SHELXTL PC program package.[5] Atomic coordinates are deposited at the Cambridge Crystallographic Data Centre.*

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09784a) and the International Science Foundation (Grant MHW 300).

---

* Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW, England.

References

1. V. A. Nikanorov, V. I. Rozenberg, and O. A. Reutov, *Proc. Indian Natl. Sci. Acad.*, 1989, **55**, A, 363.
2. V. A. Nikanorov, G. V. Gavrilova, S. V. Sergeev, V. I. Rozenberg, and O. A. Reutov, *Metalloorg. Khim.*, 1989, **2**, 102 [*Organomet. Chem. USSR*, 1989, **2**, 51 (Engl. Transl.)].
3. V. A. Nikanorov, S. V. Sergeev, V. I. Rozenberg, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 925 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 804 (Engl. Transl.)].
4. V. G. Kharitonov, V. A. Nikanorov, S. V. Sergeev, M. V. Galakhov, S. O. Yakushin, V. V. Mikul'shina, V. I. Rozenberg, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1991, **319**, 177 [*Dokl. Chem.*, 1991, **319** (Engl. Transl.)].
5. W. Robinson and G. M. Sheldrick, SHELX, in *Crystallographic Techniques and New Technologies*, Eds N. W. Isaac and M. R. Taylor, Oxford Univ. Press, Oxford, England, 1988, 366.

Received January 16, 1996

Synthesis of 1,1-dihydroperfluorooxaalkan-1-ols and their interaction with terephthaloyl chloride

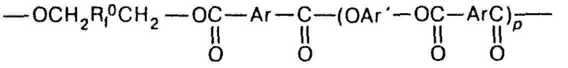
E. N. Ushakova, O. V. Konyushko, A. A. Glazkov, and S. P. Krukovsky*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

A series of 1,1-dihydroperfluorooxaalkan-1-ols and α,α,ω,ω-tetrahydroperfluorooxaalkanediols has been synthesized. Some terephthalates were synthesized by the reaction of these alcohols and diols with terephthaloyl chloride.

Key words: 1,1-dihydro-3,6,9-trioxaperfluorodecan-1-ol, 1,1-dihydro-3,6,9,12,15-pentaoxaperfluorohexadecan-1-ol, 1,1-dihydro-3,6,9,12,15,18-hexaoxaperfluorononadecan-1-ol, 1,1-dihydro-2,5-perfluorodimethyl-3,6-dioxaperfluorononan-1-ol, 1,1,3-trihydro-2,2,3,3-tetrafluoropropan-1-ol, terephthaloyl chloride, terephthalates of fluorinated alcohols.

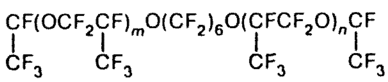
Block-copolymers consisting of macromolecular fragments of different chemical natures make it possible to create materials possessing valuable properties. Block-copolymers of simple perfluoropolyesters (flexible blocks) with polyarylates and polyarylsulfones (rigid blocks) have not been much studied. In the present work, the synthesis of fluorine-containing alcohols and diols is performed, and their reaction with terephthaloyl chloride is studied. This interaction is a model of one of the pathways of the formation of block-copolymers of the following structure:



$$\text{—OCH}_2\text{R}_f^0\text{CH}_2\text{—OC(=O)—Ar—C(=O)—(OAr'—OC(=O)—ArC(=O))}_p\text{—}$$

$\text{Ar} = \text{C}_6\text{H}_4$ *etc.*; $\text{Ar}' = \text{C}_6\text{H}_4\text{—C(CH}_3)_2\text{—C}_6\text{H}_4$ *etc.*;

$\text{R}_f^0 = (\text{CF}_2\text{CF}_2\text{O})_k(\text{CF}_2\text{O})_l\text{CF}_2$;



$$\text{CF(CF}_3\text{)(OCF}_2\text{CF(CF}_3\text{))}_m\text{O(CF}_2\text{)}_6\text{O(CF(CF}_3\text{)CF}_2\text{O)}_n\text{CF(CF}_3\text{)}$$

The vitrification temperature (T_g) of perfluoropolyesters depends primarily on the structure of the monomer

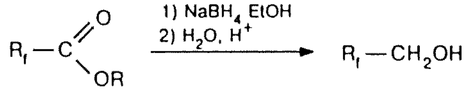
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1573—1576, June, 1996.

1066-5285/96/4506-1501 $15.00

unit; the values of T_g are −53, −73 and −175 °C (the calculated value),[1] for the polymers of $(\underset{CF_3}{C}FCF_2O)_n$, $(CF_2CF_2O)_n$, and $(CF_2O)_n$, respectively.

Perfluoropolyesters of $(CF_2CF_2O)_k(CF_2O)_l$ are distinguished exclusively by the high thermodynamic and kinetic flexibility of their chains ("superflexibility")[2] and possess extremely low T_g values (below −140 °C).[1] Oligomers containing the above units in their chains are formed by the anion polymerization of perfluoroolefin oxides or in the photochemical oxidation of perfluoroolefins with oxygen. The alcohols and diols with different structures of perfluoroalkyl radicals presented in Table 1 represent the model compounds of perfluoropolyesters prepared by the methods listed above.

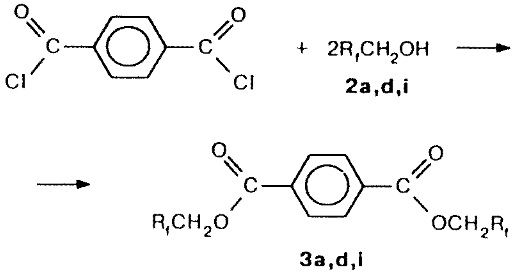
Methods for the reduction of the esters of perfluorinated acids or the corresponding acyl halides to fluorine-containing alcohols of the general formula R_f—CH_2OH are known.[3] We prepared a series of 1,1-dihydroalcohols containing perfluoropolyester fragments of different structures (see Table 1) by the reduction of perfluorooxaalkanecarboxylates with $NaBH_4$.



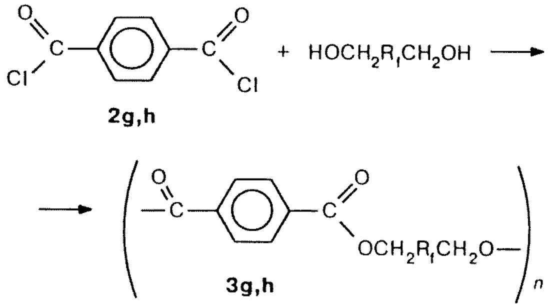
1a—g **2a—g**

R = Me, Et

The reaction of alcohols **2a—h** with terephthaloyl chloride affords the corresponding terephthalates **3a,d,i,g,h** in high yields. Depending on the type of the fluorine-containing group, these terephthalates are liquids or crystalline solids; the characteristic band at 1745 cm^{-1} (C=O) is present in their IR spectra.



i: R_f = CF_2CF_2H



Experimental

The ^1H and ^{19}F NMR spectra were recorded with a Bruker AC-200P spectrometer using HMDS and $CFCl_3$, respectively, as standards. The IR spectra were measured with a Specord IR-75 spectrophotometer.

Esters **1a—g** were prepared using the known procedure from Ref. 1 (b.p. of esters: **1a** — 49—50 °C (20 Torr);

Table 1. Characteristics of alcohols **2a—h**

Compound	B.p./°C (p/Torr)	Yield (%)
$CF_3O(CF_2CF_2O)_2CF_2CH_2OH$ (**2a**)	123—126	87
$CF_3O(CF_2CF_2O)_4CF_2CH_2OH$ (**2b**)	70—71 (20)	72
$CF_3O(CF_2CF_2O)_5CF_2CH_2OH$ (**2c**)	78—79 (20)	74
$CF_3CF_2CF_2O\underset{CF_3}{C}FCF_2OCF\underset{CF_3}{C}H_2OH$ (**2d**)	147—148	70
$CF_3CF_2CF_2O(\underset{CF_3}{C}FCF_2O)_{4,7}CF\underset{CF_3}{C}H_2OH$ (**2e**)	127—130 (2)	61
$CF_3CF_2CF_2O(\underset{CF_3}{C}FCF_2O)_{8,2}CF\underset{CF_3}{C}H_2OH$ (**2f**)	146—150 (0.1)	66
$HOCH_2C\underset{CF_3}{C}F(OCF_2\underset{CF_3}{C}F)_mO(CF_2)_6O(\underset{CF_3}{C}FCF_2O)_n\underset{CF_3}{C}FCH_2OH$ (**2g**) $m + n = 4.5$	—	66
$HOCH_2CF_2O(CF_2CF_2O)k(CF_2O)lCF_2CH_2OH$ (**2h**) $\overline{M}_n = 1600$ $k/l = 1/3.2$	—	71

Table 2. Characteristics of terephthalates (**2**)

Compound	B.p./°C (*p*/Torr) [M.p./°C]	Yield (%)	^{1}H and ^{19}F NMR, δ (*J*/Hz)
3a	131 (1) [20—21]	93	^{1}H: 5.03 (t, 2 CH_2O, J = 9.5); 8.20 (4 H, C_6H_4) ^{19}F: −54.99 (CF_3O), −76.38 ($O\underline{C}F_2CH_2$), −88.10, −88.23 ($2CF_2O$), −90.09 (CF_2O)
3d	146 (1)	95	^{1}H: 4.85 (CH_2O), 7.89 (4 H, C_6H_4) ^{19}F: −80.56, −82.12, −83.48 ($3CF_3$), −81.3 (CF_2O), AB spin system CF_2O −73.45, −83.1 (J = 150), −130.17 (CF_2), −134.28 (CF), −145.2 (CF)
3i	[68—69]	98	^{1}H: 4.90 (tt, 2 CH_2O, ^1J = 13.48, ^2J = 1.6); 6.55 (tt, 2 CHF_2, ^1J = 52.32, ^2J = 4.76); 8.22 (4 H, C_6H_4) ^{19}F: −124.26 ($2CF_2$), −138.24 (d, 2 CF_2H, J = 52.32)

1b — 88 °C (20 Torr); **1d** — 123—125 °C; **1c** — 208—211 °C; **1e** — 135—141 °C (2 Torr); **1f** — 146—150 °C (0.1 Torr). The degree of oligomerization of compounds **1e** and **1f** and the values of ($m + n$) in **1g** and ($k + l$) in **1h** were determined by the ^{19}F NMR method, and the average molecular weights (M_n) of compounds **1g** and **1h** were determined by ebullioscopy (in C_6F_6). The synthesis of **1g** was described previously,[5] and the synthesis of **1h** was described in Refs. 4 and 6. Terephthaloyl chloride was recrystallized from petroleum ether, m.p. 78—79 °C.

1,1-Dihydro-2,5-perfluorodimethyl-3,6-dioxaperfluorononan-1-ol (2d). Anhydrous EtOH (75 mL) and $NaBH_4$ (3.63 g, 101 mmol) were placed into a flask equipped with a stirrer, a reflux condenser, and a dropping funnel, and ethyl 2,5-dimethyl-3,6-dioxaperfluorononanoate (50 g, 32 mmol) was added dropwise with vigorous stirring and cooling (−10 °C). The mixture was warmed to *ca.* 20 °C and stirred for 2.5 h. Then the mixture was heated to 70 °C and kept for 3 h. The mixture was allowed to cool to 20 °C and 2 *M* HCl (50 mL) was added. Hydrolysis was carried out at 40 °C for 2 h. The fluoroorganic layer was separated, washed with H_2O (4×50 mL), dried over $MgSO_4$, and distilled, affording **2d** (35.1 g, 70 %), m.p. 147—148 °C. ^{1}H NMR, δ: 4.21 (d, 2 H, CH_2O, J = 13.10 Hz); 4.95 (1 H, OH). ^{19}F NMR, δ: −81.16, −82.7, −83.4 (3 CF_3), −82.3 (CF_2O). AB spin system (CF_2O) $\delta_A = -79.4$, $\delta_B = -83.1$, J_{AB} = 150 Hz, −130.7 (CF_2), −137.2 (CF), −145.7 (CF).

Alcohols **2a,b,c,e,f,g,h** were obtained similarly, and their yields and boiling points are presented in Table 1. The ^{1}H and ^{19}F NMR spectral parameters of alcohols **2**: 1,1-dihydro-3,6,9-trioxaperfluorodecan-1-ol **2a**: ^{1}H NMR, δ: 3.10 (t, CH_2O, J = 9.5 Hz), 4.34 (OH). ^{19}F NMR, δ: −57.38 (CF_3O), −82.25 (OCF_2CH_2), −89.90 and −90.09 (3 CF_2O), −92.12 (OCF_2).

The ^{1}H and ^{19}F NMR of 1,1-dihydro-3,6,9,12,15-pentaoxaperfluorohexadecan-1-ol (**2b**) and 1,1-dihydro-3,6,9,12,15,18-hexaoxaperfluorononadecan-1-ol (**2c**) are identical to that of alcohol **1a** and differ only in the intensity of the signals in the ^{19}F NMR spectra.

1,1-Dihydro-2,5-perfluorodimethyl-3,6-dioxaperfluorononan-1-ol (2d): ^{1}H NMR, δ: 4.24 (d, CH_2O, J = 13.05 Hz); 4.94 (OH). ^{19}F NMR, δ: −81.16, −82.69, −83.41 (3 CF_3), −82.28 (OCF_2CF_2). AB spin system (CF_2O) $\delta_A = -79.40$, $\delta_B = -82.90$, J_{AB} = 150 Hz, −130.76 (CF_2CF_3), −137.22 ($CFCH_2$), −145.69 (CF).

The ^{1}H and ^{19}F NMR spectra of compounds **2e** and **2f** are identical to that of alcohol **2d** and differ in the intensity of the signals in the ^{19}F NMR spectra.

Diol 2g: ^{1}H NMR, δ: 4.24 (d, CH_2O, J = 13.10 Hz); 4.98 (OH). ^{19}F NMR, δ: −81.21, −83.72, (all CF_3 and CF_2O), −122.31, −125.69 ($(CF_2)_4$), −131.83 ($CFCH_2$), −145.45 (CF).

Diol 2h: ^{1}H NMR, δ: 3.62, 3.97 (br.s, CH_2O); 4.42 (OH). ^{19}F NMR, δ: −52.79, −54.44, −56.18 (OCF_2O), −88.68, −88.80, −81.48 (CF_2CF_2O), −81.98, −83.77, −84.03 (CF_2CH_2). M_n = 1600 (ebullioscopy in C_6F_6).

Reactions of terephthaloyl chloride (TC) with alcohols 2a,d,g,h,i. A mixture of 1,1-dihydro-3,6,9-trioxaperfluorodecan-1-ol (2.22 g, 5.6 mmol) and TC (0.45 g, 2.2 mmol) was heated at 130—140 °C for 20 h. Then excess alcohol was removed and the residue was distilled to afford terephthalate **3a** (1.93 g, 95 %). Terephthalates **3d,i** were synthesized similarly (Table 2).

The reaction of TC with diols **2g,h** under analogous conditions (140—160 °C; 20 h) gave oily or waxy products.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09416a).

References

1. S. P. Krukovsky, A. A. Yarosh, and A. A. Glazkov, *Intern. Symp. Advanced Technologies and Production of Organic and Inorganic Chemistry-95, Moscow, April 25—28*, Section B, Reports, 1995, 102.
2. V. A. Ponomarenko, V. M. Men'shov, and L. A. Kiseleva, *Vysokomol. Soedin., Ser. B*, 1981, **23**, 403 [*Polym Sci. USSR*, 1981, **B23** (Engl. Transl.)].
3. *Syntezy ftororganicheskhikh sodenenii* [*Syntheses of Fluoroorganic Compounds*], Ed. I. L. Knunyants, Khimiya, Moscow, 1973 (in Russian).
4. V. A. Ponomarenko, S. P. Krukovsky, and A. Yu. Alybina, *Ftorsoderzhashchie geterotsepnye polimery* [*Fluorine-containing Heterochain Polymers*], Nauka, Moscow, 1979 (in Russian).
5. A. A. Glazkov, A. V. Ignatenko, S. P. Krukovsky, and V. A. Ponomarenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2512 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28**, 2327 (Engl. Transl.)].
6. G. Caporiccio, E. Strepparola, and M. A. Scarati, *Eur. Pat. Appl.* 0165.649 (1985), *Chem. Abstr.*, 1986, **104**, 130510t.

Received January 19, 1996