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Journal of Fluorine Chemistry 128 (2007) 493–499

JOURNAL OF FLUORINE CHEMISTRY

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Synthesis and characterization of tri-block fluorinated-n-alkanes

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Received 27 July 2006; received in revised form 23 December 2006; accepted 28 December 2006
Available online 13 January 2007

Abstract

A series of triblock semifluorinated n-alkanes of general formula $F(CF_2)_n(CH_2)_m(CF_2)_nF$ ($n = 6$, 8 and $m = 4$, 6, 8) have been synthesized and characterized. The synthesis of triblock compounds was performed in two different ways according to the length of the hydrogenated moiety. Coupling of two molecules of β-(perfluoro-n-alkyl)ethyl iodides leads to the triblock materials $F(CF_2)_6(CH_2)_4(CF_2)_6F$ and $F(CF_2)_8(CH_2)_4(CF_2)_8F$. The synthesis of compounds with larger hydrogenated part is accomplished in two steps by the addition of perfluoro-n-alkyl iodide $F(CF_2)_nI$ to 1,5-hexadiene and 1,7-octadiene, respectively to give the diiodo-adducts which are subsequently deiodinated to the final triblock products $F(CF_2)_6(CH_2)_6(CF_2)_6F$, $F(CF_2)_6(CH_2)_8(CF_2)_6F$, $F(CF_2)_8(CH_2)_6(CF_2)_8F$ and $F(CF_2)_8(CH_2)_8(CF_2)_8F$. The obtained triblock semifluorinated n-alkanes are characterized by low surface free energies with good lubricant properties usable as additives in ski-wax formulations.

Keywords: Tri-block fluorinated-n-alkane; Perfluorinated chains; Surfactants; Surface free energy

1. Introduction

Triblock semifluorinated n-alkanes $F(CF_2)_n(CH_2)_m(CF_2)_nF$ have interesting and useful physical and chemical properties. Their melting points are lower than those of the perfluoro-n-alkanes of the same molecular weight but their quite high molecular weight provide low vapour pressure. By varying the length of the hydrogenated and fluorinated moieties we can obtain compounds with different surface properties. Due to the presence of the unsymmetrical $–CF_2–CH_2–$ group these triblock molecules are more polar than either perfluorocarbons or hydrocarbons and consequently are more soluble in polar solvents, e.g. methanol. Diblock and triblock semifluorinated n-alkanes maintain many of the characteristical properties (i.e. chemical and thermal stability) of perfluorocarbons [1]. Mass spectrometric studies on a series of partially fluorinated alkanes have confirmed their great stability [2]. The main applications for triblock and diblock semifluorinated n-alkanes ranging from biomedical field, as oxygen-carrying agents for blood substitutes [3–8], ophthalmology applications [9–13], perfluorocarbons emulsion stabilization [14,15], to applications as solid lubricants.

Perfluoro-n-alkanes, diblock semifluorinated n-alkanes, 1,1,2,2-tetrakis(perfluoro-n-alkyl-methylene)-ethanes and perfluoropolyethers can be essentialy used for ski-applications [16–19].

Perfluoro-n-alkanes give excellent performances in terms of sliding capabilities but they have only poor adhesion on polyethene ski soles because of their completely fluorinated backbone and their high vapour pressure [20,21]. Hemifluorinated n-alkanes being compatible with classical waxes (paraffines) and with polyethene, represent a good compromise between adhesion and surface properties.

Recently we reported the syntheses of 1,1,2,2-tetrakis(perfluoro-n-alkyl-methylene)-ethanes which are symmetrical arrangements of four perfluorinated chains attached to an hydrogenated core. This structure yields low melting points, lack of crystallinity and a certain compatibility with polyethene [22].

Perfluoropolyethers have only poor water repellency because of the presence of ethereal moieties.

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doi:10.1016/j.jfluchem.2006.12.016

2. Results and discussion

2.1. Syntheses of triblock semifluorinated n-alkanes

The general procedure to synthesize triblock semifluorinated *n*-alkanes could be carried out under conditions similar to those used for diblock compounds [23–34]. An alternative method [35] involves treatment of $F(CF_2)_n(CH_2)_{m/2}I$ with Mg in an aprotic anydrous solvent at 40–140 °C under normal or high pressure. In the present paper the syntheses of triblock semifluorinated *n*-alkanes were performed in two different ways according to the hydrogenated chain length.

The syntheses of triblock semifluorinated *n*-alkanes with four hydrogenated carbon atoms is performed according to the procedure reported in Refs. [36–38] starting from β-(perfluoro-*n*-alkyl)-ethyl iodides.

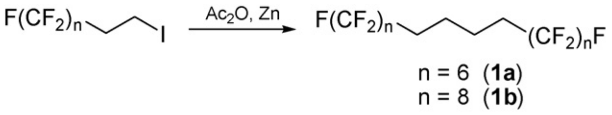
Two molecules of β-(perfluoro-*n*-alkyl)-ethyl iodides ($C_6F_{13}CH_2CH_2I$ and $C_8F_{17}CH_2CH_2I$) are coupled by treatment with zinc in acetic anhydride yielding the final products 1,4-bis(perfluoro-*n*-hexyl)-butane (**1a**) and 1,4-bis(perfluoro-*n*-octyl)-butane (**1b**), as reported in Scheme 1.

This Wurtz-type reaction involves the formation of an organometallic complex due to iodine-zinc exchange that reacts with a second molecule of β-(perfluoro-*n*-alkyl)-ethyl iodide to form the triblock semifluorinated *n*-alkane [39].

GLC analyses of the reaction mixtures show that the conversion of the starting compounds are almost complete, but the yield in the desired products varies between about 52% for (**1a**) and 47% for (**1b**) with respect to β-(perfluoro-*n*-hexyl)-ethyl iodide and β-(perfluoro-*n*-octyl)-ethyl iodide.

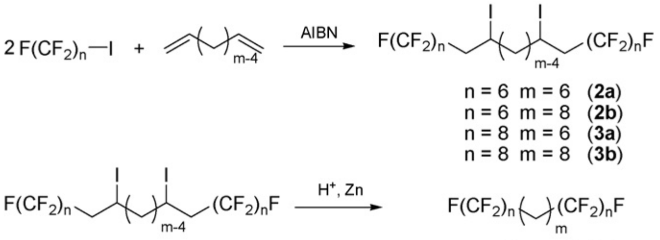
The syntheses of triblock semifluorinated *n*-alkanes with six and eight hydrogenated carbon atoms was performed via a two steps procedure [40] reported in Scheme 2 by radicalic addition of the corresponding perfluoroalkyl iodides to dienes.

The unsatured compounds used were 1,5-hexadiene and 1,7-octadiene. The reaction was performed in an inert atmosphere by dropping the diene in a suspension composed by $F(CF_2)_nI$ (10% molar excess), 2,2′-azobis(2-methylpropionitrile) (AIBN) and a water solution of sodium metabisulfite ($Na_2S_2O_5$) at a temperature of 80–85 °C. It was observed that under these conditions a substantial suppression of side reactions such as the oligomerization of the diene is obtained. GLC analyses of the reaction mixtures show that the yields in the desired diiodo-adducts were about 85% for 1,6-bis(perfluoro-*n*-hexyl)-2,5-diiodo-hexane (**2a**) and 1,6-bis(perfluoro-*n*-octyl)-2,5-diiodo-hexane (**3a**) and 80% for 1,8-bis(perfluoro-*n*-hexyl)-2,7-diiodo-octane (**2b**) and 1,8-bis(perfluoro-*n*-octyl)-2,7-diiodo-octane (**3b**) based on diene.



n = 6 (**1a**)
n = 8 (**1b**)

Scheme 1.



n = 6 m = 6 (**2a**)
n = 6 m = 8 (**2b**)
n = 8 m = 6 (**3a**)
n = 8 m = 8 (**3b**)

n = 6 m = 6 (**4a**)
n = 6 m = 8 (**4b**)
n = 8 m = 6 (**5a**)
n = 8 m = 8 (**5b**)

Scheme 2.

The subsequent reductive deiodination step is not so efficient. The reaction goes to completion but there is significant formation of by-products (the most abundant being the unsatured addition products of the type $F(CF_2)_nCH{=}CH(CH_2)_{m-4}CH{=}CH(CF_2)_nF$) as confirmed by GC/MS analyses. The yield in the desired products 1,6-bis(perfluoro-*n*-hexyl)-hexane (**4a**), 1,8-bis(perfluoro-*n*-hexyl)-octane (**4b**), 1,6-bis(perfluoro-*n*-octyl)-hexane (**5a**) and 1,8-bis(perfluoro-*n*-octyl)-octane (**5b**) varied between 55 and 62% based on diiodo-adducts (**2a**), (**2b**), (**3a**) and (**3b**), respectively. The yield of the entire process is about 48% for (**4a**) and (**4b**) and 51% for (**5a**) and (**5b**) based on the diene.

2.2. Characterization of triblock semifluorinated n-alkanes

The triblock semifluorinated *n*-alkanes synthesized are white crystalline solids with low melting points, which were characterized by different analytical techniques.

Their thermal stability is shown by DSC thermograms recorded in the temperature range −30 to 220 °C. No weight loss is observed. Calorimetric studies show for these compounds one solid–solid transition. Below the solid–solid transition temperature, Raman spectra and X-ray diffraction experiments indicated that the alkyl segment packing is similar to that observed in *n*-alkanes. Above the solid–solid transition, the hydrocarbon chain tends to become conformationally disordered but the linkage of both chain ends to rigid fluorocarbon substituents hinders the hydrocarbon segment disordering [41–43,40,44]. DSC curves of the synthesized triblock semifluorinated *n*-alkanes show a strong melting endotherm, plus a weaker endotherm associated with a solid–solid phase transition whose temperature increases with the hydrogenated segment length. Melting and solid–solid phase transitions temperatures for the synthesized compounds are reported in Table 1.

It is noteworthy that the melting points of (**4b**) and (**5b**) are the lowest of their corresponding series. In Fig. 1, DSC thermograms for (**1b**), (**5a**) and (**5b**) are reported.

Mass spectra of (**1a**), (**4a**) and (**4b**) have been detected as perfluorodecaline solutions (by GC/MS) and (**1b**), (**5a**) and (**5b**) as solids in EI conditions. It is noteworthy that fragments easily related with the molecular ions are detected in all cases, as reported in Section 4.

These compounds are not enough soluble in common organic solvents (acetone, chloroform), thus NMR characterization in solution is precluded. The ^{13}C MAS NMR spectra for compounds (**1b**), (**5a**) and (**5b**) are reported in Fig. 2.

Table 1
Values of contact angles, surface energies, melting and solid–solid phase transition temperatures for tri-block fluorinated-*n*-alkanes synthesized

Compound	Structure	$\Theta_{\mathrm{H_2O}}$[a] (degrees)	$\Theta_{\mathrm{CH_2I_2}}$[b] (degrees)	γ_{tot}[c] ($mN\ m^{-1}$)	γ_{disp}[d] ($mN\ m^{-1}$)	γ_{pol}[e] ($mN\ m^{-1}$)	Melting point (°C)	Solid–solid phase transition (°C)
(**1a**)	$F(CF_2)_6(CH_2)_4(CF_2)_6F$	125.2 ± 1.8	114.1 ± 1.2	3.85	3.71	0.14	59.7	15.4
(**4a**)	$F(CF_2)_6(CH_2)_6(CF_2)_6F$	129.0 ± 1.3	115.0 ± 1.0	3.70	3.60	0.10	56.5	17.4
(**4b**)	$F(CF_2)_6(CH_2)_8(CF_2)_6F$	130.1 ± 1.7	116.2 ± 1.4	3.49	3.40	0.10	51.3	19.6
(**1b**)	$F(CF_2)_8(CH_2)_4(CF_2)_8F$	125.4 ± 1.1	116.3 ± 1.7	3.44	3.30	0.14	91.4	24.7
(**5a**)	$F(CF_2)_8(CH_2)_6(CF_2)_8F$	128.9 ± 1.3	116.0 ± 1.0	3.46	3.36	0.10	86.0	25.8
(**5b**)	$F(CF_2)_8(CH_2)_8(CF_2)_8F$	131.7 ± 1.2	102.9 ± 1.3	5.30	5.20	0.10	80.2	27.4
(–)	TK6[f]	138.3 ± 1.0	128.9 ± 1.3	(1.8)	(1.6)	(0.2)	76.0	–
(–)	TK8[g]	137.4 ± 1.3	127.5 ± 1.5	(2.0)	(1.8)	(0.2)	93.0	–
(–)	$C_{16}F_{34}$	119.4 ± 1.7	107.4 ± 2.1	6.7	5.5	1.2	127.0	–
(–)	$F(CF_2)_{12}(CH_2)_8H$	105.5 ± 1.4	87.2 ± 1.9	20.1	19.6	0.5	85.0	57.0
(–)	$F(CF_2)_{12}(CH_2)_6H$	106.5 ± 1.9	87.3 ± 2.0	19.3	18.4	0.9	81.0	46.0
(–)	PTFE	108.5 ± 1.2	88.2 ± 1.1	19.1	18.6	0.5	327.0	–

The same parameters for other perfluorinated compounds and polymers are reported.

[a] Contact angle with water.

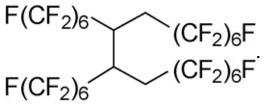
[b] Contact angle with diiodomethane.

[c] Total surface energy.

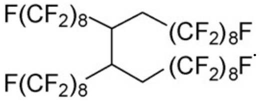
[d] Dispersion component of surface energy.

[e] Polar component of surface energy.

[f] 1,1,2,2-Tetrakis-(perfluoro-*n*-hexyl-methylene)-ethane



[g] 1,1,2,2-Tetrakis-(perfluoro-*n*-octyl-methylene)-ethane



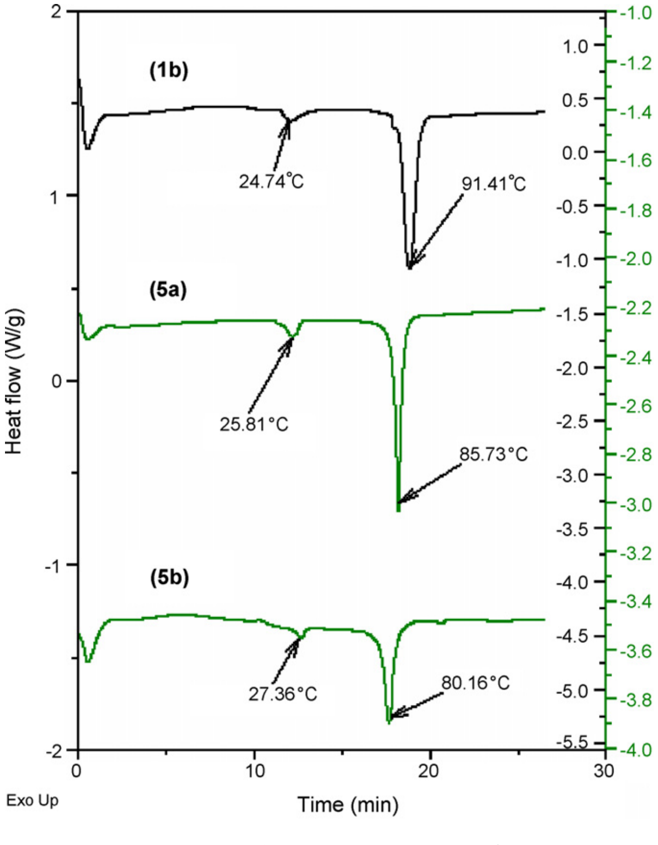


Fig. 1. DSC thermograms of $F(CF_2)_8(CH_2)_4(CF_2)_8F$ (**1b**), $F(CF_2)_8(CH_2)_6(CF_2)_8F$ (**5a**), $F(CF_2)_8(CH_2)_8(CF_2)_8F$ (**5b**).

The aliphatic part of these molecules gives rise to a broad resonance centered about at 25 ppm, while the signals of the perfluorinated moieties are detected as a broad band in the range 105–120 ppm. The ^{13}C chemical shift of methylene group (CF_2–CH_2) bonded to the fluorinated segment and of the internal chain methylene carbon atoms ($CH_2CH_2CH_2$) are reported separately in Section 4, as obtained by the deconvolution of the original aliphatic band into two components. Even if the resonance of the fluorinated carbons

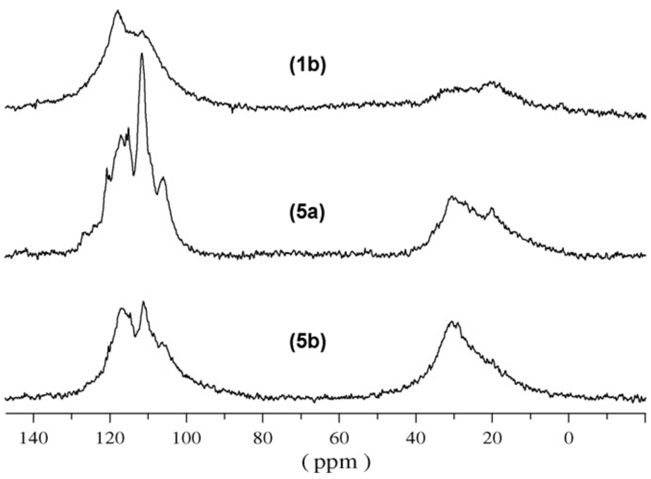


Fig. 2. ^{13}C MAS NMR spectra of $F(CF_2)_8(CH_2)_4(CF_2)_8F$ (**1b**), $F(CF_2)_8(CH_2)_6(CF_2)_8F$ (**5a**), $F(CF_2)_8(CH_2)_8(CF_2)_8F$ (**5b**).

are broad, the integration ratio of these signals with respect to the aliphatic ones is in good agreement with the expected value in both (**1a**), (**4a**), (**4b**) and (**1b**), (**5a**), (**5b**) series.

Surface free energies of the solids, γ_{tot}, were calculated using the contact angle method proposed by Owens and Wendt [45,46].

The deposition of a thin film of triblock semifluorinated *n*-alkanes on polyethene ski soles will produce an extremely hydrophobic surface. The high water repellency, determined by contact angle measurements, may indicate that fluorinated chains are capable of organizing into an ordered structure leading to the formation of a layer primarily composed of tightly packed –CF_3 groups. A uniformly organized array of trifluoromethyl groups at the interface ski/snow minimizes the adhesion of water to the moving surface responsible for kinetic losses during snow sliding [47,48].

The values of surface tensions are comparable with those of perfluoro-*n*-alkanes but the presence of a central hydrogenated chain of variable length assures compatibility and miscibility in all proportions with paraffines based ski-waxes. This allows the formulation of ski-waxes with low (0.5–2.0%), medium (2.5–5.0%) and high (5.0–15.0%) fluorine content. This parameter is of crucial importance when the characteristics of snow (temperature, water content, presence of dirt) change. The central hydrogenated core assures good adhesion and excellent retention of triblock semifluorinated *n*-alkanes on the polyethene ski soles due to good compatibility with classical ski-waxes (paraffines) and long retention on ski soles made of polyethene. Melting points of triblock semifluorinated *n*-alkanes are lower than those of diblock semifluorinated *n*-alkanes with the same balance between fluorinated and hydrogenated carbon atoms. This feature is essential to allow an easy and uniform application of the wax on ski soles. Compounds (**4a**) and (**4b**) have the lowest melting points (56.5 °C for (**4a**) and 51.3 °C for (**4b**)).

The values of contact angles and surface energies for triblock semifluorinated *n*-alkanes compared with other fluorinated compounds and polymers are reported in Table 1. There is no great variation of contact angles with the hydrogenated and fluorinated chain lengths. This result should be expected for the polar component of surface energy. In fact, both the hydrogenated core and the fluorinated tails give a comparable effect on hydrophobicity. Compounds (**1a**) and (**1b**) (4 hydrogenated carbon atoms) have a polar component of $0.14\ \text{mN m}^{-1}$. Compounds (**4a**), (**5a**) and (**4b**), (**5b**) (6 and 8 hydrogenated carbon atoms, respectively) have polar component of $0.10\ \text{mN m}^{-1}$. This suggests that an increase in the methylene sequence from 4 to 6 units have a minimal but detectable effect on the polar component of surface energy ($0.04\ \text{mN m}^{-1}$). A further increase in the hydrogenated chain length (from 6 to 8 methylene units) have no visible effect. The lengthening of fluorinated tails from 6 to 8 carbon atoms does not influence this parameter. In the series of triblock semifluorinated *n*-alkanes $F(CF_2)_6(CH_2)_m(CF_2)_6F$ (compounds (**1a**), (**4a**) and (**4b**)), the increase in the number of hydrogenated carbon atoms from 4 to 8 reduces the dispersion component of surface energy from 3.71 to $3.40\ \text{mN m}^{-1}$. The results are quite different for the series $F(CF_2)_8(CH_2)_m(CF_2)_8F$ (compounds (**1b**), (**5a**) and (**5b**)). The dispersion component is practically the same for compounds (**1b**) ($m = 4$) and (**5a**) ($m = 6$), even if a small increase ($0.06\ \text{mN m}^{-1}$) is detectable. For compound (**5b**) ($m = 8$) the value of this parameter is surprisingly high ($5.20\ \text{mN m}^{-1}$). This is probably due to an imperfect surface orientation of the perfluorinated tails. The rapid cooling from melt of (**5b**) (melting temperature, 80.2 °C) could cause a disordered superficial molecular packing of perfluorinated tails. In the case of compound (**4b**), the lower melting temperature (51.3 °C) probably allows a slower crystallization process resulting in a more ordered segregation of fluorinated chains at the interface with air.

3. Conclusion

The results described show that triblock semifluorinated *n*-alkanes synthesized in the present work have good surface properties and exhibit excellent performances as potential ski-waxes. Compounds (**4a**) and (**4b**) are the most promising. They have a long central hydrogenated core (6 carbon atoms for (**4a**) and 8 for (**4b**)) that assures excellent compatibility with paraffines, where they are incorporated as additives through a moulding process. In addition, their affinity with polyethene assures long retention on ski soles. Low melting points (56.5 °C for (**4a**) and 51.3 °C for (**4b**)) are essential to allow an easy and uniform application of the ski-wax on ski soles. Their surface energies are as low as those of perfluoro-*n*-alkanes.

4. Experimental

4.1. General experimental procedures

Perfluoro-*n*-hexyl iodide and perfluoro-*n*-octyl iodide were commercial grade reagents supplied by Elf Atochem S.A.; 1,5-hexadiene, 1,7-octadiene, 2,2′-azobis(2-methylpropionitrile) and benzoyl peroxide were purchased from Aldrich Chemical Co. A detailed description of the syntheses of the β-(perfluoro-*n*-alkyl)ethyl iodides ($C_6F_{13}CH_2CH_2I$ and $C_8F_{17}CH_2CH_2I$) is given in Ref. [49]. Other reagents employed were common laboratory materials. All the chemical reagents were used as received. All the reactions were performed under a nitrogen atmosphere.

4.1.1. Analyses

GLC analyses of the reaction mixtures were performed using a CARLO ERBA GC6000 VEGA SERIE 2 instrument (15 m × 0.25 mm silica fused capillary column, PS264 stationary phase). Typical operative conditions were: temperature program 60 °C, $15\ ^\circ\text{C min}^{-1}$ to 250 °C; He gas carrier $1\ \text{mL min}^{-1}$.

GC/MS spectra were measured on a CARLO ERBA INSTRUMENT MFC 500/QMD1000 using a silica fused capillary PS264 column (30 m × 0.25 mm) on a Finnigan Mat TSQ7000 (capillary column 30 m × 0.32 mm). Typical conditions were: temperature program 60 °C for 2 min, $10\ ^\circ\text{C min}^{-1}$ to 280 °C; He as gas carrier $1\ \text{mL min}^{-1}$.

Mass spectra of the solids were obtained on a AUTOSPEC Macromass Manchester (UK) double focusing instrument operating in electron impact (EI) mode (70 eV, 200 μA).

FTIR spectra were measured using a Nicolet Avatar 330 FT-IR spectrophotometer. Scan band width: 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200 AC spectrometer operating at 200.13 and 50.32 MHz, respectively. Peak positions are relative to Me_4Si and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). ^{19}F NMR measurements were recorded on a Varian FT 80 spectrometer operating at 74.844 MHz. Peak positions are reported relative to $CFCl_3$.

Solid state NMR analyses were performed using a Bruker AC200 spectrometer equipped for solid state analyses and operating at 50.26 MHz. Samples were spun at room temperature at 3000 kHz in 7 mm diameter zirconia rotors with Kel-F caps. The ^{13}C SPE MAS NMR (SPE = single pulse experiment, MAS = magic angle spinning) spectra were obtained with high power proton decoupling during acquisition, 30 Relaxation Delay, and processed with a 15 Hz exponential line broadening. ^{13}C chemical shifts were externally referred to solid sodium 3-(trimethyl-silyl)-1-propane sulfonate at 0 ppm. Magic angle conditions were adjusted by observing ^{79}Br spinning side bands pattern in a rotor containing 5% of KBr [50].

Differential scanning calorimetry (DSC) was performed using a TA Instrument model DSC 2920 operating with sealed stainless steel caps. The measurement were carried out in the range −30 to 220 °C and at a heating rate of 10 °C min^{-1}.

The elementary analyses were performed with a CHNS Fisons instrument, mod. EA 1108.

The surface free energies were determined using a Kruss G10/DSA10 goniometer interfaced to image-capture software. Measurements were made with de-ionized water and diiodomethane taking an average of 10–15 μL drops with each type of liquid.

4.1.2. General procedures

4.1.2.1. Preparation of 1,4-bis(perfluoro-n-alkyl)-butanes: general procedure. In a three necked Pyrex glass round bottomed flask equipped with a mechanical stirrer, thermometer and a condenser, 2-perfluoro-*n*-alkyl-1-iodo-ethane (100 mmol) was mixed with 70–100 mL of acetic anhydride which had been previously treated with powdered zinc to remove traces of acetic acid. The resulting mixture was heated at 55 °C for 5 h, during which time dust zinc (170 mmol) was added in small portions.

The solid product was separated from acetic anhydride by decantation. The excess zinc remaining was destroyed by heating the solid to 80 °C and by adding a solution of 20% aqueous HCl. The solution was cooled and the solid was recovered by vacuum filtration and it was purified by recrystallization in isopropyl ether. The purity of compounds was established by gas-liquid cromatography (GLC).

*4.1.2.2. 1,4-Bis(perfluoro-n-hexyl)-butane (**1a**).* Fifty-two percentage yield; white solid; melting point 59–60 °C; spectral data: MS *m/z* (rel. ab.%): 694 ($[M]^+$, 1%); 535 ($[M-\mathrm{CF_3CF_2},-\mathrm{HF},-\mathrm{HF}]^+$, 4%), 485 ($[M-\mathrm{CF_3(CF_2)_2},-\mathrm{HF},-\mathrm{HF}]^+$, 38%), 435 ($[M-\mathrm{CF_3(CF_2)_3},-\mathrm{HF},-\mathrm{HF}]^+$, 4%), 425 ($[M-\mathrm{CF_3(CF_2)_4}]^+$, 8%), 385 ($[M-\mathrm{CF_3(CF_2)_4},-\mathrm{HF},-\mathrm{HF}]^+$, 31%), 341 ($[M-\mathrm{CF_3(CF_2)_4},-\mathrm{CHCF},-\mathrm{HF},-\mathrm{HF}]^+$, 6%), 327 ($[M-\mathrm{CF_3(CF_2)_4},-\mathrm{CH_2CHCF},-\mathrm{HF},-\mathrm{HF}]^+$, 5%), 277 ($[M-\mathrm{CF_3(CF_2)_5},-\mathrm{CH_2CH_2},-\mathrm{HF},-\mathrm{CF_2}]^+$, 7%), 147 ($[M-\mathrm{CF_3(CF_2)_5},-\mathrm{CH_2CH_2},-(\mathrm{CF_2})_4]^+$, 35%), 91 ($[\mathrm{CF_2CH_2CH_2CH}]^+$, 100%), 77 ($[\mathrm{CF_2CH_2CH}]$, 65%), 69 ($[\mathrm{CF_3}]^+$, 100%); FTIR: $\nu_{\mathrm{C-F}}$ 1122–1321 cm^{-1}, $\nu_{\mathrm{C-H}}$ 2883–2960 cm^{-1}. δ ^{13}C SPE MAS NMR (ppm): 18.7 (–$\mathrm{CF_2}C\mathrm{H_2CH_2}$–), 28.7 (–$\mathrm{CH_2}C\mathrm{H_2CH_2}$–), 110.5–117.5 (*C*–F). Anal. calcd. for $C_{16}H_8F_{26}$: C, 27.7%; F, 71.2%. Found: C, 27.1%; F, 71.6%.

*4.1.2.3. 1,4-Bis(perfluoro-n-octyl)-butane (**1b**).* Forty-seven percentage yield; white solid; melting point 91–92 °C; spectral data: MS *m/z* (rel. ab.%): 874 ($[M-\mathrm{HF}]^+$, 1%); 854 ($[M-\mathrm{HF},-\mathrm{HF}]^+$, 1%), 635 ($[M-\mathrm{HF},-\mathrm{HF},-\mathrm{CF_3(CF_2)_3}]^+$, 1%), 525 ($[M-\mathrm{CF_3(CF_2)_6}]^+$, 6%), 505 ($[M-\mathrm{CF_3\ (CF_2)_6},-\mathrm{HF}]^+$, 50%), 377 ($[M-\mathrm{CF_3(CF_2)_7},-\mathrm{CH_2CH_2},-\mathrm{HF},-\mathrm{CF_2}]^+$, 90%); MS (EI), *m/z* (rel. ab.%): 866 ($[M-\mathrm{C_2H_4}]^{+\bullet}$, 5%); 868 ($[M-\mathrm{C_2H_2}]^{+\bullet}$, 5%), 848 ($[M-\mathrm{C_2H_2\text{-}HF}]^{+\bullet}$, 50%), 828 ($[M-\mathrm{C_2H_2\text{-}2HF}]^{+\bullet}$, 21%); FTIR: $\nu_{\mathrm{C-F}}$ 1122–1321 cm^{-1}, $\nu_{\mathrm{C-H}}$ 2883–2960 cm^{-1}; δ ^{13}C SPE MAS NMR (ppm): 18.6 (–$\mathrm{CF_2}C\mathrm{H_2CH_2}$–), 28.7 (–$\mathrm{CH_2}\ C\mathrm{H_2CH_2}$–), 110.7–117.0 (*C*–F). Anal. calcd. for $C_{20}H_8F_{34}$: C, 27.0%; F, 72.2%. Found: C, 26.8%; F, 71.1%.

4.1.3. Preparation of 1,6-bis(perfluoro-n-alkyl)-hexanes and 1,8-bis(perfluoro-n-alkyl)-octanes: general procedure

4.1.3.1. Preparation of 1,6-bis(perfluoro-n-alkyl)-2,5-diiodo-hexanes and 1,8-bis(perfluoro-n-alkyl)-2,7-diiodo-octanes

Perfluoro-*n*-alkyl iodide (200 mmol) was heated to 80 °C in a four necked Pyrex glass round bottomed flask equipped with a mechanical stirrer, thermometer, dropping funnel and a condenser. A 22% aqueous solution of $Na_2S_2O_5$ (80 mL) was then added. The resulting mixture was first flushed with nitrogen and then AIBN (8 mmol) was added. The linear diene (97 mmol) was then added dropwise and the solution was stirred for 100 min at 80 °C. The white solid that formed was decanted off, washed by stirring with water (160 mL at 80 °C), and, after cooling, was filtered off. The product was finally purified by recrystallization in chloroform.

*4.1.3.1.1. 1,6-Bis(perfluoro-n-hexyl)-2,5-diiodo-hexane (**2a**).* Eighty-five percentage yield; white solid; melting point 41–42 °C; spectral data: MS *m/z* (rel. ab.%): 720 ($[M-\mathrm{I},-\mathrm{I}]^+$, 3%); 719 ($[M-\mathrm{I},-\mathrm{HI}]^+$, 12%), 699 ($[M-\mathrm{I},-\mathrm{HI},-\mathrm{HF}]^+$, 6%), 488 ($[M-\mathrm{I},-\mathrm{C_6F_{13}CH_2CHCH_2}]^+$, 7%), 327 ($[\mathrm{C_6F_{12}{=}CH\ CH_2}]^+$, 12%), 277 ($[M-\mathrm{I},-\mathrm{HF},-\mathrm{CF_2}]^+$, 8%), 127 ($[\mathrm{I}]^+$, 30%), 69 ($[\mathrm{CF_3}]^+$, 100%); FTIR: $\nu_{\mathrm{C-F}}$ 1122–1321 cm^{-1}, $\nu_{\mathrm{C-H}}$ 2883–2960 cm^{-1}, $\nu_{\mathrm{C-I}}$ 700–734 cm^{-1}; ^{1}H NMR ($CD_3\ COCD_3$), δ: 4.52 (m, CHI, 2H); 3.0 (m, CH_2CF_2, 4H), 2.06 (m, CH_2, 4H); ^{19}F NMR (CD_3COCD_3), δ: 82.28 (m, CF_3), −114.24 (CF_2CH_2), −122.93, −123.99, −124.73, −127.35 (CF_2). Anal. calcd. for $C_{18}H_{10}F_{26}I_2$: C, 22.2%; F, 50.7%. Found: C, 21.6%; F, 49.3%.

*4.1.3.1.2. 1,8-Bis(perfluoro-n-hexyl)-2,7-diiodo-octane (**2b**).* Eighty percentage yield; white solid; melting point 29–30 °C; spectral data: MS *m/z* (rel. ab.%): 750 ($[M-\mathrm{I},-\mathrm{I}]^+$, 7%); 749 ($[M-\mathrm{I},-\mathrm{HI}]^+$, 12%), 729 ($[M-\mathrm{I},-\mathrm{HI},-\mathrm{HF}]^+$, 6%), 517 ($[M-\mathrm{I},-C_6F_{13}CH_2CHCH_2]^+$, 15%), 327 ($[C_6F_{12}{=}CHCH_2]^+$, 20%), 699 ($[M-\mathrm{I},-\mathrm{HF},-CF_2]^+$, 12%), 127 ($[\mathrm{I}]^+$, 35%), 69 ($[CF_3]^+$, 100%); FTIR: $\nu_{C\text{–}F}$ 1122–1321 cm^{-1}, $\nu_{C\text{–}H}$ 2883–2960 cm^{-1}, $\nu_{C\text{–}I}$ 700–734 cm^{-1}; ^1H NMR (CD_3COCD_3), δ: 4.47 (m, CHI, 2H); 3.04 (m, CH_2CF_2, 4H), 2.03 (m, CH_2, 4H), 1.98 (m, CH_2, 4H); ^{19}F NMR (CD_3COCD_3), δ: 82.35 (m, CF_3), −114.29 (CF_2CH_2), −122.97, −124.04, −124.60, −127.41 (CF_2). Anal. calcd. for $C_{20}H_{14}F_{26}I_2$: C, 24.0%; F, 49.3%. Found: C, 24.8%; F, 50.1%.

*4.1.3.1.3. 1,6-Bis(perfluoro-n-octyl)-2,5-diiodo-hexane (**3a**).* Eighty-six percentage yield; white solid; melting point 68–69 °C; spectral data: MS *m/z* (rel. ab.%): 920 ($[M-\mathrm{I},-\mathrm{I}]^+$, 1%); 880 ($[M-\mathrm{I},-\mathrm{I},-\mathrm{HF},-\mathrm{HF}]^+$, 1%), 601 ($[M-\mathrm{I},-C_8F_{17}CH_2CH]^+$, 1%), 587 ($[C_8F_{17}CH_2CH(I)CH_2]^+$, 1%), 474 ($[C_8F_{17}CH_2CHCH_2CH_2]^+$, 20%), 446 ($[C_8F_{17}CH_2CH]^+$, 15%), 426 ($[C_8F_{16}{=}CHCH]^+$, 15%), 377 ($[C_7F_{14}CH_2CH]^+$, 5%), 127 ($[\mathrm{I}]^+$, 35%), 77 ($[CF_2CH_2CH]^+$, 100%), 69 ($[CF_3]^+$, 80%); FTIR: $\nu_{C\text{–}F}$ 1122–1321 cm^{-1}, $\nu_{C\text{–}H}$ 2883–2960 cm^{-1}, $\nu_{C\text{–}I}$ 700–734 cm^{-1}; ^1H NMR (CD_3COCD_3), δ: 4.52 (m, CHI, 2H); 3.1 (m, CH_2CF_2, 4H), 2.07 (m, CH_2, 4H); ^{19}F NMR (CD_3COCD_3), δ: 82.24 (m, CF_3), −114.22 (CF_2CH_2), −122.91, −123.97, −124.71, −127.33 (CF_2). Anal. calcd. for $C_{22}H_{10}F_{34}I_2$: C, 22.5%; F, 55.0%. Found: C, 22.0%; F, 53.1%.

*4.1.3.1.4. 1,8-Bis(perfluoro-n-octyl)-2,7-diiodo-octane (**3b**).* Eighty-two percentage yield; white solid; melting point 57–58 °C; spectral data: MS *m/z* (rel. ab.%): 947 ($[M-\mathrm{HI},-\mathrm{HI}]^+$, 1%); 927 ($[M-\mathrm{I},-\mathrm{HI},-\mathrm{HF}]^+$, 1%), 601 ($[C_8F_{17}CH_2CH(I)CH_2CH_2]^+$, 1%), 587 ($[C_8F_{17}CH_2CH(I)CH_2]^+$, 3%), 488 ($[C_8F_{17}CH_2CH(I)(CH_2)_3]^+$, 10%), 427 ($[C_8F_{16}CHCH_2]^+$, 20%), 127 ($[\mathrm{I}]^+$, 22%), 69 ($[CF_3]^+$, 100%); FTIR: $\nu_{C\text{–}F}$ 1122–1321 cm^{-1}, $\nu_{C\text{–}H}$ 2883–2960 cm^{-1}, $\nu_{C\text{–}I}$ 700–734 cm^{-1}; ^1H NMR (CD_3COCD_3), δ: 4.47 (m, CHI, 2H); 2.97 (m, CH_2CF_2, 4H), 2.02 (m, CH_2, 4H), 1.99 (m, CH_2, 4H); ^{19}F NMR (CD_3COCD_3), δ: 82.19 (m, CF_3), −114.17 (CF_2CH_2), −122.95, −123.81, −124.65, −127.29 (CF_2). Anal. calcd. for $C_{24}H_{14}F_{34}I_2$: C, 24.0%; F, 53.7%. Found: C, 23.0%; F, 52.6%.

4.1.3.2. Preparation of 1,6-bis(perfluoro-n-alkyl)-hexanes and 1,8-bis(perfluoro-n-alkyl)-octanes

In a four necked Pyrex glass round bottomed flask equipped with a mechanical stirrer, condenser, thermometer, 1,6-bis(perfluoro-*n*-alkyl)-2,5-diiodo-hexanes or 1,8-bis(perfluoro-*n*-alkyl)-2,7-diiodo-octanes (130 mmol) was mixed with 130 mL of ethanol and 70 mL of HCl 37%. The resulting mixture was heated at 80 °C with stirring. Powdered zinc (330 mmol) was added in small portions over a period of 5 h and the reaction mixture was stirred for further 4 h.

Aqueous HCl 37% (70 mL) was added and the mixture was stirred for further 2 h at 80 °C to destroy excess zinc. The white solid that formed was decanted off, washed by stirring with water (480 mL at 80 °C), and, after cooling, was filtered off. The product was finally purified by recrystallization in methyl-*tert*-butyl ether.

*4.1.3.2.1. 1,6-Bis(perfluoro-n-hexyl)-hexane (**4a**).* Fifty-five percentage yield; white solid; melting point 56–57 °C; spectral data: MS *m/z* (rel. ab.%): 721 ($[M-\mathrm{H}]^+$, 1%); 453 ($[M,-C_5F_{11}]^+$, 20%), 375 ($[C_6F_{13}(CH_2)_4]^+$, 35%), 69 ($[CF_3]^+$, 80%); FTIR: $\nu_{C\text{–}F}$ 1122–1321 cm^{-1}, $\nu_{C\text{–}H}$ 2883–2960 cm^{-1}; δ ^{13}C SPE MAS NMR (ppm): 20.7 (–$CF_2\mathit{C}H_2CH_2$–), 30.9 (–$CH_2\mathit{C}H_2CH_2$–), 104.5–121.0 (*C*–F). Anal. calcd. for $C_{18}H_{12}F_{26}$: C, 29.9%; F, 68.4%. Found: C, 29.8%; F, 69.2%.

*4.1.3.2.2. 1,8-Bis(perfluoro-n-hexyl)-octane (**4b**).* Sixty-two percentage yield; white solid; mp 51–52 °C; spectral data: MS *m/z* (rel. ab.%): 750 ($[M]^+$, 3%); 481 ($[M,-C_5F_{11}]^+$, 22%), 375 ($[C_6F_{13}(CH_2)_4]^+$, 40%), 69 ($[CF_3]^+$, 80%); FTIR: ν_{CF} 1122–1321 cm^{-1}, ν_{CH} 2883–2960 cm^{-1}; δ ^{13}C SPE MAS NMR (ppm): 20.0 (–$CF_2\mathit{C}H_2CH_2$–), 29.5 (–$CH_2\mathit{C}H_2CH_2$–), 105.5–120.5 (*C*–F). Anal. calcd. for $C_{20}H_{16}F_{26}$: C, 32.0%; F, 65.8%. Found: C, 31.5%; F, 65.2%.

*4.1.3.2.3. 1,6-Bis(perfluoro-n-octyl)-hexane (**5a**).* Sixty-two percentage yield; white solid; mp 85–86 °C; spectral data: MS *m/z* (rel. ab.%): 903 ($[M-\mathrm{F}]^+$, 1%); 883 ($[M-\mathrm{F},-\mathrm{HF}]^+$, 1%), 553 ($[C_8F_{17}(CH_2)_6CF_2]^+$, 1%), 489 ($[C_8F_{17}(CH_2)_5]^+$, 45%), 455 ($[C_8F_{16}CHCH_2CH_2CH_2]^+$, 40%), 441 ($[C_8F_{16}CHCH_2CH_2]^+$, 12%), 426 ($[C_8F_{16}{=}CHCH]^+$, 15%), 377 ($[C_7F_{14}CH_2CH]^+$, 5%), 91 ($[CF_2CH_2CH_2CH]^+$, 65%); MS (EI), *m/z* (rel. ab.%): 902 ($[M-\mathrm{HF}]^{+\bullet}$, 10%); 553 ($[C_8F_{17}(CH_2)_6CF_2]^+$, 45%), 533 ($[C_8F_{17}(CH_2)_6CF_2\text{-}HF]^{+\bullet}$, 7%), 489 ($[C_8F_{17}(CH_2)_5]^{+\bullet}$, 30%), 475 ($[C_8F_{17}(CH_2)_4]^+$, 36%); FTIR: $\nu_{C\text{–}F}$ 1122–1321 cm^{-1}, $\nu_{C\text{–}H}$ 2883–2960 cm^{-1}; δ ^{13}C SPE MAS NMR (ppm): 18.9 (–$CF_2\mathit{C}H_2CH_2$–), 29.4 (–$CH_2\mathit{C}H_2CH_2$–), 105.5–120.2 (*C*–F). Anal. calcd. for $C_{22}H_{12}F_{34}$: C, 28.6%; F, 70.0%. Found: C, 29.0%; F, 69.1%.

*4.1.3.2.4. 1,8-Bis(perfluoro-n-octyl)-octane (**5b**).* Sixty percentage yield; white solid; melting point 80–81 °C; spectral data: MS *m/z* (rel. ab.%): 581 ($[C_8F_{17}(CH_2)_8CF_2]^+$, 1%); 503 ($[C_8F_{17}(CH_2)_6]^+$, 40%), 489 ($[C_8F_{17}(CH_2)_5]^+$, 100%), 69 ($[CF_3]^+$, 90%); MS (EI), *m/z* (rel. ab.%): 948 ($[M-H_2]^{+\bullet}$, 4%); 930 ($[M-\mathrm{HF}]^{+\bullet}$, 0.2%); 503 ($[C_8F_{17}(CH_2)]^{+\bullet}$, 20%), 489 ($[C_8F_{17}(CH_2)_5]^{+\bullet}$, 50%), 461 ($[C_8F_{17}(CH_2)_3]^{+\bullet}$, 5%); FTIR: $\nu_{C\text{–}F}$ 1122–1321 cm^{-1}, $\nu_{C\text{–}H}$ 2883–2960 cm^{-1}; δ ^{13}C SPE MAS NMR (ppm): 22.3 (–$CF_2\mathit{C}H_2CH_2$–), 30.4 (–$CH_2\mathit{C}H_2CH_2$–), 106.0–119.8 (*C*–F). Anal. calcd. for $C_{24}H_{16}F_{34}$: C, 29.8%; F, 68.0%. Found: C, 30.3%; F, 67.1%.

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