

Synthesis and Physical Properties of Novel Perfluorinated Methylene Oxide Oligomers. The Ultimate Low Temperature Fluids

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Abstract: Perfluorinated polyethers are a class of substances which are extremely inert and have both extraordinary high temperature stability and low temperature properties. The synthesis of perfluorinated polyformaldehydes with the highest oxygen content was designed to give the maximum liquid range and low temperature properties. Novel low molecular weight perfluorinated polyformaldehydes with stable and unreactive perfluoro-*n*-butyl end groups were prepared by liquid-phase direct fluorination. The boiling point of these compounds increases by approximately 20 °C with the addition of each difluoromethylene oxide unit. This trend does not continue for longer chain lengths ($n > 4$) where the increase in boiling point per CF₂O unit diminishes. The average increase of melting temperature is ~1–2 °C as the perfluorinated polyformaldehyde chain increases one difluoromethylene oxide unit. The new perfluoropolyether fluids produced have melting points ranging from –145 to –152 °C.

Introduction

Perfluorinated ethers are a class of nonflammable substances which exhibit excellent thermal and oxidative stability, low melting point, good viscosity-temperature characteristics, and good boundary lubricating properties.^{1–3} Perfluorinated ethers may be prepared by direct fluorination,⁴ electrochemical fluorination,⁵ photooxidation of perfluoroolefins,⁶ or ring-opening addition reactions of perfluoroepoxides.⁷ Among the synthetic methods, direct fluorination is the most widely applicable because many kinds of perfluorinated ethers may be prepared in very high yield and high purity. LaMar direct fluorination has been successfully used to prepare perfluorinated crown ethers,^{8–10} perfluoropoly(ethylene glycol) ethers,^{3,11–13} highly

branched perfluorinated ethers,^{14–17} perfluoro(polypropylene oxide) ethers,¹⁸ perfluorinated cryptand,¹⁹ and perfluoropolyethers.^{20–23}

The properties of perfluorinated polyethers with high oxygen content are interesting.^{1,24} The perfluorinated polyethers with the highest oxygen content are perfluorinated poly(methylene oxide)s. However, very few reports of perfluorinated poly(methylene oxide)s appear in the literature. Oxidation of difluorocarbenes produces perfluorinated poly(methylene oxide)s terminated with acid fluoride end groups.²⁵ Perfluoro acid fluorides are easy to hydrolyze, and this process is often accompanied by decarboxylation and degradation. Furthermore, the acid fluoride functional group may significantly influence the physical properties of perfluorinated poly(methylene oxide) through dipole moments, intermolecular interactions, and asymmetric effects. Direct fluorination of paraformaldehyde in the solid state gave perfluorinated poly(methylene oxide)s²⁶ with a range of molecular weights. The polymer provided only the physical properties of a high-molecular-weight mixture. Single compound fluids are much more satisfactory models for investigating the properties of this class of materials.

This work was undertaken to synthesize novel low molecular weight single compound perfluorinated poly(methylene oxide)s capped with stable, unreactive and straight-chain perfluorobutyl end groups. Thus, among the known perfluorinated poly(methylene oxide)s, the physical properties of single compounds

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(1) Jones, W. R., Jr.; Bierschenk, T. R.; Juhlke, T. J.; Kawa, H.; Lagow, R. *J. Ind. Eng. Chem. Rev.* **1988**, *27*, 1497.

(2) Brodbelt, J.; Maleknia, S.; Liou, C.-C.; Lagow, R. *J. Am. Chem. Soc.* **1991**, *113*, 5913.

(3) Gerhardt, G. E.; Lagow, R. *J. Chem. Soc., Chem. Commun.* **1977**, 259.

(4) Bierschenk, T. R.; Juhlke, T. J.; Kawa, H.; Lagow, R. U.S. Patent 5,093,432, 1992.

(5) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*, 2nd ed.; Ellis Horwood Limited: New York, 1992; p 74.

(6) Sianesi, D.; Pasetti, A.; Corti, C. *Makromol. Chem.* **1965**, *86*, 308.

(7) Chambers, R. D. *Fluorine in Organic Chemistry*; John Wiley & Sons: New York, 1973; p 227.

(8) Lin, W.-H.; Bailey, W. I., Jr.; Lagow, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1350.

(9) Lin, W.-H.; Bailey, W. I., Jr.; Lagow, R. *J. Pure Appl. Chem.* **1988**, *60*, 473.

(10) Lin, T.-Y.; Lagow, R. *J. Chem. Soc., Chem. Commun.* **1991**, 12.

(11) Adcock, J. L.; Lagow, R. *J. Org. Chem.* **1973**, *38*, 3617.

(12) Adcock, J. L.; Beh, R. A.; Lagow, R. *J. Org. Chem.* **1975**, *40*, 3271.

(13) Gerhardt, G. E.; Lagow, R. *J. Org. Chem.* **1978**, *43*, 4505.

(14) Persico, D. F.; Huang, H.-N.; Lagow, R. *J. Org. Chem.* **1985**, *50*, 5156.

(15) Lagow, R. J.; Clark, G. B.; Rutherford, G. B.; Lin, W.-H.; Mlsna, T. E. *J. Fluorine Chem.* **1991**, *54*, 78.

(16) Huang, H.-N.; Lagow, R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 871.

(17) Huang, H.-N.; Persico, D. F.; Lagow, R. *J. Org. Chem.* **1988**, *53*, 78.

(18) Gerhardt, G. E.; Lagow, R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1321.

(19) Brodbelt, J.; Maleknia, S.; Lagow, R. J.; Lin, T.-Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1705.

(20) Persico, D. F.; Gerhardt, G. E.; Lagow, R. *J. Makromol. Chem., Rapid Commun.* **1985**, *6*, 85.

(21) Persico, D. F.; Gerhardt, G. E.; Lagow, R. *J. Am. Chem. Soc.* **1985**, *107*, 1197.

(22) Persico, D. F.; Lagow, R. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 233.

(23) Adcock, J. L.; Lagow, R. *J. Am. Chem. Soc.* **1974**, *96*, 7588.

(24) Pacansky, J.; Miller, M.; Hatton, W.; Liu, B.; Scheiner, A. *J. Am. Chem. Soc.* **1991**, *113*, 329.

(25) Sianesi, D.; Bernardi, G.; Moggi, G. U.S. Patent 3,721,696, 1973; *Chem. Abstr.* **1973**, *78*, 158970m.

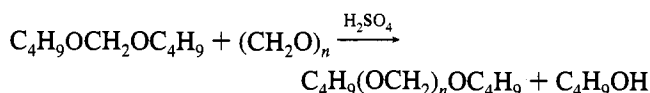
(26) Lagow, R. J.; Bierschenk, T. R.; Juhlke, T. J. U.S. Patent 4,827,042, 1989; *Chem. Abstr.* **1989**, *111*, 215161z.

capped with perfluoro(*n*-butyl) groups should be more representative of the entire class of compounds.

Results and Discussion

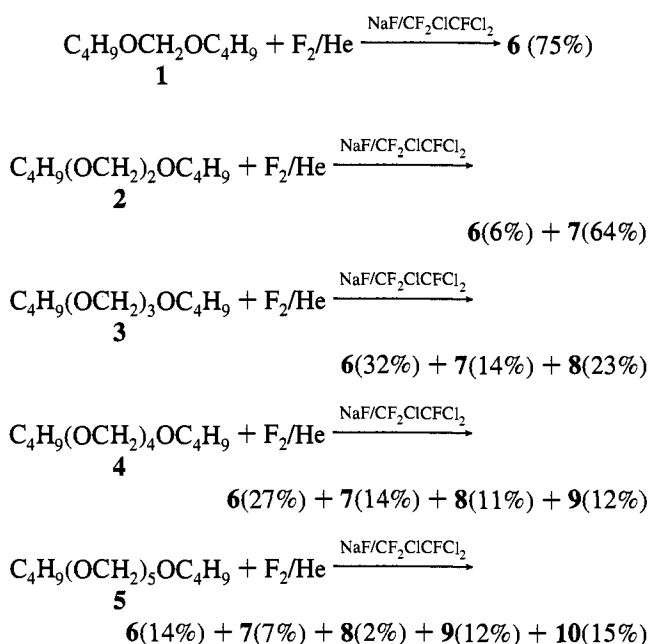
Using a literature method,²⁷ dibutoxymethane (**1**) was treated with paraformaldehyde in the presence of sulfuric acid to give a mixture of 1-butanol and the compounds **1–5**, along with polymeric material (Scheme 1). Each of the polyformaldehydes (**1–5**) can be purified simply by distillation at reduced pressure.

Scheme 1



After liquid-phase direct fluorination of the polyformaldehyde (**1–5**), **1** produces **6** (75%); **2** produces **6** (6%) and **7** (64%); **3** produces **6** (32%), **7** (14%), and **8** (23%); **4** produces **6** (27%), **7** (14%), **8** (11%), and **9** (12%); and **5** produces **6** (14%), **7** (7%), **8** (2%), **9** (12%), and **10** (15%) (Scheme 2). Perfluoro

Scheme 2^a



^aC₄F₉(OCF₂)_nOC₄F₉: **6**, *n* = 1; **7**, *n* = 2; **8**, *n* = 3; **9**, *n* = 4; **10**, *n* = 5.

poly(methylene oxide) oligomers are very sensitive to hydrogen fluoride during direct fluorination. When any such degradation occurs, carbonyl fluoride is released, resulting in lower molecular weight byproducts.

The perfluoro methylene oxide polyethers were purified by distillation and preparative GLC separation. In Table 1, ¹⁹F NMR spectra support the reported structures of the perfluorinated polyformaldehydes based on chemical shifts and integration data. The IR spectra of the perfluorinated polyformaldehydes are similar and show strong absorption between 1317 and 1060 cm⁻¹ representing C–F and C–O stretching vibrations. Mass spectra of the perfluorinated polyformaldehydes do not show parent peaks and only the CI mass spectrum of **6** has the peak (M – F + H)⁺. These compounds fragment readily under EI and CI conditions. All EI mass spectra of the

Table 1. ¹⁹F NMR Data of the Perfluorinated Polyformaldehydes

compd	chemical shift/ppm
6	–53.6 (s, 2F, OCF ₂ O), –84.1 (s, 6F, CF ₃), –87.4 (s, 4F, CF ₂ O), –128.8 (s, 8F, CF ₂)
7	–55.4 (s, 4F, OCF ₂ O), –84.1 (s, 6F, CF ₃), –87.4 (s, 4F, CF ₂ O), –128.8 (s, 8F, CF ₂)
8	–55.5 (s, 4F, OCF ₂ O), –57.4 (s, 2F, OCF ₂ O), –84.1 (s, 6F, CF ₃), –87.4 (s, 4F, CF ₂ O), –128.8 (s, 8F, CF ₂)
9	–55.2 (s, 4F, OCF ₂ O), –57.2 (s, 4F, OCF ₂ O), –83.7 (s, 6F, CF ₃), –87.1 (s, 4F, CF ₂ O), –128.5 (s, 8F, CF ₂)
10	–55.2 (s, 4F, OCF ₂ O), –57.2 (s, 6F, OCF ₂ O), –83.7 (s, 6F, CF ₃), –87.1 (s, 4F, CF ₂ O), –128.5 (s, 8F, CF ₂)

Table 2. Physical Properties of the Perfluorinated Polyformaldehydes (C₄F₉(OCF₂)_nOC₄F₉)

compd	<i>n</i>	bp (°C)	mp (°C)
6	1	125	–152
7	2	146	–151
8	3	166	–149
9	4	186	–147
10	5	200	–145

perfluorinated polyformaldehydes have the same base peak at 219 representing C₄F₉ cation.

Table 2 lists the boiling and melting temperatures of the perfluorinated polyformaldehydes. Initially, the boiling point of these compounds increases by approximately 20 °C with the addition of each difluoromethylene oxide unit. This trend does not continue for a longer chain length (*n* = 5), and the increase in boiling point per unit decreases. Melting points of the perfluorinated polyformaldehydes increase slowly as their molecular weights increase. The average increase of the melting temperature is ~1–2 °C as the perfluorinated polyformaldehyde chain increases one difluoromethylene oxide unit. Pacansky and co-workers investigated the structure of perfluorinated ethers using ab initio methods and reconfirmed internal rotation of perfluoroalkyl groups about the C–O bonds, stating that repulsive interactions between lone pairs of electrons on the oxygen and fluorine atoms and/or lone pairs of electrons on the adjacent fluorine atoms on each perfluoroalkyl group promote lower temperature rotation.²⁴ Rotation at very low temperature around ether linkages is not observed for their hydrocarbon analogues.²⁴ Internal rotation does increase asymmetry about fluorocarbon ether linkages and contributes to decreases in the melting point.

Decomposition tests were performed with a DSC using a liquid sample in a stainless steel capsule sealed with a Viton O-ring. As the temperature increased, the liquid sample boiled, causing high pressure inside the capsule, and a broad endothermic peak appeared. If the sample decomposes, an exothermic peak should come out. However, no exothermic peak was observed up to 300 °C for the perfluoropolyether compounds (**6–10**).

Conclusion

The perfluorinated poly(methylene oxide)s (**6–10**) were successfully prepared by liquid-phase direct fluorination with elemental fluorine. The boiling point of these compounds increases by approximately 20 °C with the addition of each difluoromethylene oxide unit. This trend does not continue for longer chain lengths (*n* > 4) where the increase in boiling point per CF₂O unit diminishes. The average increase of melting temperature is ~1–2 °C as the perfluorinated polyformaldehyde chain increases one difluoromethylene oxide unit. The perfluoropolyether backbones of these compounds are very flexible, and, as a result, these materials have a very long liquid range. At low temperatures the ether linkages store vibrational energy,

(27) Imperial Chemical Industries Ltd. U.S. Patent 2,449,469, 1948; Chem. Abstr. 1949, 43, 1051h.

while at even lower temperatures free rotation around the ether linkage provides extremely low temperature fluid properties. In fact, they are the lowest temperature properties for any known carbon containing compounds of comparable molecular weight. We note that the melting point of the five compounds we have prepared range from -145 to -152 °C. No decomposition of the compounds were found up to 300 °C by means of DSC.

Experimental Section

General Methods. All reagents and solvents were obtained from Aldrich Chemical Co. and used as received. Di(*n*-butoxyl)methane was prepared according to the literature method.²⁸ The ¹⁹F NMR analysis was done on Nicolet NT-360 and Varian EM-390 spectrometers with CFC1₃ as an internal standard. The ¹H NMR and ¹³C NMR spectra were taken on a Bruker AC250 with CDCl₃ as an internal standard. Elemental analysis were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. High resolution mass spectra were taken on a VG analytical ZAB2-E, chemical ionization mass spectra on a Finnigan MAT TSQ-70, and electron impact mass spectra with a Bell and Howell 21-491 mass spectrometer operating at 70 eV. Infrared analysis was taken with a Biorad FTS-40 fourier transform infrared spectrometer. Samples were prepared for infrared analysis by adding one drop of samples between two KBr windows. Gas chromatography separations were done by using a HP 5880A gas chromatograph equipped with thermal conductivity detector. The column used for separation of the perfluorinated compounds was a 10 ft × 0.25 in. stainless steel column containing 25% OV-210 Chromosorb A (60/80 mesh). The helium flow rate was 60 cm³ min⁻¹. Temperature for injector, column, and detector were 250, 80, and 250 °C. DSC was carried out under nitrogen on Perkin-Elmer DSC 7.

Synthesis of *n*-Butyl Capped Poly(methylene oxide). Sulfuric acid (1 mL) was added to a 500-mL flask containing di(*n*-butoxyl)methane (170 g) and paraformaldehyde (10 g). The mixture was stirred at 80 °C for 12 h. The cool solution was added to 300 mL of ether, and the solution was washed with saturated sodium bicarbonate aqueous solution several times to remove sulfuric acid. The solution was dried with anhydrous magnesium sulfate. After removal of ether using a rotary evaporator, the rest of the liquid was distilled at 0.2 mmHg. Butanol and di(butoxyl)methane came out before 35 °C. Then 95 g of **2** at 54–58 °C (lit.,²⁹ bp: 103 °C/13 mmHg), 15 g of **3** at 77–82 °C, 5 g of **4** at 98–102 °C, and 2 g of **5** at 123–127 °C came out in sequence. **2**: ¹H NMR (CDCl₃) δ 1.3 (t, 7.2 Hz, 6H), 1.8 (m, 4H), 1.9 (m, 4H), 3.9 (t, 6.2 Hz, 4H), 5.1 (s, 4H); ¹³C NMR (CDCl₃) δ 13.7, 19.6, 32.1 (CH₃CH₂CH₂), 67.8 (CH₂O), 91.4 (OCH₂O); HRMS (CI) for (C₁₀H₂₃O₃) found 191.163330, calcd 191.164720. **3**: ¹H NMR (CDCl₃) δ 1.3 (t, 7.2 Hz, 6H), 1.8 (m, 4H), 1.9 (m, 4H), 3.9 (t, 6.2 Hz, 4H), 5.1 (s, 4H), 5.2 (s, 2H); ¹³C NMR (CDCl₃) δ 13.7, 19.6, 32.1 (CH₃CH₂CH₂), 67.8 (CH₂O), 91.4 (OCH₂O), 87.4 (OCH₂O); HRMS (CI) for (C₁₁H₂₅O₄) found 221.174520, calcd 221.175285. **4**: ¹H NMR (CDCl₃) δ 1.3 (t, 7.2 Hz, 6H), 1.8 (m, 4H), 1.9 (m, 4H), 3.9 (t, 6.2 Hz, 4H), 5.1 (s, 4H), 5.2 (s, 4H); ¹³C NMR (CDCl₃) δ 13.7, 19.6, 32.1 (CH₃CH₂CH₂), 67.8 (CH₂O), 91.4 (OCH₂O), 88.0 (OCH₂O); HRMS (CI) for (C₁₂H₂₇O₅) found 251.185086, calcd 251.185849. **5**: ¹H NMR (CDCl₃) δ 1.3 (t, 7.2 Hz, 6H), 1.8 (m, 4H), 1.9 (m, 4H), 3.9 (t, 6.2 Hz, 4H), 5.1 (s, 4H), 5.2 (s, 4H), 5.23 (s, 2H); ¹³C NMR (CDCl₃) δ 13.7, 19.5, 32.0 (CH₃CH₂CH₂), 68.0 (CH₂O), 92.0 (OCH₂O), 88.0 (OCH₂O), 88.5 (OCH₂O); HRMS (CI) for (C₁₃H₂₉O₆) found 281.196117, calcd 281.196414.

Liquid-Phase Direct Fluorination with Elemental Fluorine. Liquid-phase direct fluorination of the poly(methylene oxide)s (**1–5**) was carried out by slowly injecting a trichlorotrifluoroethane solution of a hydrocarbon methylene oxide ether into a reactor containing trichlorotrifluoroethane, sodium fluoride,³⁰ and saturated fluorine. The reactor design of the liquid-phase direct fluorination has been described

Table 3. Fluorination Conditions of the Perfluorinated Polyformaldehydes

temp (°C)	time (h)	He (mL/min)	F ₂ (mL/min)
-28	0.5	850	0
-28	4–9 ^a	850	100
0	12	12	12
16	72	12	12

^a Adding sample during this time.

previously.⁴ The fluorination conditions are shown in Table 3. After the fluorination, the mixture was filtered, and trichlorotrifluoroethane was recovered by distillation of the filtrate. The rest of the solution was purified by preparative gas chromatograph to give **6–10**, respectively. The ¹⁹F NMR data are in Table 2. **6**: IR (neat) 1376 (w), 1316 (s), 1220 (s, br), 1144 (s), 1110 (s), 1011 (w), 960 (m), 899 (m), 870 (m), 830 (m), 746 (m) cm⁻¹. Anal. Calcd for C₉F₂₀O₂: C, 20.79; F, 73.06. Found: C, 20.56; F, 72.75. **7**: IR (neat) 1377 (w), 1317 (s), 1223 (s, br), 1145 (s), 1089 (s, br), 970 (w), 891 (m), 850 (w), 824 (w), 746 (m) cm⁻¹. Anal. Calcd for C₁₀F₂₂O₃: C, 20.49; F, 71.32. Found: C, 20.31; F, 70.97. **8**: IR (neat) 1377 (w), 1317 (s), 1223 (s, br), 1145 (s), 1089 (s, br), 970 (w), 891 (m), 850 (w), 824 (w), 746 (m) cm⁻¹. Anal. Calcd for C₁₁F₂₄O₄: C, 20.26; F, 69.92. Found: C, 20.12; F, 69.68. **9**: IR (neat) 1376 (w), 1369 (s), 1220 (s, br), 1144 (s), 1096 (s), 1060 (s, br), 997 (w), 958 (w), 893 (m), 823 (w), 746 (m) cm⁻¹. Anal. Calcd for C₁₂F₂₆O₅: C, 20.07; F, 68.79. Found: C, 19.89; F, 68.41. **10**: IR (neat) 1376 (w), 1369 (s), 1221 (s, br), 1144 (s), 1096 (s), 1065 (s, br), 981 (w), 951 (w), 893 (m), 823 (w), 746 (m) cm⁻¹. Anal. Calcd for C₁₃F₂₈O₆: C, 19.91; F, 67.84. Found: C, 19.81; F, 67.69.

Measurement of Boiling and Melting Points. The boiling points of the perfluorinated poly(methylene oxide)s (**6–10**) were determined by the Siwoloboff's method³¹ with uncertainty of ±1 °C. For the determination of melting point, the samples were sealed in capillaries, solidified by liquid nitrogen, and quickly transferred to a -160 °C cooling bath prepared by mixing liquid nitrogen and 2-methylbutane. The melting points were determined by observing melting of the compounds in the sealed capillaries as the temperature-homogenous cooling bath slowly warmed up.³² Trichlorofluoromethane, which was used to test the accuracy of the method, melted at -111 °C (lit.³³ -111 °C).

Decomposition Test. Decomposition tests were carried out by DSC with 10 mg of the compounds contained in stainless steel capsules sealed with Viton O-rings, which can be used at temperatures as high as 300 °C. The tests were run under nitrogen from 50 to 300 °C at the heating rate of 40 °C/min.

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Supplementary Material Available: ¹⁹F NMR spectra of the five perfluorinated polyformaldehydes (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(28) Vinokurov, D. M. *Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol.* **1960**, *3*, 190; *Chem. Abstr.* **1960**, *54*, 17255c.

(29) Rieche, A.; Gross, H. *Chem. Ber.* **1960**, *93*, 259.

(30) (a) Bierschenk, T. R.; Juhlke, T. J.; Lagow, R. J. U.S. Patent 4,755,567, 1988; *Chem. Abstr.* **1988**, *108*, 6684w. (b) Bierschenk, T. R.; Juhlke, T. J.; Lagow, R. J. U.S. Patent 4,859,747, 1989; *Chem. Abstr.* **1988**, *108*, 6684w.

(31) Furniss, B. S.; Hannaford, A. J.; Roger, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman Group Limited: London, 1978; p 230.

(32) Wang, B.-H.; Adcock, J. L.; Mathur, S. B.; Hook, W. A. V. *J. Chem. Thermodynamics* **1991**, *23*, 699.

(33) Budavari, S.; O'Neil, M. J.; Smith, A.; Heckelman, P. E. *The Merck Index*, 11th ed.; Merck & Co.: NJ, 1989; p 9559.