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Surface modification of halogenated polymers
3. Influence of additives such as alkali cations or nucleophiles on the magnesium reductive treatment of polytetrafluoroethylene

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Abstract

The presence of a small amount of an alkali cation in a magnesium solution dramatically increases the rate of defluorination of PTFE and enhances oxygenation. Evidence of this effect is observed for concentrations down to 1 mM and treatment durations of only 10 s. The presence of the alkali cation also makes the polymer porous. The rate of defluorination and the depth of attack increase both with the alkali cation concentration and with the duration of the treatment. Sodium is more reactive than potassium which is itself more reactive than lithium. The phenomenon is not limited to alkali cations and is also evident with the tetrabutylammonium cation. When nucleophiles such as diethylphosphite, thiophenoxide or the anions of 2-mercaptopyridine and thiourea are present in a solution of magnesium containing a moderate amount of solvated electrons ($<$ 50 mM), the grafting of the nucleophile to the polymer occurs but leads to poor yields. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: PTFE; Solvated electrons; Liquid ammonia

1. Introduction

Polytetrafluoroethylene (PTFE) which is certainly the most known among perfluorinated polymers is used in lots of devices that take advantage of some of its remarkable properties (mechanical resistance, chemical inertness, temperature stability, low dielectric constant, etc.) [1,2]. Due to its low surface free energy, surface modification of PTFE has to be carried out prior to bonding it to other materials [3–8] and can be performed by different methods (photochemistry [9], γ irradiation, ion introduction [10] and reduction [11,12]) of which we have focused only on reductive treatments. Different reductive reagents can be used: alkali metals whose reaction with the polymer is very fast but poorly controlled and results in the carbonization of the polymer [11–17], milder reactants such as the benzoin dianion which has to be reacted for several hours to obtain carbonization [3,18], and magnesium solutions in liquid ammonia which were described in Part 1 of this paper. The latter solutions do not carbonize the polymer and do not destroy its surface which presents a controlled hydrophilic character. In contrast, the polymer treated by alkali metals becomes porous [19–22].

Here, the influence of additives such as alkali cations or nucleophiles to the magnesium reactant has been studied. It is predicted that small amounts of alkali cations would allow control of the surface porosity since magnesium alone does not make the polymer porous whilst alkali metals do. Nucleophiles were expected to undergo electron-induced substitution of the fluorine atoms by trapping the radicals generated during the first reduction step of the polymer by the magnesium solution according to an electro-induced radicalar nucleophilic substitution ($S_{RN}1$ mechanism). Under photochemical stimulation grafting of nucleophiles on the PTFE surface has already been reported [23].

The results have been analysed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF SIMS).

2. Experimental

All the chemical reagents were purchased from Aldrich

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(Fallavier, France) and used without further purification. Teflon plaques were supplied by 3P Ltd (Langres, France). Before treatment, the samples (2–3 cm^2 and 1 mm thick) were pretreated in order to decrease surface contamination, this consisted of refluxing in isopropanol for 1 h and then drying in an oven (100°C).

The different treatments were performed in solutions of liquid ammonia (80 ml) which was condensed into an electrochemical cell via an already described set-up [24]. Liquid ammonia was handled under atmospheric pressure and maintained at -40°C by a cryocooler. Electrolyses were performed under conditions of controlled current (10^{-1} A per cm^2) using a stainless steel cathode (10 cm^2, 156 mesh per cm^2) and a magnesium anode.

After treatment the samples were washed sequentially with aqueous HCl (0.1 M), then distilled water in order to eliminate adsorbed mineral fluorinated compounds and acetone.

2.1. Preparation of the solutions of solvated electrons in the presence of magnesium and an alkali cation

These solutions were obtained in three steps: (i) electrochemical reduction of a solution of ammonium tetrafluoroborate (0.3 M, 24 mmol) into magnesium tetrafluoroborate; (ii) addition of an alkali salt; and (iii) electrolysis of the solution to obtain solvated electrons. The electrolysis ((i) + (iii)) was stopped when 6000 Cb (62 mF) were passed through the circuit. The first 24 mF permitted the reduction of ammonium tetrafluoroborate into magnesium tetrafluoroborate. The next 38 mF allowed the reduction of the acidic impurities contained in the medium and the formation of the solvated electron solution. The concentration of the solvated electron solution was measured after treatment by titrating with ammonium bromide until the disappearance of the blue colour characteristic of the solvated electrons. The concentration was estimated to be about 0.2 M. In step (ii), the desired amount of Li^+, Na^+ or K^+ cations were, respectively, obtained by addition of lithium chloride, sodium or potassium tetrafluoroborate. The concentrations of the alkali cations ranged from 0.5 to 10 mM. Treatments were also performed with the tetrabutylammonium cation by addition of tetrabutylammonium tetrafluoroborate instead of the alkali salt.

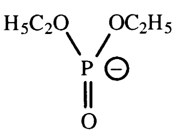
Treatment consisted of immersing the samples in the solution of solvated electron for different time durations ranging from 10 s to 30 min.

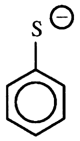
2.2. Preparation of the solutions of solvated electrons in the presence of magnesium and a nucleophile

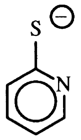
These solutions were obtained in three electrochemical steps. The first step (j) was similar to step (i) of the last procedure and consisted of the reduction of a solution of ammonium tetrafluoroborate (0.02 M, 1.6 mmol, 160 Cb) into magnesium tetrafluoroborate. The last two steps were as follows: (jj) reduction of the acidic form of the nucleophile NuH into Nu^- (i.e. $MgNu_2$) (NuH, 0.2 M, 16 mmol, 1.6×10^3 Cb), (jjj) formation of the solvated electron solution (1–40 mM). The reduction of NH_4BF_4, NuH and the acidic impurities contained in the medium (e.g. water) involved generally about 2×10^3 Cb, after which the characteristic blue colour of solvated electrons appeared and the passage of additional charge was used to produce the solvated electrons solution (step (jjj)). The concentration of the solvated electron solution was calculated from the charge passed through the circuit in step (jjj) (8 Cb for a 1 mM solvated electron solution).

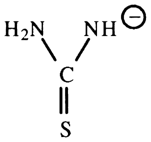
Treatment consisted of immersing the samples into the solvated electron solution until the blue colour of the solvated electron had disappeared. Slightly different treatments were also performed: (k) samples were treated in the presence of additional sodium which was introduced in the form of the tetrafluoroborate salt (0.3 M, 2.65 g); (kk) in a first step the magnesium treatment was performed in the absence of a nucleophile and in a second step the PTFE plaques were immersed into a solution of pure $(EtO)_2PO^-$ which was made in situ by deprotonation of $(EtO)_2POH$ by the stoichiometric amount of potassium *tert*-butoxide; (kkk) the same treatment as in (kk) was performed with $(EtO)_2POH$ instead of $(EtO)_2PO^-$ as the nucleophile and (kv) the treatment was performed during the last step of the standard procedure and 83 Cb (or 190 Cb) were passed through the circuit under a 45 mA (or 125 mA) intensity in 30 min (or 25 min); the concentration of the solvated electrons varied therefore between 0 and 11 mM (or 23 mM).

The nucleophiles tested were diethylphosphite, thiophenoxide and the anions of 2-mercaptopyridine and thiourea:









2.3. XPS analysis

The experimental conditions of XPS analysis of the samples have already been given in Part 1 [21] and will only be summarized in Part 3.

The chemical composition of a superficial layer (about 5 nm) of the samples was determined by XPS. The calculation of the fractional atomic concentrations of one element relative to carbon 1 s was achieved using wide scan spectra. For each polymer, the sensitivity factors of oxygen, fluorine, nitrogen and phosphorus relative to carbon were taken from the literature: $S_O = 3.1$ (reference value for various oxygenated polymers), $S_F = 3.7$ (reference value for PTFE), $S_P = 1.6$ and $S_S = 2.2$ (reference values for organic compounds) [25].

The chemical environments neighbouring the carbon atoms could be deduced from the high-resolution XPS spectra.

The accuracy of the XPS measurements is between 10% and 20%. The limit of detection of an element is around 0.04% (calculated from Ref. [28], p. 587).

2.4. SEM analysis

A JEOL JSM-5200 SEM operating at an accelerating voltage of 5 kV was used to examine the polymer morphology. For the elemental profile, a Pentafet Link ISIS Oxford analyser was used. The samples were set in epoxy resin and coated with gold using a Polaron SEM coating system.

2.5. ToF SIMS analysis

The ToF SIMS measurements were performed with a Phi-Evans Trift 1 ToF SIMS spectrometer [26]. The samples were bombarded with a pulsed Ga^+ (15 kV) ion beam with 800 pA d.c. current and pulsed at 5 kHz repetition rate with a 4 ns pulse width. The beam was rastered on a $190 \times 190\ \mu m^2$ surface area. The secondary ions were extracted perpendicular to the sample surface and accelerated up to ± 3 keV (depending on the mode). The spreading of the initial kinetic energies of the secondary ions was compensated by a 270° deflection in three electrostatic hemispheric analysers before detection. This compensation allowed a mass resolution ($m/\Delta m > 10^3$) high enough to separate the contributions of isobar ions at the same nominal mass. In order to avoid the charging of the insulating polymer samples, a charge compensation was achieved with a pulsed electron gun operated at 20 eV. Secondary ions in the mass range 0–5000 *m*/*z* were collected during 5 min, this corresponds to a total primary ion fluence per spectrum of 5×10^{11} ions/cm^2, ensuring static analysis conditions. The data acquisitions and treatments were made with the cadence software from Charles Evans & Associates [26]. The mass calibration of the spectra was performed by using reference peaks of molecular ions with a known composition.

2.6. Modelling simulation

Modelling simulation was performed with Insight II® (Biosym Technologies).

3. Results and discussion

3.1. Preparation of the reactant solutions

The concentrations used are shown in Table 1.

The reactant solution was prepared in three stages for both the alkali cations and nucleophiles. The first step was the same in each case and consisted of the preparation of the supporting electrolyte.

Table 1
Concentrations in the solutions of solvated electron

	Mg/alkali treatment	Mg/nucleophile treatment
$[Mg(BF_4)_2]$	0.15 M	0.02 M
$[e^-, NH_3]$	0.20 M	1–20 mM
Alkali salt	0.5–20 mM	0
Nucleophile	0	0.20 M

3.1.1. Supporting electrolyte

The supporting electrolyte had to be suited to the subsequent electrolysis conditions, and in particular had to be inert towards solutions of solvated electrons in the presence of magnesium cations. Since (i) Mg^{2+} readily precipitates with many anions (e.g. halides) and (ii) carbonization of PTFE occurs quickly when PTFE is exposed to solvated electrons in the presence of alkali cations, halide anions and alkali cations had to be avoided. We have chosen to use $Mg^{2+}2BF_4^-$, which was prepared in situ by reduction of ammonium tetrafluoroborate at the cathode:

$$NH_4^+\,BF_4^- + e \rightarrow NH_3 + 1/2H_2 + BF_4^- \qquad (1)$$

and oxidation of magnesium from the electrode at the anode:

$$Mg \rightarrow Mg^{2+} + 2e \qquad (2)$$

leading to the overall reaction for step (i):

$$2(NH_4^+\,BF_4^-) + Mg \rightarrow 2NH_3 + H_2 + Mg^{2+}\,2BF_4^- \qquad (3)$$

We have checked that the amounts of alkali impurities contained in $NH_4^+BF_4^-$ were negligible. The percentages by mass of lithium, sodium and potassium in $NH_4^+BF_4^-$, measured by flame emission spectroscopy were, respectively: < 0.0007%, 0.016% and 0.001% which corresponds to the following concentrations in the solution of liquid ammonia: < 0.03, 0.2 and 0.008 mM. As expected these concentrations are negligible, particularly when compared to the amounts of alkali cations added to the magnesium solutions, which were always higher than 0.5 mM.

The concentration of the electrolyte was smaller when a nucleophile was present in the medium since the conductivity of the solution was insured by the nucleophile itself.

3.1.2. Solutions of magnesium in the presence of a small amount of an alkali cation

In the second step (ii) when there were no more ammonium cations present in the medium, small amounts of alkali salts were added to the preceding solution. In order not to interfere with the species in solution, we have first chosen to add tetrafluoroborate salts. Unfortunately lithium tetrafluoroborate is highly hygroscopic and the addition of a small amount was nearly impossible; lithium chloride whose solubility in liquid ammonia at − 40°C is about 0.03 M [27] was used instead. Such problems did not occur with sodium or potassium tetrafluoroborates.

In step (iii), solvated electrons were generated at the cathode:

$$e^-_{\text{cathode}} \rightarrow e^-_{\text{solution}} \quad (4)$$

whilst reaction (2) remained valid at the anode, leading to the following overall equation for step (iii):

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-_{\text{solution}} \quad (5)$$

3.1.3. *Solutions of magnesium in the presence of a nucleophile*

In step (jj) the nucleophile Nu^- was obtained at the cathode according to:

$$\text{NuH} + e \rightarrow 1/2\text{H}_2 + \text{Nu}^- \quad (6)$$

whilst magnesium was oxidized at the anode via reaction (2), giving the following overall reaction for step (jj):

$$2\text{NuH} + \text{Mg} \rightarrow \text{H}_2 + \text{Mg}^{2+} 2\text{Nu}^- \quad (7)$$

In step (jjj) solvated electrons in the presence of magnesium could accumulate in the solution according to what was observed in step (iii) of the last procedure.

Diethylphosphite, thiophenoxide and the anions of 2-mercaptopyridine and thiourea were chosen as nucleophiles since their incorporation should result in the etching of a new atom whose characterization by XPS or ToF SIMS should be possible: a phosphorus peak should be detected with diethylphosphite and a sulfur peak in the case of thiophenoxide and the anions of 2-mercaptopyridine and thiourea.

3.2. *Magnesium treatment in the presence of a small amount of an alkali cation*

3.2.1. *SEM*

3.2.1.1. Physical aspect of the plaques. The visible aspect of PTFE plaques did not change upon the magnesium treatment but changed dramatically when a small amount of an alkali cation was added to the magnesium solution. After some seconds of treatment, the PTFE samples became dark and porous. Such an effect was greater with sodium or potassium than with lithium.

By analysis of the backscattered and secondary electron emissions from the sample, SEM allowed the imaging of the surface morphology. Fig. 1 shows an untreated PTFE surface and Figs 2–4 surfaces treated by magnesium/alkali cation (≈ 1.5 mM) solutions for 5 min (Fig. 2, Li^+; Fig. 3, Na^+; Fig. 4, K^+). For the untreated sample (cf. Fig. 1) the image shows the surface to be fairly homogeneous with a regular series of parallel lines across the surface possibly due to machine finishing. These lines have completely disappeared when the samples have been treated by the magnesium/alkali solutions for 5 min (cf. Figs 2–4). The surface treated in the presence of lithium (cf. Fig. 2) looked approximately the same as that of the untreated sample (cf. Fig. 1), whilst that of the sodium-treated sample was no longer homogeneous and white ‘scars’ of about 2 μm wide, due to accumulations of charge and indicating where surface modification has occurred, could be seen all over the sample surface. This effect was even more noticeable for the potassium-treated sample (cf. Fig. 4), for which the scars were often more than 10 μm long. The absence of change of the PTFE surface with either the magnesium[21] or the magnesium/lithium treatment must be considered with care and referred to the observation scale (about 1–2 μm for a 20 μm sale bar). Changes may be taking place on the sub-micron scale.

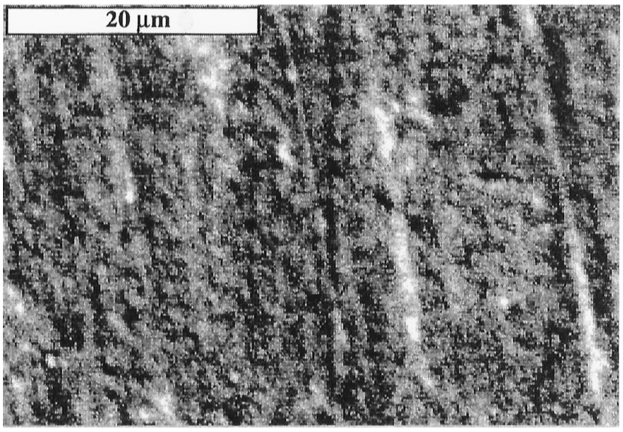


Fig. 1. SEM of an untreated PTFE sample.

3.2.1.2. X-ray fluorescence. By analysing the X-rays emitted from the irradiated sample under SEM conditions, fluorescence spectra were obtained. The depth of the explored zone depends on the analysed element and on the energy of the incident electron beam. For a 5 keV beam the different atoms are analysed up to about 1 μm from the surface. The X-ray fluorescence spectra of an untreated sample and a sample treated for 5 min in a 1.22 mM solution of potassium are, respectively, represented in Fig. 5a and Fig. 5b (analogous figures were

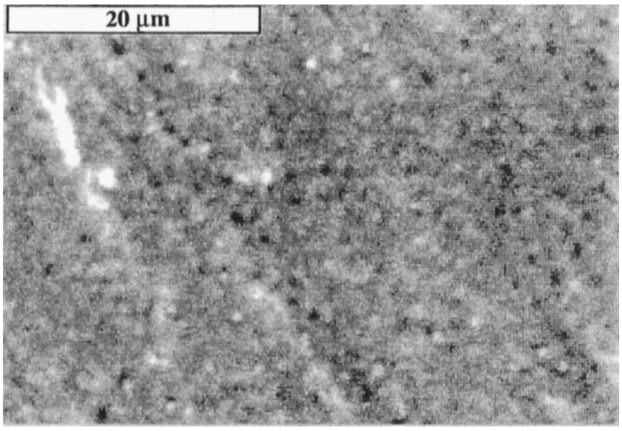


Fig. 2. SEM of a PTFE sample treated in a Mg/Li^+ solution. $[\text{Mg(BF}_4)_2] = 0.15$ M, $[e^-, \text{NH}_3] = 0.20$ M, $[\text{LiCl}] = 1.24$ mM; treatment time, 15 min.

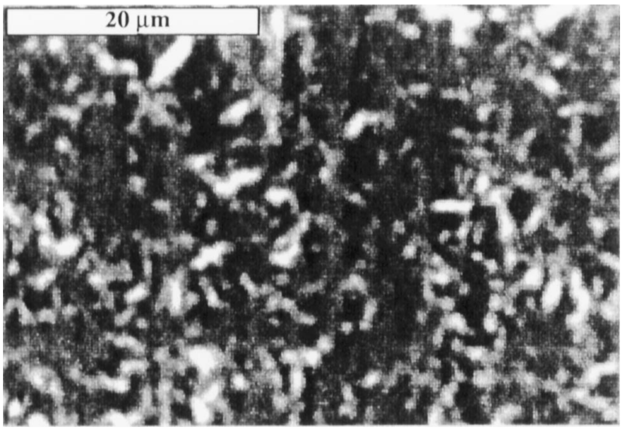


Fig. 3. SEM of a PTFE sample treated in a Mg/Na$^+$ solution. [Mg(BF$_4$)$_2$] = 0.15 M, [e$^-$, NH$_3$] = 0.20 M, [NaBF$_4$] = 1.77 mM; treatment time, 15 min.

obtained with lithium and sodium). Upon treatment the carbon peak remained unchanged, the fluorine peak decreased by a factor about 2, whilst the oxygen peak nearly doubled.

A quantitative microanalysis of the relative amounts of each element was achieved by normalizing the F/C ratio of the different treated samples assuming that the F/C ratio of pure PTFE was equal to 2. The results are reported in Table 2. Sodium was found to be more reactive than potassium which was itself more reactive than lithium (cf. entries 1 and 2 of Table 2). The increase of defluorination with the time of treatment and the concentration of the alkali cation was clearly evident (compare entries 1, 2 and 3 for the influence of treatment time and entries 2 and 4 for the influence of concentration). When the depth of the explored zone increased by increasing the energy of the incident electron beam, the F/C ratios were higher because a larger proportion of untreated PTFE was then analysed (cf. entries 4 and 5 of Table 2).

3.2.1.3. Depth of attack. Images of the morphology of slices through PTFE samples were also obtained. The above part of Fig. 6 represents the morphology of a slice through a PTFE sample which had been treated by potassium (analogous figures were obtained with lithium and sodium); the horizontal line indicates the position from where the profile was taken and the spectrum below shows the fluorine composition along the line indicated (in the same way carbon profiles were also obtained). The depth of attack of the reactant through the PTFE plaque was taken as the distance between the surface and the point where the amount of fluorine detected was the same as in the bulk sample, corrected by the size of the X-ray probe (about 1.5 ± 0.5 μm). The elemental profile of an untreated sample (cf. Fig. 4 of Ref. [21]) shows that the amount of fluorine in the sample is approximately constant throughout the sampling depth and drops off as soon as the fluorine-free resin starts, whilst the profile of the sample which was treated by the K$^+$ solution shows an area of gradual decline in the amount of fluorine that was detected. For samples treated for 30 min in alkali cation solutions the following depths of attack, *d* were measured: for [Li$^+$] = 8.6 mM, $d \approx 2.0 + 0.5$ μm, for [Na$^+$] = 5.9 mM, $d \approx 2.5 + 0.5$ μm and for [K$^+$] = 4.7 mM, $d \approx 2.0 + 0.5$ μm. The comparison of the depths of attack observed with the

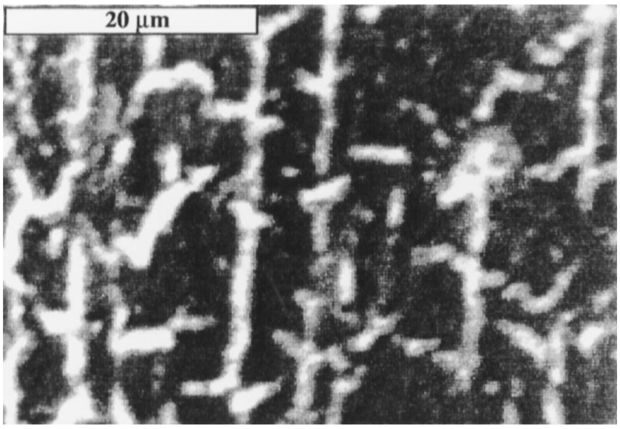


Fig. 4. SEM of a PTFE sample treated in a Mg/K$^+$ solution. [Mg(BF$_4$)$_2$] = 0.15 M, [e$^-$, NH$_3$] = 0.20 M, [KBF$_4$] = 1.22 mM; treatment time, 15 min.

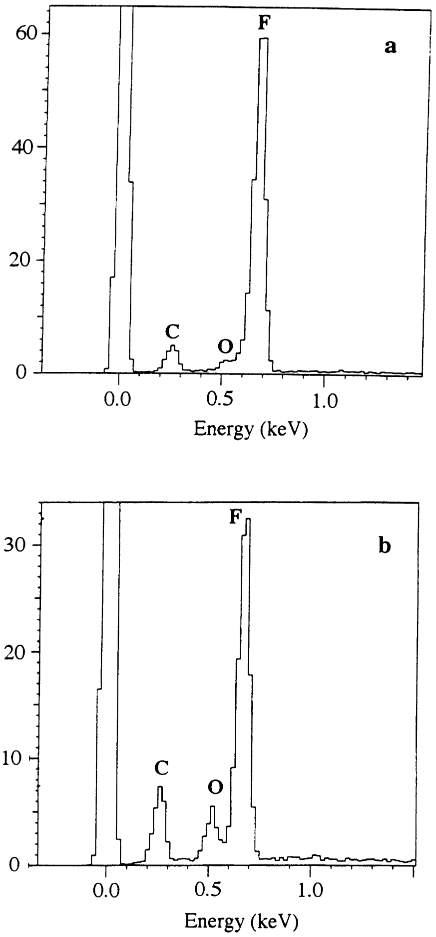


Fig. 5. X-ray fluorescence spectra of PTFE samples. (a) Untreated; (b) treated for 5 min in a potassium solution. [Mg(BF$_4$)$_2$] = 0.15 M, [e$^-$, NH$_3$] = 0.20 M, [KBF$_4$] = 1.22 mM.

Table 2
Scanning electron microscopy, X-ray fluorescence analysis of samples of PTFE plaque treated by magnesium/alkali cations solutions[a]

Entry	$[M^+]^b$ (mM)	Time of treatment (min)	$E^{\circ c}$ (keV)	F/C		
				Li	Na	K
1	4.7	1	10	1.3	0.52	0.84
2	4.7	5	10	0.35	0.07	0.22
3	4.7	30	10			$< 0.10^d$
4	1.2	5	10	2	1.2	
5	1.2	5	5	2	0.85	
6	5.9	30	10		$< 0.15^d$	
7	8.6	30	10	$< 0.12^d$		

[a] Estimated from the X-ray fluorescence spectra of the PTFE surface
[b] $[M^+]$: [LiCl] or $[NaBF_4]$ or $[KBF_4]$
[c] Energy of the incident X-ray beam
[d] Estimated from the profile image

different alkali cations confirms therefore the higher reacticity of sodium compared to lithium or potassium. At such depths, the order of magnitude of the F/C ratios could be deduced from the C and F profiles; they were always lower than 0.10 (cf. entries 3, 6, 7 of Table 2). When the concentration of the alkali cation increased, the depth of attack increased too: in a previous paper it was estimated to $\approx 8.0\ \mu m$ for a 15 min treatment in a 0.3 M sodium solution [21].

3.2.2. XPS [25, 28, 29]

3.2.2.1. XPS spectra. X-ray photoelectron spectra of untreated PTFE plaques consist mainly of two elemental peaks relative to carbon and fluorine atoms (cf. entry 1 of Table 3). Upon a 1 min treatment in a magnesium solution (i) the peak of fluorine decreased a little (F/C = 1.75 instead of 2) largely until about 90%; (ii) the peak of carbon, which corresponded mainly to $\mathbf{C}F_2$ groups (at ~293 eV) for untreated PTFE could be divided into three sub-peaks: still the $\mathbf{C}F_2$ peak which was 25% smaller and two additional peaks: the first one at ~285 eV which corresponded mainly to carbon or hydrogen elements ({**C**–C, **C**=C, **C**H}), and the second one at ~288 eV, which corresponded to oxygen or monofluorinated atoms ({**C**OH, **C**=O, **C**HF, $\mathbf{C}O_2H$}) and represented between 5% and 15% of the total carbon atoms (cf. entry 2 of Table 3).

When a small amount (< 10 mM) of alkali cation was present in the magnesium solution the same type of XPS spectrum was observed as with magnesium alone. The main change was the increase of the intensity of the {**C**–C, **C**=C, **C**H} peak which represented between 44% and 68% of the total carbon peak. The peak relative to {**C**OH, **C**=O, **C**HF, $\mathbf{C}O_2H$} also increased upon addition of the alkali cation. The intensity of that peak did not significantly depend on the alkali cation concentration nor on the time of treatment, and represented about 15%–20% of the total carbon atoms peak intensity. The {**C**OH, **C**=O, **C**HF, $\mathbf{C}O_2H$} peak itself could be deconvoluted into three sub-peaks at ~287 eV {**C**OH}, ~288 eV {**C**=O, **C**HF} and ~289 eV {$\mathbf{C}O_2H$}, among which the {**C**OH} sub-peak was the largest (about 15% of the total carbon atoms peak intensity). An example of such a deconvolution is represented in Fig. 7 for a PTFE sample treated for 30 min in a Mg/Li^+ solution and clearly demonstrates the observations already mentioned: the main carbon peak is that of {**C**–C, **C**=C, **C**H} groups and the largest peak among the oxygenated peaks corresponds to {**C**OH} groups. In this case, the {$\mathbf{CF_2}$} peak has nearly totally disappeared which resulted from both the long treatment time and the relatively high concentration of the alkali cation added; such a disappearance was not observed for lower treatment times and concentrations.

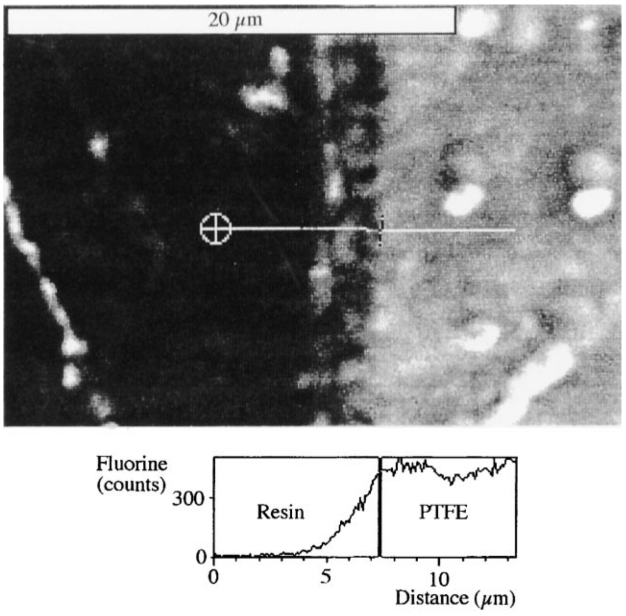


Fig. 6. SEM profile image of a sample of PTFE. The spectrum below shows the fluorine composition along the line indicated. $[Mg(BF_4)_2] = 0.15$ M, $[e^-, NH_3] = 0.20$ M, $[NaBF_4] = 5.9$ mM; treatment time, 30 min.

Table 3
XPS analysis of samples of PTFE plaque treated by magnesium in the presence of small amounts of various cations

Entry	Sample (eV)	Proportion of C at binding energy, E_b			Relative proportions of O and F	
	E_b^a	285.0 ± 0.5 C–C, C=C CH	287.0–289.0 ± 0.5 COH, C=O, CO$_2$H, CHF	293.3 ± 0.5 CF$_2$	O/C ($S_O = 3.1$)	F/C ($S_F = 3.7$)
1	Untreated	0	2	98	0.04	2.00
2	Mg[b,c]	13	14	73	0.05	1.75
3	Mg/Li$^+$[b,d]; θ[e] = 0°	44	16	40	0.15	0.98
4	Mg/Li$^+$[b,d]; θ[e] = 45°	54	15	31		0.86
5	Mg/Li$^+$[b,d]; θ[e] = 60°	61	14	25		0.72
6	Mg/Na$^+$ [b,f]	68	16	16	0.15	0.33
7	Mg/K$^+$ [b,g]	59	24	17	0.19	0.43
8	Mg/NBu$_4^+$[b,h]	64	12	24	0.17	0.54
9	Mg/NBu$_4^+$[i,j]	65	21	14	0.18	0.34

[a] Binding energy
[b] Treatment time, 1 min
[c] [NH_4BF_4]: 0.3 M; [e^-, NH_3]: 0.15 M
[d] [LiCl]: 1.24 mM added to solution *c*.
[e] Take-off angle
[f] [$NaBF_4$]: 1.77 mM added to solution *c*
[g] [KBF_4]: 1.22 mM added to solution *c*
[h] [NBu_4BF_4]: 3.1 mM added to solution *c*
[i] Treatment time: 2 min
[j] [NBu_4BF_4]: 3.1 mM added to solution *c*

3.2.2.2. Influence of the alkali cation. The XPS analyses of PTFE samples treated for 1 min in magnesium solutions in the presence of 1–2 mM solutions of different cations are summed up in Table 3. The proportions of {**C**OH}, {**C**=O, **C**HF} and {**C**O$_2$H} were not reported in the table since they did not vary significantly in the different experiments and were similar to those observed in Fig. 7.

The same trends were observed for sodium or potassium (cf. entries 6, 7 of Table 3). In such cases, the treatment resulted in the {**C**–C, **C**=C, **C**H} ratio increasing to about 60–70% and the {**C**F$_2$} ratio decreasing to about 15%; the proportions of oxygen and fluorine relative to carbon were in agreement with the deconvolution of the carbon peak (O/C ≈ 0.15–0.20, F/C ≈ 0.30–0.50). Lithium was found to be the least reactive among the alkali cations: the {**C**–C, **C**=C,

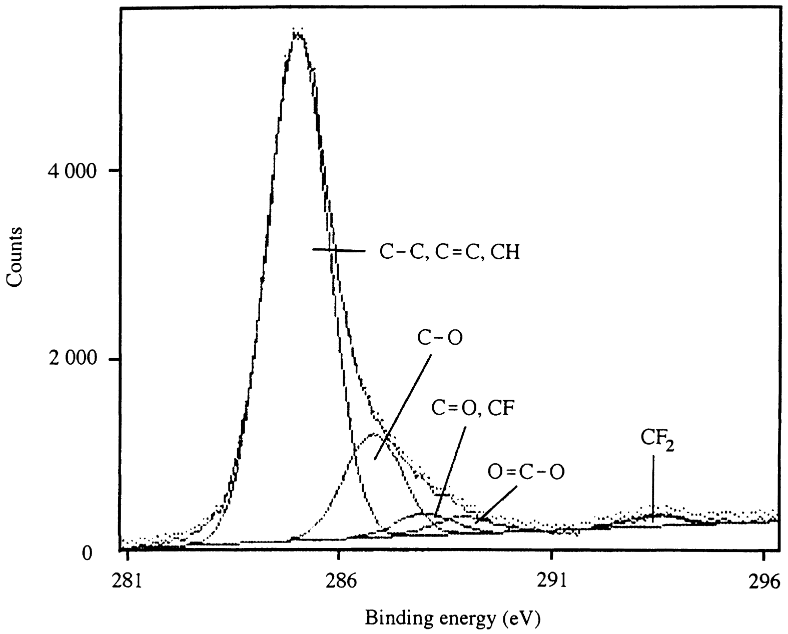


Fig. 7. High-resolution XPS spectrum of a Mg/Li$^+$-treated PTFE sample, carbon atom peaks. [$Mg(BF_4)_2$] = 0.15 M, [e^-, NH_3] = 0.20 M, [LiCl] = 1.24 mM; treatment time, 30 min.

CH} ratio was lower at ≈ 45% and the F/C ratio higher at ≈ 0.98 (cf. entry 3 of Table 2).

The phenomena observed are not limited to alkali cations since when similar experiments were performed in the presence of the tetrabutylammonium cation instead of alkali cations, similar observations were made: (i) the PTFE samples became dark and porous; and (ii) the same variation of the surface carbon composition was observed as with sodium or potassium (cf. entry 8 of Table 3).

3.2.2.3. Depth profile. XPS analyses at different emission angles, θ (measured from the normal to the surface) of the lithium-treated samples provided a depth profile (cf. entries 3–5 of Table 3) since when θ increases, surface emission is increasingly favoured over bulk emission. As expected, when θ increased the amount of {**C**–C, **C**=C, **C**H} also increased whilst the {**C**F$_2$} percentage and the F/C ratios decreased. This suggested a lower severity of attack than the depth explored by XPS (about 5 nm), which is in agreement with the results obtained by X-ray fluorescence (cf. entries 4, 5 of Table 2, C/F ≈ 2). This result is specific to small concentrations of lithium (1.2 mM) and short treatment times (1 min).

3.2.2.4. Influence of the concentration of the alkali cation. The influence of the concentration of the alkali cation added to a magnesium solution on the composition of the surface is represented in Fig. 8 in the case of the lithium treatment. For a treatment time of 1 min, when the concentration of lithium chloride increased up to about 9 mM, the {**C**–C, **C**=C, **C**H} percentage increased to about 65%, whilst the {**C**F$_2$} percentage and the F/C ratio decreased, respectively, to about 5% and 0.1. In the same range of concentrations, no effect was observed with more efficient reagents, such as sodium or potassium, for which the depth of attack is larger than 5 nm; with lower concentrations an effect should possibly be observed, but from an experimental point of view, it would not have been reasonable to precisely handle concentrations lower than 1 mM. In the case of the X-ray fluorescence method, the influence of the concentration has been evidenced with the three alkali cations since the explored depth is larger than with XPS (1 μm instead of 5 nm).

3.2.2.5. Influence of the treatment time. In the range of concentrations 1–10 mM, the time of treatment had an influence with the three alkali cations investigated. The influence of the treatment time on the composition of the surface is represented in Fig. 9 in the case of the lithium treatment (1.24 and 8.61 mM). Similar curves were observed with the other two alkali cations except that the increase of {**C**–C, **C**=C, **C**H} and the decrease of F/C were quicker than for lithium. The {**C**–C, **C**=C, **C**H} percentage increased up to about 80% in all cases but the increase was sharper with the most concentrated solution: the 80% value was observed after only 1 min of treatment with the 8.61 mM solution and after 10 min with the least concentrated solution. In the same way, the {**C**F$_2$} percentage and the F/C ratio decreased to approximately 0 after 1 min of treatment in the 8.61 mM solution and after 10 min in 1.24 mM solution. The influence of the treatment time was also observed with the tetrabutylammonium cation (cf. entries 8 and 9 of Table 1).

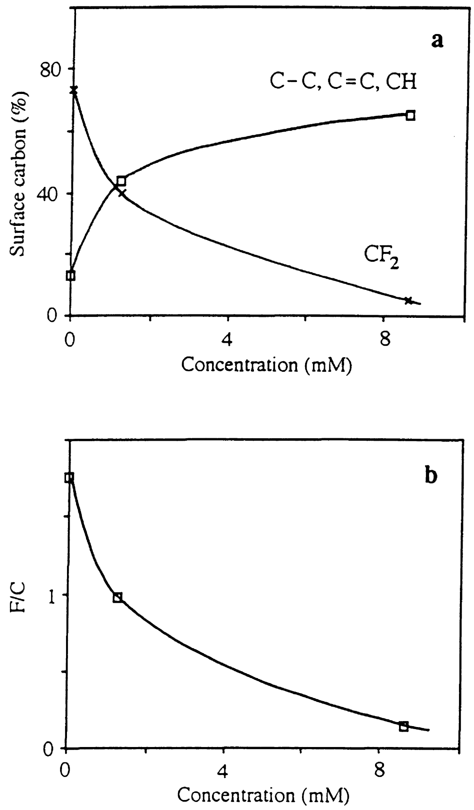


Fig. 8. Variation of the functionality of the surface carbon (a) and the F/C ratio (b) with the concentration of the lithium chloride added to a magnesium solution. [Mg(BF$_4$)$_2$] = 0.15 M, [e$^-$, NH$_3$] = 0.20 M; treatment time, 1 min.

3.3. Magnesium treatment in the presence of nucleophiles (Nu$^-$ in MgNu$_2$)

3.3.1. Evidence of chemical grafting of the nucleophile

The XPS results obtained with diethylphosphite are shown in Table 4.

In a first experiment we have immersed a PTFE sample into a 0.2 M solution of diethylphosphite in the absence of solvated electrons (cf. entry 1 of Table 4). The XPS spectrum corresponded to that of pure PTFE: each carbon atom was surrounded by two fluorine atoms, the F/C ratio was about 2 (a little lower) and no phosphorus was detected.

In the following experiments the concentrations of the solvated electron varied between 1 and 40 mM. The XPS spectra of samples treated in the presence of both magnesium and diethylphosphite were comparable to those observed in the absence of nucleophile: the samples were defluorinated whilst their oxygen and nitrogen content increased and the signal at 285 eV for {**C**–C, **C**=C, **C**H} represented the main contribution to the carbon peak. The main new factor was the detection of a phosphorus peak (cf. Fig. 10) whose intensity was rather low (0.25% $P/C < 0.5\%$). Since the P amounts observed by XPS were close to the XPS limit of detection, we used ToF SIMS which is a more sensitive and more superficial technique to detect fragments of the nucleophile at the surface of the polymer. Both the negative and positive ToF SIMS spectra exhibited some differences upon addition of the nucleophile, but the effects were more easily observed in the negative ion spectra. The latter are represented in Figs 11 and 12 for samples treated in the absence (entry 10 of Table 4) and in the presence (entry 3 of Table 4) of diethylphosphite, respectively. The chemical composition of the prominent peaks observed in the spectra is given in Table 5. Upon addition of the nucleophile, the main effect observed on the spectra was the appearance of peaks at 137 and 207 *m*/*z* which correspond to the nucleophile itself and to the nucleophile bonded to a polymer fragment (see in Table 5), respectively. Peaks observed at 59, 149, 163 *m*/*z* are due polydimethylsiloxane $(Me_2Si{-}O)_n$, a very common surface contaminant. Some less important trends might also be mentioned: (i) the increases of the peaks at 19.00 (F), 38.00 (F_2), 69.00 (CF_3) which corresponded to a smaller extent of defluorination of the surface in the presence of the nucleophile (already noticed by XPS) since the treatment solution used was less reductive (concentration of the solvated electron: 5 mM instead of 150 mM); (ii) the single peak at 31.00 (CF) had become a double peak because of the

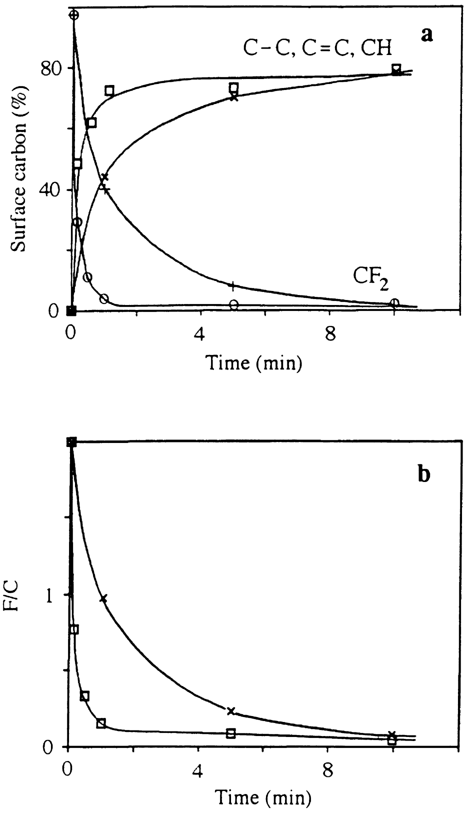


Fig. 9. Variation of the functionality of the surface carbon (a) and the F/C ratio (b) with treatment time. Reactant, Mg/Li$^+$. $[Mg(BF_4)_2] = 0.15$ M, $[e^-, NH_3] = 0.20$ M, $[LiCl] = 1.24$ mM (x, +) or 8.61 mM (□, ○).

Table 4
XPS analysis of samples of PTFE plaque treated by magnesium/magnesium diethylphosphite solutions

Entry	$[e_s]^b$ (mM)	Proportion of C at binding energy, E_b (%)			Relative proportions of O, F and P		
	E_b^a (eV)	285.0 ± 0.5 **C**–C, **C**=C, **C**H	287.0–289.0 ± 0.5 **C**OH, **C**=O, **C**O$_2$H, **C**HF	293.0 ± 0.5 **C**F$_2$	O/C ($S_O = 3.1$)	F/C ($S_F = 3.7$)	P/C ($S_P = 1.6$)
1	0^c	11	7	82	0.05	1.70	0
2	1^c	75	12	13	0.15	0.25	0.0035
3	5^c	75	9	16	0.20	0.30	0. 0050
4	10^c	73	11	16	0.22	0.24	0. 0037
5	20^c	71	4	25	0.16	0.56	0. 0037
6	40^c	79	4	17	0.10	0.43	0. 0025
7	40^d	79	19	2	0.22	0.08	0. 0028
8	150^e	75	7	18	0.12	0.40	0. 0009
9	150^f	52	9	39	0.09	0.08	0
10	150^g	85	7	8	0.21	0.23	0

[a] Binding energy

[b] Solvated electrons concentration

[c] $[(EtO)_2PO^-]$: 0.2 M

[d] $[(EtO)_2PO^-]$: 0.2 M; [NaBF4]: 0.3 M; treatment time, 1 min

[e] $[(EtO)_2PO^-]$: 0; treatment time, 30 min. Then the plaque was immersed into a solution of $(EtO)_2POH$ + *tert*-BuOK for 30 min

[f] $[(EtO)_2PO^-]$: 0; treatment time, 30 min. Then the plaque was immersed into a solution of $(EtO)_2POH$ for 30 min

[g] $[(EtO)_2PO^-]$: 0; treatment time, 30 min

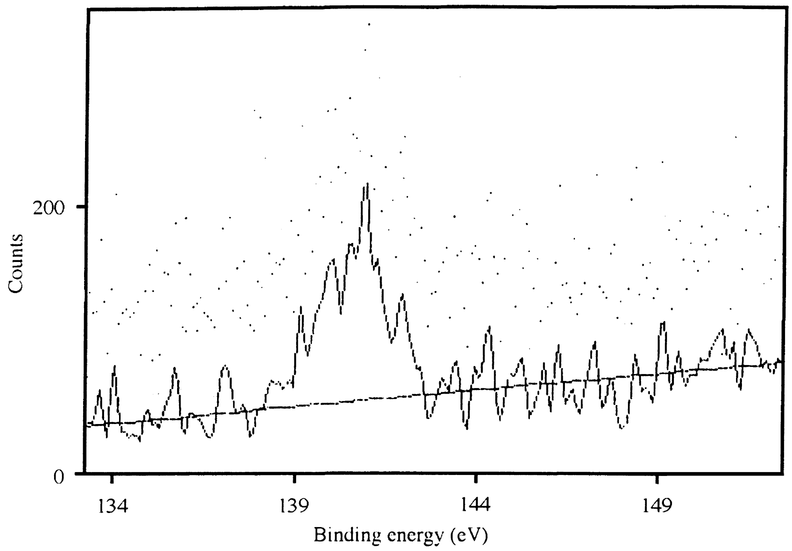


Fig. 10. High-resolution XPS spectrum of a PTFE sample, phosphorus atom peak. [e^-, NH_3] = 5 mM, [$(EtO)_2PO^-$] = 0.2 M.

emergence of P fragments at 30.97 (cf. Fig. 13); (iii) the appearance of a fragment at 62.96 (PO_2).

Additional experiments were also performed according to slightly different procedures. When the treatment was performed in the presence of sodium, the phosphorus amount was nearly the same and defluorination was higher (entry 7, Table 4). This has already been observed when magnesium and sodium treatments were compared. When $(EtO)_2PO^-$ was added after the magnesium reductive treatment had been performed (cf. entry 8, Table 4), phosphorus was present at the surface of the sample at a smaller extent (0.09% instead of 0.25–0.50%) but in an analogous procedure with $(EtO)_2POH$ instead of $(EtO)_2PO^-$ no phosphorus was detected (cf. entry 9, Table 4).

In the cases of thiophenoxide and the anions of 2-mercaptopyridine and thiourea, the same effects were observed by XPS: the surface composition was roughly the same as that observed in the absence of nucleophile and sulfur was present on the XPS spectra (cf. entries 1–5 of Table 6). The greatest effect was observed with thiophenoxide which led to a proportion of sulfur relative to carbon of about 4%. In the other cases the sulfur content was lower than 1%.

In all cases the variations of the oxygen content as a function of the presence of the nucleophile could not reliably be taken into account since its dispersion was too high. Interpretations related to the nitrogen content were also difficult to make since the magnesium treatment in the absence of nucleophile resulted in a nitrogen content different from zero (2% at maximum). Anyway, when using nitrogen nucleophiles such as the anions of thiourea or norvaline ($CH_3(CH_2)_2CH(NH_2)CO_2^-$), one trend can be mentioned: the nitrogen content increased to values higher than 2% (3% and 5% for thiourea and norvaline, respectively). In the case of diethylphosphite and the sulfur anions, the phosphorus (or sulfur) peaks could not be attributed to physical pollution of the sample since in the absence of nucleophile, no phosphorus peak (nor sulfur) was detected (cf. entries 10 of Table 4 and 6 of Table 6). In all cases it seemed to us that it was reasonable to postulate the chemical grafting of the nucleophile to the polymer and to interpret the results in view of already-known mechanisms of nucleophilic substitutions. Furthermore, grafting of various reducing agents to PTFE had already been mentioned under photochemical inducement [30].

3.3.2. Interpretation

The processes of chemical reduction of fluoropolymers were discovered in the 1950s but their mechanism is not yet completely clear [11]. Most authors agree on the first step which consists of partial defluorination [31,32]:

$$-CF_2- \; + \; e^- \longrightarrow -\dot{C}F- \; + \; F^- \qquad (8)$$

This assumption is in agreement with studies of molecular reactions involving perfluoroalkyl halides [33,34] in which the existence of perfluoroalkyl radicals $R_F^\cdot$ has been pointed out. These radicals may be obtained from perfluoroalkyl halides by photolysis [35], thermolysis [36], through metals or metal complexes [37], anions [38] and radical anions [39]. They can also be produced by simple decomposition of unstable sulfonyl iodides [40], thermal decomposition of perfluoro- and polyfluoro- acyl peroxides [41] or perfluoro carboxylic acids [42]. Electrochemistry is another means to obtain $R_F^\cdot$ radicals, which may be obtained at the anode by oxidation of perfluorocarboxylic anions [43], or at the cathode by reduction of perfluoroalkyl halides [44–46].

Perfluoroalkyl radicals were reported to react with nucleophiles such as 2,6-di-*tert*-butylphenoxide, 2-mercaptothiazolinethiolates and imidazolates under electrochemical inducement via a $S_{RN}1$ type reaction [33]. In our case, the electron induction is necessary to obtain a 0.25–0.50% of phosphorus since in the absence of electron

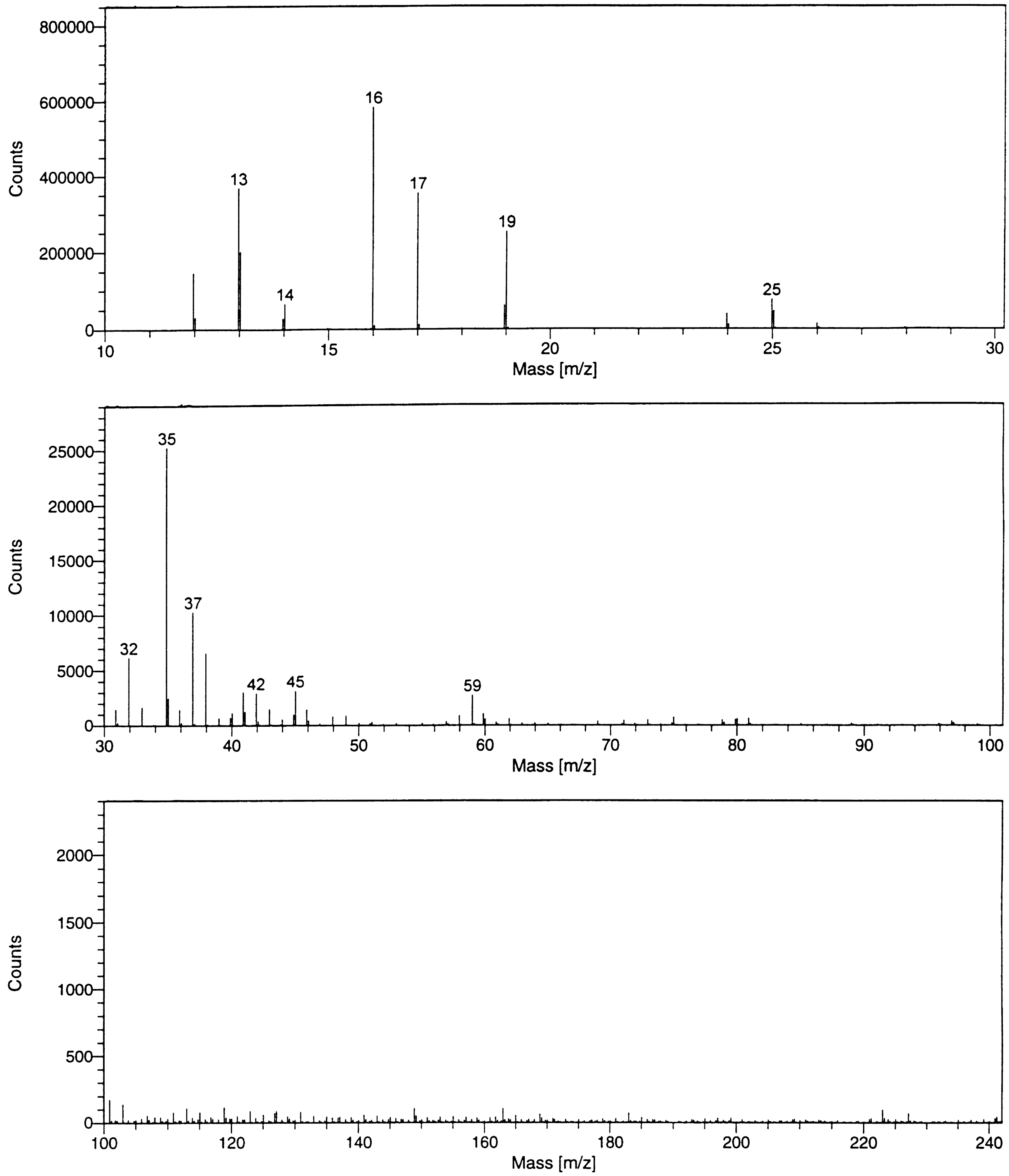


Fig. 11. ToF SIMS spectrum of a magnesium-treated PTFE sample, negative peaks. [e^-, NH_3] = 150 mM; treatment time, 30 min.

induction (cf. entry 8 of Table 4) phosphorus was detected at the PTFE surface to a smaller extent (0.09% only). Substitution of PTFE by nucleophiles in the presence of the solvated electron can therefore be interpreted by a nucleophilic substitution at the level of the perfluoroalkyl radical obtained by the reductive cleavage (8). The addition of the perfluoroalkyl radical to the nucleophile leads to the anion radical of the substitution product:

$$—\dot{C}F— \xrightarrow{Nu^-} (>CF—Nu)^{\dot{}-} \quad (9)$$

which is readily oxidized:

$$(>CF—Nu)^{\dot{}-} - e^- \longrightarrow >CF—Nu \quad (10)$$

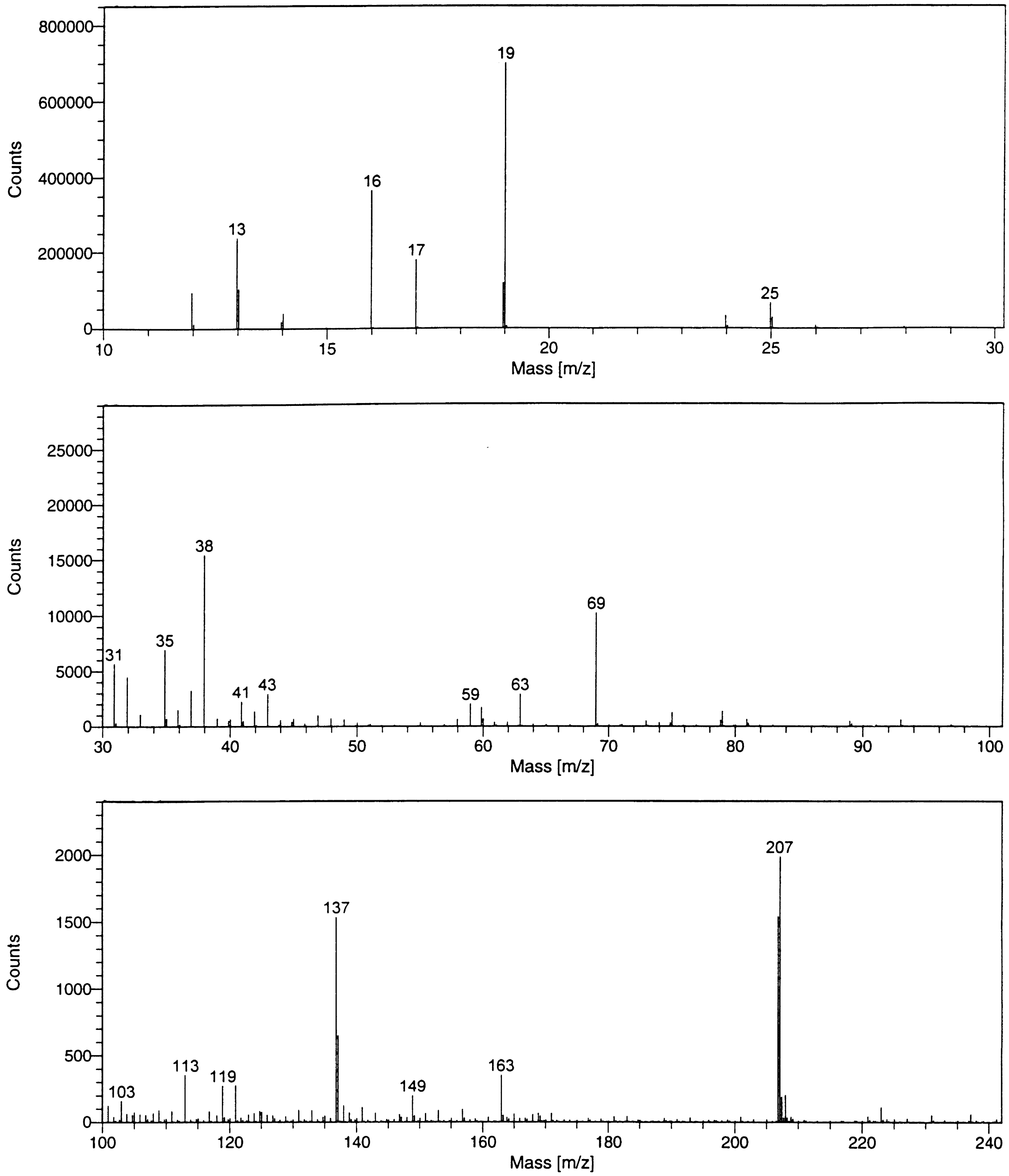


Fig. 12. ToF SIMS spectrum of a magnesium-treated PTFE sample in the presence of diethylphosphite, negative peaks. [e^-, NH_3] = 5 mM, [$(EtO)_2PO^-$] = 0.2 M.

The nucleophilic addition is in competition with a second reduction of the perfluoroalkyl radical leading to a double bond:

$$-\dot{C}F-CF_2- \;+\; e^- \longrightarrow -CF{=}CF- \;+\; F^- \tag{11}$$

or to a carbanion:

$$-\dot{C}F- \xrightarrow{e^-} -CF^- - \tag{12}$$

which can undergo further protonation by any acidic impurity in the solvent (or by the solvent itself) or elimination of hydrofluoric acid with a vicinal hydrogenated carbon atom.

When the sample was immersed into an $(EtO)_2PO^-$ solution after the reductive treatment and not at the same time (cf. entry 8 of Table 4), the phosphorus content was smaller

Table 5
ToF SIMS spectrum of a magnesium-treated PTFE sample in the presence of magnesium diethylphosphite, negative peaks

m/*z*	Chemical composition
12	C
13	CH
16	O
17	OH
19	F
25	C_2H
31	P/CF
32	O_2
35	Cl
37	Cl
38	F_2
59	$SiOCH_3$
63	PO_2
69	CF_3
137	$(EtO)_2PO$
149	$Si_2O_3C_3H_9$
163	$Si_2O_2C_5H_{15}$
207	$(EtO)_2POHCF_3$

$[e^-, NH_3] = 5$ mM; $[(EtO)_2PO^-]$: 0.2 M

and in that case an $S_{RN}1$ type reaction does not uphold because of the absence of induction. However, since the PTFE sample had been first activated by the magnesium treatment a classical nucleophilic substitution could be assumed. It is well-known that highly fluorinated compounds cannot undergo nucleophilic substitutions whilst less-fluorinated compounds can [33]. In the same way, when PVDF was immersed into solutions of either *tert*-butoxide or ethoxide, the F/C ratio decreased to about 15% whilst the O/C ratio increased to about 25% [22]. Such reactions are not possible with untreated PTFE (cf. entry 1 of Table 4, P/C = 0). However, defluorinated PTFE obtained after the magnesium reductive treatment could undergo nucleophilic substitution in the same way as PVDF. But the phenomenon could also be interpreted by physical adsorption of the anion at the surface of PVDF or PTFE. Our present results are not sufficient to postulate one of the two mechanisms. When $(EtO)_2POH$ was used as the nucleophile (cf. entry 9 of Table 4), no phosphorus was detected since the nucleophilic character of the acid is weaker than that of the corresponding basic species.

Since (i) the relative proportions of phosphorus or sulfur obtained by XPS were often close to the detection limit (0.04%) and (ii) ToF SIMS gives qualitative information only, a quantitative interpretation of the results obtained in the presence of solvated electrons is not reasonable. The low yields observed could be explained by a too high concentration of the solvated electrons which would be in favour of reduction instead of substitution. The difference between the different yields obtained could be due to the following. (i) A poor control of the concentration of the solvated electron in the medium; this problem could be circumvented by the voltammetric control of the oxidation peak of the solvated electrons during the reaction. (ii) Different reactivities of the nucleophiles; the reactivity of the nucleophiles investigated towards aryl radicals in ammonia containing magnesium salts is not known at present (it is only known in ammonia containing alkali salts). (iii) A difference between the diffusion coefficients of the nucleophiles inside the polymer; computer modelling showed that the smallest nucleophile was the anion of thiourea and the largest diethylphosphite; diffusion coefficients are expected to follow the same trend. In the case of thiourea, the situation is more complicated since (i) the electrochemical reduction of thiourea may lead to the dianion and not only to the monoanion and (ii) the solubility of such anions in a

Table 6
XPS analysis of samples of PTFE plaque treated by magnesium/sulfur nucleophiles solutions

Entry	$[e_s]^b$ (mM)		Proportion of C at binding energy, E_b (%)			Relative proportions of O, F and P		
		E_b^a (eV)	285.0 ± 0.5 **C**–C, **C**=C, **C**H	287.0–289.0 ± 0.5 **C**OH, **C**=O, **C**O$_2$H, **C**HF	293.0 ± 0.5 CF$_2$	O/C ($S_O = 3.1$)	F/C ($S_F = 3.7$)	S/C ($S_S = 2.2$)
1	$C_6H_5S^-$	5^c	68	18	14	0.14	0.31	0.043
2	$C_6H_5S^-$	$0–11^d$	70	9	21	0.09	0.54	0.016
3	$C_6H_4NS^-$	20^e	41	17	41	0.13	0.95	0.009
4	$SCNH_2NH^-$	5^f	75	18	7	0.15	0.18	0. 0007
5	$SCNH_2NH^-$	$0–23^g$	75	18	7	0.19	0.18	0. 0048
6		150^h	85	7	8	0.21	0.23	0

Nucleophiles: magnesium salts of thiophenoxide and the anions of 2-mercaptopyridine and thiourea
[a] Binding energy
[b] Solvated electrons concentration
[c] $[C_6H_5S^-]$: 0.14 M
[d] $[C_6H_5S^-]$: 0.14 M; the solvated electrons were obtained continuously by passing 83 Cb through the circuit under a 45 mA intensity; treatment time, 30 min
[e] $[C_6H_4NS^-]$: 0.056 M.
[f] $[SCNH_2NH^-]$: 0.2 M
[g] $[SCNH_2NH^-]$: 0.2 M; the solvated electrons were obtained continuously by passing 190 Cb through the circuit under a 125 mA intensity; treatment time, 25 min
[h] $[Nu^-]$: 0; treatment time, 30 min

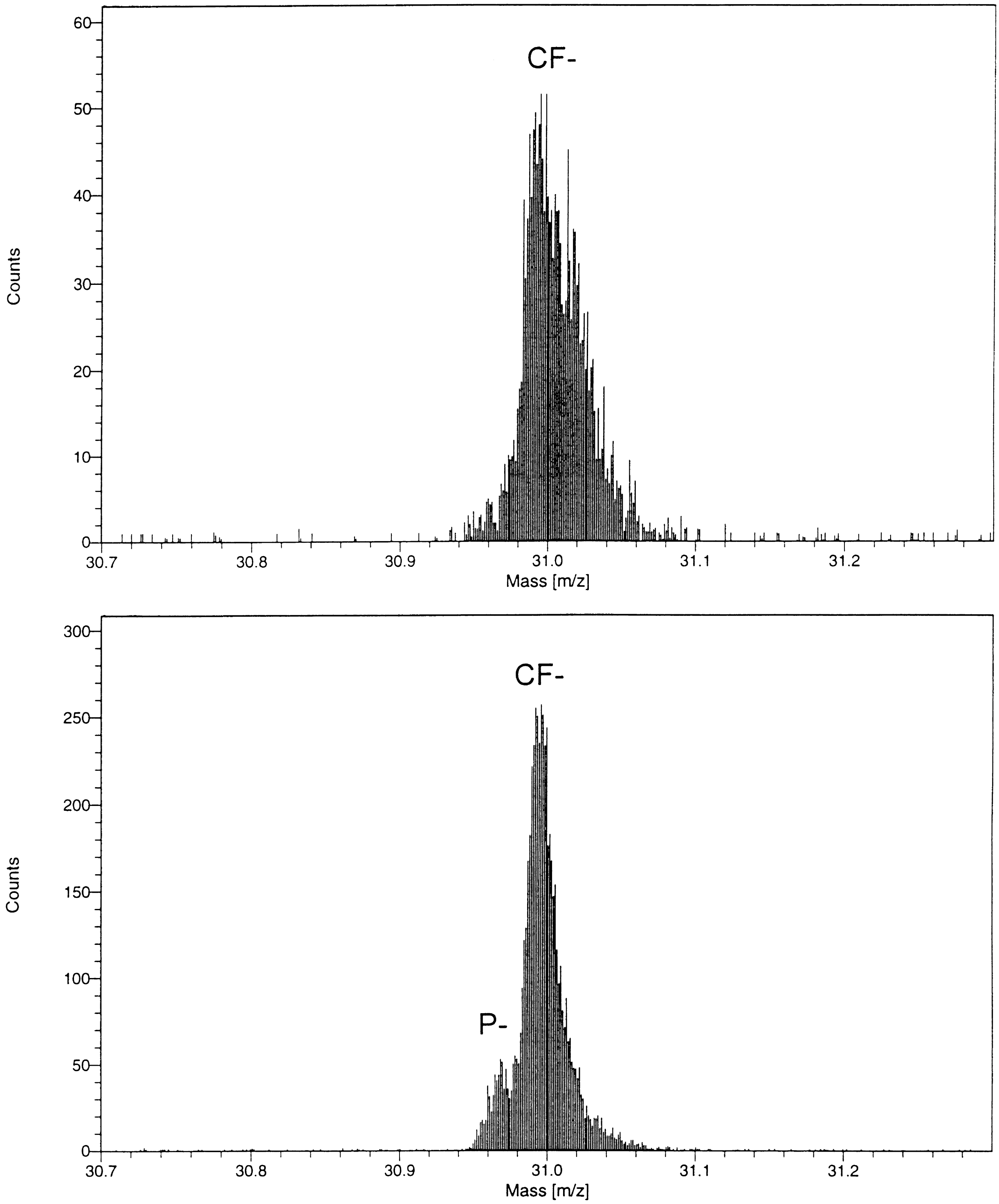


Fig. 13. ToF SIMS spectrum of a magnesium-treated PTFE sample in the presence of diethylphosphite, negative peaks, expansion of the zone around *m*/*z* = 31. [e^-, NH_3] = 5 mM, [$(EtO)_2PO^-$] = 0.2 M.

medium containing magnesium cations is lower than that in a medium containing alkali cations only and could be lower than the expected 0.2 M.

4. Conclusion

The reactivity of a magnesium solution towards PTFE was affected by the presence of an alkali cation or a nucleophile but the magnitude of the change was very different in the two cases.

The presence of a small amount of an alkali cation in the magnesium solution dramatically increased the rate of defluorination. The effect was observed for concentrations down to 1 mM and treatment durations of only 10 s. The rate of defluorination increased with the concentration of the alkali cation and the treatment time. In the presence of the alkali cation oxygenation of the surface was enhanced. Oxygenated substituents were mainly COH groups (O/C $\approx$ 15%–20% by XPS whatever the concentration of the alkali cation and the treatment time). The presence of the alkali cation made the polymer porous. The depth of attack also increased with the concentration of the alkali cation and the treatment time. For 30 min treatments in 5–8 mM solutions of alkali cations, the depths of attack were about 2–3 μm. Sodium was found to be more reactive than potassium which was itself more reactive than lithium. The phenomenon was not limited to alkali cations since it was also observed with the tetrabutylammonium cation.

When a nucleophile such as diethylphosphite, thiophenoxide or the anions of 2-mercaptopyridine and thiourea was present in a solution of magnesium containing a moderate amount of solvated electrons ($<$ 50 mM), the grafting of the nucleophile to the polymer was detected by XPS and ToF SIMS. The results could be interpreted by an electron-induced $S_{RN}1$ type reaction. However the proportions of either phosphorus or sulfur relative to carbon were too low ($<$ 5% determined by XPS) to allow a quantitative interpretation. The low yields of substitution observed could be due either to a too high concentration of solvated electrons or to a poor reactivity of the nucleophiles in the magnesium medium or to a weak diffusion of the nucleophile inside the polymer.

Efforts are devoted at present to the increase of the yields of substitution. The efficiency of nucleophilic substitution of PTFE should be increased by using both alkali cations and nucleophiles. Since PTFE becomes porous when an alkali cation is present in a magnesium solution, the role of the alkali would be to insure the diffusion of the nucleophile into the polymer. The amount of alkali should be low ($\approx$ 1 mM) in order to favour substitution of PTFE instead of reduction.

By using nucleophiles possessing specific properties, such as the ability to complex to or to adsorb onto some selected organic compounds, new perfluorinated membranes could be obtained with possible applications in the purification of effluents and the concentration of traces. Nucleophiles such as phosphonic and phosphinic acids, pyrazolones, oxazolones or calixarenes should be interesting for that purpose.

Acknowledgements

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References

[1] Carlson DP, Schmiegel W. In: Ullmann's encyclopedia of industrial chemistry, vol A11, 5th ed. New York: Wiley, 1988:393–429.

[2] Gangal SV. In: Encyclopedia of polymer science and engineering. New York: Wiley, Vol. 16, 1989.

[3] Hung MH, Burch RR. J Appl Polym Sci 1995;55:549.

[4] Lee KW, McCarthy T. J Macromol 1987;20:1439.

[5] Dias AJ, McCarthy T. J Macromol 1987;20:2068.

[6] Lee KW, McCarthy T. J Macromol 1988;21:2318.

[7] Kolb BU, Patton PA, McCarthy T. J Macromol 1990;23:366.

[8] Cross EM, McCarthy T. J Macromol 1990;23:3916.

[9] Allmer K, Feiring AE. Macromol 1991;24:5487.

[10] Said MA, Balik CM, Carlson JD. J Polym Sci Polym Phys 1988;26:1457.

[11] Kavan L. In: Chemistry and physics of carbon, vol 23. New York: Marcel Dekker, 1991:71–171.

[12] Kavan L. Chem Rev 1997;97:3061.

[13] Brecht H, Mayer F, Binder H. Angew Makromol Chem 1973;33:89.

[14] Dwight DW, Riggs WM. J Colloid Interf Sci 1974;47:650.

[15] Riggs WM, Dwight DW. J Electron Spectrosc Rel Phen 1974;5:447.

[16] Lepoutre G, Sienko MJ. In: Benjamin WA, editor. Metal-ammonia solutions—physicochemical properties. New York, 1964.

[17] Kavan L, Bastl Z, Dousek FP, Jansta J. Carbon 1984;22:77.

[18] Costello CA, McCarthy T. J Macromol 1984;17:2940.

[19] Combellas C, Kanoufi F, Marzouk H, Thiébault A. French patent 95 09726.

[20] Brace K, Combellas C, Delamar M, Fritsch A, Kanoufi F, Shanahan MER, Thiébault A. J Chem Soc Chem Commun 1996:403.

[21] Brace K, Combellas C, Delamar M, Dujardin E, Kanoufi F, Shanahan MER, Thiébault A. Polymer 1997;38:3295.

[22] Belzung B, Brace K, Combellas C, Delamar M, Kanoufi F, Shanahan MER, Thiébault A. Polymer 1997:in press.

[23] Allmer K, Feiring AE. Macromol 1991;24:5487.

[24] Combellas C, Lu Y, Thiébault A. J Appl Electrochem 1993;23:841.

[25] Beamson G, Briggs D. In: High resolution XPS of organic polymers. The scienta ESCA 300 database.

[26] Schueler B, Sander P, Reed DA. Vacuum 1990;41:1661.

[27] Nicholls. In: Inorganic chemistry in liquid ammonia, Monograph 17. Amsterdam: Elsevier, 1979:9,16.

[28] Eberhart JP. In: Analyse structurale et chimique des matériaux, Dunod, 1983. Méthodes physiques d'étude des minéraux et des matériaux solides.

[29] Briggs D, Seah MP. In: Practical Surface Analysis, 1, Auger and X-ray Photoelectron Spectroscopy. New York: Wiley, 1990.

[30] Allmer K, Feiring AE. Macromol 1987;20:2819.

[31] Costello CA, McCarthy TJ. Macromol 1987;20:2819.

[32] Chakrabarti N, Jacobus J. Macromol 1988;21:3011.

[33] Médebielle M, Pinson J, Savéant JM. J Am Chem Soc 1991;113:6872.
[34] Wakselman C. J Fluorine Chem 1992;59:367.
[35] Andrieux CP, Gélis L, Savéant JM. Tetrahedron Lett 1989;30:4961.
[36] Cowell A, Tamborski C. J Fluorine Chem 1981;17:345.
[37] Chen QY, Qiu ZM. J Fluorine Chem 1988;39:289.
[38] Wakselman C, Tordeux M. J Org Chem 1985;50:4047.
[39] Wakselman C, Tordeux M, Clavel JL, Langlois B. J Chem Soc Chem Commun 1991:993.
[40] Huang WY, Hu LQ. J Fluorine Chem 1989;44:25.
[41] Yoshida M, Yoshida T, Kobayashi M, Kagimata N. J Chem Soc Perkin Trans 1989;1:909.
[42] Tanabe Y, Matsuo N, Ohno N. J Org Chem 1988;53:4582.
[43] Muller N. J Org Chem 1986;51:263.
[44] Andrieux CP, Gélis L, Médebielle M, Pinson J, Savéant JM. J Am Chem Soc 1990;112:3509.
[45] Andrieux CP, Gélis LJ, Savéant JM. J Am Chem Soc 1990;112:786.
[46] Amatore C, Gomez L, Calas P, Commeyras A. J Fluorine Chem 1990;49:247.