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Surface fluorination of PEEK film by selective wet-chemistry

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The PEEK–OH film, obtained by surface reduction of the native PEEK film, was designed as a versatile key-intermediate for the development of mild and selective fluorination processes. Reaction with diethylaminosulfur trifluoride in $CFCl_3$, and 4-trifluoromethylbenzamide in HOAc (H_2SO_4 catalysis) gave the PEEK–F and PEEK–$PhCF_3$ films, in 92% and 36% yields, respectively. Reaction of PEEK–ONa with heptadecafluoro-10-iododecane in DMF produced the PEEK–C_8F_{17} film in 6% yield. The modified PEEK surfaces were analysed by X-ray photoelectron spectroscopy (X.p.s.). © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high-performance thermoplastic exhibiting excellent mechanical properties, thermal stability and environmental resistance[1]. Recently, this polymer, mainly used for constructive elements in industry, has found new developments in the medical sector, and in biotechnology. Indeed, carbon-fibre-reinforced PEEK gave rise to new composite materials that are used as implants for bone reconstruction[2–6]. In our laboratory, supports for the *in vitro* cultivation of anchorage-dependent mammalian cells are made from surface-modified PEEK films[7,8].

Incorporation of fluorine motifs[9,10] into organic polymers has attracted considerable interest over the last decade, due to the unique surface properties of the resulting materials, like non-sticking behaviour and improved biocompatibility[11–14].

As a part of a programme for developing new biomaterials from synthetic polymers[15–17], we became interested in the tailor-made derivatization of PEEK[7,8]. In this article, we report the selective surface fluorination of PEEK films using the wet-chemistry technique, i.e. organic synthesis carried out at the solid–liquid interface.

EXPERIMENTAL

Polymer sample

Amorphous PEEK film was received from ICI (UK); the sample was Stabar K200 (reference number K0310902; depth of $25\,\mu m$). The contact angle of water was 71.2° (±1.5°), and the X.p.s. analysis revealed an O/C atomic ratio of 0.20 (theoretical value for $C_{19}H_{12}O_3$: O/C = 0.158). This results from an industrial surface treatment by corona discharge. Native PEEK film was obtained as follows: (i) immersion of Stabar K200 in refluxing acetone for 48 h; (ii) rinsing twice with acetone; (iii) drying

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under vacuum (1 mmHg) for 3 h at 60°C. After this treatment, the contact angle of water was 82° (±1.2°)[18]. From X.p.s. analysis we found an atomic O/C ratio of 0.148, close to the theoretical value[19]; C_{1s} (87.13%): 284.8 eV (C–C, C–H), 286.4 eV (C–O), 287.1 eV (C = O), 291.5 eV (π); O_{1s} (12.87%): 531.5 eV (O = C), 533.3 eV (O–C) (*Figure 1*).

Reagents and solvents

Organic reagents (99+% purity) were purchased from Acros Chimica (Beerse, Belgium) or Aldrich (Bornem, Belgium) and used as received. Inorganic reagents (analytical grade) were obtained from UCB (Braine-l'Alleud, Belgium) or Merck (Darmstadt, Germany) and used as received. Dimethylformamide (DMF), dimethylsulfoxide (DMSO), chloroform and tricholorofluoromethane were distilled before use. Acetone was dried over $CaCl_2$ and distilled. Methanol, ethanol and isopropanol were dried over CaO and distilled. Acetic acid (glacial, 99.8%) was used as received. Water (h.p.l.c. grade) was obtained with a Milli-Q system (Millipore, Bedford, MA)

Methods

The contact angles of water were measured at room temperature using the sessile drop technique and an image analysis system (CCD camera of MXR 5010 type and contour processor PIO-12 with computer monitor 80 from Electronish Ontwerp Bureau De Boer, Holland). The values given in *Table 1* are the average of 10 measurements. The standard deviation is indicated in parentheses. The X.p.s. spectra were obtained with a SSI X probe (SS-100/206) spectrometer from Fisons (Surface Science Laboratories, Mountain View, CA), equipped with an aluminium anode and a quartz monochromator. The direction of photoelectron collection made angles of 55° and 75° with the normal to the sample and the incident X-ray beam, respectively. The electron flood gun was set at 6 eV. The vacuum in the analysis chamber

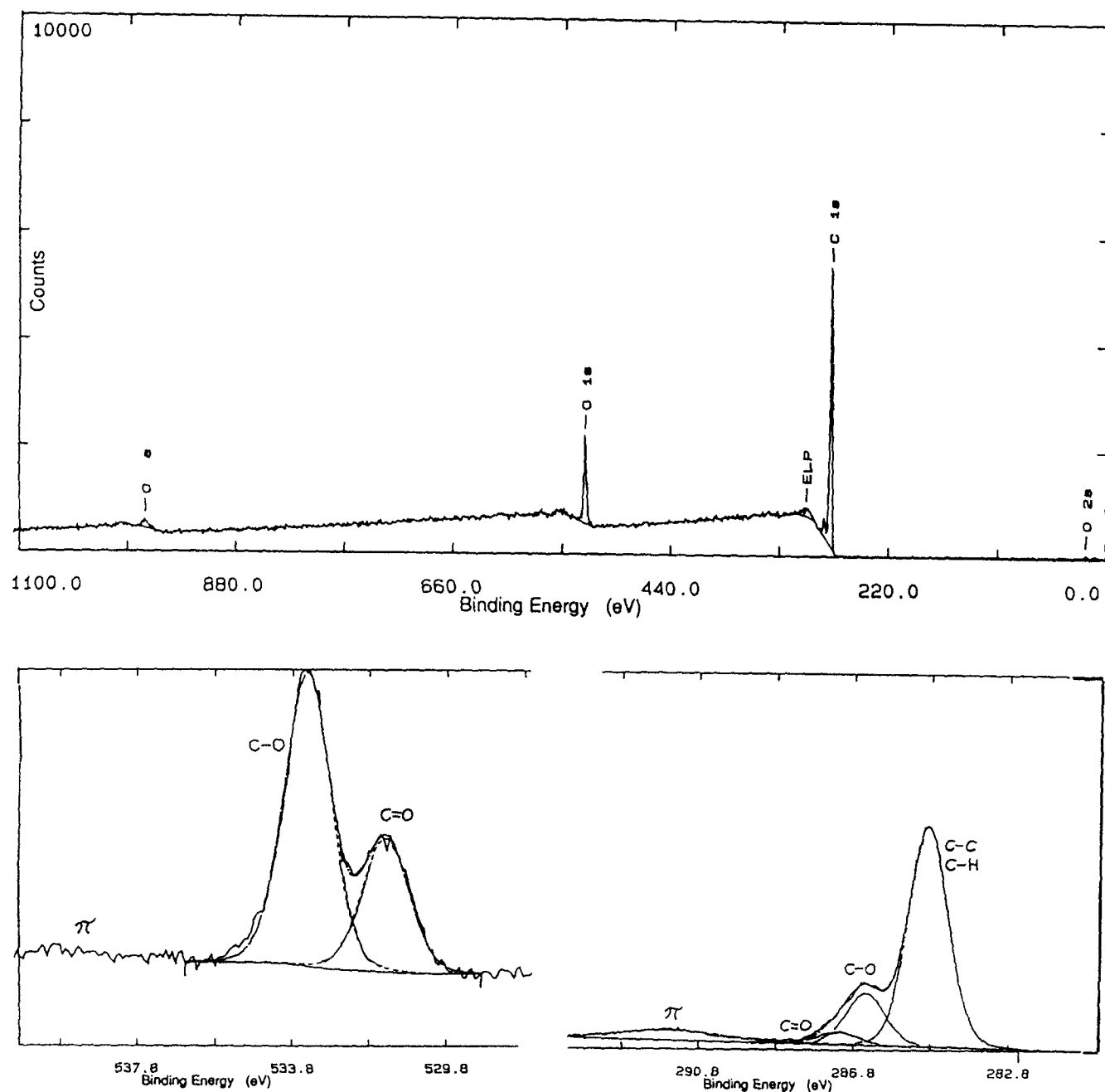* To whom correspondence should be addressed

Figure 1 X.p.s. spectrum of native PEEK

was 2.5×10^{-7} Pa. The binding energies of the peaks were determined by setting the C_{1s} component due to carbon only bound to carbon and hydrogen at a value of 284.8 eV. The peak areas were determined with a nonlinear background subtraction. Intensity ratios were converted into atomic concentration ratios by using the SSI ESCA 8.3 D software package. The peaks were curved fitted using a nonlinear least squares routine and assuming a Gaussian/Lorentzian (85/15) function.

Surface chemistry

Large film samples (rectangles of 30 cm in length and 5–15 cm in width) were fixed on a home-made glass cylinder (height: 16 cm; diameter: 8.5 cm) and placed into a 1.5 l wide neck (diameter: 12 cm) reaction flask (Sovirel glassware) containing the reactive solution (0.5–1.2 l). The neck was fitted, with a large diameter flange joint, in a lid with a two-socket neck equipped with a reflux

condenser and a drying tube. The external side of the film was marked and considered for the surface analyses (X.p.s. and contact angle with water). After chemical treatment and suitable rinsing, the film samples were dried under vacuum ($p \leq 1$ mmHg) at 60°C. We used a Gallenkamp oven and an Edwards E2M5 pump, connected through two vapour-condensers cooled with liquid air.

Preparation of PEEK–OH film

DMSO (1.2 l) and sodium borohydride (2.4 g) were introduced in the reaction flask and heated at 120°C under stirring (dissolution occurred). The PEEK film sample (30 cm × 15 cm) fixed on the glass cylinder was totally immersed into the reactive solution for 3 h at 120°C, then removed from the support and rinsed, successively with methanol (15 min), water (10 min), 0.5 N HCl (10 min), water (10 min) and ethanol (15 min). After

Table 1 Modified PEEK films

| | Film sample | Origin of the sample | θ_w^a | F/C atomic ratio | | Yield[c] |
				Calcd	Exp.[b]	
1	PEEK	Stabar K200 film washed in refluxing acetone for 2 days	82.0° (1.2)	–	–	–
2	PEEK–ONa	PEEK film reduced in $NaBH_4$/DMSO, at 120°C, for 3 h	64.6° (1.4)	–	–	–
3	PEEK–OH	PEEK film reduced as above, and neutralized in 0.5 N HCl	69.8° (1.1)	–	–	80%
4	PEEK–F (1)	PEEK–OH film treated in DAST/$CHCl_3$, at 20°C, for 40 h	74.6° (1.5)	0.0526	0.030	57%
5	PEEK–F (2)	PEEK–OH film treated in DAST/$CFCl_3$, at 20°C, for 48 h	79.1° (1.4)	0.0526	0.0412	74%
6	PEEK–OH ($CFCl_3$)	PEEK–OH film immersed in $CFCl_3$, at 20°C, for 48 h	–	–	0.0022	–
7	PEEK–$PhCF_3$ (1)	PEEK–OH film treated in HOAc/H_2NCO–C_6H_4–CF_3 (H^+ catal), at 20°C, for 48 h	74.4° (1.6)	0.1111	0.0265	18%
8	PEEK–$PhCF_3$ (2)	PEEK–OH film treated in HOAc/H_2NCO–C_6H_4–CF_3 (H^+ catal), at 20°C, for 75 h	77.9° (2.1)	0.1111	0.040	29%
9	PEEK–OH(H_2NCO–Ph–CF_3)	PEEK–OH film immersed in HOAc/H_2NCO–C_6H_4–CF_3 without catalyst	–	–	0.0	–
10	PEEK–C_8F_{17}	PEEK–ONa film treated in I–CH_2–CH_2–C_8F_{17}/DMF at 20°, for 2 days	78.1° (1.1)	0.5862	0.0382	4.5%
11	PEEK–OH(I–C_2H_4–C_8F_{17})	PEEK–OH film immersed in I–CH_2–CH_2–C_8F_{17}/DMF at 20°, for 2 days	–	–	0.0	–

[a] Contact angle of water
[b] X.p.s. analysis
[c] Percentage of modified polymer units in the domain investigated by X.p.s., i.e. about 10 atomic layers, or 50–80 Å depth

drying under vacuum (3 h, 60°C), the sample (PEEK–OH) was stored, in the dark, in a polystryrene box (damp and dust proof).

X.p.s. analysis: C_{1s} (85.16%): 284.8 eV (C–C, C–H), 286.4 eV (C–O), 287.1 eV (C = O), 291.6 eV (π); O_{1s} (14.84%): 531.5 eV (O = C), 532.4 eV (O–H), 533.3 eV (O–C), 539.8 eV (π) (*Figure 2*).

Preparation of PEEK–ONa film

The PEEK film sample (30 cm × 5 cm) was treated as above with $NaBH_4$ in DMSO, then rinsed with isopropanol (3 × 10 min) and dried under vacuum (2 h, 60°C).

Reaction of PEEK–OH film with DAST

Trichlorofluoromethane (450 ml) and DAST (diethylaminosulfur trifluoride, 3 ml) were introduced in the reaction flask. The PEEK–OH film sample (30 cm × 5 cm) fixed on the glass cylinder was immersed into the reactive solution for 48 h at room temperature, then removed and washed with $CFCl_3$ (2 × 10 min) and acetone (2 × 10 min). The film sample was dried (1 mmHg, 60°C, 3 h).

X.p.s. analysis: C_{1s} (~285 eV, 78.92%); O_{1s} (~533 eV, 15.39%); F_{1s} (~686 eV, 3.25%) (*Figure 3*)—Blank sample: C_{1s} (~285 eV, 79.21%); O_{1s} (~533 eV, 18.52%); F_{1s} (~686 eV, 0.18%).
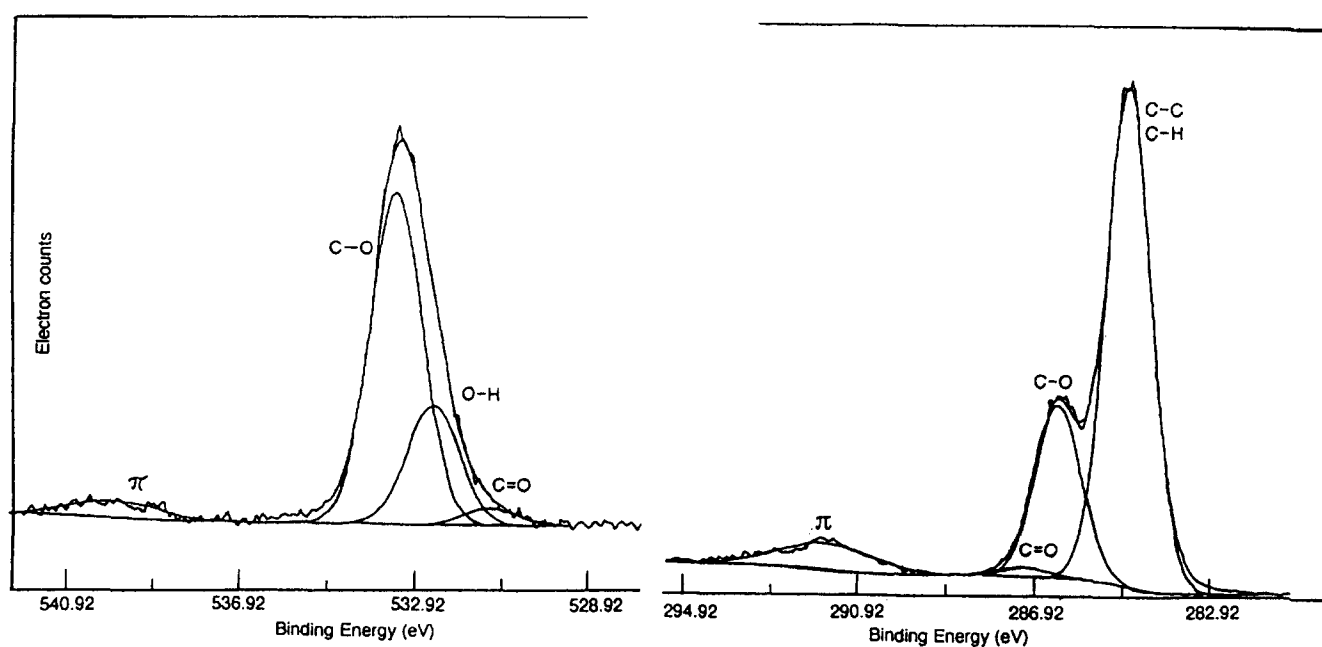
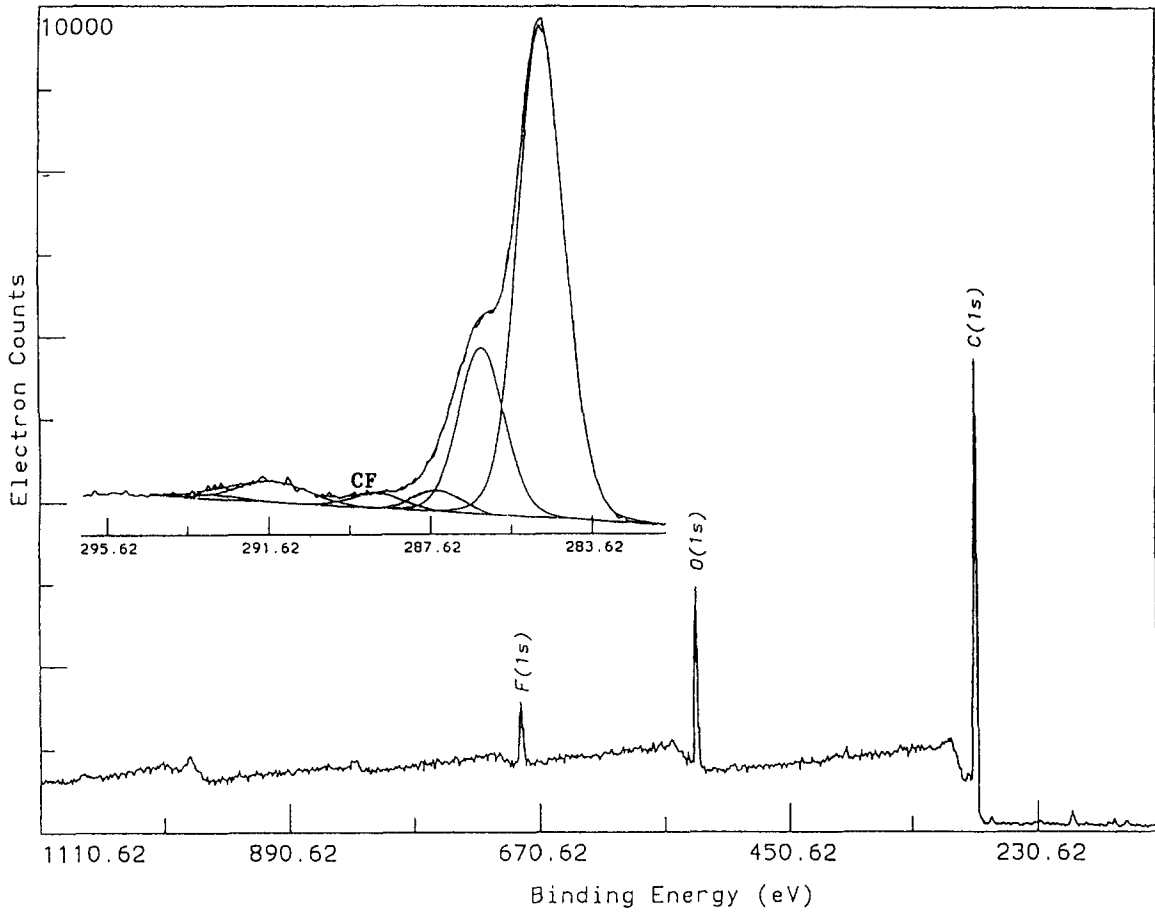

Figure 2 X.p.s. spectrum of PEEK–OH

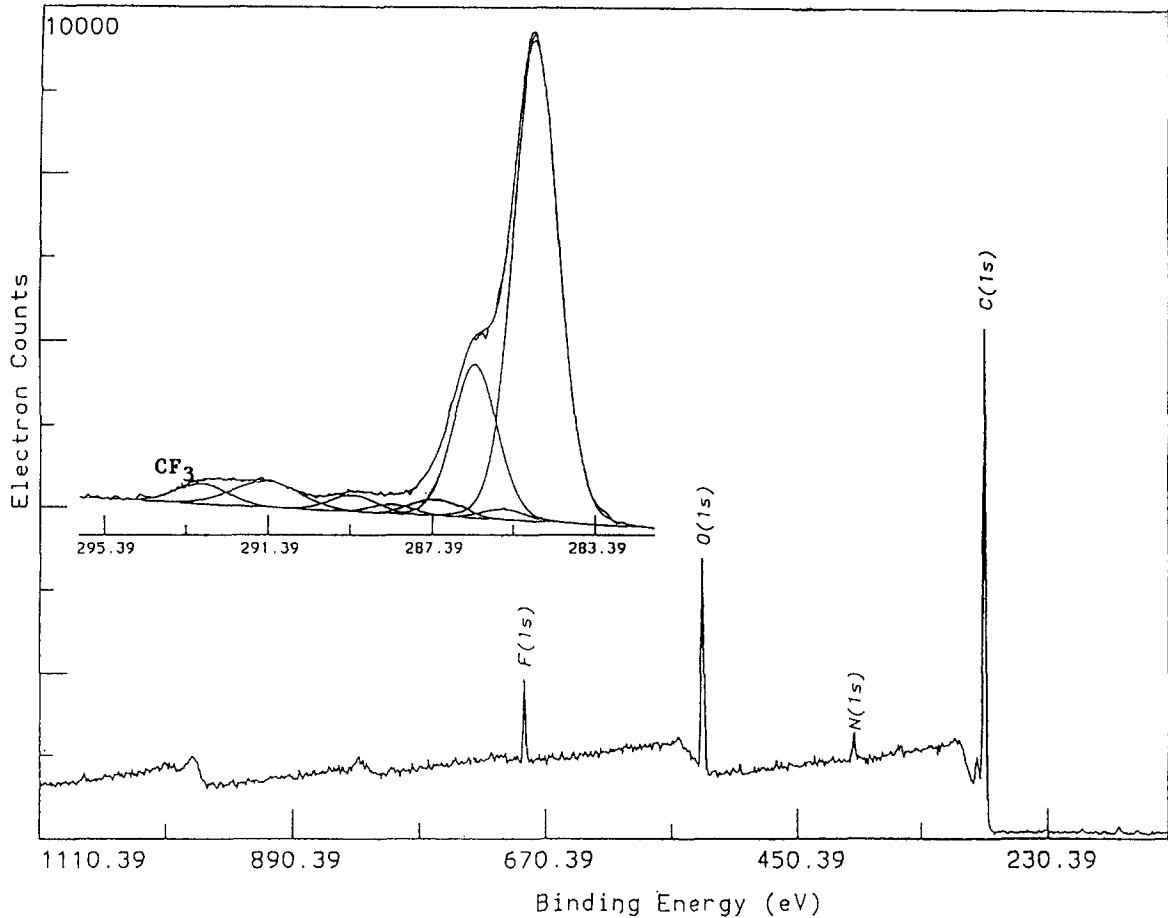**Figure 3** X.p.s. spectrum of PEEK–F

Figure 4 X.p.s. spectrum of PEEK–PhCF₃

Reaction of PEEK–OH film with 4-trifluoromethylbenzamide

Acetic acid (460 ml), 4-trifluoromethylbenzamide (6.94 g) and sulfuric acid (0.2 ml) were introduced in the reaction flask and stirred until dissolution occurred. The PEEK–OH film sample (30 cm × 5 cm) fixed on the glass cylinder was immersed into the reactive solution for 76 h at room temperature, then removed and washed with HOAc (3 × 15 min) and acetone (2 × 15 min). The film sample was dried (1 mmHg, 60°C, 3 h).

X.p.s. analysis: C_{1s} (~285 eV, 79.52%); N_{1s} (~399 eV, 1.11%); O_{1s} (~533 eV, 15.77%); F_{1s} (~688 eV, 3.18%) (*Figure 4*).

Reaction of PEEK–ONa film with heptadecafluoro-iododecane

A solution of 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane (1 g) in N,N-dimethylformamide (80 ml) was placed in an Erlenmeyer flask. The PEEK–ONa film sample (disk of 2.2 cm in diameter) was introduced and left for 48 h at 20°C, under smooth shaking.

The sample was removed from the reactive solution and rinsed, successively with DMF (1 × 15 min) and acetone (1 × 15 min), then dried under vacuum (2 h, 60°C).

X.p.s. analysis: Si_{2s} (~150 eV, 3.50%); C_{1s} (~283 eV, 74.06%); O_{1s} (~530 eV, 15.46%); F_{1s} (685 eV, 2.83%).

RESULTS AND DISCUSSION

Several techniques for polymer surface fluorination have been developed, for instance plama treatments[20] and radical insertion reactions.[21] However, PEEK fluorination is poorly documented; one paper describes the reaction of PEEK with fluorine atoms and ions produced by glow discharge excitation of CF_4.[22] Bulk-fluorinated polymers usually result from the polymerization of fluorinated monomers; novel copolymers of PEEK containing ring trifluoromethyl substituents have been recently synthesized by starting with trifluoromethyl-benzophenone units[23].

Due to the polymer insolubility in common organic solvents, the direct functionalization of PEEK has been reported to be a very arduous process, limited to the sulfonylation[24] and nitration reactions[25]; indirect methods were thus developed using the soluble methyl–PEEK as starting material[26,27]. On the other hand, this solvent resistance of PEEK allowed us to perform selective surface wet-chemistry based on the benzophenone motif derivatization[28,29]. Therefore, we selected this approach as first strategy for the direct fluorination of the native PEEK film. Diethylaminosulfur trifluoride (DAST) was chosen as mild fluorinating agent[30]. The transformation of carbonyl precursors into gem-difluoride derivatives using DAST is widely exemplified in classical organic synthesis (liquid phase), mainly in the
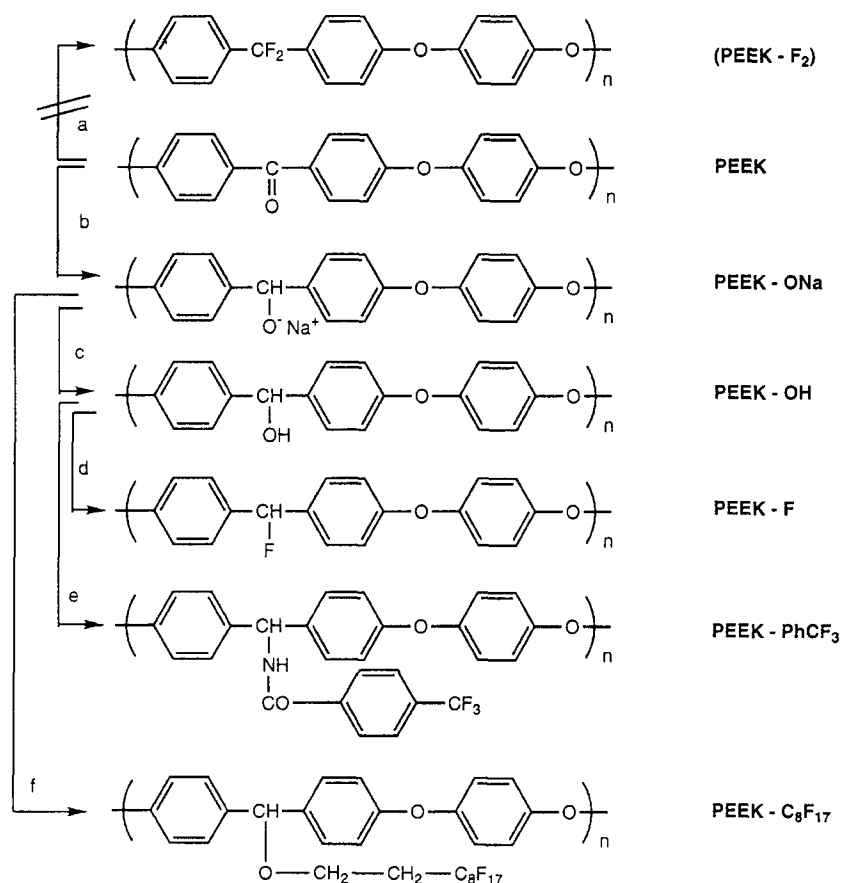
Reagents and conditions: (a) Et_2NSF_3 (DAST), $CFCl_3$, 20°C, 8 days; (b) $NaBH_4$, DMSO, 120°C, 3h; (c) 0.5NHCl, 20°C, 10 min; (d) Et_2NSF_3 (DAST), $CHCl_3$ or $CFCl_3$, 20°C, 40 -48h; (e) H_2NCO - C_6H_4 - CF_3, HOAc, H_2SO_4 catal., 20°C, 2-3 days, (f) I - CH_2 - CH_2 - C_8F_{17}, DMF, 20°C, 2days.

Scheme 1 Strategies for PEEK film fluorination

aliphatic series. Unfortunately, we found that the PEEK film surface could not be transformed into PEEK-F_2 (*Scheme 1a*) after immersion of the sample in DAST solutions during several days (X.p.s. analysis). This lack of reactivity could be due to the poor electrophilic character of the diarylketone motif[31]. In a control experiment made in solution, we similarly observed that DAST is unreactive towards 4,4'dimethoxybenzophenone at room temperature. This result prompted us to consider an alternative strategy that makes use of the derived alcohol (PEEK-OH) as reactive precursor for the development of fluorination processes.

Surface reduction of PEEK film samples into PEEK-OH (*Scheme 1b, c; Table 1*, entry 3) with sodium borohydride in dimethylsulfoxide at 120°C for 3 h, followed by neutralization in aqueous HCl, has been previously reported[8]. The percentage of surface hydroxylation was determined by X-ray photoelectron spectroscopy (X.p.s.), from the experimental $\underline{C} = O/\underline{C}-O$ and $\underline{O} = C/\underline{O}-C$ atomic ratios, measured in the fine structures of the C_{1s} and O_{1s} peaks respectively. In comparison to the native PEEK sample (*Figure 1*), the C_{1s} peak of PEEK-OH (*Figure 2*) showed a significant diminution of the $\underline{C} = O$ component at 287.1 eV, and a related increase of the $\underline{C}-O$ component at 286.4 eV including the contributions of both the ether- and alcohol functions. The fine structure of the O_{1s} peak (*Figure 2*) revealed an important diminution of the $\underline{O} = C$ component at 531.5 eV, the maintenance of the $\underline{O}-C$ component at 533.3 eV, and the emergence of a new component at 532.4 eV attributed to the H$\underline{O}-C$ alcohol function[32]. The reduction affected about 80% of the monomer units contained in the ten outermost atomic layers (50–80 Å depth, i.e. the interface domain explored by the X.p.s. technique)[8].

The direct fluorination of PEEK-OH with DAST[33] was first considered. Indeed, this reagent has been previously used for the transformation of benzhydrol derivatives into diarylmethyl fluorides[34] and bis(diarylmethyl)ethers[35] resulting from an intermolecular dehydration process; for steric reasons, this competitive reaction should be minimized at the solid (PEEK-OH) interface. PEEK-OH film samples were thus immersed in DAST solutions (1% w/v) in chloroform (*Table 1*, entry 4), and in trichlorofluoromethane (*Table 1*, entry 5) for two days at room temperature, then suitably washed and dried (*Scheme 1d*). The X.p.s. analysis of the samples clearly showed the presence of fluorine atoms at 686.22 eV corresponding to the C-$\underline{F}$ motif (*Figure 3*). Accordingly, in the fine structure of the C_{1s} peak, a new component was found at 288.95 eV ($\underline{C}-F$). Depending on the nature of the solvent, the experimental F/C atomic ratios were 0.030 ($CHCl_3$) and 0.0412 ($CFCl_3$); this second value was corrected into 0.0388, considering the solvent adsorption contribution (*Table 1*, entry 6). From the F/C atomic ratios, we calculated the percentages of fluorinated units[36]: the reaction in $CHCl_3$ gave 57% of substitution, while the reaction in $CFCl_3$ afforded 74%. Taking into account the level of hydroxylation of the starting material PEEK-OH (80%), we concluded that the surface chemistry yields were 71% and 92% respectively. It should be mentioned that the X.p.s. spectra of the PEEK-F samples did not reveal the presence of sulfur or nitrogen atoms, meaning that the DAST reagent is not adsorbed on the modified interfaces and that the fluorine incorporation well results from the hydroxyl group substitution. The contact angles of water

were 74.6° (entry 4) and 79.1° (entry 5), showing a significant enhancement of the hydrophobic character of the PEEK-F surfaces, as compared to the PEEK-OH precursor ($\theta_w = 69.8°$, entry 3).

In a model study carried out with 4,4'-dimethoxybenzhydrol as PEEK-OH mimic, we found that the hydroxyl group could be easily substituted by a large variety of primary amides in acetic acid containing 0.1% (w/v) of sulfuric acid as catalyst[37]. This practical reaction was successfully applied for the PEEK-OH derivatization with a perfluorinated amide. Immersion of PEEK-OH film samples into a solution of 4-trifluoromethylbenzamide (1.5%, w/v) and sulfuric acid catalyst (0.1%, w/v) in acetic acid, followed by the appropriate washings and drying, gave the fluorinated surfaces PEEK-PhCF$_3$ (*Scheme 1e*). After two days of reaction at room temperature, the X.p.s. analysis of the film samples showed fluorine atoms at 688.34 eV, with a F/C atomic ratio of 0.0265 (*Table 1*, entry 7) corresponding to 18% of substitution[38]. After three days of reaction, the surface derivatization reached 29% (entry 8), as determined from the F/C atomic ratio of 0.040[38]. Nitrogen atoms were detected in X.p.s. at 399.85 eV (*Figure 4*), with a N/C atomic ratio of 0.0139 corresponding to 30% substitution[39], a value in excellent agreement with the previous one determined from the F/C atomic ratio. Moreover, the fine structure of the C_{1s} peak showed three new components, at 293.04 eV ($\underline{C}F_3$)[40], 288.40 eV (N-$\underline{C}$ = O) and 285.67 eV ($\underline{C}$-N), fully consistent with the PEEK-PhCF$_3$ chemical structure. We controlled (X.p.s. analysis) that the substitution reaction did not occur in the absence of a strong acid catalyst (*Table 1*, entry 9). The corrected yields of surface derivatization were 22% and 36% for the PEEK-OH samples treated with the amide during two days (entry 7) and three days (entry 8) respectively. The corresponding contact angles of water were 74.4° and 77.9°, resulting from the replacement of some surface OH groups with trifluorosubstituted hydrophobic motifs.

Finally, we examined the possibility of fixing a perfluoroalkyl chain on the polymer surface via a Williamson etherification. The PEEK-ONa film sample (*Scheme 1b*), obtained by the reductive treatment of PEEK omitting the acidification, was immersed in a solution of heptadecafluoro-10-iododecane (1.25%, w/v) in dimethylformamide for two days at room temperature, then rinsed and dried (*Scheme 1f*). The X.p.s. analysis of the resulting PEEK-C_8F_{17} sample (*Table 1*, entry 10) revealed the presence of fluorine atoms at 686.5 eV, with a F/C atomic ratio of 0.0382 corresponding to 4.5% of coupling[41] (corrected yield: 5.6%). This value appears relevant, since a PEEK-OH film sample similarly treated with heptadecafluoro-10-iododecane did not show the incorporation of fluorine atoms (entry 11). This low yield of Williamson coupling most probably results from the competition between iodide substitution of C_8F_{17}-CH_2-CH_2-I with the surface alkoxide functions (SN_2), and destruction of the electrophilic reagent by the polymer playing the role of a base for eliminating HI (E2)[42,43]. This last reaction path should be favoured by the presence of a strong electron withdrawing group (C_8F_{17}).

CONCLUSION

Wet-chemistry was readily performed on the surface of

amorphous PEEK film. The main advantages of this technique[44], over plasma treatment for instance, are the simpleness of the procedure which does not require special equipment, the selectivity of the chemical transformations that parallels the specificity usually reached in organic synthesis performed in homogeneous phase with well-defined reagents, and the possibility of controlling the extent and depth of functionalization depending on the reagent concentration, solvent wettability, temperature and duration of the treatment. Yet, some problems, related to the presence of a liquid phase surrounding the solid sample, should be pointed out: the experimental conditions have to be carefully selected in order to avoid the dissolution of the modified polymer interface; several rinsings are needed to desorb the unreacted chemicals.

The surface fluorination of poly(ether ether ketone) (PEEK) film has been successfully achieved, using the reduced polymer (PEEK–OH) as a versatile key-intermediate. The direct replacement of the hydroxyl group with fluorine could be realized in high yield by reaction with DAST. On the other hand, the coupling of 4-trifluoromethylbenzamide under acidic catalysis was performed in moderate yield. However, this original hydroxyl substitution could be applied to the anchorage of primary amides bearing selected functional groups and chemical architecture able to modulate the polymer surface properties.

Since fluorinated polymers are generally blood compatible materials, due to their protein-repulsive properties[45], we realized a rapid, qualitative, evaluation of the biological response induced by our modified PEEK films. In a standard blood coagulation test[46], we found that the clots formed on the fluorinated surfaces PEEK–F (2) and PEEK–PhCF₃ (2) were significantly less important than the clots formed on the native PEEK film (reference) and on the reduced PEEK–OH films (which behaves as PEEK). We noted a 20–30% diminution of the weight of clots. Under similar condition of testing, the native PEEK film coated with heparin[47] induced a 45–55% diminution of the weight of clots. The moderate improvement in blood biocompatibility could not be obviously correlated to the water contact angles of the various samples.

ACKNOWLEDGEMENTS

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36   We considered a theoretical monomer unit consisting of [(PEEK–OH)$_x$ + (PEEK–F)$_y$], i.e. [(C₁₉H₁₄O₃)$_x$ + (C₁₉H₁₃FO₂)$_y$], where $(x+y) = 1$. For $x = 0.43$ and $y = 0.57$, the calculated F/C atomic ratio was $0.57/19 = 0.03$. For $x = 0.26$ and $y = 0.74$, the calculated F/C atomic ratio was $0.74/19 = 0.0389$
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SYNOPSIS

As part of a program for developing new biomaterials from synthetic polymers, we are interested in the surface modification of poly(ether ether ketone) (PEEK) using the wet-chemistry technique.

Reduction of PEEK film gives an hydroxylated surface (PEEK–OH), that further reacts with DAST to furnish the fluorinated surface (PEEK–F). Coupling of PEEK–OH with 4-trifluoromethylbenzamide, under acid catalysis, produced the trifluoromethylated surface (PEEK–PhCF$_3$).

Reaction of PEEK–ONa with heptadecafluoro-10-iododecane is not very efficient.

The modified PEEK surfaces are characterized by X.p.s. spectroscopy and contact angle of water. Their biocompatibility has been evaluated in a standard blood coagulation test.