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Synthesis of aliphatic diamine and polyetherimide with long perfluoroalkyl side chain

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Abstract

The monomer, 2-(perfluorohexylmethyl)butan-1,4-diamine (TFD), was prepared from itaconic acid dimethyl ester via the addition of perfluorohexyl iodide followed by the gradual transformation of ester groups into amino groups. The polymerization of bisphenol-A diphthalic anhydride (BAPA) with TFD led to hydrophobic fluorinated polyetherimide (FPEI) with $R_F = C_6F_{13}$ side chain. This polymer makes it possible to cast films.

Keywords: Fluorinated-alkylmethyldiamines; Fluorinated polyetherimide; Hydrophobic non-porous films

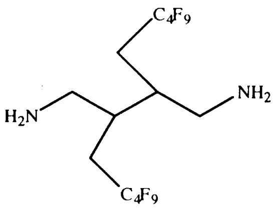
1. Introduction

Fluoropolymers [1] and particularly fluorinated polyimides [2,3] are the subject of an intensive development with regard to their interesting thermal, chemical and physical properties. The hydrophobic nature of the fluorinated polyimides makes them potentially attractive for coating applications, casing and sheathing as well as specific technologies. Recently, they were selected for preparing selective dense membranes used in organic–organic liquid mixtures separation [4]. However, the transformation processing of these thermoplastic materials and the mechanical properties of the film products are often sensitive points due to the rigidity of the macromolecules chains. Indeed, more often than not the aromatic groups that are involved in the polymer structure may lead to brittleness.

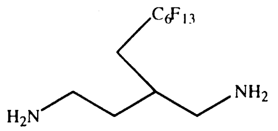
The most common fluorinated polyimides are obtained via the polymerization of 2,2′-bis[3,4-(dicarboxyphenyl)-hexafluoropropan]dianhydride (6FDA) with fluorinated or non-fluorinated aromatic diamines [5–8] giving materials showing a variable fragility. Bisphenol-A diphthalic anhydride (BAPA), with or without fluoromethyl groups, brings to some extent flexibility properties to the polymer chain thanks to the ether linkage. On the other hand, very few fluorinated diamines are available and often they do not show sufficient structural qualities to enhance the flexibility.

It seems proved that a strong hydrophobicity of polymers is generally connected to the presence of long fluorinated alkyl chains $-(CF_2)_n-CF_3$ fixed on the main chain [9–12]. Moreover, according to the n value, these pendant chains can gradually change the interchain distances, the solid morphology and the bulk structure, finally bringing about important consequences for the rigidity–flexibility characteristics of the materials.

All things considered, hydrophobicity and easy processing, we performed the synthesis of a new series of polyetherimides and copolyetherimides containing pendant perfluoroalkyl chains by polymerizing BAPA with a mixture of *m*-phenylenediamine (*m*-PDA) and 2,3-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)butan-1,4-diamine (NFD) [13]. This series is now extended using 2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)butan-1,4-diamine; 2-(perfluorohexylmethyl)butan-1,4-diamine (TFD). This article describes the synthesis and characterization of TFD and the related polyetherimide based on the polymerization of BAPA with TFD.



NFD



TFD

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2. Results and discussions

2.1. Synthesis of 2-(perfluorohexylmethyl)butan-1, 4-diamine

The synthesis of the perfluorinated diamine began by introducing the perfluorinated side chain. The starting molecule was itaconic acid dimethyl ester which can react efficiently with various perfluorinated alkyl iodides (R_FI with $R_F = C_4F_9$, C_6F_{13}) [14]; then the two diesters groups were transformed into amine groups in good yield using classic reactions.

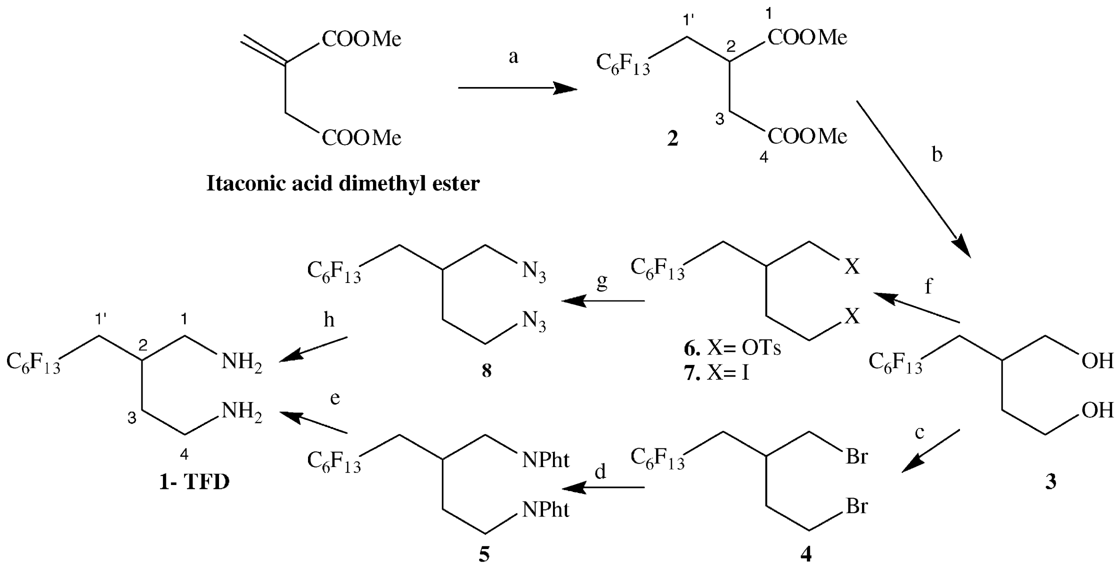
The synthesis of the diamine was carried out as outlined in Scheme 1. The reaction between perfluorohexyl iodide and itaconic acid dimethyl ester in presence of active zinc led to fluorinated diester **2** which was reduced to the corresponding diol **3** using $LiAlH_4$ and THF as a solvent. The transformation of the diol into the corresponding dihalide (**4** or **7**) was done using various procedures (HBr/H_2SO_4, PBr_3, $I_2/H_3PO_4–P_2O_5$). The best results were obtained by substitution of the tosylated derivative (**6**) with NaI; diiodide **7** was obtained in more than 80% yield.

Starting with the dihalide (**4** or **7**), the diamine was formed following the classic method of Gabriel. The treatment of the bromide derivative **4** with potassium phthalimide in DMF at 80 °C provided the corresponding diphthalate **5** in a good yield (65%). The deprotection of **5** with hydrazine gave the crude diamine **1** (TFD) in satisfactory yield (59%). Another method was to treat the diiodide derivative **7** with sodium azide. This gave the corresponding azide **8** which was reduced to the desired diamine **1** with H_2/Pd–C in a good yield (89%). Many attempts to purify **1**, obtained from **5** or **8**, were unsuccessful. Particularly, we tried the purification by salt formation as well as by column chromatography. We noticed the instability of the molecule and its partial degradation in such experimental conditions. In fact, diamines of this kind are very sensitive to the carbonation and require to be protected from air. An alternative solution was the purification of the diphthalate **5** by column chromatography using silica and a 25% ethyl acetate/75% petroleum ether mixture as eluant. The deprotection of **5**, leading to **1**, was carried out just before the polymerization. The NMR spectra were consistent with the TFD structure and showed no impurity above 3% concentration. Currently, we are attempting to elaborate a specific purification method of **1**.

2.2. Synthesis of fluorinated polyetherimide (FPEI)

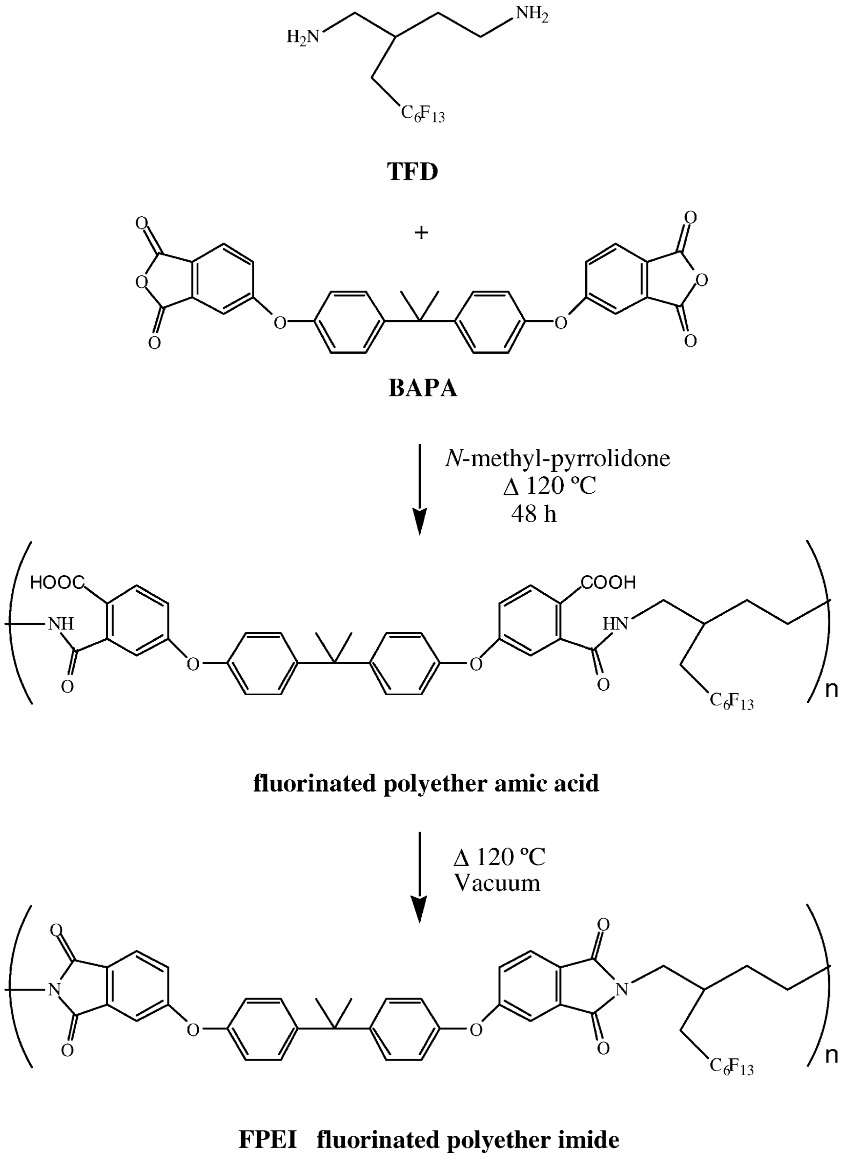
Fluorinated polyetherimide (FPEI) was prepared by heating an equimolar amount of BAPA and fresh TFD in *N*-methyl-pyrrolidinone (NMP) under argon atmosphere at 120 °C for 48 h (Scheme 2).

Generally, non-fluorinated diamines react with dianhydrides at room temperature. In the case of fluorinated diamines, we observed a slow increase of the solution viscosity with time and we deduced a lower reactivity of the fluorinated diamine than those of the non-fluorinated diamines. This most probably results from its strong electron-withdrawing nature. Therefore, to convert the full amount of TFD, 120 °C temperature and long reaction time conditions were indispensable. An incomplete imidization of the polymer was first obtained. In this kind of step-reaction, generally a poly(ether amic acid) intermediate



a. $C_6F_{13}I$ / $Zn/CH_3CH_2COOH/CH_2Cl_2$ b. $LiAlH_4$ / THF c. PBr_3 d. Potassium phthalimide/DMF e. Hydrazine/ EtOH f. 1. TsCl / py 2. NaI / acetone g. NaN_3 DMF h. H_2 / Pd-C

Scheme 1.



Scheme 2.

was obtained by the opening of the anhydride ring of BAPA [15]. Then, one carboxylic acid group and one amide group result from the reaction of BAPA with the diamine. So, the poly(ether amic acid) intermediate and the expected polyetherimide were present together in the solution. The mixture of the polymers was precipitated in a EtOH/H_2O mixture. To achieve chain extension to higher molecular weights and to complete imidization, the mixture of polymers was dried in a vacuum oven at 140 °C for 12 h, allowing the dehydration of the amid-acid structure to lead to the imide structure and to give FPEI as the only product.

In order to evaluate the characteristics of FPEI we also polymerized BAPA with *m*-PDA. The resulting polymer, that we named UPEI, was obtained by a similar procedure. It provided us with a useful comparison. In fact, UPEI is the normal ULTEM 1000 polyether imide developed by General Electric Plastics.

According to the gel permeation chromatography (GPC) data, molecular weights M_n and M_w are not very high but the polydispersity value seems to be correct (Table 1). The purity degree of TFD can account for the relatively low molecular weight. Differential scanning calorimetry (DSC) showed that FPEI is amorphous. The glass transition temperature, T_g, decreases from 217 °C for the UPEI sample to 113 °C for FPEI. This can be attributed to the aliphatic chain segments leading to an easy change in the conformation of the macromolecules. Furthermore, the bulky fluorinated side chains keep the macromolecules away from each other and may allow a few movements of all chain segments.

UPEI and ULTEM showed slightly different degradation temperatures, respectively 385 and 430 °C (literature data) under atmosphere of argon, partly because the polymer samples were not prepared in the same manner. UPEI

Table 1
Characteristics of polyetherimides

	M_w	M_n	T_g (°C)	T_d (°C, air)[a]		T_d (°C, argon)[a]	
				10%	50%	10%	50%
UPEI	30,000	12,000	217	385	–	375	–
FPEI	12,200	6,000	113	440	545	485	525

[a] Atmosphere under which thermal degradation temperature, defined as *x*% weight loss, was measured.

Table 2
Contact angles and surface energies of polyetherimide

	θ_{H_2O} (°)	$\theta_{CH_2I_2}$ (°)	γ_s^d (mN m^{-1})	γ_s^p (mN m^{-1})	γ_s (mN m^{-1})
UPEI	88	32	44.5	0.8	45.3
FPEI	90	77	15.8	7.0	22.8

samples result from the cast-evaporation method and ULTEM samples result from extrusion.

The degradation temperature is affected by the fluorinated side chains. A loss of 10% weight of polymer occurred above 440 °C under air and 485 °C under argon indicating reasonable stability of the polymers (Table 1).

The wettability, measured by the water contact angle, slightly decreases from UPEI to FPEI. The combination of water and diiodomethane contact angles shows the increase of hydrophobicity ($\gamma_s = 22.8$ mN m^{-1}) of the FPEI film surface (Table 2).

We tried to elaborate films from a 10% weight polymer solution in NMP which was cast on a glass plate and then the solvent evaporated. The first attempts gave films greater than 30 μm thick standing the test of handling.

3. Experimental

3.1. General

^{1}H, ^{13}C, ^{19}F NMR spectra were recorded with a Bruker AC instrument. Tetramethyl silane (TMS) and fluorotrichloromethane were used as internal references for ^{1}H and ^{19}F NMR spectra, respectively. FTIR spectra were recorded with a Bruker IFS 25 spectrophotometer. Molecular weights of polymers were determined by GPC with a Waters instrument using tetrahydrofuran (THF) as eluant. The system was calibrated with polystyrene standards. DSC data were obtained using a Mettler DSC 30 instrument under N_2 atmosphere. Thermogravimetric analysis (TGA) was effected using a Netzch Garatebau STA 409 instrument under atmosphere of air or argon.

Static measurements of the contact angle were made with a Kruss G1 apparatus. The polymer solution was placed on a metal support and when the solvent evaporated, a thin film was formed and the measurements were made with water and diiodomethane.

The method developed by Owens and Wendt [16] allows the calculation of the surface energy γ_s, its dispersive (γ_s^d) and polar (γ_s^p) components, from the contact angle values (θ), the superficial energy of two liquids ($\gamma_{L\,H_2O} = 78.8$ m Nm^{-1} and $\gamma_{L\,CH_2I_2} = 50.8$ mN m^{-1}), the dispersive component ($\gamma^d_{L\,H_2O} = 21.8$ m Nm^{-1} and $\gamma^d_{L\,CH_2I_2} = 49.5$ mN m^{-1}) and polar component ($\gamma^p_{L\,H_2O} = 51$ mN m^{-1} and $\gamma^p_{L\,CH_2I_2} = 1.3$ m Nm^{-1}).

3.2. 2-(Perfluorohexylmethyl) succinic acid dimethyl ester (**2**)

To a stirred solution of itaconic acid dimethyl ester (70.5 ml, 0.5 mol), propionic acid (37 ml, 0.5 mol) and activated zinc (32.7 g, 0.5 mol) in CH_2Cl_2 (250 ml), perfluorohexyliodide (108 ml, 0.5 mol) was added dropwise during 1.5 h. The temperature of the mixture rose to 40 °C. The reaction mixture was dissolved in Et_2O (2 l) and the solution was successively washed with 10% aqueous HCl (3 × 200 ml), water (3 × 200 ml) and dried over Na_2SO_4. Removal of solvent gave crude perfluorohexyl derivated **2** (215.6 g, 90%), which was used for the next step without further purification.

IR (ν_{max}, cm^{-1}): 2959, 1740, 1440, 1351, 1145, 1034.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.53 (s, 3H, OMe), 3.49 (s, 3H, OMe), 3.02 (q, 1H, $J = 6$ Hz, H-2), 2.60 (dd, 1H, $J = 17$ and 7 Hz, H-3$_A$), 2.51 (dd, 1H, $J = 17$ and 6 Hz, H-3$_B$), 2.45 (m, 1H, H-1$'_A$), 2.20 (m, 1H, H-1$'_B$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 173.4 (C-1), 171.6 (C-4), 52.9, 52.4 (2OMe), 35.8 (C-3), 34.7 (C-2), 31.9 (C-1$'$) and 118.7 (m, CF_3), 116.1, 113.7, 113.2, 111.4, 108.9 (5m, 5CF_2).

^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm): −81.9 (CF_3), −114.3, −122.8, −123.9, −124.5, −127.2 (5CF_2).

FABMS: *m/z* (%): 479 $(M + H)^+$ (28), 447 (100), 403 (23), 433 (14), 389 (19), 377 (26), 209 (5), 169 (17), 117 (12), 55 (100), 31 (86).

3.3. 2-(Perfluorohexylmethyl)butan-1,4-diol (**3**)

$LiAlH_4$ (9.25 g, 0.24 mol) was added to a solution of **2** (105.8 g, 0.22 mol) in dry THF (2 l) at 0 °C. The reaction mixture was stirred for 2 h at room temperature. After that, few drops of water were added at 0 °C until the excess $LiAlH_4$ was eliminated. Then, ether (2 l) and a mixture of $Na_2SO_4/NaHCO_3$ (1:1, 200 g) were added and the mixture was stirred for 2 h. After filtration and evaporation of the solvent, compound **3** (84.5 g, 91%) was obtained as a pale viscous liquid.

IR (ν_{max}, cm^{-1}): 3330, 2944, 1237, 1145, 1047, 695.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.7–3.5 (m, 4H, H-1,4), 2.2–1.7 (m, 5H, H-2,3,1$'$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 65.4 (C-1), 60.3 (C-4), 35.7 (C-3), 32.6 (C-2), 31.9 (C-1$'$) and 121.8 (m, CF_3), 119.3, 116.1, 113.3, 111.2, 108.2 (5 m, 5CF_2).

^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm): −81.5 (CF_3), −113.7, −122.5, −123.6, −124.2, −126.9 (5CF_2).

FABMS: *m/z* (%): 423 $(M+H)^+$ (28), 405 (100), 403 (23), 387 (22), 119 (14), 69 (95), 31 (85).

3.4. 1,4-Dibromo-2-(perfluorohexylmethyl) butane (**4**)

PBr_3 (3 ml, 30 mmol) was added to diol **3** (10.1 g, 23.9 mmol) at 0 °C. After 30 min, the mixture was heated at 80 °C for 12 h. After that, 10 ml of water was added at 0 °C and two layers appeared. The aqueous layer was extracted with Et_2O (3×100 ml). The Et_2O solutions were added to the organic layer. All the solutions were washed with 10% aqueous Na_2CO_3 (3×50 ml), followed by brine (3×50 ml) and dried over Na_2SO_4. The filtrate was concentrated to give an oil which was purified by distillation. The dibromo derivated **4** (6.3 g, 48%) was obtained as a colorless oil.

IR (ν_{max}, cm^{-1}): 2972, 1230, 1150, 490.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.52 (m, 2H, H-1), 3.38 (m, 2H, H-4), 2.49 (s.a., 1H, H-2), 2.3 (m, 1H, $\text{H1}'_{\text{A}}$), 2.1–1.9 (m, 3H, H-3,$1'_{\text{B}}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 37.5 (C-1), 35.9 (C-3), 33.5 (C-1′), 31.3 (C-2), 39.9 (C-4) and 121.3 (m, CF_3), 118.8, 116.3, 113.8, 111.4, 108.6 (5m, $5CF_2$).

^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm): -81.5 (CF_3), -113.5, -122.5, -123.6, -124.2, -126.9 ($5CF_2$).

FABMS: *m/z* (%): 548 $(M+H)^+$ (8), 467 (38), 387 (55), 367 (9), 327 (10), 113 (18), 109 (34), 69 (100), 41(82).

3.5. 1,4-(Di-N-phthalimide)-2-(perfluorohexylmethyl) butane (**5**)

Solid potassium diphthalimide (0.928 g, 4.86 mmol) was added to a stirred solution of **4** (1.065 g, 1.94 mmol) in DMF (5 ml) and the mixture was heated at 80 °C for 4 h. Then, water was added (5 ml) and the formed precipitate was filtrated off, dissolved in CH_2Cl_2 and the solution was washed many times with water and dried over Na_2SO_4. The filtrate was concentrated to give **5** (0.822 g, 62%) as a white solid.

IR (ν_{max}, cm^{-1}): 3027, 2950, 2870, 1780, 1720, 1623, 1487.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.85 (m, 4H, Ar), 7.74 (m, 4H, Ar), 3.84 (m, 4H, H-1,4), 2.48 (q, 1H, $J = 6$ Hz, H-2), 2.40–2.26 (m, 2H, H1′), 1.88 (c, 2H, $J = 6$ Hz, H-3).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 168.6, 167.0 (4CO), 134.6, 134.4 (4CH, *m*-Ar), 132.4, 132.2 (4C, Ar), 123.9, 123.6 (4CH, *o*-Ar), 42.1 (C-1), 35.6 (C-4), 33.2 (C-1′), 31.5 (C-3), 29.9 (C-2) and 121.4 (m, CF_3), 119.1, 116.2, 113.3, 115.5, 108.8 (5m, $5CF_2$).

^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm): -81.4 (CF_3), -113.2, -122.4, -123.5, -124.0, -126.8 ($5CF_2$).

FABMS: *m/z* (%): 681 $(M+H)^+$ (25), 551 (6), 534 (9), 404 (11), 160 (100), 105 (40), 31 (58).

3.6. 2-(Perfluorohexylmethyl)butan-1,4-diol ditosylate (**6**)

To a solution of **3** (84.5 g, 0.20 mol) in pyridine (500 ml) at 0 °C was added TsCl (99.1 g, 0.52 mol). The mixture was stirred at 0–5 °C for 12 h, then ice (100 g) was added and the stirring continued for 30 min. The solution was extracted with Et_2O (3×1 l) and the combined organic layers were successively washed with water (3×200 ml), 10% aqueous HCl (3×200 ml), 5% aqueous $NaHCO_3$ (3×200 ml), brine (3×200 ml) and dried over Na_2SO_4. Removal of the solvent gave crude tosyl derivate **6** as pale yellow oil.

IR (ν_{max}, cm^{-1}): 2972, 2950, 1599, 1440, 1401, 1366, 665.

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm): 7.71 (d, 4H, $J = 8$ Hz, Ar), 7.31 (d, 2H, $J = 8$ Hz, Ar), 7.27 (d, 2H, $J = 8$ Hz, Ar), 3.95 (m, 4H, H-1,4), 2.40 (s, 6H, Ar*CH₃*), 2.24 (m, 1H, H-2), 2.2–1.9 (m, 2H, H-1′), 1.78 (m, 2H, $J = 6$ Hz, H-3).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 145.8, 145.6 (C*p*, Ar), 130.4 (4CH, *m*-Ar), 128.3 (4CH, *o*-Ar), 133.0, 132.6 (2C, Ar), 70.7 (C-1), 67.2 (C-4), 31.4 (C-1′), 30.8 (C-3), 28.8 (C-2), 22.0 ($2CH_3Ar$) and from 108 to 122 (6 m, weak intensity, CF_3–$(CF_2)_5$–).

^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm): -81.4 (CF_3), -113.7, -122.5, -123.6, -124.2, -126.8 ($5CF_2$).

FABMS: *m/z* (%): 731 $(M+H)^+$ (4), 638 (100), 559 (6), 482 (7), 403 (11), 387 (11), 173 (35), 155 (98), 91 (100), 31 (52).

3.7. 1,4-Diiodo 2-(perfluorohexylmethyl) butane (**7**)

Solid NaI (26.3 g, 175.2 mmol) was added to a stirred solution of **6** (32 g, 43.8 mmol) in acetone (300 ml) and the mixture was heated under reflux for 3 h. Then, the solvent was evaporated and the residue diluted with water (300 ml). The aqueous phase was extracted with Et_2O (3×500 ml) and the combined organic layers were washed with H_2O (3×150 ml), 10% aqueous solution of Na_2SO_3 (3×150 ml), 5% aqueous $NaHCO_3$ (3×150 ml), brine (3×150 ml) and dried over Na_2SO_4. The filtrate was concentrated to give an oil which was purified by column chromatography with petroleum ether–Et_2O (98/2) as eluant affording iodo derivate **7** (23 g, 82%) as a colorless oil.

IR (ν_{max}, cm^{-1}): 2950, 1263, 1234, 1182, 1145, 714.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.32 (d, 1H, $J = 11$ Hz, H-1_{A}), 3.27 (dd, 1H, $J = 11$ and 3 Hz, H-1_{B}), 3.16 (dd, 1H, $J = 11$ and 6 Hz, H-4_{A}), 3,04 (dd, 1H, $J = 10.6$ Hz, H-4_{B}), 2.30 (m, 1H, H-2), 2,00–1,80 (m, 4H, H-3,1′).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 38.8 (C-3), 35.1 (C-1′), 32.7 (C-2), 13.6 (C-1), 2.0 (C-5) and 121.3 (m, CF_3), 118.9, 116.1, 113.8, 113.2, 111.4 (5m, $5CF_2$).

^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm): -81.9 (CF_3), -113.4, -122.7, -123.8, -124.4, -127.2 ($5CF_2$).

FABMS: *m/z* (%): 642 $(M+H)^+$ (8), 641 (7), 515 (91), 387 (4), 327 (8), 155 (35), 119 (28), 69 (100), 31 (92).

3.8. 2-(Perfluorohexylmethyl) butane 1,4-diazide (**8**)

Solid NaN_3 (5 g, 77.1 mmol) was added to a stirred solution of **4** (12.4 g, 19.3 mmol) in DMF (50 ml) and the mixture was heated at 80 °C for 4 h. Then, water was added

(100 ml) and the mixture was extracted with Et_2O (3×500 ml). The combined organic layers were washed with brine (3×100 ml) and dried over Na_2SO_4. The filtrate was concentrated to give an oil which was purified by column chromatography with petroleum ether–Et_2O (95/5) as eluent giving diazide derivate **8** (8.8 g, 96%) as a colorless oil.

IR (ν_{max}, cm^{-1}): 2950, 2084, 1366, 1236, 1147, 812, 732.

^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.42 (dd, 1H, $J = 13$ and 5 Hz, H-1_A), 3.39 (dd, 1H, $J = 13$ and 4 Hz, H-1_B), 3.31 (t, 2H, $J = 7$ Hz, H-4), 3.04 (dd, 1H, $J = 10.6$ Hz, H-4_B), 2.30 (m, 1H, H-2), 2.00–1.80 (m, 4H, H-3, 1′).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 53.1 (C-1), 47.7 (C-4), 31.1 (C-1′), 30.4 (C-3), 28.7 (C-2) and 121.5 (m, CF_3), 118.9, 116.1, 113.8, 111.2, 108.8 (5m, $5CF_2$).

^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm): −82.0 (CF_3), −113.7, −122.7, −123.8, −124.5, −127.3 ($5CF_2$).

FABMS: *m/z* (%): 642 $(M + H)^+$ (8), 641 (7), 515 (91), 387 (4), 327 (8), 155 (35), 119 (28), 69 (100), 31 (92).

3.9. 2-(Perfluorohexylmethyl)butan-1,4-diamine (1)

Method A: H_2 was added at room temperature and under atmospheric pressure to a vigorously stirred suspension of 10% Pd/C catalyst (50 mg) and 1.31 g (2.8 mmol) of **8** in MeOH (15 ml). After 4 h, the reaction was completed. The mixture was filtered through celite and concentrated to give diamine **1** (1.05 g, 89%) as a white pale oil.

Method B: To a solution of **5** (0.800 g, 1.17 mmol) in EtOH (5 ml), hydrazine (1 ml) was added and the mixture was stirred and heated with reflux until a white solid appeared. Then, it was cooled to 0 °C, acidified (pH 1) with aqueous hydrochloric acid and refluxed again for 30 min. After this time, the precipitate of *N*,*N*-phthaloylhydrazine was filtrated off and washed with water. The water solution was alkalined with aqueous NaOH, extracted with ether and dried over Na_2SO_4. The filtrate was concentrated to give crude diamine **1** (0.290 g, 59%) as pale white oil.

IR (ν_{max}, cm^{-1}): 3372, 3300, 2936, 1587, 1147, 1365, 1238, 812.

^1H NMR (400 MHz, CD_3OD): δ (ppm): 2.6 (m, 4H, H-1,4), 2.22 (m, 1H, $H1'_A$), 1.99 (m, 1H, $H1'_B$), 1.90 (spt., 1H, $J = 6$ Hz, H-2), 1.55 (m, 2H, H-3).

^{13}C NMR (100 MHz, CD_3OD): δ (ppm): 44.6 (C-1), 38.7 (C-4), 34.8 (C-3), 32.4 (C-2), 32.2 (C-1′) and 121.2 (m, CF_3), 118.6, 116.0, 113.3, 111.2, 108.7 (5m, $5CF_2$).

^{19}F NMR (235 MHz, CD_3OD): δ (ppm): −80.8 (CF_3), −112.0, −121.3, −122.4, −122.9, −125.8 ($5CF_2$).

FABMS: *m/z* (%): 421 $(M + H)^+$ (100), 404 (98), 402 (92), 388 (10), 384 (9), 136 (12), 169 (100), 31(100).

3.10. Fluoropolyetherimide FPEI

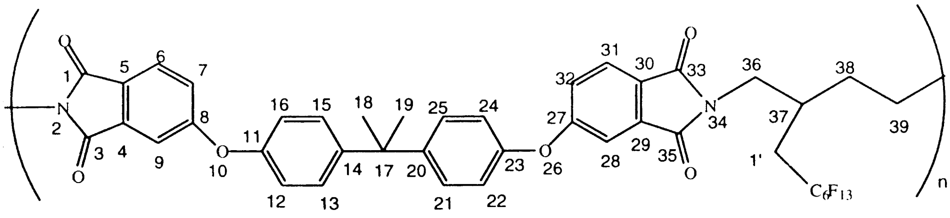
Solid BAPA (2.134 g, 4.1 mmol) was added to a stirred solution of **1** (1.801 g, 4.1 mmol) in NMP (*N*-methyl-pyrrolidone, 33 ml) under atmosphere of argon. The mixture was heated at 120 °C for 2 days. Then, it was poured into aqueous ethanol (200 ml H_2O and 100 ml EtOH) and the formed precipitate was filtrated off and dried under vacuum at 140 °C for 12 h. A brown dark solid of FPEI was obtained (3.52 g, 90%).

IR (ν_{max}, cm^{-1}): 2959, 1740, 1440, 1351, 1145, 1034.

^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.67 (m, 2H, H-7, H-32), 7.22 (m, 6H, H-9, H-12, H-16, H-22, H-24, H-28), 7.18 (m, 2H, H-6, H-31), 6.42 (m, 4H, H-13, H-15, H-22, H-24), 3.66 (m, 4H, H-36, H-39), 2.33 (m, 1H, H-37), 2.30–2.05 (m, 2H, H-1′), 1.72 (m, 2H, H-38), 1.65 (s, 6H, H-18, H-19).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 168.5, 168.1 (C-1, C-3, C-33, C-35); 164.1, 163.9 (C-8, C-27); 153.2, 153.1 (C-11, C-23); 148.0, 147.9 (C-14, C-20); 134.3 (C-4, C-29); 129.1 (C-13, C-15, C-21, C-25); 125.8, 125.6 (C-6, C-31); 125.5, 125.3 (C-5, C-30); 123.0, 122.8 (C-7, C-32); 120.4 (C-12, C-16, C-22, C-24); 43.0 (C-17); 42.1 (C-36), 35.1 (C-39), 33.1 (C-1′); 31.6 (C-38); 31.4 (C-18, C-19); 28.1 (C-37) and 120.3 (m, CF_3), 119.5, 116.1, 114.0, 112.4, 109.0 (5m, $5CF_2$).

^{19}F NMR (235 MHz, $CDCl_3$): δ (ppm): −81.4 (CF_3), −113.1, −122.4, −123.5, −124.0, −126.8 ($5CF_2$).



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