A New Synthetic Approach to Poly- and Perfluorinated Polyethers[1]

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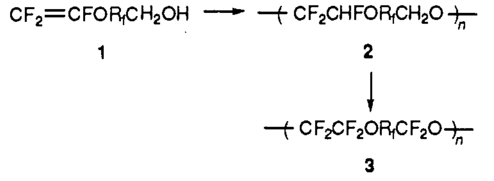
Abstract: Linear and cyclic perfluorinated polyethers are prepared by a new route involving polymerization of a trifluorovinyl ether alcohol ($CF_2{=}CFOR_fCH_2OH$ (**1**), $R_f = CF_2CF(CF_3)OCF_2CF_2$) followed by fluorination of the intermediate polyfluorinated polyethers. Polymerization occurs by ionic addition of OH groups to trifluorovinyl ether groups. In the absence of solvent, linear polymers with M_n values up to 29000 are obtained in excellent yield. In glyme solution, cyclic oligomers are the major products and a cyclic dimer is obtained in yields as high as 60%. Fluorinated macrodiols with M_n values to 5000 are obtained by copolymerization of **1** with a fluorinated diol. The intermediate linear and cyclic partially fluorinated polyethers have excellent solubility in organic solvents and the cyclics can complex anions through hydrogen bonding. Photofluorination of these polyethers with elemental fluorine in perfluorinated solvents proceeds smoothly with little fragmentation to afford the corresponding perfluorinated analogues in excellent yield.

Introduction

Perfluorinated polyethers exhibit high thermal stability, excellent chemical resistance, and low surface energy and are useful as lubricants, elastomers, and heat transfer fluids under demanding conditions.[2] They are generally prepared by ring opening polymerization of hexafluoropropylene oxide or by the random copolymerization of tetrafluoroethylene and hexafluoropropylene with oxygen under ultraviolet irradiation.[3] Direct fluorination of hydrocarbon ethers has been reported,[4] but it must be done very slowly under carefully controlled conditions to avoid decomposition of the substrates. A few perfluorinated polyethers have also been prepared by fluorination of partially fluorinated vinyl ether polymers.[5]

We now report a new approach to fluorinated polyethers with well-defined structures involving the polymerization of readily available fluorinated vinyl ether alcohols **1** (Scheme I). Polymerization occurs by ionic addition of OH groups to trifluorovinyl ethers. Although additions of nucleophiles to fluorinated olefins are well-known, few examples of additions to trifluorovinyl ethers have been reported[6] and no polymerizations by this method have been described. Both linear and cyclic polyethers **2** can be prepared, as can novel fluorinated macromonomers by polymerization in the presence of fluorinated diols. The cyclic, polyfluorinated crown ethers can be obtained in surprisingly high yields without employing high dilution. The partially-fluorinated polyethers have unusual and potentially useful properties, including high solubility in organic solvents and the ability to complex ions. Since these intermediates are already mostly fluorinated, replacement of the remaining hydrogens using elemental fluorine can be accomplished without extraordinary measures to give their perfluorinated analogues **3** in high yield with little loss of molecular weight.

Scheme I



R_1 = perfluoroalkylene or perfluoroalkyleneoxy

Results and Discussion

The trifluorovinyl ether esters **4a,b**, currently used as comonomers for the preparation of fluorinated ion exchange resins,[7] are convenient precursors to the trifluorovinyl ether alcohols[8] **1a,b**. Controlled $NaBH_4$ reduction of **4** provides **1** without the need to protect the sensitive vinyl ether group. In contrast, the fluorinated double bonds are reduced by more powerful reagents, such as lithium aluminum hydride.

The vinyl ether alcohol **1a** undergoes a catalyzed condensation reaction to give products consisting of the repeat unit **2** (Scheme

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(1) Contribution No. CR-6533 from Central Research & Development; presented in part at the 11th Winter Fluorine Conference, St. Petersburg, FL, January 1993.

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(5) Farnham, W. B.; Roe, D. C.; Dixon, D. A.; Calabrese, J. C.; Harlow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 7707. Farnham, W. B. In *Synthetic Fluorine Chemistry*; Olah, G. A., Chambers, R. D., Prakash, G. K. S., Eds.; J. Wiley & Sons: New York, 1992.

(6) We have recently described the high yield addition reaction of phenols to trifluorovinyl ethers as a useful process for other polymer systems: Feiring, A. E.; Wonchoba, E. R. *J. Org. Chem.* **1992**, 57, 7014.

(7) (a) Grot, W. G.; Molnar, C. J.; Resnick, P. R. U.S. Patent 4,544,458, 1985. (b) England, D. C.; Resnick, P. R. U.S. Patent 4,487,668, 1984. (c) Miyake, H.; Sugaya, Y.; Yamabe, M. *Reports Res. Lab. Asahi Glass Co., Ltd.* **1987**, *37*, 241.

(8) Hung, M.-H. U.S. Patent 5,093,446, 1992. Farnham, W. B.; Hung, M.-H. U. S.Patent 5,134,211, 1992. The alcohols **1a,b** are also useful as comonomers in free radical polymerizations.

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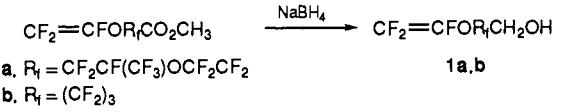
Scheme II



$$CF_2{=}CFOR_fCO_2CH_3 \xrightarrow{NaBH_4} CF_2{=}CFOR_fCH_2OH$$

4a, $R_f = CF_2CF(CF_3)OCF_2CF_2$ **1a,b**

4b, $R_f = (CF_2)_3$

Table I. Polymerization of 1a

catalyst (wt %)	solvent	T (°C)	$\bar{M}_n$[a]	$\bar{M}_w$[a]
KH (0.5)	glyme	0	4210[b]	6530[b]
K_2CO_3 (3.0)	none	100	6120	8570
CsF (0.1) + Cs_2CO_3 (0.3)	none	120	25800	52600
CsF (5) + Cs_2CO_3 (17)	none	25–80	12900	22400
Cs_2CO_3 (1)	none	120	27200	57900
Bu_4NCl (1)	none	120	23400	41300
Me_4NCl (0.2)	none	107	26700	52800
PPNCl (0.5)	none	120	20200	37800
Ph_4PCl (0.5)	none	120	no polymer	
TASCl[c] (0.4)	none	120	d	
CsF (0.4)	none	120	16700	31100
Cs_2CO_3 (0.4)	none	120	28500	65500
Cs_2CO_3 (4)	tetraglyme	25	5700[b]	6500[b]
KOt-Bu (1.4)	DMF	10	3400[b]	5920[b]
K_2CO_3 (3)	DMSO	50	5010[b]	8870[b]

[a] GPC analysis. [b] Analysis of residue after removing cyclic oligomer 5. [c] TAS = tris(dimethylamino)sulfonium. [d] Apparent decomposition.

I). The course of the reaction is highly dependent upon reaction conditions, including the nature of the catalyst and reaction medium, and monomer purity is, of course, of utmost importance in obtaining high molecular weight material.[9] Catalyst selection was made with the aim of minimizing formation of unreactive chain ends. Most of the catalysts found are bases (Table I), but we have not examined in detail the propagating species or determined the various acid/base equilibria which are presumably involved.

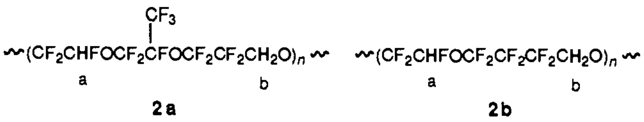
Linear Polymers. To produce a linear polymer with the highest molecular weight, reactions were carried out neat to avoid formation of cyclomers. Although the addition reaction of alcohol to vinyl ether takes place readily at 25 °C in ethereal or dipolar aprotic solvents, neat polymerization reactions require substantially higher temperatures. Typical catalyst screening experiments were carried out at 110-120 °C in order to achieve reasonable reaction rates. For the polymerization reactions whose results are summarized in Table I, monomer **1a** and catalyst (typically at 200/1 to 800/1 weight ratio) were combined in screw-cap vials under nitrogen, sealed, and heated in stages to 120 °C. Viscosity increases were apparent visually and magnetic stirring was effective only at early stages of polymerization.

Polymerization catalysts preferred because of their selectivity are the alkali metal (especially cesium) carbonates, tetraalkylammonium and bis(triphenylphosphoranylidene)ammonium (PPN) chlorides, and bicarbonates. Undesired side reactions are minimized by using relatively low (<0.5% by weight) catalyst levels. Under these conditions, the fraction of cyclic dimer **5** (see below) was usually 5% or less and was easily removed from the desired polymer by Kugelrohr distillation. Conversions of **1a** were essentially quantitative as judged by product weights and lack of detectable amounts of unreacted monomer by GLC.

By using carefully refined monomer, polymers with an M_n value of about 28500, corresponding to a degree of polymerization of about 72, were obtained. Alcohol end groups can be detected by NMR, and M_n values calculated from integrals of these signals are in reasonably good agreement with GPC results based upon polystyrene standards. Signals for residual trifluorovinyl groups have not been detected in these samples.

The highly fluorinated homopolymers **2**, in contrast to typical perfluorinated polymers, exhibit unusually good solubility in common organic solvents, so characterization by GPC and NMR is straightforward, and spectral assignments are provided in the Experimental Section. ¹H NMR shifts of the CHF and CF_2CH_2 moieties in **2** are highly solvent dependent, and spectral shifts are in the direction expected from hydrogen-bonding interactions with donor solvents (Table II).[5]

Table II. Proton Chemical Shifts[a] of Polyethers 2



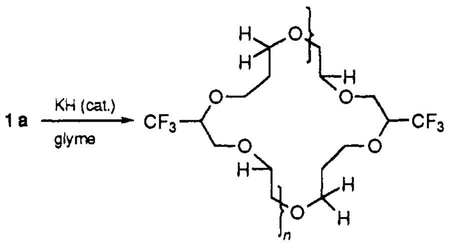
$$\sim(\underset{a}{CF_2CHF}OCF_2\overset{CF_3}{CF}OCF_2\underset{b}{CF_2CH_2}O)_n\sim \quad \sim(\underset{a}{CF_2CHF}OCF_2CF_2\underset{b}{CF_2CH_2}O)_n\sim$$

2a **2b**

solvent	H_a (**2a**)	H_b (**2a**)	H_a (**2b**)	H_b (**2b**)
DMSO-d_6	7.10	4.69	7.12	4.76
acetone-d_6	6.81	4.72	6.80	4.60
THF-d_8	6.67	4.63	6.68	4.60
methanol-d_4	6.60	4.52	6.60	4.58
acetonitrile-d_3	6.40	4.56	6.35	4.53
nitromethane-d_3	6.34	4.58	6.25	4.53
chloroform-d_1	5.95	4.32	5.94	4.37
benzene-d_6	5.17	3.77	5.42	3.90

[a] Chemical shifts in ppm, TMS internal standard.

Cyclic Oligomers. At a concentration of about 0.4 M in glyme, **1a** reacts with a catalytic amount of potassium hydride to give the cyclic dimer **5** in 55-60% isolated yield. Cyclic trimers (**6**), tetramers, and pentamers constitute a significant fraction of the remaining product. The yield of cyclic dimer is diminished in other solvents, such as tetraglyme or DMSO. Although condensation polymerizations are known to feature competitive ring formation and linear chain growth,[10] the substantial fraction of cyclic oligomers obtained from **1a** at moderate concentrations is worthy of note. The degree of polymerization for the linear polymer obtained in solution was limited to modest values, typically in the range 10-15. The cyclic dimer, trimer, and tetramer, which occur as families of stereoisomers,[11] were characterized by NMR and GC/MS as detailed in the Experimental Section.



5, $n = 1$
6, $n = 2$

all unspecified bonds to fluorine

Cyclic dimer **5** forms a 2/1 complex with Bu_4NCl: 1 mmol of tetrabutylammonium chloride is solublized in tetrahydrofuran by the addition of 2 mmol of cyclic dimer **5**. The resulting large downfield shifts and dispersion observed in the ¹H NMR signals for the CHF groups of the macrocycle (and relatively small shift differences for the CH_2 groups) suggest that hydrogen bonding (CH---Cl) is the organizing feature in a tetracoordinate chloride ion complex (Table III). Exchange involving chloride ion complex and free cyclic dimer appears to be rapid on the NMR time scale at 25 °C.

Interactions of the cyclic oligomers with fluoride ion are also observed, but the stoichiometry of the complexes is not known with certainty. The ¹H NMR spectrum of a sample prepared from cyclic dimer (0.125 mmol) and $(Me_2N)_3SMe_3SiF_2$ (0.065

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(9) Billmeyer, Jr. F. W., *Textbook of Polymer Science*; J. Wiley & Sons: New York, 1984: Chapter 2.

(10) See, for example: *Cyclic Polymers*; Semlyen, J. A., Ed.; Elsevier: New York, 1986.

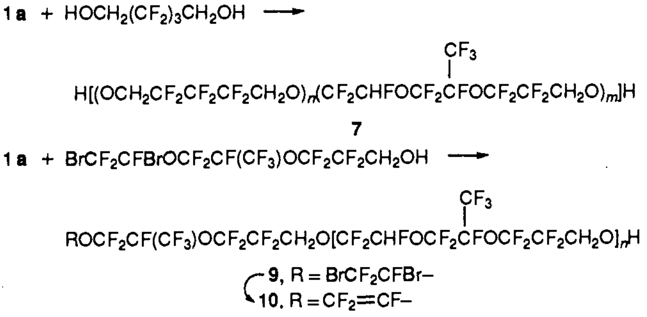
(11) Some reflection reveals a total of ten possible stereoisomers for **5**. Of these, two have (time averaged) inversion symmetry, two have (time averaged) C_2 symmetry, while the others lack symmetry and occur as pairs of enantiomers. Thus, the maximum possible number of CHF shifts is limited to 8.

Table III. ^{1}H NMR Chemical Shifts for Cyclic Dimer 5 and Ion Complexes[a]

group	**5**	2:1 **5**:Bu_4NCl	2:1 **5**:$TASMe_3SiF_2$	2:1 **5**:TASF
CHF	6.74–6.70 (five peaks (dd))	7.44	8.27	8.72
		7.16	7.96[b]	8.44
		7.14	7.65	8.40
		6.98	7.35	8.07
		6.92	7.30	7.64
		6.91	7.25	7.57
		6.90	7.19	7.51
		6.88		7.39
CH_2CF_2	4.45–4.74	4.55–4.80	4.65–5.20	4.65–5.45

[a] 6% (by weight of cyclic dimer) in THF-d_8; all CHF signals exhibit $^2J_{HF}$ = 51–52 Hz. [b] Two overlapping bands.

Scheme III



$$\textbf{1a} + HOCH_2(CF_2)_3CH_2OH \longrightarrow$$

$$H[(OCH_2CF_2CF_2CF_2CH_2O)_n(CF_2CHFOCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}FOCF_2CF_2CH_2O)_m]H$$

7

$$\textbf{1a} + BrCF_2CFBrOCF_2CF(CF_3)OCF_2CF_2CH_2OH \longrightarrow$$

$$ROCF_2CF(CF_3)OCF_2CF_2CH_2O[CF_2CHFOCF_2\overset{\overset{\displaystyle CF_3}{|}}{C}FOCF_2CF_2CH_2O]_nH$$

9, R = $BrCF_2CFBr-$

10, R = $CF_2{=}CF-$

mmol) in THF-d_8 exhibited downfield shifts for the CHF doublets (Table III). The CH_3Si singlet at 0.03 suggests a rapidly exchanging mixture of $(CH_3)_3SiF$ and $[(CH_3)_3SiF_2]^-$. Removal of $(CH_3)SiF$ under reduced pressure is easily accomplished, and this results in larger downfield shifts for the CHF groups in the residual mixture. Solutions containing equimolar quantities of cyclic dimer and $TASMe_3SiF_2$ exhibit slightly greater downfield shifts for the CHF groups, but instability of the species generated by $(CH_3)_3SiF$ removal has hampered further analysis.

Macromonomers. The alcohol/vinyl ether A–B monomers **1** can also be used to prepare telechelic macromonomers if the condensation reaction is conducted in the presence of calculated amounts of an A–A monomer. Thus, condensation of **1a** in the presence of a fluorinated diol should afford fluorinated macrodiols[12] which are of considerable interest for the preparation of segmented block copolymers.[13,14] Reaction of **1a** and 2,2,3,3,4,4-hexafluoropentane-1,5-diol with a basic catalyst afforded the macrodiols **7** with molecular weights in the range of 2-5 × 10^3 and excellent difunctionality (Scheme III). Approximately 5% of monomer **1a** was converted to cyclic dimer **5** under these conditions, but this side product was easily removed by distillation. Polydispersities, determined by GPC, were generally about 1.3 and M_n values were in good agreement with those estimated from ^{19}F NMR measurements. 1,5-Pentanediol was not incorporated under these conditions, presumably because the hydrocarbon alcohol is far less acidic. In a similar fashion, reaction of **1a** with the brominated alcohol **8** afforded the the macromonomer **9** which could, with some difficulty, be converted to a macro vinyl ether alcohol **10** by reductive elimination of bromine.

Perfluorinated Derivatives. The oligomers and polymers described above retain a number of protons which may be undesirable for some demanding applications. The obvious solution is to replace hydrogen with fluorine, and it appears that the only prospect for such transformation is radical fluorination.

Fluorinations of this type are known in the literature. Lagow has described the fluorination of selected hydrocarbon compounds using elemental fluorine wherein both temperature and fluorine concentration are gradually increased.[15] Adcock developed another process termed "aerosol fluorination", in which the substrate was deposited on solid NaF and then reacted with fluorine.[16] In all cases, however, only relatively small molecules were fluorinated[17] and it was not obvious that replacing relatively few hydrogens in large chains would proceed smoothly without chain scission. We decided to try an approach based on treating the substrates with relatively concentrated fluorine under irradiation.[18]

In order to minimize the chances of cracking the macromolecule, reactions were conducted in solution. Although dilution decreases somewhat the chances for radical chain reactions, it helps to absorb part of the energy released when hydrogen atoms are replaced by fluorine. The choice of solvent is not a trivial matter. Hydrogen-containing solvents are obviously not suitable, but even halogenated ones such as $CFCl_3$ or CCl_2FCF_2Cl, usually stable to fluorine, can react violently with this element when irradiated at temperatures near 0 °C. We chose two perfluorinated solvents which proved safe and suitable for radical fluorination: perfluoro-2-butyltetrahydrofuran (FC-75) and hexafluoropropylene oxide (HFPO) oligomers known as Krytox.[19] Although these solvents are expensive they can be reused.

Cyclic dimer **5**, which contains six hydrogen atoms, was dissolved in FC-75 and treated with a ca. 10-fold excess of fluorine (per hydrogen) while undergoing irradiation with a medium pressure mercury lamp. Fluorination could be monitored by gas chromatography. After full conversion was achieved, the cyclic product **11** was isolated by distillation in very good yield with no evidence for oligomerization or fragmentation. Its boiling point is very similar to that of the starting material. Its ^{1}H NMR spectrum did not show any signal, while the ^{19}F NMR spectrum shows CF_3 and OCF_2 groups in a narrow region between −80 and −84.5 ppm, the OCF_2CF_2O groups are found at somewhat higher field (−89 to −90 ppm), and signals for the two "internal" CF_2 groups ($CF_2\mathit{CF_2}CF_2$) appear at higher field (−129.5 and −129.6 ppm) for the two diastereomers. The tertiary fluorines appear at −145.6 and −146.3 ppm. The high resolution mass spectrum exhibits characteristic m/z at 829.9426 [$(M - CF_2O)^+$] and other fully fluorinated fragments (see experimental section). Gel permeation chromatography (GPC) indicates the molecular weight as ca. 1000.

Higher cyclic and linear oligomers were also successfully fluorinated. The cyclic trimer **6** was converted to its fully fluorinated derivative **12** in greater than 80% yield. In addition to the characteristic ^{19}F NMR spectrum, its mass spectrum exhibited m/z 1277.8754 [$(M - CF_2O)^+$] and GPC analysis indicated a molecular weight of ca. 1300. Fluorination of low molecular weight oligomers **13** (n = 7–12) also proceeded cleanly. In this case Krytox was found to be a better solvent because of solubility problems encountered with FC-75. The product **14** was obtained in very good yield and both ^{1}H NMR (which shows no signals) and ^{19}F NMR are in accord with essentially complete replacement of all the hydrogen atoms by fluorine. That little fragmentation occurred was shown by GPC analysis (M_n ca. 3200). A similar mixture of oligomers, but with higher molecular weight (**15**, n = 20–40), was also fluorinated to produce **16** with almost identical NMR spectral properties found for the above cases. Gel permeation chromatography (GPC) indicated that cleavage processes were minimal and the average molecular weight exceeds 14000. The thermal stability of the perfluorinated product

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(12) Boutevin, B.; Robin, J. J. *Adv. Polym. Sci.* **1992**, *102*, 105.

(13) Cohen, G. M.; Farnham, W. B.; Feiring, A. E. U.S. Patent 5,185,421, 1993.

(14) Yang, S.; Xiao, H. X.; Higley, D. P.; Kresta, J.; Frisch, K. C.; Farnham, W. B.; Hung, M. H. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A30*, 241.

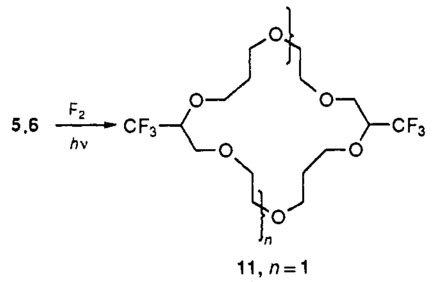
(15) See for example: Huang, H.-N.; Persico, D. F.; Lagow R. J. *J. Org. Chem.* **1988**,*53*, 78.

(16) Adcock, J. L.; Cherry, M. L. *Ind. Eng. Chem. Res.* **1987**, *26*, 208.

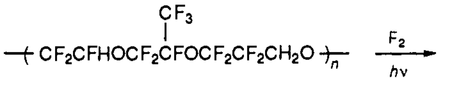
(17) For a rare exception however, see: Gerhardt, G. E.; Dumitru, E. T.; Lagow, R. T. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *18*, 157.

(18) A similar method has recently been reported: Sievert, A. C.; Tong, W. R.; Nappa, M. J. *J. Fluorine Chem.* **1991**, *53*, 397.

(19) Several oligomers by this name with different molecular weight are commercially available from DuPont.

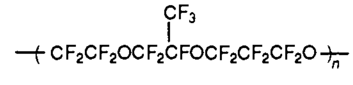


11, n = 1
12, n = 2
all unspecified bonds to fluorine



$$-\!\!\left(CF_2CFHOCF_2\overset{\displaystyle CF_3}{\overset{|}{C}}FOCF_2CF_2CH_2O\right)_{\!n}\!- \xrightarrow[h\nu]{F_2}$$

13, n = 7–12
15, n = 20–40



$$-\!\!\left(CF_2CF_2OCF_2\overset{\displaystyle CF_3}{\overset{|}{C}}FOCF_2CF_2CF_2O\right)_{\!n}\!-$$

14, n = 7–12
16, n = 20–40

in air was compared with the parent hydrogen-containing polymer by thermal gravimetric analysis (10 °C/min, air). While the latter started to lose weight at 340 °C and practically disappeared at 370 °C, the perfluorinated material completely degraded only around 450 °C.

The importance of the irradiation in this process is better appreciated when compared with another method of perfluorination. When **13** was dissolved in CCl_2FCF_2Cl and reacted under 10 atm of 25% fluorine in nitrogen at +80 °C for 4 h, mainly the end groups CH_2OH were affected, apparently oxidized to the corresponding acyl fluorides. Even after repeating the procedure three times, about 10% of the protons, mainly those geminal to a fluorine atom (CF_2CFHO), were still present.

Conclusions

The two-step process described by Scheme I provides a useful new approach to the synthesis of valuable perfluorinated polyethers. Both steps, condensation polymerization and fluorination, occur in high yield under mild reaction conditions. Although most of our work has been conducted with materials derived from the vinyl ether alcohol **1a**, since it is most readily available to us, preliminary work with **1b** suggests that this approach is quite general. The linear perfluorinated polyethers derived from **1a** can be considered as exactly alternating copolymers of tetrafluoroethylene oxide, hexafluoropropylene oxide, and hexafluorooxetane and cannot currently be made directly from these monomers. Although a few perfluorinated crown ethers are known, the tedious fluorination process required for their syntheses from the hydrocarbon analogues limits their availability.[4] In contrast, our process readily provides multigram quantities of the cyclic dimer **5** in over 50% yield.

The intermediate polyfluorinated species **2**, themselves, show an interesting combination of properties, including high solubility in organic solvents and the ability of the cyclics to complex anions. The strong hydrogen bonds formed by $-CF\mathit{H}-$ and $-CF_2C\mathit{H}_2O-$ protons with various acceptors have been noted previously[5,6] and presumably account for the solubility and complexation behavior. Although the reason for the unusually high yields of cyclic formed in solution oligomerization of **1a** is not known, it is tempting to speculate on the existence of a template effect.

The versatility of this synthetic approach is also illustrated by the formation of the macromonomers **7**, **9**, and **10** with well-defined structures by conducting the polymerization in the presence of appropriate mono- and difunctional reagents. The fluorinated macrodiols **7** have already been used to prepare an interesting new series of partially fluorinated segmented polyurethanes,[14] and we are investigating other novel polymers which can be prepared from these intermediates.

Experimental Section

^1H NMR spectra were recorded with a GE QE plus instrument at 300MHz. ^{19}F NMR spectra were recorded using Nicolet NT200 (188.2 MHz), GE QE-300 (283.1 MHz), or GE Omega (470.5 MHz) spectrometers and are reported in parts per million from $CFCl_3$. IR spectra were recorded on a Perkin-Elmer 983G spectrometer. Mass spectra were measured with a VG 7070H instrument. GC was done using a Hewlett Packard 5890 with a 25 m × 0.2 mm HP1 cross-linked methyl silicone capillary column, operating at 60–250 °C. THF, dimethoxyethane, and ether were distilled from sodium/benzophenone and stored under nitrogen. Other solvents were distilled and stored over activated molecular sieves. All polymerization reactions were carried out in an atmosphere of dry nitrogen, and manipulation of hygroscopic and water sensitive catalysts was done in a Vacuum Atmospheres drybox.

9,9-Dihydro-9-hydroxyperfluoro-3,6-dioxa-5-methyl-1-nonene (1a). In a dry flask with a magnetic stirring bar, 211 g (0.50 mol) of the ester precursor (**4a**)[20] was dissolved in absolute ethanol (300 mL). Sodium borohydride (11.34 g, 0.30 mol) was added slowly from a solid addition funnel. The reaction was somewhat exothermic and the reaction pot was kept at <10 °C by external cooling. After the addition of sodium borohydride was completed, the reaction mixture was stirred for 1 h at room temperature. The mixture was added to ice water (600 mL) and 6 N HCl (600 mL). The bottom product layer was separated, washed with water, and distilled to give the desired product as a clear, colorless liquid, bp 68–70 °C (25 mmHg). Yield: 168.7 g (85.6%). ^1H NMR ($CDCl_3$): δ 4.00 (dt, J = 13.5 Hz, 1.0 Hz, 2H), 2.12 (s, br, 1H). ^{19}F NMR ($CDCl_3$): –80.4 (s, br, 3F), –84.2 (s, br, 2F), –85.3 (m, br, 2F), –126.6 (t, J = 14 Hz, 2F), –145.7 (t, J = 21.8 Hz, 1F), –113.7, (dd, J = 66, 84.6 Hz 1F), –121.1 (ddt, J = 84.6, 112.1, 5.2 Hz, 1F), –135.7 (ddt, J = 66, 112.2, 5.8 Hz, 1F).

Anal. Calcd for $C_8H_3F_{13}O_3$: C, 24.38; H, 0.77; F, 62.67. Found: C, 23.96; H, 0.68; F, 62.78. MS (NCI) [M + F]: calcd 412.9859; found 412.9843.

1a was further refined by spinning band distillation using a 46 ×1 cm column at 75 °C (25 mmHg) and center cuts were used for subsequent polymerization studies. Saturated components, $CF_3CHFOCF_2CF(CF_3)OCF_2CF_2CH_2OH$ and $HCF_2CHFOCF_2CF(CF_3)OCF_2CF_2CH_2OH$, were the most abundant contaminants.

7,7-Dihydro-7-hydroxyperfluoro-3-oxa-1-heptene (1b).[21] A dry flask was charged with methyl perfluoro-5-oxa-6-heptenoate[22] (61.2 g, 0.2 mol) in absolute ethanol (120 mL). Sodium borohydride (4.54 g, 0.12 mol) was added slowly into the reaction solution via a solid additional funnel while the temperature was kept at about 10 °C. The mixture was allowed to stir at room temperature for 1 h after the addition of $NaBH_4$ was completed. The mixture was then added to ice water/6 N HCl (1:1 v/v, 500 mL) and worked up as described for **1a**. The product was distilled to provide 47.6 g (85.6% yield) of product as a clear, colorless liquid, bp 54–55 °C (30 mmHg). ^1H NMR ($CDCl_3$): δ 4.10 (t, J = 14.5 Hz, 2H), 2.65 (s, br, 1H). ^{19}F NMR (188.24 MHz, $CDCl_3$): –85.7 (m, 2F), –123.4 (m, 2F), –127.6 (s, br, 2F), –114.2, (dd, J = 65.5, 85.5 Hz, 1F), –122.4, (ddt, J = 85.5, 112.1, 5.6 Hz, 1F), –135.4, (ddt, J = 66, 112.2, 5.6 Hz, 1F).

Cyclic Dimer 5. A mixture oil-free potassium hydride (117 mg) and glyme (150 mL) was cooled to 0 °C and treated dropwise with **1a** (23.4 g, 59.4 mmol). A mild exotherm warmed the reaction mixture to ca. 8 °C during the addition, and stirring was continued for 4 h at 25 °C. The reaction mixture was cooled, treated with ca. 0.2 mL of isopropyl alcohol, diluted with ether (200 mL), and washed several times with water. The organic layer was dried and evaporated to give 23.5 g of colorless oil. Kugelrohr distillation (0.2 mmHg) afforded 12.8 g of colorless oil, bp 55–75 °C, identified as cyclic dimer **5**, 3.6 g (bp 130–165 °C) of material identified as cyclic trimer **6** contaminated with a minor amount of dimer **5**, and 5.6 g of higher-boiling residue (M_n = 4200 by GPC analysis). ^1H NMR of cyclic dimer **5**: see Table III. ^{19}F NMR (THF-d_8, 470.5 MHz) of **5**: –79.50 to –79.84 (m, CF_3), –82.4 to –85.7 (m, overlapping CF_2), –86.31 to –86.98 (six lower-field signals for OCF_2 AB patterns, J =

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[20] The ester precursor, $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2COOMe$, is a DuPont product.

[21] Munekata, S.; Ukihashi, H.; Yamabe, M.; Kaneko, I. U.S. Patent 4,209,635, 1985.

[22] Yamabe, M.; Kumai, S.; Munekata, S. U.S. Patent 4,275,226, 1981.

144.3–146.3 Hz), –90.29 to –92.62 (eight higher-field signals for OCF_2 AB patterns, J = 143.7–146.4 Hz), –122.5 to –124.4 (m, CF_2CH_2), –143.3 to –145.42 (m, CF), –146.0 to –146.44 (m, CHF), see also footnote 11. GC/MS showed for cyclic dimer **5** a parent ion with m/z 787.974152 (calcd for $C_{16}H_6F_{26}O_6$ 787.974922); for the cyclic trimer **6** a parent ion with m/z 1181.952957 (calcd for $C_{24}H_9F_{39}O_9$ 1181.962383); and for the cyclic tetramer a parent ion with nominal m/z 1579.

Polymerization of 1a with Cs_2CO_3. Cesium carbonate (10 mg) and **1a** (1.0 g) were placed in a vial which was sealed and heated in an oil bath maintained at 120 °C. Within 1 h, the mixture had thickened considerably. The reaction mixture was maintained at 120 °C for 88 h. ^{1}H NMR (THF-d_8): 6.65 (d, J = 52 Hz, CHF), 4.58 (t, J = 13 Hz, internal CF_2CH_2O), 3.90 (t, J = 13 Hz, terminal CH_2O); integrated area internal CH_2O/terminal CH_2O was ca. 55/1. Size exclusion analysis showed the major peak (90%) with M_n = 27 200 and M_w = 57 900 with use of polystyrene standards. ^{19}F NMR (THF-d_8) showed –79.97 (s, CF_3), –82.5 to –85.0 (overlapping AB patterns, OCF_2), –90.4 and –90.9 (AB pattern, J = 146, OCF_2), –123.6 (m, CF_2CH_2), –144.95 (m, CF), –145.7 (d of m, J = 52, CHF), –125.6 (m, CF_2CH_2OH end groups). Integration of internal CF_2CH_2O (–123.6) and terminal CF_2CH_2O groups (–125.6) gave relative areas of 85/1. No signals for residual trifluorovinyl groups were observed. NMR and size exclusion analyses were in reasonably good agreement and were consistent with the desired linear condensation polymer $(CF_2CHFOCF_2CF(CF_3)OCF_2CF_2CH_2O)_n$. TGA (20 °C/min) of a similarly prepared sample showed onset of thermal decomposition at ca. 300 °C (air) and 400 °C (N_2). DSC exhibited T_g at –60 °C.

Polymerization of 1a with R_4NCl. Tetramethylammonium chloride (2 mg) and **1a** (1.0 g) were placed in a vial which was sealed and heated in an oil bath at 107 °C for 65 h. ^{1}H NMR analysis of the colorless, viscous grease showed the ratio of signals at 4.6 and 3.90 ppm as ca. 60/1. The small amount of cyclic dimer formed (GC analysis) was removed by Kugelrohr distillation (up to 100 °C/ 0.05 mmHg). ^{19}F NMR featured the internal/terminal CF_2CH_2O group ratio as ca. 83/1. Size exclusion chromatography showed the major peak with M_n = 26 700 and M_w = 52 800, consistent with condensation polymer **2**.

Tetrabutylammonium chloride (2 mg) and 1.0 g of **1a** were placed in a vial which was sealed and heated to 107 °C for 65 h. ^{1}H NMR analysis showed the ratio of in-chain CH_2O/terminal CH_2OH groups to be ca. 60/1. Size exclusion analysis showed M_w = 46 700 and M_n = 24 000. T_g = ca. –60 °C.

Macrodiol 7. A mixture of alcohol **1a** (40.0 g, 102 mmol) and hexafluoropentane-1,5-diol (2.84 g, 13.4 mmol) was treated with cesium carbonate (0.4 g) in a three-necked flask, and the mixture was heated to 120 °C over a 1-h period. The mixture was maintained at 120 °C for 18 h. Depending on the purity of **1a**, initiation can appear difficult and may require additional catalyst. Once started, the reaction takes place rapidly and with considerable evolution of heat. The product was dissolved in 1,1,2-trichlorotrifluoroethane, washed with 2 N hydrochloric acid and water, and dried. The solution was treated with activated charcoal, filtered through Celite, concentrated in vacuum, and subjected to Kugelrohr distillation (120 °C/0.05 mmHg) to remove cyclic dimer **5** to afford 37.8 g of colorless, viscous oil. ^{1}H NMR (THF-d_8) showed 6.69 (d of m's, J = 51 Hz, CHF), 5.21 (bd s, OH), 4.62 (pseudotriplet, internal CH_2O), 3.95 (t, J = 15 Hz, terminal CH_2OH), consistent with the M_n = 3100 copolymer (assuming 100% difunctionality). ^{19}F NMR (THF-d_8) showed the following shifts and integrated intensities (a): –79.9 (s, a = 40), –82.5 to –85.0 (m, a = 52), –90.6 (center of m, a = 25), –120.3 (br s, a = 4.5), –120.65 (m, a = 1.25), –122.0 (m, a = 1.25), –123.6 (br s, a = 20), –125.05 (s, a = 2.5) –125.7 (m, a = 6), –125.95 (s, a = 1.25), –145.0 (m, a = 12.5), –145.7 (overlapping doublets of multiplets, $^2J_{HF}$ = 52 Hz, a = 12.5). Integration of the small doublet at –147.3, assigned to CF_3CHF non-functional ends, indicated the fraction of monofunctional product to be ca. 1%. ^{19}F NMR was suitable for determining M_n using the following assignments and shifts: for $C_5F_6H_4$ fragments, in-chain {CF_2CH_2 = –120.3, central CF_2 = –125.05} and terminal {OCH_2CF_2 = –120.65, –122.0, central CF_2 = –125.95}; for **1a**-derived fragments, in-chain CF_2CH_2O = –123.6, terminal CF_2CH_2OH = –125.7. Size exclusion analysis showed the major peak with M_w = 4060 and M_n = 3120 with use of polystyrene standards.

Dibromo Alcohol 8. A sample of **1a** (7.85 g, 19.9 mmol) was treated in small portions with bromine (3.2 g, 20 mmol) with the temperature controlled at 15–22 °C. When the reaction was judged to be complete by GC analysis, excess bromine was removed under a stream of nitrogen and the product was isolated by Kugelrohr distillation at 50 °C (0.2 mmHg) providing 8.70 g of product. ^{19}F NMR (THF-d_8): –64.13 (m, 2F, CF_2Br), –72.2 (apparent dq, J_d = 24 Hz, J = 9 Hz), and –72.55 (apparent dq, J = 23, 9 Hz, 1F, CFBr for two diastereomers), –80.5 to –86.2 (overlapping AB patterns, 4F, OCF_2), –79.4 (apparent q, J = 9 Hz, 3F), –125.38 (t, J = 14.8 Hz, 2F), –145.4 (m, 1F, tertiary CF).

Dibromo Alcohol 9. A mixture of alcohol **1a** (2.0 g, 5.08 mmol) and dibromide **8** (83 mg, 0.15 mmol) was treated with cesium fluoride (10 mg) and heated at 120 °C for 15 h. ^{19}F NMR (THF-d_8): –80.0 (s, and minor s at –79.5), –82.5 to –85.0 (OCF_2 AB patterns), –90.7 (center of AB pattern, J = 150 Hz), –123.7 (m, J = 22 Hz), –145.0 and –145.7 (d of m), end group signals at –125.7 (CF_2CH_2), –64.25 (m, CF_2Br), and –72.5 (m, CFBr). Size exclusion analysis showed the major peak with M_w = 13 100 and M_n = 8 370, consistent with ^{19}F NMR end-group analysis.

Alternate Preparation of Dibromo Alcohol 9 (Cs_2CO_3 Catalysis). A mixture of **1a** and **8** as described above was treated with cesium carbonate (8 mg) and heated at 120 °C for 64 h. ^{19}F NMR spectrum was as described above except that integration yielded M_n = 9100. Size exclusion analysis showed M_w = 14 700 and M_n = 9 510.

Macro Vinyl Ether Alcohol 10. Since standard debromination conditions (Zn dust, DMF, moderately elevated temperature) were not satisfactory, the dibromo alcohol **9** was dissolved in 1,1,2-trichlorotrifluoroethane (CFC-113), washed with water containing a small amount of hydrochloric acid (to remove catalyst residues from the previous step), dried, stripped, and evacuated. Toluene was added and solvent was again removed. The resulting product was treated as follows: Zinc dust (630 mg, 9.6 mmol) and dry DMF (4 mL) were treated with 1,2-dibromoethane (288 mg, 1.5 mmol) and the mixture was stirred for 0.5 h at ambient temperature. A 6.0-g sample of dibromo alcohol **9** in DMF (10 mL) was added and the mixture was stirred for 1.0 h at 25 °C. The reaction mixture was filtered, and the solid was rinsed with DMF. The filtrate was added to water and the resulting supernatant was decanted. The product was rinsed several times with water, dissolved in CFC-113, washed again with water, dried, and concentrated to give 4.9 g of oligomer. ^{19}F NMR (THF-d_8): –79.8 (s, CF_3), –82.1 to –84.6 (OCF_2 AB patterns), –89 to –91.2 (OCF_2 AB patterns), –123.3 (CF_2CH_2O), –144.8 and –145.8 (m and d of m's, tertiary CF and CHF), and trifluorovinyl end group signals at –113.1 (dd, J = 66, 86 Hz), –121.4 (dd, J = 86, 113 Hz), –136.1 (d of d of triplets, J_d = 66, 113 Hz), –125.2 (m, terminal CF_2CH_2OH). Integration was in reasonable agreement with size exclusion analysis which showed M_w = 11 800 and M_n = 7 360.

Caution. Fluorine is a strong oxidizer and a very corrosive material. An appropriate vacuum line made from copper or monel in a well-ventilated area should be constructed for working with this element. The reactions themselves were carried out in Teflon vessels. If elementary precautions are taken, work with fluorine is relatively simple.

General Procedure Substituting Hydrogens with Fluorine. Mixtures of 25–30% F_2 diluted with nitrogen were used in this work. The gas mixtures were prepared in a secondary container. The appropriate polyether was dissolved either in perfluoro-2-Bu-THF (FC-75) or in Krytox GPL 100 (a fluorinated oil) which also contained about 5 g of pulverized NaF to absorb the released HF. The reaction mixture was cooled to –10 °C, stirred with the aid of a vibromixer, and irradiated with a 450-W medium-pressure mercury lamp. A stream of fluorine in nitrogen (ca. 140 mL/min) was passed into the mixture such that the temperature did not rise above +10 °C . The reaction was stopped after 200 mmol of fluorine had been passed through. The mixture was poured into water and the organic layer was washed with sodium bicarbonate solution. The water layer was extracted twice with $CFCl_3$. The combined fluorocarbon fractions were washed with water, dried with $MgSO_4$, and filtered and the solvent was removed under reduced pressure.

Fluorination of Cyclic Dimer 5. A cold solution (–10 °C) of 3.66 g of the cyclic dimer **5** in perfluoro-2-Bu-THF (FC-75) was prepared. NaF (5 g) was added and the reaction was performed as described above. The main product was distilled at 50 °C/0.25 mmHg, by Kugelrohr distillation and was identified as perfluorinated cyclic dimer **11**, 3.4 g (82% yield). No protons were detectable in the ^{1}H NMR. ^{19}F NMR (THF-d_8/$CFCl_3$, 470.5 MHz): –80.94 (apparent q, J = 9.8 Hz, CF_3), –81.08 (apparent q, J = 10.2 Hz, CF_3), –81.1 to –85.1 and –89.7 to –90.2 (overlapping OCF_2 AB patterns), –129.5 (s) and –129.6 (d, J = 6.7 Hz) of equal intensity (–CF_2–), –145.6 (triplet of doublets, J = 21.7, 12.8 Hz, CF), –146.3 (triplet of doublets, J = 21.7, 12.8 Hz). MS, m/z 829.9426 [$(M - CF_2O)^+$], 691.9580 [$(M - CF_2O - (CF_2)_2 - 2F)^+$], 428.9638 [$(M/2 - F)^+$], 146.9876 [$(CF_2CF(CF_3)O - F)^+$].

Fluorination of Cyclic Trimer. A suspension of 3.5 g of **6** was fluorinated and worked up as described above. Traces of the solvent were removed by Kugelrohr distillation at 50 °C under 0.25 mmHg. The residue **12**

(3.4 g, 85% yield) showed no detectable protons in the ^{1}H NMR. The ^{19}F NMR is characteristic of the repeating unit: −80 to −84.5 (m, 9F), −89 to −89.7 (m, 4F), −129.5 (m, 2F), −145.9 ppm (m, 1F). The mass spectrum shows the same pattern as for **10**. MS, *m/e* 1277.8754 [$(M - CF_2O)^+$], 1139.9061 [$(M - CF_2O - (CF_2)_2 - 2F)^+$], 428.9587 [$(M/3 - F)^+$], 146.9863 [$(CF_2CF(CF_3)O - F)^+$].

Fluorination of Oligomer Mixture 13 (*n* = 7–12). The oligomeric mixture (2.6 g) was reacted as above using Krytox GPL 100 as solvent. Upon completion of the reaction, the Krytox was removed by distillation and the reaction mixture was left at 125 °C under 2 mmHg for 4 h. The residue (2.05 g, 78% yield) showed no detectable protons in the ^{1}H NMR. The ^{19}F NMR is characteristic of the repeating unit: −82 to −91.5 (m, 13F), −131.5 (m, 2F), −147.3 ppm (m, 1F).

Fluorination of Oligomer Mixture 15 (*n* = 20–40). The oligomers (1.05 g) were reacted as before with Krytox GPL 100 as solvent. Upon completion of the reaction the solvent was distilled and the reaction mixture was left at 150 °C under 2 mmHg for 4 h. The residue **16** (0.75 g, 70% yield) showed no protons in the ^{1}H NMR. The ^{19}F NMR is characteristic of the repeating unit: −82 to −91.5 (m, 13F), −129.8, 130.5 (n m, 2F), −146, 146.7 ppm (m, 1F).