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Synthesis and characterization of a new class of polyfluorinated alkanes: tetrakis(perfluoroalkyl)alkane

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Abstract

The synthesis and physico-chemical characterization of 1,1,2,2-tetrakis(perfluoroalkyl-methylene)ethane { $[F(CF_2)_nCH_2]_2CH$ }₂ (n = 6, *TK6*; n = 8, *TK8*) are reported. The synthesis consists of four steps: (1) addition of allyl alcohol to a perfluoroalkyl iodide, $F(CF_2)_nI$ (n = 6, 8) to give the corresponding iodo-adduct; (2) dehalogenation of the adduct by treatment with zinc in aqueous acetic acid, yielding 3-perfluoro-*n*-alkyl-1-propene; (3) addition of 3-perfluoro-*n*-alkyl-1-propene to perfluoroalkyl iodide, $F(CF_2)_nI$ (n = 6, 8) to give 1,3-perfluoro-*n*-alkyl-2-iodo-propane; (4) coupling of 1,3-perfluoro-*n*-alkyl-2-iodo-propane by zinc in acetic anhydride giving the final products. TK6 and TK8 are characterized by very low surface tension values and exhibit very good properties as potential ski-waxes. \bigcirc 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well known that perfluorinated materials are characterized by extremely low surface tension values [1] which makes them very useful in the field of lubrication, in particular, in the formulation of lubricants for polyethylene snow articles such as skis, snowboards and sleds [2–4]. The phenomenon of kinetic loss during snow sliding is very complex, but it can be separated into two components: dry friction (caused by the friction of snow particles against the running surface) and, more important, capillary suction (adherence of water to the moving surface producing a suction effect) [5,6]. This latter effect can be minimized by using water-repellent materials like perfluorinated compounds. Perfluoropolyethers, diblock semifluorinated-*n*alkanes and perfluoro-*n*-alkanes are among the best known and most commonly used compounds in this class.

Although *perfluoropolyethers* [7] (Fomblin[®], Kritox[®]) are very good lubricants for extreme operating conditions, their performance is not optimal because they contain an ethereal bond that gives them only a moderate water-repellence. Semifluorinated-*n*-alkanes, R_F - R_H , which are partially compatible with paraffins, where they are incorporated as additives through a moulding process in order to improve water repellence as ski-waxes, are generally prepared in two steps:

(1) Addition of a perfluoroalkyl iodide, $F(CF_2)_n I$, n = 4, 6, 8, 10, 12, to a linear 1-alkene, $CH_2=CH(CH_2)_{m-2}H$, m = 10-24, to give the corresponding iodo-adduct (Eq. (1)):

$$F(CF_2)_n I + CH_2 = CH(CH_2)_{m-2} H$$

$$\rightarrow F(CF_2)_n - CH_2 - CHI - (CH_2)_{m-2} H$$
(1)

The reaction is induced by means of a radical initiator (generally AIBN, 2,2'-azobis(2-methylpropionitrile) that abstracts the iodine atom from R_FI forming an R_F radical that adds irreversibly to the alkene [7–21].

(2) The second step consists of the reductive dehalogenation of the iodo-adduct (Eq. (2)):

$$F(CF_{2})_{n}-CH_{2}-CHI-(CH_{2})_{m-2}H$$

$$\stackrel{-HI}{\rightarrow}F(CF_{2})_{n}-CH=CH-(CH_{2})_{m-2}H;$$

$$F(CF_{2})_{n}-CH=CH-(CH_{2})_{m-2}\stackrel{Zn,H^{+}}{\rightarrow}F(CF_{2})_{n}(CH_{2})_{m}H$$
(2)

which can be accomplished by treatment with zinc powder in acetic acid [22], or alternatively in either gaseous [23,24] or aqueous [20,25] HCl in ethanol (or a different suitable solvent) or employing lithium

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aluminium hydride in anhydrous diethyl ether [16, 17,20].

Perfluoro-*n*-alkanes, in principle telomers of polytetrafluoroethylene, are generally prepared by the coupling of perfluoroalkyl iodide, $F(CF_2)_nI$, n = 6, 8, 10, 12, using zinc [14,26,27] (Eq. (3)):

$$F(CF_2)_n I + F(CF_2)_m I + Zn \rightarrow F(CF_2)_{n+m} F + ZnI_2$$
(3)

Perfluoro-*n*-alkanes are characterized by very low surface tension (15–17 mN m⁻¹) and very high chemical inertness. Their high repellence to water and dirt gives the resulting perfluoro-paraffin ski-waxes excellent performance in terms of sliding capability. However, the melting temperatures of these compounds [MP($C_{12}F_{26}$) = 73.7 °C, MP($C_{16}F_{34}$) = 126.8 °C] are rather high, which makes their application to polyethylene ski soles difficult. Moreover they possess high vapor pressures that cause sublimation of the product and consequent loss from the surface onto which it is applied [28,29]. Finally, perfluoro-*n*-alkanes are insoluble in the polyethylene ski surfaces and are therefore only absorbed physically on the porous ski soles inducing further loss of material.

In the present paper, the synthesis and characterization of a new class of fluorinated compounds 1,1,2,2-tetrakis-perfluoro-*n*-alkyl-alkanes, in particular of { $[F(CF_2)_nCH_2]_2$ -CH}₂ with n = 6 (TK6) and n = 8 (TK8), are reported. These compounds consist of a symmetrical arrangement of four perfluorinated chains attached to a hydrogenated core. This particular structure opposes crystallization and therefore the melting temperature is lower than that of a perfluoro-*n*-alkane of the same molecular weight. These compounds exhibit improved performance in the field of ski-waxes. The high molecular weights ($MW(C_{30}H_{10}F_{52})$, 1358 and $MW(C_{38}H_{10}F_{68})$, 1758) provide very low vapor pressure and the water repellence, as determined by contact angle measurement, even higher than that of perfluoro-paraffins.

2. Results and discussion

2.1. Syntheses of TK6 and TK8

The synthesis of 1,3-perfluoro-*n*-alkyl-1-propanes TK6 and TK8 was performed as reported in Scheme 1 via the following four steps:

- (1) addition of allyl alcohol to a perfluoroalkyl iodide, F(CF₂)_nI (n = 6, 8) to give the corresponding iodoadducts **1a** and **1b**, respectively (Eq. (4));
- (2) dehalogenation of the adduct by treatment with zinc in aqueous acetic acid, yielding 3-perfluoro-*n*-alkyl-1-propenes 2a and 2b, respectively (Eq. (5));
- (3) addition of the 3-perfluoro-*n*-alkyl-l-propene to the corresponding perfluoroalkyl iodide, F(CF₂)_nI (n = 6, 8) giving the 1,3-perfluoro-*n*-alkyl-2-iodo-propanes **3a** and **3b**, respectively (Eq. (6));
- (4) coupling of the compounds **3** by zinc in acetic anhydride yielding the final products TK6 and TK8 (Eq. (7)).

The synthesis can be accomplished starting from an allylic compound (either chloride or alcohol). The first trials were performed by using allyl choride [30]. Since the boiling

$$F(CF_{2})_{n}I + CH_{2}=CHCH_{2}-OH \xrightarrow{AIBN} F(CF_{2})_{n}CH_{2}CHCH_{2}OH \qquad (4)$$

$$Ia, n=6$$

$$Ib, n=8$$

$$F(CF_{2})_{n}CH_{2}CHCH_{2}OH \xrightarrow{Zn} F(CF_{2})_{n}CH_{2}CH=CH_{2} \qquad (5)$$

$$2a, n=6$$

$$2b, n=8$$

$$F(CF_{2})_{n}CH_{2}CH=CH_{2} + F(CF_{2})I \longrightarrow F(CF_{2})_{n}CH_{2}CHCH_{2}(CF_{2})_{n}F \qquad (6)$$

$$I$$

$$3a, n=6$$

$$3b, n=8$$

$$2 F(CF_{2})_{n}CH_{2}CHCH_{2}(CF_{2})_{n}F \xrightarrow{Zn} F(CF_{2})_{n}CH_{2}CHCH_{2}(CF_{2})_{n}F \qquad (7)$$

$$I$$

$$TK-6, n=6$$

$$TK-6, n=6$$

$$TK-6, n=6$$

Scheme 1.

point of this compound (BP_{allyl chloride} = 45 $^{\circ}$ C) is lower than the decomposition temperature of the initiator AIBN $(T_{\rm dec} = 75 \,^{\circ}{\rm C})$, the synthesis must be performed in an autoclave. Under these reactions conditions $(T = 80 \degree C;$ P = 10 atm; reagent ratio R_FI:allyl chloride = 2:1) a mixture of products is formed and the conversion of reagents is not complete (90% conversion after 3 h). The reactions have been followed by GLC and the chromatograms obtained showed the formation of the $F(CF_2)_n CH_2 CHICH_2 CI$ adducts, together with small quantities of the corresponding olefins 2 and adducts 3. Separation of products 2 by fractional distillation is difficult because their boiling points are close to those of the corresponding perfluoroalkyl iodide compounds. Thus, the yield of the desired products, $F(CF_2)_n CH_2 CHICH_2 Cl$ (n = 6, 8), is not higher than 54% based on R_FI used. The dehalogenation reaction of $F(CF_2)_n CH_2 CHICH_2 Cl$ proceeds smoothly with little formation of by-products (yield ca. 90%). The yield of the entire process is about 50% [31].

An alternative method to produce the olefins **2** proceeds from addition of perfluoroalkyl iodides to allyl alcohol. This process is easier because it is not necessary to perform the alkylation reaction in an autoclave (BP_{alcohol} = 97.1 °C). GLC analysis of the reaction mixture shows that in this case the yield in **1** is very high (ca. 90%) with very low formation of by products. A great improvement in the rate of reaction was achieved by the synergic action of sodium metabisulfite and AIBN [32]. It has been proposed that bisulfite suppresses side reactions that slow the R_FI addition reaction. The azonitrile initiator gives rise to the radical CH₂CHCH(·)OH, to which a rapid transfer of an hydrogen atom occurs [33,34]. The reaction goes to completion in about 4 h whereas the reaction requires more than 20 h and a considerable excess of alcohol if the bisulfite is not added.

The dehalogenation of adducts **1**, $F(CF_2)_nCH_2CHI-CH_2OH$ (n = 6, 8) with zinc in acetic acid is not so efficient (Eq. (5), Scheme 1); the reaction goes rapidly to completion, but there is significant formation of by-products (predominantly $F(CF_2)_nCH_2CH_2CH_2OH$) together with the olefins **2** in about 70% yield. Further addition of the perfluoroalkyl iodide (n = 6, 8) on allyl substrates $F(CF_2)_nCH_2CH=CH_2$ (n = 6, 8) is performed (Eq. (6), Scheme 1) to obtain the iodine adducts **3**, $F(CF_2)_nCH_2CHICH_2(CF_2)_nF$ in the presence of AIBN.

The final products TK6 and TK8 were obtained by coupling of $F(CF_2)_nCH_2CHICH_2(CF_2)_nF$ by treatment with zinc in acetic anhydride (Wurtz-type reaction) [35]. The suggested mechanism for the Wurtz reaction involves the iodine-metal exchange to form an organometallic compound which then reacts with a second molecule of halide to form the final perfluoroalkane product in a high yield (usually >95%). The dimerization reaction of **3** is less efficient: there is almost complete conversion of the starting compound, but the yield of the desired product is about 50%. The mixture obtained contains two other compounds which have not been identified.

2.2. Characterization of TK6 and TK8

The compounds TK6 and TK8 are low melting point colorless solids, which have been characterized with spectroscopic techniques. As *TK6* and *TK8* are soluble exclusively in perfluorinated compounds (such as perfluorodecalin or CFCs) ¹H and ¹³C NMR spectra were recorded in perfluorinated solvents. The particularly broad signals of the proton resonances indicate a restricted molecular motion, probably due to the fact that the protons are isolated from the solvent molecules by the perfluoroalkyl groups wrapped in around the nonfluorinated core. For this reason it was not possible to obtain crystals suitable for X-ray determinations, even at low temperature.

¹³C NMR spectra of solid products *TK6* and *TK8* are reported in Fig. 1, with indication of the particular pulse sequence employed. Two broad signals were detected for each sample, attributable to carbons in the R_F and R_H moieties, respectively. The signals occur practically at the same chemical shift for *TK6* and *TK8* (CH, CH₂ = 25 ppm, CF₃ and CF₂ = 110 ppm).

The ability of the CP sequence to yield more intense signals for carbons bonded to protons is emphasized in both TK samples, while in the HPDEC spectra signals of R_F and R_H carbons display a relative intensity that corresponds more closely to the effective molecular formula.

Both sequences employed revealed the rigid character of R_F and R_H moiety in *TK6* and *TK8* materials, as the signal to noise ratio is low and bandwidth is very large.

DSC analyses of *TK6* and *TK8* show an intense melting endotherm peak, which occurs at 97.16 and 82.58 °C, respectively. It is noteworthy that the melting point of the heavier *TK8* compound is lower than that of *TK6*. These melting temperatures are significantly lower than those of perfluorinated *n*-alkane compounds, semifluorinated *n*-alkanes or *n*-alkanes with the same number of carbon atoms [23].

In Table 1, the values of contact angles and surface tensions for *TK6* and *TK8* are reported, in comparison with other perfluorinated compounds and some fluorinated polymers. Surface free energy of the solid, γ_s , was calculated using the contact angles with the Eqs. (8) and (9), which were proposed by Owens and Wendt [36b] who extended the Fowkes concept [36a]:

$$1 + \cos \theta = 2\sqrt{\gamma_s^{d}} \left(\frac{\sqrt{\gamma_1^{d}}}{\gamma_1}\right) + 2\sqrt{\gamma_s^{p}} \left(\frac{\sqrt{\gamma_1^{p}}}{\gamma_1}\right)$$
(8)

$$\gamma_{\rm s} = \gamma_{\rm s}^{\rm d} + \gamma_{\rm s}^{\rm p} \tag{9}$$

where θ is the contact angle, γ_1 the surface free energy of the liquid and γ_1^d and γ_1^p are its dispersion and polar components, respectively; γ_s is the solid free energy and γ_s^d and γ_s^p are its components. The dispersion and the polar components of the surface free energy of water are 21.8 and 51.0 mN m⁻¹, respectively, and those of the di-iodomethane are 49.5 and 1.3 mN m⁻¹, respectively [36b].



Fig. 1. ¹³C NMR spectra of solid products TK6 and TK8, with indication of the particular pulse sequence employed.

Table 1				
Contact angles values	and surface tension	calculated according to	Owens method	36] of <i>TK6</i> and <i>TK8</i>

Compound	$\varTheta_{\rm H_2O(deg)}$	$\Theta_{\mathrm{CH}_2\mathrm{I}_2(\mathrm{deg})}$	$\gamma_{tot} \ (mN \ m^{-1})$	$\gamma_{\rm disp}~({\rm mN}~{\rm m}^{-1})$	$\gamma_{pol} \ (mN \ m^{-1})$
TK6	138.3 ± 1.0	128.9 ± 1.3	(1.8)	(1.6)	(0.2)
TK8	137.4 ± 1.3	127.5 ± 1.5	(2.0)	(1.8)	(0.2)
$C_{16}F_{34}$	122.3 ± 2.1	103.0 ± 1.3	7.7	7.3	0.4
$C_{20}F_{42}$	119	107	6.7	5.5	1.2
Poly(tetrafluoroethylene)	108	88	19.1	18.6	0.5

 $\Theta_{H_2O(deg)}$: contact angle of water on the compound; $\Theta_{CH_2I_2(deg)}$: contact angle of di-iodomethane on the compound; γ_{tot} (mN m⁻¹): interfacial energy; γ_{disp} (mN m⁻¹): interfacial energy (dispersion component); γ_{pol} (mN m⁻¹): interfacial energy (polar component).

It is noteworthy that the values of Θ_{H_2O} and $\Theta_{CH_2I_2}$ for *TK6* and *TK8* are significantly higher than those of the other fluorinated compounds, with lower energy tension values (either molecular dispersion energies and polar interaction term). In this context, the limitations of the model and equation used must be taken into account [36].

In conclusion, the compounds *TK6* and *TK8*, on the basis of their high molecular weight, low vapor pressure, and at the same time low melting point and low surface tension, appear to be good candidates for ski-waxes, as indicated by some preliminary results.

3. Experimental

3.1. Reagents and general procedure

Perfluorohexyl iodide and perfluorooctyl iodide were commercial grade reagents supplied by Elf Atochem S.A. Allyl chloride, allyl alcohol and AIBN (2,2'-azobis(2-methylpropionitrile) were purchased from Aldrich Chemical Co. All other reagents employed were common laboratory materials. All the chemical reagents were used as received. All the reactions were performed under inert atmosphere (N_2) .

3.2. Analysis

GLC analyses of the reaction mixtures were performed using a Shimadzu GC-8A instrument ($2 \text{ m} \times 2 \text{ mm}$ stainless steel column packed with FS on 100–120 mesh Chromosorb P) connected to a Shimadzu C-R3A integrator. Typical operative conditions were: temperature programme 50 °C for 6 min, 20 °C/min to 250 °C; He as gas carrier 24 ml/min.

GC/mass spectra were measured on a Carlo Erba Instrument MFC 500/QMD1000 using a silica fused capillary PS264 column ($30 \text{ m} \times 0.25 \text{ mm}$) and on a Finnigan Mat TSQ7000 (capillary column $30 \text{ m} \times 0.32 \text{ mm}$). Typical

conditions were: temperature programme 60 $^{\circ}$ C for 2 min, 10 $^{\circ}$ C/min to 280 $^{\circ}$ C; He as gas carrier 1 ml/min).

FTIR spectra were measured using a Nicolet Avatar spectrophotometer.

¹H and ¹³C {¹H} NMR spectra were recorded on a Bruker 200 AC spectrometer operating at 200.13 and 50.32 MHz, respectively. Peak positions are relative to Me₄Si and were calibrated against the residual solvent resonance (¹H) or the deuterated solvent multiplet (¹³C). ¹⁹F NMR measurements were recorded on a Varian FT 80 spectrometer operating at 74.844 MHz. Peak positions are reported relative to CFCl₃.

Solid-state NMR analyses were performed using a Bruker AC200 spectrometer. Samples were spun at room temperature at 3000 kHz in 7 mm diameter zirconia rotors with Kel-F caps. All spectra were obtained by using both the standard Bruker cross-polarization pulse sequence (CP/MAS) and single pulse experiments with high power decoupling (HPDEC/MAS). In both cases, decoupling was applied during acquisition. The 50.32 MHz solid-state ¹³C CP/ MAS NMR spectra were obtained with a 3 ms contact time and a 10 s relaxing delay, recording the free induction decay over a sweep width of 50 kHz, during an acquisition time of 0.08 s in a 8 K data set, and were processed with 40 Hz exponential line broadening. ¹³C cross-polarization experiments were optimized using adamantane. The Magic Angle condition was adjusted observing ⁷⁹Br spinning side bands pattern in a rotor containing 5% KBr [37]. The ¹³C chemical shifts were externally referenced to solid sodium 3-(trimethyl-silyl)-1-propane-sulfonate at 0 ppm.

Differential scanning calorimetry (DSC) was measured using a TA Instruments model DSC 2920 operating under nitrogen flow. The measurements were carried out in the range 30–350 °C and at a heating rate of 10 °C/min.

The surface free energy of TK6 and TK8 samples were determined using a Kruss G10/DSA10 goniometer interfaced to image-capture software. Measurements were made with de-ionized water and di-iodomethane taking an average of 10 15 μ l drops with each type of liquid.

3.3. General procedure

3.3.1. 3-Perfluoro-n-hexyl-2-iodo-l-propanol, F(CF₂)₆CH₂CHICH₂OH (**1***a*)

Perfluoro-*n*-hexyl iodide (177 g, 0.40 mol) was heated to 75 °C in a four necked 2 l Pyrex glass round bottomed flask equipped with a mechanical stirrer, thermometer, dropping funnel and a condenser. A 30% aqueous solution of Na₂S₂O₅ (35 ml) was then added [38]. The resulting mixture was heated at 80 °C and AIBN (0.80 g, 0.0048 mol) was added. The allyl alcohol (24 g, 0.41 mol) was then added dropwise and the solution was stirred for 90 min at 80 °C. The white solid that formed was decanted off, washed by stirring with water (400 ml at 80 °C), and, after cooling, was filtered off. The product was finally purified by distillation (70–76 °C/2 Torr). Yield 187.3 g, 93%. MS *m*/*z* (rel. ab. %): 503 ([*M* – H]⁺, 1%); 487 ([*M* – OH]⁺, 3%); 377 ([*M* – I]⁺, 80%); 357 ([*M* – I – HF]⁺, 58%); 337 ([*M* – I – 2HF]⁺, 8%); 69 ([CF₃]⁺, 100%). FTIR (nujol): v_{OH} 3365 cm⁻¹, v_{CF} 1122–1321 cm⁻¹, v_{C-O} 1043 cm⁻¹. ¹H NMR: (CD₂Cl₂) δ 2.90 (m, CH₂); 4.41 (tt, ³*J*_{HH} 6.6, ³*J*_{HH} 6.7, CHI); 3.79 (d, ³*J*_{HH} 6.6, CH₂O), 2.19 (s br, OH). (CD₃COCD₃) δ 3.30 (m, CHCF₂); δ 2.77 (m, CHCF₂); 4.34 (m, CHI); 3.92 (m, CH₂O), 3.01 (s br, OH). ¹⁹F NMR (CD₂Cl₂): δ –81.2 (t, ³*J*_{FF} 9.7, CF₃); -113.7 (m, CF₂CH₂); -122.1, -123.2, -123.9, -126.4 (m, CF₂). ¹³C NMR (CD₃COCD₃): δ 20.55 (s, CHI), 38.11 (t, ²*J*_{CF} 20.73, CH₂CF₂), 69.26 (s, CH₂O), 108–130 (m, CF).

3.3.2. 3-Perfluoro-n-octyl-2-iodo-l-propanol, F(CF₂)₈CH₂CHICH₂OH (**1b**)

The synthesis was performed according to the procedure described for **1a** starting from perfluoro-*n*-octyl-iodide (742 g, 1.36 mol), $Na_2S_2O_5$ (80.7 g in 253 g H₂O), AIBN (6.7 g, 0.04 mol) and allyl alcohol (118.2 g, 2.038 mol). The final product obtained as a white solid was purified by distillation (107–110 °C/10 Torr). Yield: 657 g, 74%.

MS *m*/*z* (rel. ab. %): 603 ([*M* – H]⁺, 1%); 587 ([*M* – OH]⁺, 2%); 477 ([*M* – I]⁺, 80%); 457 ([*M* – I – HF]⁺, 40%); 437 ([*M* – I – 2HF]⁺, 10%); 69 ([CF₃]⁺, 100%). FTIR (nujol): v_{OH} 3372 cm⁻¹, v_{CF} 1147–1241 cm⁻¹, v_{C-O} 1041 cm⁻¹. ¹H NMR (CD₃COCD₃) δ 3.30 (m, CHCF₂); δ 2.82 (m, CHCF₂); 4.34 (m, CHI); 3.83 (m, CH₂O), 2.05 (s br, OH). ¹⁹F NMR (CD₂Cl₂): δ –80.74 (m, CF₃); –113.1 (m, CF₂CH₂); –122.4, –121.8, –123.2, –125.7 (m, CF₂). ¹³C NMR (CD₃COCD₃): δ 20.51 (s, CHI), 38.07 (t, ²*J*_{CF} 20.73, CH₂CF₂), 69.22 (s, CH₂O), 106–124 (m, CF).

3.3.3. 3-Perfluoro-n-hexyl-l-propene, $F(CF_2)_6CH_2CH=CH_2$ (2a)

In a four necked Pyrex glass round bottomed flask equipped as for the preparation of **1a**, $F(CF_2)_6CH_2CHI-CH_2OH$ (187.3 g, 0.37 mol) was mixed with a 30% aqueous solution of acetic acid (221.4 g). The resulting mixture was heated at 85 °C with stirring. Powdered zinc (35.4 g, 0.54 mol) was added in small portions over a 4 h period and reaction mixture was stirred for a further 2 h. Aqueous HCl (3 ml) was added and mixture was stirred for further 4 h at 80 °C to destroy excess zinc. The two resulting phases were separated and the organic phase was distilled (80–85 °C/680 Torr) obtaining 80.2 g (60%) of **2a**.

MS m/z (rel. ab. %): 361 ($[M + H]^+$, 2%); 360 (M^+ , 15%); 295($[M - C_2H_3F_2]^+$, 16%); 169 ($[C_3F_7]^+$, 4%); 119 ($[C_2F_5]^+$, 20%); 91 ($[C_4H_5F_2]^+$, 100%); 69 ($[CF_3]^+$, 50%); 41 ($[C_3H_5]^+$, 99%). FTIR (nujol): v_{CF} 1122– 1348 cm⁻¹, $v_{C=C}$ 1649 cm⁻¹. ¹H NMR (CD₂Cl₂): δ 2.87 (dtt, ³J_{HH} 6.9, ³J_{HF} 11.5, ⁴J_{HH} 1.29, CH₂); 5.81 (m, CH=); 5.37 (m, CH=); 5.31 (m, CH=). ¹⁹F NMR (CD₂Cl₂): δ -81.2 (m, CF₃); -113.5 (m, CF₂CH₂); -122.1, -123.2, -126.4 (m, CF₂). ¹³C NMR (CD₃COCD₃): δ 36.94 (t, ²J_{CF} 21.2, CH₂CF₂), 126.97 (CH=), 123.88 (CH₂=), 110–124 (m, CF).

3.3.4. 3-Perfluoro-n-octyl-l-propene, $F(CF_2)_8CH_2CH=CH_2$ (**2b**)

The synthesis was performed according to the procedure described for **2a** starting from $F(CF_2)_8CH_2CHICH_2OH$ (657 g, 1.09 mol), aqueous solution of acetic acid (200 g) and zinc (71.2 g, 1.08 mol).The product was distilled (60–63 °C/20 Torr).Yield 280 g, 56%.

MS m/z (rel. ab. %): 461 ($[M + H]^+$, 1%); 460 ($[M]^+$, 10%); 395 ($[M - C_2H_3F_2]^+$, 15%); 91 ($[C_4H_5F_2]^+$, 95%); 69 ($[CF_3]^+$, 30%); 41 ($[C_3H_5]^+$, 100%). FTIR (nujol): v_{CF} 1115–1348 cm⁻¹, $v_{C=C}$ 1650 cm⁻¹. ¹H NMR (CD₃COCD₃): δ 3.05 (dt, ³ J_{HH} 7.0, ³ J_{HF} 19.1, C H_2); 5.84 (m, CH=); 5.40 (m, C $H_2=$). ¹⁹F NMR (CD₃COCD₃): δ -80.99 (t, ³ J_{FF} 9, C F_3); -112.7, -113.9 (m, C F_2 CH₂); -121.6, -122.4, -123.2, -126.0 (m, C F_2). ¹³C NMR (CD₃COCD₃): δ 37.05 (t, ² J_{CF} 22.3, CH₂CF₂), 126.97 (CH=), 123.75 (CH₂=), 113–121 (m, CF).

3.3.5. 1,3-Perfluoro-n-hexyl-2-iodo-propane, F(CF₂)₆CH₂CHICH₂(CF₂)₆F (**3***a*)

 $F(CF_2)_6CH_2CH=CH_2$ (201 g, 0.56 mol) was mixed with $F(CF_2)_6I$ (256 g, 0.58 mol) in a 1 l four necked flask equipped with a condenser, mechanical stirrer and a thermometer. The mixture was heated under nitrogen to 85 °C and AIBN was added (5.1 g, 0.03 mol), then the solution was heated at 85 °C for 20 h, with the further addition of AIBN during the reaction time (ca. 1 g every 4 h). The product was purified by distillation (100–107 °C/1 Torr). Yield 440 g (97%).

MS *m*/*z* (rel. ab. %): 679 ([M - I]⁺, 4%); 659 ([M - I - HF]⁺, 12%); 345 ([$C_8H_2F_{13}$]⁺, 17%); 295 ([$C_7H_2F_{11}$]⁺, 36%); 169 ([C_3F_7]⁺, 10%); 119 ([C_2F_5]⁺, 27%); 69 ([CF_3]⁺, 80%). FTIR (nujol): v_{CF} 1236, br. ¹H NMR (CD₂Cl₂): δ 4.53 (q, ³ J_{HH} 6.6, *CH*); 2.97 (m, *CH*₂). ¹⁹F NMR (CD₂Cl₂): δ -81.2 (tt, ³ J_{FF} 9.7, ⁴ J_{FF} 2.2, *CF*₃); -113.6 (m, *CF*₂CH₂); -121.9, -123.1, -123.7, -126.3 (m, *CF*₂). ¹³C NMR (CD₃COCD₃): δ 0.93 (CHI), 42.38 (t, ² J_{CF} 20.3, *CH*₂CF₂), 104–126 (m, *CF*).

3.3.6. 1,3-Perfluoro-n-octyl-2-iodo-propane, F(CF₂)₈CH₂CHICH₂(CF₂)₈F (**3b**)

This compound was prepared according to the procedure described for **3a** starting from $F(CF_2)_8CH_2-CH=CH_2$ (280 g, 0.61 mol), $F(CF_2)_8I$ (365.6 g, 0.67 mol) and AIBN (10 g, 0.06 mol). **3b** was distilled at 128–134 °C/7 Torr. Yield 490 g (80%).

MS m/z (rel. ab. %): 779 ([M - I]⁺, 5%); 759 ([M - I - HF]⁺, 10%); 119 ([C_2F_5]⁺, 30%); 69 ([CF_3]⁺, 80%). FTIR v_{CF} 1241 cm⁻¹, br. ¹H NMR (CD₃COCD₃): δ 4.66 (q, ³ J_{HH} 5.6, CH); 3.24 (m, CH₂). ¹⁹F NMR (CD₂Cl₂): δ -81.0 (t, ³ J_{FF} 10.0, CF₃); -113.6 (m, CF₂CH₂); -121.5, -122.5, -123.6, -126.0 (m, CF₂). ¹³C NMR (CD₃COCD₃): δ 0.94 (CHI), 42.22 (t, ² J_{CF} 20, CH₂CF₂), 106–124 (m, CF).

3.3.7. 1,1,2,2-Tetrakis(perfluorohexyl-methylene)ethane ${[F(CF_2)_6CH_2]_2CH}_2$ (TK6)

 $F(CF_2)_6CH_2CHICH_2(CF_2)_6F$ (320 g, 0.40 mol) was mixed with acetic anhydride (580 ml) which had been

previously treated with powdered zinc (3 g) to remove traces of acetic acid. The resulting mixture was heated at 60-65 °C for 4 h, during which time powdered zinc (27.5 g, 0.42 mol) was added in small portions. The solid product was separated from acetic anhydride by decantation. The excess zinc remaining in the solid product was destroyed by heating the solid to 80 °C and continuously adding a solution of 10% aqueous HCl. This solution was then cooled and the desired product was separated from the aqueous phase by decantation and was then purified by distillation at 170–175 °C/ 1 Torr. Yield 205 g, 37%. Calcd. for C₃₀H₁₀F₅₂: C 26.53, H 0.74; Found: C 26.37, H 0.70. FAB/MS (m-nitrobenzylalcohol) (*m*/*z*, rel. ab. %): 1511 ([M + NBA]^{•+}, 30%); 1471 $([1511-2HF]^{\bullet+}, 40\%)$. FTIR: v_{CF} 1122–1246 cm⁻¹, br. ¹H NMR (CD₃COCD₃, perfluorodecaline): δ 0.93 (m, CH₂); δ 1.85 (m, CH). ¹³C NMR (CD₃COCD₃, freon 113): δ 28.24 (s, CH), δ 31.40 (t, ²J_{CF} 21.6, CH₂CF₂), 106–124 (m, CF).

3.3.8. 1,1,2,2-Tetrakis(perfluorooctyl-methylene)ethane { $[F(CF_2)_8CH_2]_2CH_2$ (TK8)

TK8 was prepared according to the procedure described for TK6, starting from $F(CF_2)_8CH_2CHICH_2(CF_2)_8F$ (490 g, 0.49 mol), zinc (32 g,0.49 mol) and acetic anhydride (500 ml). The product was separated from the aqueous phase by decantation and purified by distillation at 213–217 °C/ 1 Torr. Yield 214 g (25%). FAB/MS (*m*-nitrobenzylalcohol) (*m*/*z*, rel. ab. %): 1758 ([*M*]^{•+}, 30%). Calcd. for C₃₈H₁₀F₆₈: C 25.96, H 0.57; Found: C 26.61, H 0.52. FTIR: *v*_{CF} 1100– 1250 cm⁻¹, br. ¹H NMR (CD₃COCD₃, perfluorodecaline): δ 0.95 (m, *CH*₂); δ 1.66 (m, *CH*). ¹³C NMR (CD₃COCD₃, CFC 113): δ 29.33 (s, *CH*), δ 31.27 (t, ²*J*_{CF} 20.9, *CH*₂CF₂), 100–130 (m, *CF*).

References

- (a) T.W. Del Pesco, Handbook of Lubrication and Tribology, CRC Press, Boca Raton, FL, 1994, p. 287;
 (b) D. Myers, Surfactant Science and Technology, VCH, Weinheim, 1988.
- [2] A. Karydas, US Patent 5 914 298 (1999).
- [3] E. Traverso, et al., US Patent 5 202 041 (1993).
- [4] G.P. Gambaretto, US Patent 4 724 093 (1988).
- [5] G. Albanesi, Chim. Ind. (Milan) 77 (1995) 377.
- [6] G. Albanesi, Chim. Ind. (Milan) 80 (1998) 749.
- [7] K. von Werner, J. Fluorine Chem. 28 (1985) 229.
- [8] M. Kuroboshi, T. Ishihara, J. Fluorine Chem. 39 (2) (1988) 299.
- [9] A. Probst, K. Raab, K. Ulm, K. Werner, J. Fluorine Chem. 37 (1987) 223.
- [10] E. Traverso, Eur. Patent Appl. 0 444 752 A1, 1991.
- [11] E.S. Lo, Germ. Offen. 2 047 475, 1971.
- [12] T. Enokida, G. Katu, Jpn. Kokai, Tokyo Koho JP 07 48 294, 1995.
- [13] T. Durenroth, R.A. Falk, J. Haan, Eur. Patent Appl. EP 690 027, 1996.
- [14] A.L. Henne, J. Am. Chem. Soc. 57 (1953) 5750.
- [15] N.O. Brace, J. Org. Chem. 28 (1963) 3093.
- [16] N.O. Brace, J. Org. Chem. 27 (1962) 3033.
- [17] N.O. Brace, J. Org. Chem. 27 (1962) 4491.
- [18] N.O. Brace, US Patent 3 145 222 (1964).
- [19] N.O. Brace, J. Fluorine Chem. 20 (1982) 213.

- [20] M. Napoli, C. Fraccaro, L. Conte, G.P. Gambaretto, E. Legnaro, J. Fluorine Chem. 57 (1970) 219.
- [21] R.E. Banks, B.E. Smart, J.C. Taylor, Organofluorine Chemistry, Principles and Commercial Applications, Plenum Press, New York, 1994.
- [22] A. Hassner, R.P. Hoblitt, C. Heatcock, J.E. Kropp, M. Lorber, J. Am. Chem. Soc. 92 (1970) 1326.
- [23] J.F. Rabolt, T.P. Russel, R.J. Twieg, Macromolecules 17 (1984) 2786.
- [24] R.J. Twieg, J.F. Rabolt, Macromolecules 21 (1988) 1806.
- [25] M.V.D. Puy, A.J. Poss, P.J. Persichini, L.A.S. Ellis, J. Fluorine Chem. 67 (1994) 215.
- [26] J.L. Howell, WO Patent 92 0 60 60A1, 1992.
- [27] T. Enokida, Jpn. Patent 07 04 294, 1995.
- [28] D.L. Dorset, Macromolecules 23 (1990) 894.
- [29] G.T. Dee, B.B. Sauer, B.J. Haley, Macromolecules 27 (1994) 6106.

- [30] M. Napoli, G.P. Gambaretto, J. Fluorine Chem. 84 (1997) 101.
- [31] M. Napoli, R. Bertani, J. Fluorine Chem. 111 (2001) 49.
- [32] N.O. Brace, J. Fluorine Chem. 93 (1999) 1.
- [33] P.D. Bartlett, R. Aitschul, J. Am. Chem. Soc. 67 (1945) 812.
- [34] C. Walling, Free Radicals in Solution, Wiley, New York, 1957, 259 pp.
- [35] (a) A.J. Henne, J. Am. Chem. Soc. 75 (1953) 5750;
 (b) J. March, Advanced Organic Chemistry, fourth ed., Wiley, New York, 1992, p. 449.
- [36] (a) F.M. Fowkes, J. Phys. Chem. 67 (1963) 2538;
 (b) D.K. Owens, R.C. Wendt, J. Appl. Polym. Sci. 13 (1969) 1741;
 (c) S. Wu, J. Polym. Sci.: Part C 34 (1971) 19.
- [37] J.S. Frye, G.E. Maciel, J. Magn. Res. 48 (1982) 125.
- [38] M. Kotora, M. Hajek, B. Ameduri, B. Boutevin, J. Fluorine Chem. 68 (1994) 49.