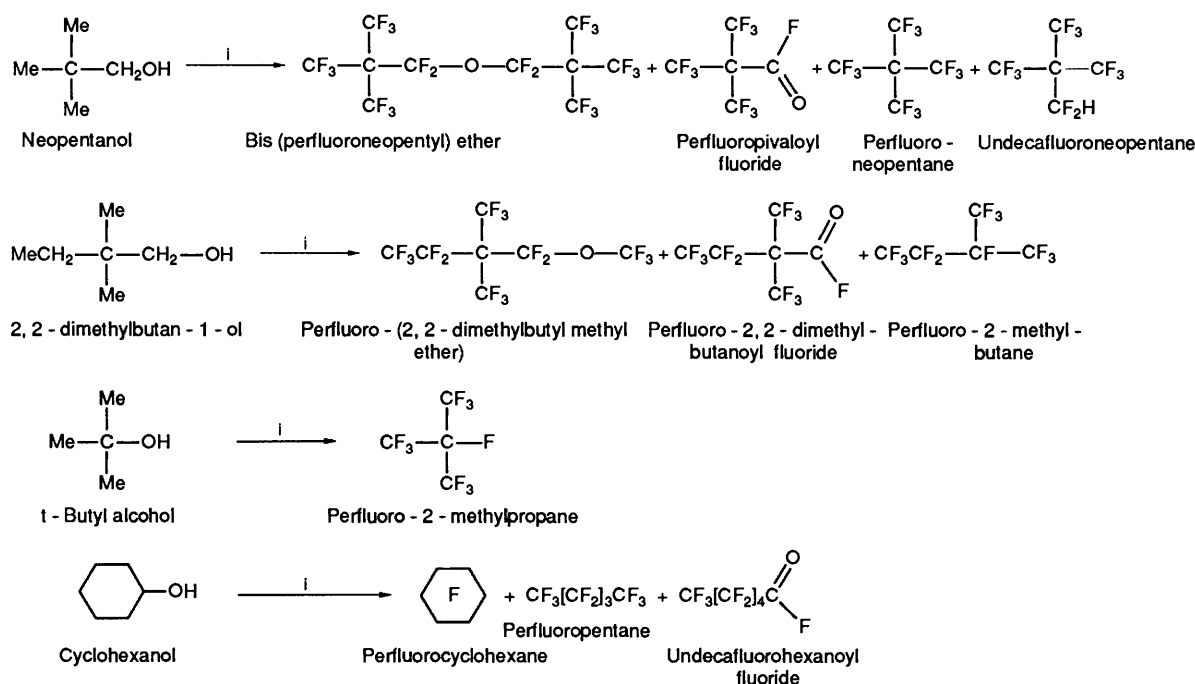
### Experimental

**Materials, Analyses and Physical Measurements.**—1,1,1-Tris(hydroxymethyl)ethane, diethyl carbonate, 4-chlorobenzene-diazonium hexafluorophosphate, ethylene glycol, anhydrous potassium fluoride, neopentanol, t-butyl alcohol, cyclohexanol and 2,2-dimethylbutan-1-ol were obtained from Aldrich Chemical Co. Fluorine gas was technical grade and supplied by Air Products and Chemicals, Inc. All the starting materials were used as received except where stated differently. Elemental analyses and molecular-weight determinations were performed at Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York. Mass spectra were measured on a Bell and Howell model 21-490 mass spectrometer at 70 eV. NMR spectra were taken on a Varian EM 390 spectrometer at 84.67 MHz for fluorines and 89.33 MHz for protons. All the <sup>19</sup>F NMR spectra were run as neat samples for liquid products. The *J*-value is in Hz. Freon 11, CFC1<sub>3</sub>, was used as the solvent for solid products. IR spectra were obtained with a Beckman Acculab 8 or Digilab FTS-40 Fourier transform infrared spectrometer using a gas cell with KBr windows for volatile products. Gas chromatography separations were made using a Bendix model 2300 programmable gas chromatograph equipped with a cryogenic controller and thermal conductivity detector. The column used for separation of the fluorinated products was either a 20 ft ×  $\frac{3}{8}$  in 20% Fomblin Y-45 on Chromosorb P (60–80 mesh) or a 24 ft ×  $\frac{1}{4}$  in 10% Fluorosilicone (QF-1-0065) on Chromosorb P (60–80 mesh). The helium flow rate was 60 cm<sup>3</sup> min<sup>-1</sup>. B.p.s and m.p.s were measured in sealed 6 mm glass tubes as described previously.<sup>7</sup> Thermal analyses were performed on a duPont Model 990 thermogravimetric analyser.

**Fluorination Apparatus.**—The four-zone cryogenic reactor, tube reactor, and other fluorination devices have been described previously.<sup>8</sup>

**Preparation of 3-Methyloxetane-3-methanol.**—3-Methyloxetane-3-methanol was prepared from 1,1,1-tris(hydroxymethyl)ethane, and diethyl carbonate was prepared according to the literature method.<sup>9</sup>

† NAFION® is a registered trademark of E. I. DuPont de Nemours and Company, and FLEMION® is a registered trademark of the ASAHI Glass Co., Ltd., Japan.



**Scheme 2** Direct fluorination of hydrocarbon-derived alcohols. *Reagents and conditions:* i,  $F_2$ , He,  $-120^\circ C$  to room temp.

**Table 1** Fluorination conditions for poly-(3-methyloxetane-3-methanol)

Time (t/days)	He flow ( $cm^3 min^{-1}$ )	$F_2$ flow ( $cm^3 min^{-1}$ )	Temp. ( $T/^\circ C$ )
1	30	1	a
1	30	2	a
1	15	2	a
1	0	2	a
1	0	2	45
1	0	2	60
0.5	60	0	60
0.5	100	0	60

<sup>a</sup> Ambient temperature.

**Polymerization of 3-Methyloxetane-3-methanol and its Characterization.**—Methyl chloride gas (15 psig at room temp.;  $100 cm^3$ ) was dried using a glass tube filled with silica gel and was then condensed into a  $500 cm^3$ , four-necked flask equipped with a mechanical stirrer, thermometer, solid  $CO_2$  condenser and gas-inlet tube. The flask was cooled to  $-78^\circ C$  by solid  $CO_2$ -acetone slush. Freshly distilled 3-methyloxetane-3-methanol (25 g, 0.25 mol) was then added all at once. The mixture was refluxed  $\sim -22^\circ C$  after the slush was removed.

Phosphorus pentafluoride gas was prepared by the thermal decomposition of 4-chlorobenzenediazonium hexafluorophosphate (12 g, 0.04 mol) at ca.  $165^\circ C$  and was swept into the polymerization vessel via a stream of dry nitrogen. A white precipitate was observed 20 min after the initial introduction of phosphorus pentafluoride. The reaction mixture was kept for another hour at the reflux temperature. The methyl chloride was then evaporated off and the hard, white solid products were removed from the flask and then ground to a powder. After being washed several times with diethyl ether, the solid, powdered material was held *in vacuo* for 24 h to remove any volatile chemicals and afforded a fine powder (20 g, 80%), m.p.  $118-120^\circ C$  {Found: C, 56.80; H, 9.6; F, 3.75; P, 0.4.  $[CH_2CMeCH_2(OH)CH_2O]$  requires C, 58.82; H, 9.80%};  $\delta_H$  0.7 (3.2 H, Me), 3.07 (3.7 H,  $2 \times CH_2$ ), 3.18 (1.8 H,  $CH_2OH$ ) and 4.31 (1 H, OH);  $\nu_{max}/cm^{-1}$  3450 br and 1040 (OH) and

1100 (COC). According to osmotic-pressure measurements of a methanolic solution, the average number molecular weight,  $\bar{M}_n$ , of our product was found to be 1500 daltons, which corresponds to an average *n*-value of 14.7 in the above structure. The presence of phosphorus and fluorine in the powdered products results from the destruction of the catalyst by reaction with the polymer. This destructive behaviour is well known for phosphorus pentafluoride-catalysed cyclic ether polymerization.<sup>10</sup>

**Fluorination of Poly-(3-methyloxetane-3-methanol) and Characterization of the Products.**—The starting material was fluorinated initially at room temperature using dilute fluorine (diluted by helium gas) followed by a stepwise increase in fluorine concentration until pure fluorine conditions were achieved, and then the higher-temperature conditions were used. The fluorination conditions are shown in Table 1.

In a typical reaction, solid poly-(3-methyloxetane-3-methanol) (0.71 g) was ground and sieved to give fine powder ( $< 100$  mesh), and then was put into a nickel boat to be placed in the centre of a hollow nickel tube reactor. The assembled apparatus was flushed with He overnight ( $100 cm^3 min^{-1}$ ) before the fluorination was started. The reaction yielded a fluorinated, snow-white powder (1.48 g, 87%), m.p.  $218^\circ C$  (initial decomp.) and  $430^\circ C$  (complete decomp.) {Found: C, 24.3; H,  $< 0.05$ ; F, 60.7.  $[CF_2C(CF_3)(COF)CF_2O]_n$  requires C, 24.59; F, 62.30%}; the IR spectrum showed  $\nu_{max}/cm^{-1}$  3150br (OH), 1900s, 1875s and 1812s (CO), 1350br (CF) and 1050 (COC). The trace amount of hydrogen could result from an unreplaced carbon-hydrogen bond or from hydrolysis of a carbonyl fluoride group (F-CO-F). After the solid had been refluxed with aq. sodium hydroxide ( $2 mol dm^{-3}$ ) at  $95^\circ C$  for 24 h, the carbonyl absorptions of the fluorinated powder shifted to  $1650 cm^{-1}$ . The IR spectra matched exactly the reported data.<sup>5</sup> The dried, alkali-treated, brown powder was washed successively with aq. hydrochloric acid ( $0.5 mol dm^{-3}$ ) and with water. After being dried *in vacuo* the H-form resin was mixed with aq. sodium chloride ( $1 mol dm^{-3}$ ) at room temperature and was then titrated with sodium hydroxide ( $1 mol dm^{-3}$ ) using phenolphthalein as indicator. The number of exchange sites of our fluorinated powder was found to be  $4.7 \times 10^{-3} mol g^{-1}$ . The

volatile liquid (0.3 g) was collected in a  $-78^{\circ}\text{C}$  glass trap, attached to the end of a metal trap filled with sodium fluoride pellets. IR analysis of the carefully separated liquid indicated C-H and COF absorptions as well as strong C-F absorptions.

**Fluorination of Neopentanol.**—Neopentanol (2 g, 25 mmol) was vacuum-sublimed into a four-zone cryogenic reactor with zones 3 and 4 cooled to  $-78^{\circ}\text{C}$  by means of a liquid nitrogen cryogenic system. The inside of the hollow nickel tube reactor was tightly packed with copper turnings. Two hours after complete sublimation, all of the zones were cooled to  $-120^{\circ}\text{C}$  and the assembled apparatus was flushed with He overnight ( $60\text{ cm}^3\text{ min}^{-1}$ ). Fluorinations were conducted under the conditions listed in Table 2.

A mixture (6 g) consisting of (GC assay) 58.3% of bis(perfluoroneopentyl) ether, 14.2% of perfluoropivaloyl fluoride, 2.9% of undecafluoroneopentane, 3.3% of perfluoroneopentane, and other relatively less volatile products were collected in the  $-78^{\circ}\text{C}$  glass trap. These products were separated by vacuum-line distillation followed by gas chromatographic purification on the Fluorosilicone column at  $75^{\circ}\text{C}$ . The volatile, crystalline, major component was bis(perfluoroneopentyl) ether (3.4 g, 55%), m.p.  $68^{\circ}\text{C}$  (lit.,<sup>11</sup>  $68-68.5^{\circ}\text{C}$ );  $\nu_{\text{max}}/\text{cm}^{-1}$  1270br, 1200s, 1085s and 729br;  $\delta_{\text{F}}$   $-64.2$  (18 F, P, J 5.9,  $6 \times \text{CCF}_3$ ) and  $-67.5$  (4 F, M,  $2 \times \text{CF}_2$ ). The  $^{19}\text{F}$  NMR, mass and IR spectra agreed with the previously reported data.<sup>11</sup> The proposed reaction schemes are presented in the Discussion section. The characterization of the other by-products was by comparison with reported data.<sup>8</sup>

**Fluorination of 2,2-Dimethylbutan-1-ol.**—2,2-Dimethylbutan-1-ol (2  $\text{cm}^3$ , 16.6 mmol) was evaporated via a He flow of  $150\text{ cm}^3\text{ min}^{-1}$  into a four-zone cryogenic reactor with zones 3 and 4 cooled with solid  $\text{CO}_2$  and the heating coil held at  $140^{\circ}\text{C}$  by an oil-bath. Two hours after injection, all the zones were cooled to  $-120^{\circ}\text{C}$  by means of a liquid nitrogen cryogenic system and the assembled apparatus was flushed overnight with He ( $60\text{ cm}^3\text{ min}^{-1}$ ). The reaction conditions were the same as those used for the fluorination of neopentanol.

The liquid products (2.6 g) contained (GC assay) 25.3% of undecafluoro-2,2-dimethylbutanoyl fluoride, b.p.  $88^{\circ}\text{C}$  (Found: C, 23.0; F, 72.6.  $\text{C}_6\text{F}_{12}\text{O}$  requires C, 22.79; F, 72.15%);  $\delta_{\text{F}}$  43.6 (1 F, COF),  $-64.2$  (3 F,  $\text{CF}_3\text{CF}_2$ ),  $-82.8$  (2 F,  $\text{CF}_2$ ) and  $-111.3$  [6 F,  $\text{C}(\text{CF}_3)_2\text{COF}$ ];  $m/z$  297 ( $\text{M}^+ - \text{F}$ ) and 247 ( $\text{M}^+ - \text{CF}_3$ ).

Perfluoro-(2,2-dimethylbutyl methyl ether) was obtained in 17% yield, b.p.  $90^{\circ}\text{C}$  (Found: C, 20.7; F, 75.3.  $\text{C}_7\text{F}_{16}\text{O}$  requires C, 20.78; F, 75.25%);  $\delta_{\text{F}}$   $-58.1$  (3 F, t,  $\text{OCF}_3$ ),  $-64.2$  [6 F,  $\text{C}(\text{CF}_3)_2$ ],  $-81.0$  (3 F, h = heptet,  $\text{CF}_3$ ) and  $-110.1$  (2 F, h,  $\text{CF}_2$ );  $m/z$  319 ( $\text{M}^+ - \text{OCF}_3$ ).

Perfluoro-(2-methylbutane) was also obtained, in 28% yield;  $\delta_{\text{F}}$   $-75.2$  [6 F, m,  $\text{C}(\text{CF}_3)_2$ ],  $-83.9$  (3 F,  $\text{CF}_3$ ),  $-121.2$  (2 F,  $\text{CF}_2$ ) and  $-188.9$  (1 F, CF);  $m/z$  269 ( $\text{M}^+ - \text{F}$ ); and other less volatile products were collected in a  $-78^{\circ}\text{C}$  glass trap. The separation of perfluoro-(2,2-dimethylbutyl methyl ether) (0.34 g) was accomplished on the Fomblin column at  $85^{\circ}\text{C}$ . As compared with the fluorination of neopentanol, the reaction could be followed by similar procedures. However, owing to the lower volatility and more sterically crowded structure of bis(perfluoro-2,2-dimethylbutyl) ether, chain cleavage occurred predominantly at the carbon-carbon bonds adjacent to the ether linkage. This degradation resulted in perfluoro-(2,2-dimethylbutyl methyl ether) and perfluoro-(2-methylbutane). On the other hand, undecafluoro-2,2-dimethylbutanoyl fluoride was the only volatile product found to contain a carbonyl fluoride functional group.

**Table 2** Fluorination conditions for neopentanol

Time (t/days)	He flow ( $\text{cm}^3\text{ min}^{-1}$ )	$\text{F}_2$ flow ( $\text{cm}^3\text{ min}^{-1}$ )	Zones ( $T/^{\circ}\text{C}$ )			
			1	2	3	4
1	60	1	-120	-120	-120	-120
1	30	1	-120	-120	-120	-120
1	30	2	-120	-120	-120	-120
1	10	1	-120	-120	-120	-120
1	10	2	-110	-110	-110	-110
1	0	1	-110	-110	-110	-110
1	0	1	-95	-95	-95	-95
1	0	1	-85	-85	-85	-85
1	0	1	-78	-78	-78	-78
1	0	1	a	-78	-78	-78
1	0	1	a	a	-78	-78
1	0	1	a	a	a	-78
1	0	1	a	a	a	a
1	30	0	a	a	a	a

<sup>a</sup> Ambient temperature.

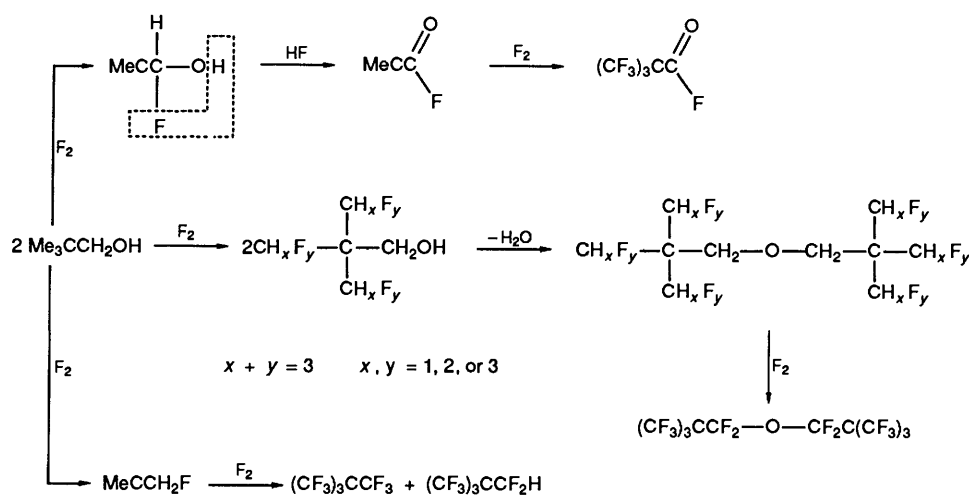
**Fluorination of *t*-Butyl Alcohol.**—*t*-Butyl alcohol (2 g, 27 mmol) was vacuum-sublimed into the four-zone cryogenic reactor and the reaction conditions were similar to those used for the fluorination of neopentanol. Cleavage of the acid-unstable tertiary C-OH bond resulted in perfluoro-(2-methylpropane) (3.3 g) as the major component of the products collected in the  $-78^{\circ}\text{C}$  glass trap. The  $^{19}\text{F}$  NMR spectrum matched that previously reported.<sup>12</sup> A key question is whether the highly sterically crowded bis(perfluoro-*t*-butyl) ether can be obtained by the proposed 'condensation' approach (see the Discussion section).

**Fluorination of Cyclohexanol.**—Cyclohexanol (2  $\text{cm}^3$ , 19.2 mmol) was evaporated into the four-zone cryogenic reactor and was fluorinated by the same procedures as used for 2,2-dimethylbutan-1-ol. A mixture (4.8 g) consisting of (GC assay) 44.5% of perfluoropentane, 7.4% of undecafluorohexanoyl fluoride and 8.1% of perfluorocyclohexane as well as other less volatile products were collected in the  $-78^{\circ}\text{C}$  trap. After gas chromatographic separation on a Fomblin column at  $65^{\circ}\text{C}$ , perfluoropentane (1.2 g) was obtained. Bis(perfluorocyclohexyl) ether was not produced, as evidenced by gas chromatographic comparison with an authentic sample.\* In contrast to the sterically crowded 'tertiary' fluorides of bis(perfluoroisopropyl) ether,<sup>13</sup> 'condensation' of partially fluorinated cyclohexanol is much less likely to occur.

Perfluorocyclohexane was produced by cleavage of the secondary C-OH bonds. Undecafluorohexanoyl fluoride was probably obtained from a reaction intermediate, the partially fluorinated cyclohexanone, by cleavage of one of the ketone bonds. Further degradation resulted in the formation of perfluoropentane. These proposed reaction mechanisms are supported by earlier results on direct fluorination of ketones.<sup>14</sup>

Liquid products (4.3 g) consisted of (GC assay) 44.5% of perfluoropentane,  $\delta_{\text{F}}$   $-84.9$  (6 F,  $2 \times \text{CF}_3$ ),  $-126.4$  (2 F,  $\text{CF}_2$ ) and  $-129.2$  (4 F,  $2 \times \text{CF}_2$ );  $m/z$  288 ( $\text{M}^+$ ) and 269 ( $\text{M}^+ - \text{F}$ ); 8.1% of perfluorocyclohexane,  $m/z$  300 ( $\text{M}^+$ ) and 281 ( $\text{M}^+ - \text{F}$ ); and undecafluorohexanoyl fluoride (7.4 g),  $\delta_{\text{F}}$  21.0 (1 F, COF),  $-84.0$  (3 F, tt,  $\text{CF}_3$ ),  $-120.2$  (2 F,  $\text{CF}_3\text{CF}_2$ ),  $-124.5$  (2 F,  $\text{CF}_2\text{COF}$ ),  $-124.6$  (2 F,  $\text{CF}_3\text{CF}_2\text{CF}_2$ ) and  $-128.2$  (2 F,  $\text{CF}_2\text{CF}_2\text{COF}$ );  $m/z$  297 ( $\text{M}^+ - \text{F}$ ) and 247 ( $\text{M}^+ - \text{CF}_3$ ).

\* Bis(perfluorocyclohexyl) ether was prepared from diphenyl ether by direct fluorination.



Scheme 3 The proposed reaction mechanisms of direct fluorination of neopentanol

## Results and Discussion

The IR carbonyl stretching vibrations of our products establish the formation of carbonyl fluoride groups during the fluorinations. The total number of exchange sites of our perfluorinated resin, based on careful titrations, indicate that nearly all of the pendant hydroxy groups have been converted into carbonyl fluoride groups. For comparison purposes, poly(ethylene oxide) resin was treated by fluorine under the same reaction conditions as used for fluorination of poly-(3-methyloxetane-3-methanol). Generally speaking, some degree of degradation always occurs during fluorination of polymers. However, only trace amounts of alkanoyl fluoride were found by FT-IR analysis of the products obtained from fluorination of poly(ethylene oxide). It appears that the majority of functionalization which occurs during fluorination of poly-(3-methyloxetane-3-methanol) does not result from chain scission. All of the fluorinations were handled in such a manner as to minimize the possibility of chain scission of the backbone and to preserve carbonyl fluoride groups generated during the reactions. The introduction of different ionic groups on the backbone of our perfluorinated polymer is made possible by very carefully controlled fluorination conditions and the choice of well designed hydrocarbon precursors.

In spite of the successful preparation of the  $\text{CF}_3\text{OF}$  by the reaction of silver fluoride with methanol,<sup>15</sup> most direct fluorinations of aliphatic alcohols produce some degradation products.<sup>6</sup> Our carefully controlled direct fluorination of neopentanol created a novel and much easier synthetic route to perfluoropivaloyl fluoride and bis(perfluoroneopentyl) ether than the previously reported method.<sup>8b,11</sup> Currently, the highly branched perfluorinated ethers are of interest in biomedical applications,<sup>11</sup> and, in general, perfluoroalkanoyl fluorides are useful intermediates in many cases. Although the reaction mechanisms are not well understood, the formation of carbonyl fluoride groups under conditions occurring during the electrochemical fluorination of alcohols,<sup>16</sup> such as those shown in Scheme 3, is believed to be the major route to functionalization. As compared with the 'oxyfluorination' of molecularly small aliphatic alcohols,<sup>17</sup> the absence of volatile difunctional products and the site of the functionalization in fluorination of 2,2-dimethylbutan-1-ol support the conclusion that the carbonyl fluoride groups were produced by conversion of hydroxy groups instead of introduction of oxygen radicals either by cleavage of carbon-oxygen bonds or other sources. On the other hand, bis(perfluoroneopentyl) ether was probably obtained by the 'condensation' approach proposed in Scheme 3.

In contrast with the industrial preparation of saturated

aliphatic ethers from aliphatic alcohols in acidic environments,<sup>18</sup> the production of hydrogen fluoride and partially fluorinated neopentanol during the fluorination would make the proposed 'condensation' mechanism much more likely. It should be noted that the acidity of the hydroxy groups on fluorinated alcohols increases with increasing perfluoroalkyl substitution,<sup>19</sup> and perfluorocyclic ethers were obtained by the electrochemical fluorination of alkanediols.<sup>20</sup> The subsequent fluorination of secondary, tertiary, or more crowded primary aliphatic alcohols indicated that steric hindrance, rearrangements, or cleavage were necessary for the 'successful' fluorination to occur. As compared with these interesting results, it is difficult to determine whether or not cross-linking occurs during the preparation of our previously discussed perfluorinated resins.

The fluorocarbons reported in this manuscript are perfluorinated ion-exchange resins, highly branched perfluorinated ethers, and monofunctional surfactants. Our successful direct fluorination technique opens the path for synthesis of new materials from inexpensive and extremely well developed hydrocarbon polymer precursors.

## Acknowledgements

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