Surface modification of poly(vinylidene fluoride) by alkaline treatment Part 2. Process modification by the use of phase transfer catalysts

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Abstract

A detailed study of the alkaline modification of poly(vinylidene fluoride) (PVdF) by a phase transfer catalyst (PTC) medium has been carried out by X-ray photoelectron spectroscopy, (XPS), secondary ion mass spectrometry (SIMS) and Raman spectroscopies, to determine the composition of the modified surface layer. The study indicates the formation of a surface layer consisting of conjugated C=C bonds, concomitant with surface defluorination and the inclusion of oxygen functionalities on treatment. A previous investigation studied the affect of alkaline treatment, however without the use of PTCs (Ross GJ, Watts JF, Hill MP, Morrissey P. Surface modification of poly(vinylidene fluoride) by alkaline treatment. 1. The degradation mechanism Polymer 2000;41: 1695–96.), that produced a surface layer with different functionalities. A mechanism for the degradation process in the presence of a PTC is proposed in this paper, which includes the formation of the polyene structure followed by hydroxide attack to yield hydroxyl and carbonyl groups and more complex oxygen functionalities. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinylidene fluoride); Conjugation; Phase transfer catalysts

1. Introduction

Surface treatment of poly(vinylidene fluoride) (PVdF) with concentrated sodium hydroxide, increases its resistance to attack by other harsh caustic environments. Although this is an effective treatment, it can take many hours to complete, which is far too long to be implemented as a commercial process. There have been a few studies [2] indicating that the process can be accelerated by the use of phase transfer catalysts (PTCs), with sodium and potassium hydroxides [3–5]. This paper sets out to expand the data presented in the literature, and compare the results with that of samples treated with concentrated sodium hydroxide [1].

According to the original definition [6], phase transfer catalysis accelerates or permits reactions between ionic compounds and organic, water insoluble, substrates in solvents of low polarity. Such catalysts are typically onium salts, which readily solubilize alkali metal ions. The basic function of the catalyst is to transfer anions of the reacting salt into the organic medium in the form of ion

pairs. As a result of the nature of the catalysts, the activity is strongly related to the hydrophilic-hydrophobic balance, i.e. the distribution of the catalyst between the aqueous and organic phase. Therefore the solvophobic nature of the polymer is considered to affect the ability of the catalyst.

Cho and Song [2] used Fourier transform infrared (FT-IR) and ultra-violet (UV–VIS) spectroscopy to investigate the reaction mechanism, and proposed the following for the PTC assisted alkaline modification of PVdF:

$$(-CH_2-CF_2-)_n + NaOH \xrightarrow[OH^-]{PTC} (-CH=CF-)_n + NaF + H_2O$$

Mechanism 1
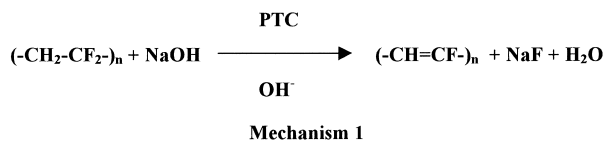
Owen et al. [7,8] investigated the surface modification of PVC, and Kise and Ogata investigated the surface modification of PVdF [3]. Both concluded that C=C double bonds were almost exclusively formed in a conjugated manner; Kise and Ogata suggested that triple bonds were also formed. Dias and McCarthy [4] and Hahn and Percec [9] also reported the formation of double and triple bonds with no apparent oxygen incorporation, with alkaline treatment of PVdF, the experiments were carried out under vacuum

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Table 1
Experiments were conducted in 250 cm^3 of 4 M NaOH solution at 80°C in a waterbath shaking at 110 revolutions per minute

Catalyst	Moles	Reaction time (hours)
TBAH	0.125	2
TBAB	0.125	0.5, 1 and 2
TBPB	0.125	2
	0.0025	1,2,4,8,12 and 24
TBAHS	0.125	2
	0.0025	1,2,8 and 24
	0.00125	1,2,8 and 24

and a nitrogen atmosphere, respectively. Brewis et al. [5] did however expand Mechanism 1 to include formation of hydroxide and carbonyl groups on the polyene chain as shown below in Mechanism 2:
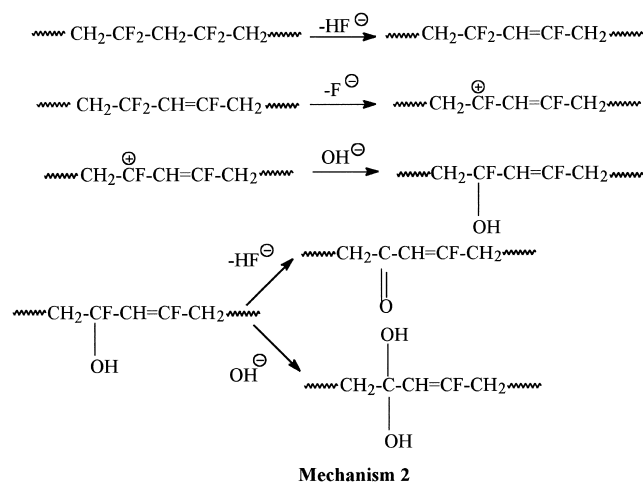
Mechanism 2

Mechanism 1 is generally accepted, however Brewis et al. have indicated that there are oxygen functionalities present on treatment, which are not accounted for by this mechanism. The aim of the current paper is to develop a mechanistic model of the alkaline degradation of PVdF in the presence of PTCs, and compare this model to that described in Ref. [1] for the alkaline treatment alone. The model will be based on chemical analysis obtained by X-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectroscopy (ToF-SIMS) and Raman spectroscopy. ToF-SIMS and XPS are surface chemical analysis techniques that complement each other well, particularly for the analysis of organic polymers. Raman spectroscopy was chosen for its unique ability to estimate the extent of conjugation within the modified layer.

2. Experimental

PVdF film samples (25, 50 and 100 μm in thickness) were mounted in polypropylene frames fixed with nylon

screws to ensure no curling of the film, to reduce contamination through handling and to prevent problems due to surface proximity effects. The films were cleaned with isopropanol, followed by rinsing in milli-Q water (0.056 Scm^{-1}). The samples were treated with 250 cm^3 of 4 M NaOH (Analar grade NaOH), and between 0.00125 and 0.125 mol (i.e. between 0.005 and 0.5 mol/dm^3) of PTC at 80°C in a shaking waterbath, at 110 revolutions per minute, between 1 and 48 h. The experimental details are summarised in Table 1, the PTCs used were:

1. Tetrabutyl ammonium bromide (TBAB). $(C_4H_9)N^+ Br^-$
2. Tetrabutyl phosphonium bromide (TBPB). $(C_4H_9)P^+ Br^-$
3. Tetrabutyl ammonium hydrogen sulphate (TBAHS). $(C_4H_9)N^+ HSO_4^-$
4. Tetrabutyl ammonium hydroxide solution (TBAH). $(C_4H_9)N^+ OH^-$

The generic structure of the catalysts is shown below:
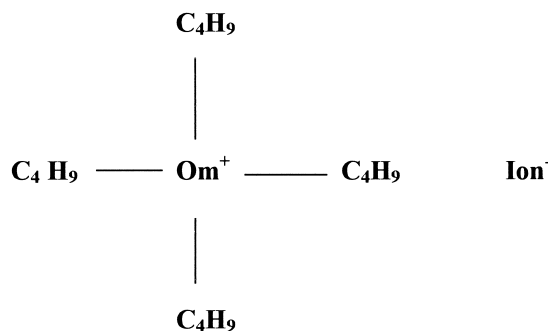
where $Om^+ =$ onium cation N^+ or P^+; $Ion^- = Br^-$, OH^-, or HSO_4^-.

On removal from the solution, the samples were rinsed in milli-Q water to quench the reaction.

Analyses were carried out by XPS, ToF-SIMS and Raman spectroscopy.

3. Analytical studies

Surface analysis was carried out using XPS and ToF-SIMS. Two spectrometers were employed for XPS; a VG Scientific ESCALAB MKII and a Scienta ESCA 300 spectrometer [10]. To account for charging, the binding energy is calibrated by adjusting all peaks by the amount required to place the C1s line representative of C–H/CH2 at 285.0 eV. The ToF-SIMS spectra were obtained using a VG Scientific Type 23 system equipped with a Poschenreider time of flight system and a MIG300PB pulsed liquid ion source. The results are normalised with regard to total ion yield to account for variations in total spectral intensity. The Raman spectra were recorded using a DILOR XY multichannel spectrometer in the backscattering mode, using a 632 or 514.53 nm resonant lines of He–Ne or Ar^+ laser, respectively.
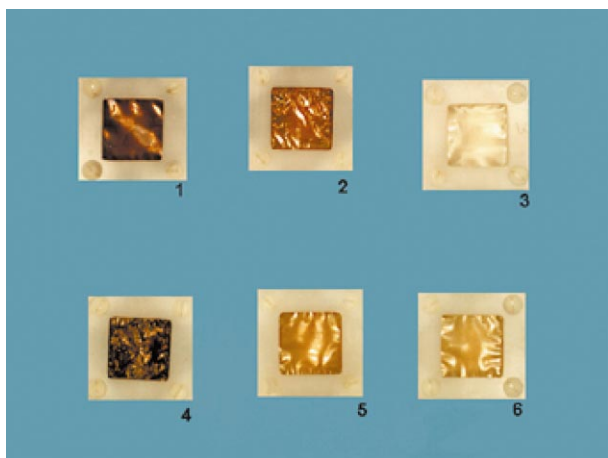
Fig. 1. Change in colour of the PVdF 50 μm films after treatment with 4 M NaOH and 0.125 mol of PTC at 80°C: (1) TBAHS 2 h; (2) TBPB 2 h; (3) TBAH 2 h; (4) TBAB 2 h; (5) TBAB 1 h; and (6) TBAB 30 min.

Full details of the spectral interpretation and modes of operation of the spectrometers have been provided in a previous publication [1].

4. Results

4.1. Phase transfer catalyst selection

Initially, four solutions of aqueous 4 M sodium hydroxide were prepared, each with 0.125 mol of a different catalyst, added to 250 cm^3 of solution. One film was placed in each solution for 2 h. Two more samples were placed in solution 1 (TBAB) and removed after 0.5 and 1 h. This catalyst was selected as the most effective for surface modification of PVdF by the literature [2], and was therefore chosen to investigate the kinetics of the surface treated reactions.

Prior to treatment the PVdF samples were translucent white in appearance. After treatment a colour change was observed for all films, as shown in Fig. 1. The TBAB, TBPB and TBAHS treated films (2 h) were a deep brown colour, whereas the TBAH treated film showed little colour change. Analytical

Table 2
Elemental concentrations of samples treated with 4 M NaOH at 80°C for 2 h with different catalysts (0.125 mol added)

Catalyst	Surface concentration (at%)				
	Carbon	Oxygen	Fluorine	Sodium	Nitrogen
PVdF	54.5	3.4	42.0	–	–
48 h[a]	64.2	9.8	24.4	–	1.6
256 h[a]	70.2	29.1	0.6	–	–
TBAHS	69.3	25.4	4.1	1.2	–
TBAB	86.5	9.1	3.3	1	–
TBPB	93.1	3.7	1.9	1.2	–
TBAH	62.3	13.5	23.7	0.5	–

[a] No catalyst; 12 M NaOH used; 48 h or 256 h treatment time.
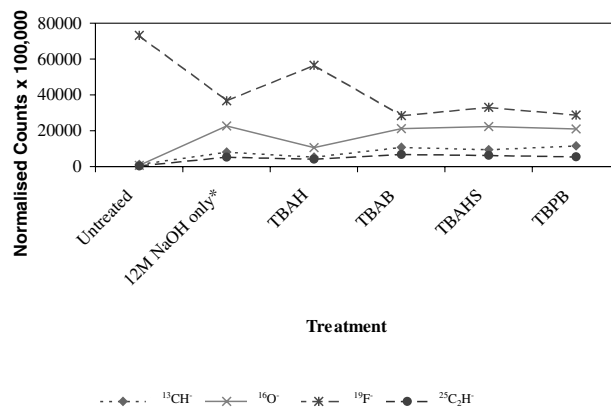
Fig. 2. Negative ToF-SIMS counts for PVdF samples treated at 80°C for 2 h with 4 M NaOH with 0.0125 mol of different catalysts added.

techniques, such as XPS and SIMS, were used to determine the chemical functionality of the resultant modified layers.

The treated PVdF samples were analysed by XPS and the results are shown in Table 2, including samples treated with no PTC present. These results clearly indicate that, over the same time periods, significantly more defluorination occurs with the catalysts than with NaOH alone, with the exception of TBAH. These data support Fig. 1, in that the catalysts may work via different mechanisms. They also show that defluorination occurs to the same extent with all the catalysts, with the exception of TBAH. The samples were also analysed by ToF-SIMS, and the change in intensity for the elemental ions F$^-$ and O$^-$ and the hydrocarbons CH$^-$ and C$_2$H$^-$ are shown in Fig. 2. The ToF-SIMS results indicate that, the catalysts reduce the F$^-$ intensity, with the exception of TBAH. This catalyst is not as effective as the others studied in this investigation, and therefore was not studied further. The ToF-SIMS results show that the catalyst treatment produces hydrocarbon intensities that are consistent with conjugated structures, as shown in Fig. 3. In choosing fragments representative of conjugated structures, there is a compromise that must be reached between low-intensity higher mass ions and those at a relatively modest mass, which have a higher intensity. Having established that such conjugated structures are a distinct possibility, the comparison between different PTCs is more readily made in the low-mass ions.
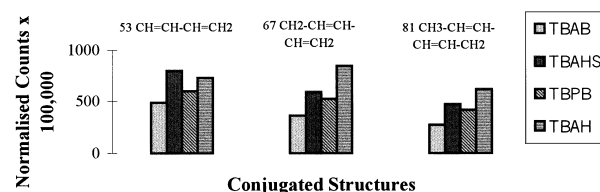

Fig. 3. Possible conjugated structures in the positive ToF-SIMS spectra of PVdF treated at 80°C for 2 h with 4 M NaOH with 0.125 mol of catalyst added.
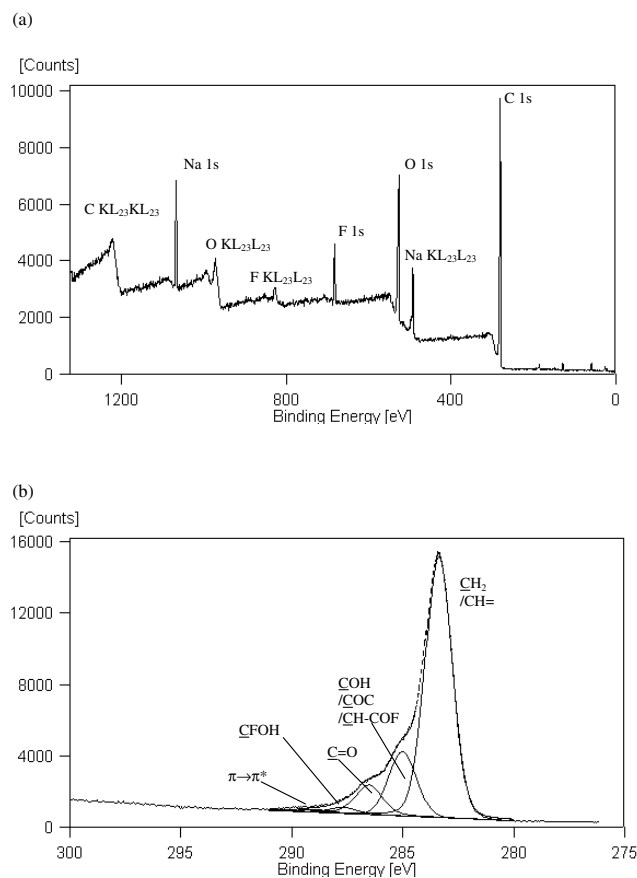
(a)

(b)

Fig. 4. XPS spectra of PVdF after treatment at 80°C for 4 h with 4 M NaOH with 0.0025 mol of TBPB added: (a) survey spectra; and (b) C 1s peaks.

To compare levels of oxidation between treatments, similar levels of defluorination must be considered, as this relates to the extent of the reaction (see Table 2). All the catalysts, with the exception of TBAHS at these concentrations, promote less oxygen inclusion than with sodium hydroxide treatment alone. The XPS results indicate that more oxygen is included in the TBAHS sample than the TBAB and TBPB samples. Therefore, TBPB with the least amount of oxygen inclusion and TBAHS with the most oxygen inclusion, were chosen for further investigations.

PVdF samples were treated with different concentrations of TBAHS, (0.00125 and 0.0025 mol in 250 cm^3 of 4 M NaOH), there was no appreciable difference in the surface

Table 3
Carbon peak assignments for PVdF after treatment with 4 M NaOH at 80°C with PTCs using the ESCA 300

Peak	Binding energy	Full width; half maximum	Assignment
1	285.0	1.3	CH–CH
2	286.6	1.5	CH–CFOH/COH/COC
3	288.0	1.5	C=O/CF
4	289.0	1.3	COHF/COOH/CF=
5	290.4	1.3	$\pi^* \rightarrow \pi^*$
6	290.4	1.2	CF$_2$

Table 4
Atomic percentage of elements of PVdF on treatment with 4 M NaOH at 80°C with 0.0025 mol of TBPB added

Time (h)	Element percentage						
	C	O	F	Na	P	N	Br
24[a]	54.5	3.4	41.6	0.0	0.4	0.0	0.0
1	75.7	16.6	2.7	2.0	1.3	1.6	0.3
2	73.3	17.0	4.1	4.0	1.5	0.0	0.5
4	70.9	18.7	4.0	4.0	1.3	0.0	0.7
8	72.4	20.5	3.0	3.0	0.6	0.0	0.5
12	72.4	20.5	3.0	3.0	0.6	0.0	0.5
24	70.1	20.3	3.4	4.6	0.9	0.0	0.7

[a] 24 h treatment with 0.01 M TBPB and no NaOH.

analysis data between the two concentrations, this is expected for catalysts that are present in excess proportions. The addition of 0.0025 mol of PTC was chosen for future experiments as it is above the minimum required concentration.

4.2. XPS analysis

XPS was used to analyse the second set of samples that were treated with 4 M NaOH and 0.0025 mol of catalyst (TBPB or TBAHS) at 80°C between 0 and 24 h. Fig. 4 shows the survey spectrum and the fitted carbon 1s spectrum of PVdF, treated with 0.0025 mol of TBPB and 4 M NaOH at 80°C after 4 h treatment. The assignments of the carbon 1s peaks are shown in Table 3. These results show that after 4 h of treatment, the surface modification involves oxygen inclusion along with almost complete defluorination at the XPS analysis depth of approximately 5 nm. It is shown that oxygen could be present in the form of hydroxyl, and carbonyl groups; however, the assignment of the peaks in Fig. 4 could be, as shown in Table 3, more than just one component. The remaining fluorine groups are present, either in the form of CF, =CF or HO–C–F groups. No CF$_2$ groups remain while the presence of a $\pi \rightarrow \pi^*$ shake-up satellite, peak 5, indicates the formation of conjugated C=C structures. Changes in the surface concentration of elements with time of treatment with TBPB, is shown in Table 4. In this table, the extent of oxygen inclusion reaches 20%, after 8 h treatment, but does not increase with longer times. At shorter treatment times (~1 h) the oxygen inclusion is at least 16%, therefore, the relative increase in oxygen between 1 and 8 h of treatment is low. Coupled with the fact that only 3–4% fluorine remains in the XPS analysis depth after 1 h of treatment, this suggests that the reaction is almost complete after 1 h. The presence of phosphorus and bromine is proof of the inclusion of the catalyst into the sample, albeit in very small quantities. Table 5 shows the surface composition with respect to carbon functionalities over treatment time with TBPB.

Tables 6 and 7 present the information, in the same format as Tables 4 and 5, but for the PTC, TBAHS. Table

Table 5
Surface composition, with respect to carbon functionalities for PVdF treated in 4 M NaOH at 80°C with 0.0025 mol of TBPB as a function of time

Time (h)	Surface concentration of carbon functionalities (at%)					
	CH_2	COH/COC/ CH–COHF	C=O/CF	COHF/	$\pi^* \rightarrow \pi^*$	CF_2
24[a]	7.3	26.0	1.3	0.0	0.0	20.2
1	53.9	14.2	4.7	2.3	1.0	0.0
2	50.6	11.7	6.1	3.0	1.5	0.0
4	50.3	12.6	6.2	1.3	0.6	0.0
8	52.6	11.8	6.1	1.8	0.6	0.0
12	48.3	15.3	4.9	3.5	0.0	0.0
24	46.7	16	4.5	2.9	0.0	0.0

[a] 24 h treatment with 0.01 M TBPB and no NaOH.

6 shows the concentration of elements of PVdF after treatment with 4 M NaOH and 0.0025 mol of TBAHS at 80°C. The presence of nitrogen indicates that the catalyst has interacted with the surface, although the concentration is very small. Again the concentration of oxygen is about 20% and does not change appreciably between 1 and 24 h of treatment. The percentage of fluorine drops to around 3% within 1 h of treatment. Table 7 shows surface composition with respect to carbon functionalities, as a function of TBAHS treatment time. These tables show the same possible types of oxygen and fluorine inclusion as for the TBPB samples described above. Again, the presence of the $\pi \rightarrow \pi^*$ shake-up satellite indicates the formation of a conjugated C=C structures.

A typical fluorine spectrum of a TBPB treated sample is shown in Fig. 5, two components can be clearly identified, one representative of sodium fluoride and the other of either CF, =CF, or HO–C–F. The peak representing CF_2 in the untreated sample lies at 688.0 eV, as expected, however after treatment the fluorine peak is shifted slightly (to 687.4 eV). This is not typical of CF which should lie at 687.0 eV, but could be shown as being representative of HO–C–F. The fluorine spectra of the TBAHS treated samples are almost identical to that of the TBPB treated samples, therefore the same conclusions can be drawn.

The catalysts, at these low-concentration levels, acceler-

Table 6
Atomic percentage of elements of PVdF on treatment with 4 M NaOH at 80°C with 0.0025 mol of TBAHS added

Time (h)	Element percentage				
	C	O	F	Na	N
24[a]	52.5	2.1	45.4	1.0	0.0
1	67.9	21.3	3.6	5.5	1.7
2	69.9	21.1	3.7	3.8	1.5
4	63.6	19.2	6.9	9.0	1.3
8	88.0	10.9	1.0	1.0	0.0
12	76.0	19.4	2.3	2.3	0.0
24	73.3	19.9	2.5	3.1	1.2

[a] 24 h treatment with 0.01 M TBAHS and no NaOH.

Table 7
Surface composition, with respect to carbon functionalities for PVdF treated in 4 M NaOH at 80°C with 0.0025 mol of TBAHS added, as a function of time

Time (h)	Surface concentration of carbon functionalities (at%)					
	CH_2	COH/COC/ CH–COHF/ CH–CF_2	C=O/ CF	COHF	$\pi^* \rightarrow \pi^*$	CF_2
24[a]	2.0	25.6	1.0	1.0	0.0	23.2
1	43.2	13.5	3.6	6.6	1.0	0.0
2	43.3	17.4	7.4	1.8	0.0	0.0
4	39.7	15.2	5.8	2.3	1.0	0.0
8	72.8	10.9	0.9	3.3	0.0	0.0
12	52.7	15.7	5.8	2.0	0.0	0.0
24	48.8	13.4	5.4	4.3	0.9	0.0

[a] 24 h treatment with 0.01 M TBAHS and no NaOH.

ate the defluorination reaction and reduce the incorporation of oxygen into the sample. Oxygen is present as hydroxyl and carbonyl groups. The fluorocarbon species that remain are not in the form of CF_2 groups. Conjugated double bonds are evident in the XPS carbon 1s spectra as shown by the presence of the $\pi \rightarrow \pi^*$ shake-up satellite at 290.4 eV. After 1 h of treatment, the reaction appears to be complete in both cases. There is no significant difference between the catalyst treatments at this level of PTC concentration, in stark contrast to the data in Table 2 where a higher concentration of TBPB leads to little oxygen incorporation.

4.3. ToF-SIMS analysis.

The negative and positive ToF-SIMS spectra of untreated PVdF are shown in Fig. 6. The negative spectrum contains fluorocarbon and hydrocarbon peaks, as shown in Fig. 6(a). The negative spectrum between *m/z* 1–19 has not been included as it is dominated by an elemental fluorine peak, this is expected as a result of the sensitivity of SIMS to fluorine, and for the fact that PVdF is 33 at% fluorine. There are also peaks representing elemental oxygen, carbon, CH and CH_2, however such peaks explain little about the overall structure. There are also chlorine peaks present at
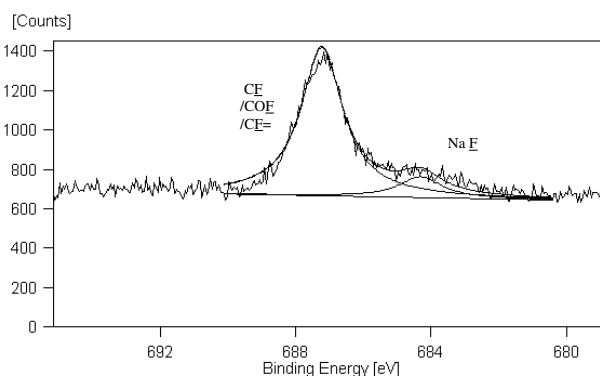

Fig. 5. F1s spectra of PVdF treated at 80°C for 4 h with 4 M NaOH with 0.0025 mol of TBPB added.
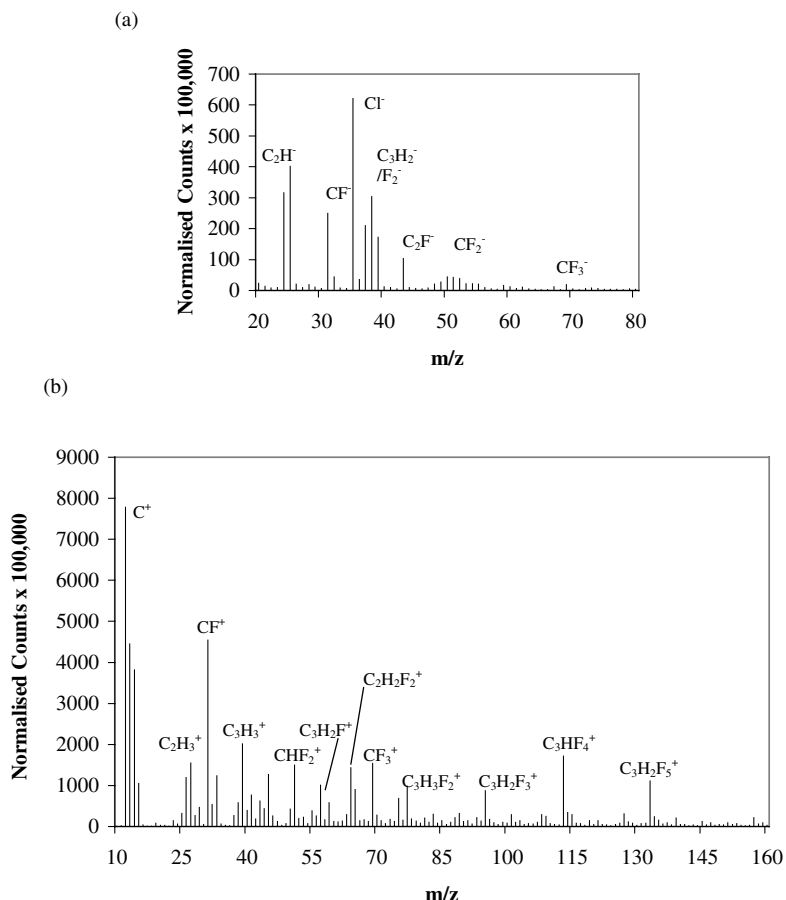
(a)

(b)

Fig. 6. ToF-SIMS spectra of untreated PVdF: (a) negative spectra; and (b) positive spectra.

$m/z = 35$ and 37, this is just contamination, negative SIMS spectra are very sensitive to electronegative ions such as F^- and Cl^-, the chlorine ion intensity is insignificant in comparison to that of the fluoride ion intensity. The fluorocarbon fragments, such as $C_3HF_4^+$ dominate the positive spectrum, Fig. 6 (b), is as expected.

Prior to interpreting the spectra obtained through the catalyst treatments, the catalysts were analysed by ToF-SIMS. Each catalyst was separately dissolved in milli-Q water, and a droplet of solution was dried onto aluminium foil. The resulting spectrum from the TBPB sample is shown in Fig. 7. The negative spectrum of TBPB has two very characteristic peaks attributed to bromine ($m/z = 79$ and 81). The positive ToF-SIMS spectrum shows a characteristic fragment pattern involving the removal of the butyl groups from the phosphonium ion. Characteristic peaks in the positive spectrum are: $m/z = 259$, $(P(C_4H_9)_4)^+$, and $m/z = 229$, $(PC_4H_9)_3)CH_2CH^+$.

A spectrum of PVDF, treated with 0.01 M TBPB at 80°C for 24 h was also acquired. Adsorption of the catalyst onto the PVdF sample is shown to occur by the presence of the characteristic catalyst peaks. The fluorocarbon groups obvious in untreated PVdF positive spectrum (Fig. 6 (b)), have now been attenuated by the presence of the catalyst. A small amount of catalyst, identifiable by a peak at $m/z = 259$, is responsible for this phenomenon. This must

be taken into account when comparing the spectra. However, after treatment with the catalyst alone the negative spectrum still has a substantial fluorine peak, there are no significant peaks higher in intensity than this, indicating that the catalyst does not attenuate the negative spectrum in this case. This demonstrates the introduction of the PTC with the organic polymer phase. Taking into account that the samples are washed after exposure to the environment, the PTCs are therefore adsorbed onto the polymer surface and this does not represent residual material.

Fig. 8 shows the spectra of PVdF after treatment with 4 M NaOH and 0.0025 mol of TBPB at 80°C. Fragments that could represent CFH^- groups and $CHFOH^-$ groups are present, as well as masses that could represent oxygen containing groups $((CH)_2(OH)_2^-)$ and conjugated structures $((CH_2)_4(CH)_5^-)$. Catalyst peaks, as expected, dominate the positive spectrum shown in Fig. 8(b). Small peaks representing PVdF can be found (e.g. CF_2H^+, $C_2HF_2^+$, $C_3H_2F_3^+$). There are some new peaks that are not representative of either the catalyst or the base PVdF. These could be interpreted either as conjugated or oxygen containing structures, as shown in Table 8.

The characteristic fragment pattern of TBAHS involves striping the butyl groups away from the ammonium ion, in some cases fragments are more stable when only partial
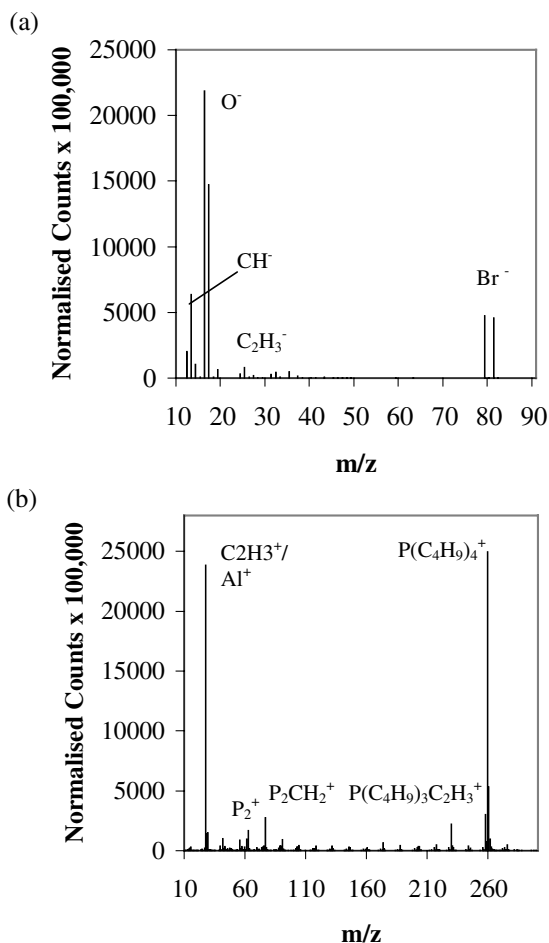
(a)

(b)

Fig. 7. TBPB ToF-SIMS spectra: (a) negative; and (b) positive.
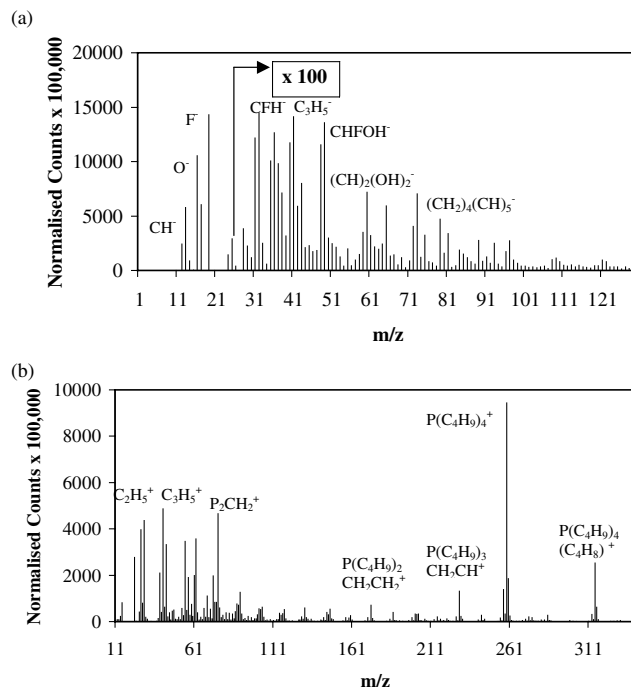
(a)

(b)

Fig. 8. ToF-SIMS spectra of PVdF treated at 80°C for 24 h with 4 M NaOH with 0.0025 mol of TBPB added: (a) negative; and (b) positive.

shown in Fig. 9 as they dominate the spectrum, therefore peaks previously attenuated are easily observed here.

4.4. Raman spectroscopy

Fig. 10 shows a Raman spectra (green laser) of untreated PVdF. The Raman spectra of PVdF after 24 h treatment in 0.01 M TBAHS and 0.01 M TBPB at 80°C are consistent with the untreated spectra, indicating that no modification of the sample has occurred.

Fig. 10 also shows Raman spectra (green laser) of the samples treated with 0.0025 mol of TBAHS between 1 and 24 h at 80°C with 4 M NaOH. Here, a dramatic change in the spectra is observed. The treated samples were found

striping of the butyl group is achieved and a CH_2 group remains, e.g. peak $m/z = 142$, $(N(C_4H_9)_2CH_2)^+$, a fragment ion characteristic of this catalyst. The other main characteristic peaks are $m/z = 242$, $(N(C_4H_9)4)^+$ and $m/z = 184$, $(N(C_4H_9)_2(C_4H_8))^+$. There are no peaks, characteristic of the catalyst in the negative spectrum that will be easily identified when on a PVdF surface. As with the TBPB, TBAHS adsorbs strongly onto the surface without modifying the PVdF surface significantly. Fig. 9 shows the ToF-SIMS spectra of PVdF after treatment with 0.0025 mol of TBAHS and 4 M NaOH at 80°C for 24 h. There are more peaks present, representative of treated PVdF in the negative spectrum, compared to that of TBPB. As shown in Fig. 9 there are intense peaks that could be representative of oxygen containing groups and conjugated structures. There is also an intense peak representing $CFHOH^-$, as is consistent with the TBPB negative spectrum and the XPS results. Catalyst peaks dominate the positive spectrum, although there are two peaks present that are not representative of the catalysts or untreated PVdF. $m/z = 135$ could be representative of $(CH)_8CH_2OH$ and $m/z = 105$, which could represent $(CH)_7CH_2$. The catalyst peaks above $m/z = 150$ (major peaks $m/z = 242$ and 184), are not

Table 8
Positive ToF-SIMS spectra assignments. Possible structures for characteristic fragments identified in Figs. 8 and 9

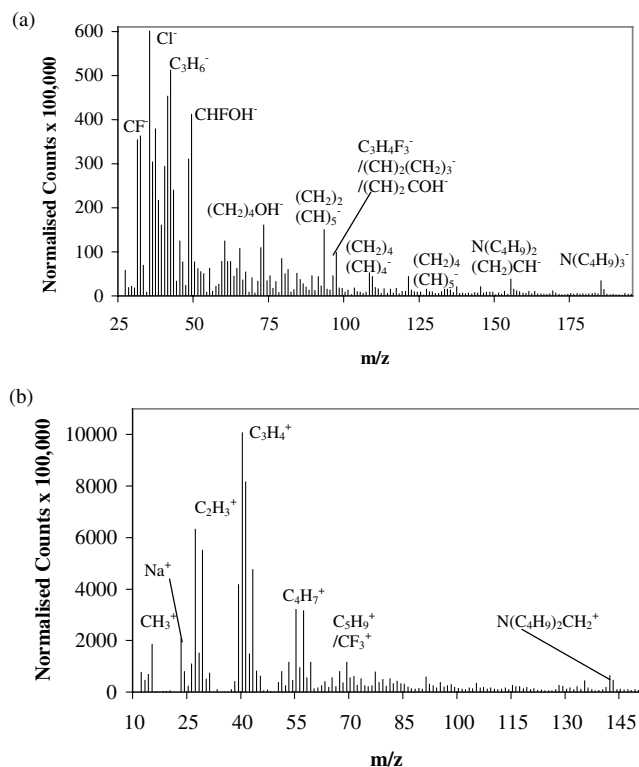| m/z	Possible structure
299	$(CH)_{23}$
	$(CH_2CHOHCHOH)_3 CHOHCHOHOH$
285	$(CH)_{21}C$
	$(CH_2)_2(CHOHCHOH)_3 CHOHCHOHOH$
273	$(CH)_{21}$
207	$(CH)_{15}C$
	$(CH_2CH)(CHOH)_6$
82	$(CH)_4CHOH$
79	$(CH)_5CH_2$
48	$CFOH$
	$CH_2(OH)_2$

Fig. 9. ToF-SIMS spectra of PVdF treated at 80°C for 24 h with 4 M NaOH with 0.0025 mol of TBAHS added: (a) negative spectra; and (b) positive spectra.

to degrade substantially under the laser, therefore the laser power was kept low (2 mW) and time was kept short (20 s), to prevent the rapid degradation of the treated films.

The majority of peaks in the fingerprint region (<900 cm^{-1}) of the spectra disappear on treatment, indicating a complete change in the structure. The peaks in the region 900–1400 cm^{-1} of untreated PVdF represent fluor-

ocarbons, most of which also disappear on treatment. The only peak to remain after treatment is the carbon–carbon single bond stretching mode, at 1129 cm^{-1}. This is shifted as it is part of a conjugated structure, as shown in Fig. 10. A new peak that appears at 1527 cm^{-1} represents the carbon–carbon double bond stretching mode of a conjugated structure. The weak vibration at 1373 cm^{-1} could be a result of the interactions of the C–C and C=C stretching modes. The Raman spectra therefore, show the formation of a conjugated carbon–carbon double bond structure.

The distance between the peaks 1129 and 1527 cm^{-1}, representing the single and double bond stretching modes, respectively, is inversely proportional to the length of the conjugated structure. This remains constant for samples treated between 1 and 24 h. However, the peak intensities do change over time, increasing in the range 1–4 h, and then decreasing rapidly with increasing fluorescence up to 24 h. The peak at 1373 cm^{-1} disappears after 8 h treatment. The increase in peak intensity is representative of an increase in the number of conjugated chains present of one specific length. After 4 h treatment, the number of chains at this specific length is reduced greatly; therefore, conjugated chain production is complete within 4 h at the Raman analysis depth. As there is a reduction in the number of chains present, a process removing these chains must be occurring, or this could represent a measure of layer stability.

The resonant enhancement of the peaks in the range analysed is a result of the π-electron polarizability and the coupling of these vibrational modes to the lowest vibrational state. Samples analysed with the red laser produced Raman spectra of inferior quality. The samples treated with 0.0025 mol of TBPB and 4 M NaOH at 80°C between 1 and 24 h, are practically identical to those obtained with TBAHS, indicating that both catalysts work in the same manner.

5. Discussion

PVdF was treated with four different catalysts, TBAH, TBAB, TBPB and TBAHS, which resulted in a colour change in all cases. The darker the colour the lower the concentration of fluorine found to be present by XPS and ToF-SIMS analysis. This is expected as it represents the formation of the conjugated layer.

Treating the samples with 12 M NaOH [1] up to 256 h reduces the fluorine concentration to approximately 99% of the initial value, and increases the oxygen concentration to 30 at%. Within 2 h of this treatment however, the fluorine has only decreased by 46%, and the oxygen incorporation has only reached 10 at%. In the experiments prepared here, the hydroxide concentration was reduced to 4 M, but the presence of the catalyst increased the rate of reduction of fluorine to greater than 90%, and oxygen incorporation to 21 at% within 2 h. The reaction had also reached completion after 1 h. The samples treated with NaOH,
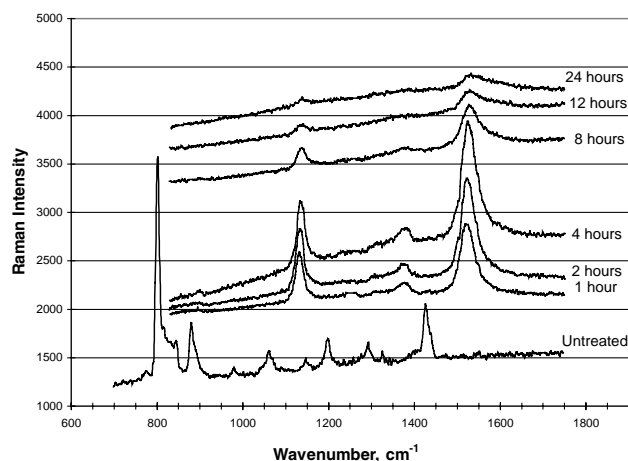

Fig. 10. Raman spectra (green laser) of PVdF samples treated with 0.0025 mol of TBPB between 0 and 24 h, at 80°C. The intensity of the lower value is indicated on the left-hand side of each spectra.

progressively defluorinate up to 256 h [1], when they reach a level practically equivalent to 1 h treatment with catalyst, however, the oxygen incorporation when not using a catalyst is almost 10 at% greater (up to 50%).

In the first set of experiments, a high catalyst concentration was utilised and resulted in a large difference in the concentration of oxygen incorporated on reaction with the different catalysts. At the lower catalyst concentration (0.0025 mol), however, this is not the case. In fact, the two catalysts produce almost identical surface studies, as shown in Table 9. The fourth peak of the C1s XPS spectrum is at 4 eV higher than the unfunctionalised carbon and may represent an HO–C–F group, the overall percentage of fluorine is consistent with the size of this component. Also, the position of the XPS F 1s component indicates that HO–C–F is present. This is consistent with the ToF-SIMS spectra that contain a significant percentage of fragments, which could represent HO–C–F groups, see Figs. 8 and 9.

There is a distinct possibility that $=$CF groups are present, within the modified structure, however both in the C1s and F 1s XPS spectra these would occur at the same position as HO–C–F functionalities. The conjugated structure gives rise to a chemical shift, which is equivalent to that of the OH group [11]. Thus, evidence for this species is not secure. It is clear that no fluorine remains as CF in its non-conjugated form, as this would lead to an extra component in the fluorine 1s XPS spectrum. ToF-SIMS does provide evidence of the CF groups (which may, or may not, be part of a conjugated structure), in the negative spectra as indicated in Figs. 8 and 9 where there are fragment ions assignable to CF and CFH. These groups could, however, result from the destruction of HO–C–F groups, as their intensity is similar to that of the CFH groups. In summary, there is no completely unambiguous spectroscopic evidence of fluorine within the conjugated structure (i.e. $=$CF). The analytical data is consistent with their presence, this point will be considered further during discussion of the degradation mechanism, where the formation of $=$CF is involved in the elimination step.

It is clear that no CF_2 groups are present after treatment, as the XPS peak, which could represent these groups (assigned as the $\pi \rightarrow \pi^*$ interaction), is not consistent with the percentage of fluorine present. Also there is no peak representative of CF_2 groups in the XPS F1s spectra. Previously [1], experiments with NaOH only, showed that both fluorine atoms were removed, one immediately after the other. The XPS results of the catalyst treated samples indicate the removal of one fluorine atom at a time.

Considering that the fluorine groups are all present as HO–C–F or $=$CF groups, this accounts for the fourth peak in the XPS C 1s spectrum, as shown in Table 3, the fluorine percentage and size of this peak are comparable. Therefore, there are no COOH groups present in the XPS C1s spectrum, as these groups would be part of component 4. This is complemented by the ToF-SIMS spectra, where

there are no sizeable peaks relating to COOH in the negative spectra of the catalyst treated samples. Therefore, there are no COOH groups present in the final structure.

Table 8 shows the possible structures that refer to the fragment ions formed on treatment of PVdF with TBPB and TBAHS. These results show the possible formation of conjugated structures, as well as the formation of oxygen containing groups in the positive spectra. The negative spectrum in Fig. 9 also shows the possible formation of oxygen containing groups and conjugated structures. XPS and ToF-SIMS both indicate the formation of conjugated structures, and they also indicate the formation of oxygen containing structures. XPS and ToF-SIMS provide evidence for the inclusion of oxygen into the sample in forms that interfere with, and therefore destroy the conjugated structure, i.e. the formation of HO–C–F groups. It is possible that chain scission is also occurring under the harsh environment of the treatment. Both these processes lead to the destruction of the conjugated structure. The Raman results show that a conjugated structure is formed; however, after 4 h treatment time there appears to be a break-up of this structure. The Raman analysis depth is considerably deeper then that of XPS and ToF-SIMS. The reactions that are occurring on the surface after 1 h may not occur at the Raman analysis depth until 4 h treatment time. This would explain the break up of structure that is observed in the Raman spectra after 4 h.

The Raman spectra that were obtained resembled spectra observed for trans-polyacetylene [12]. By use of the graph obtained in a previous publication [1], an estimation of conjugation length from our Raman results can be obtained. A separation of 399 cm^{-1} of the two Raman peaks represents a polyene with 8–9 C$=$C bonds present.

Previously, treatment of PVdF with 12 M NaOH at 80°C for up to 56 h [1] was also shown, by Raman spectroscopy, to produce a polyene of 8–9 C$=$C bonds. The intensity of the peaks for the catalyst treated samples however, is much greater, indicating that more polyene structures of this bond length were formed.

From the XPS F1s spectra it is evident that CF groups are not formed unless part of a conjugated structure. Therefore, the third peak in the XPS C1s spectra is representative of carbonyl groups. Whether or not $=$CF groups are actually formed has not been proven. There is evidence for the presence of $=$CF groups in the ToF-SIMS spectra, as well as the possibility in the XPS C1s and F1s spectra, therefore it is more likely that these groups are formed.

From the XPS, Raman spectroscopy and ToF-SIMS results it is evident that HO–C–F groups and conjugated structures are formed. XPS and ToF-SIMS also indicate the formation of COH groups and $=$CF groups. Carbonyl groups are present as shown by the XPS C1s spectra. The interpretation of the Raman spectroscopy indicates the formation of conjugated chains of length 8–9 double bonds.

## 6. The Degradation mechanism

It is proposed that the mechanism for the defluorination of PVdF in aqueous alkaline solution with the addition of PTC, which is consistent with our model for NaOH induced egradation [1], is as follows with regard to the PTC TBPB:

(a) Deprotonation
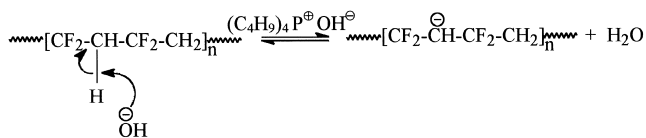
The PTCs interact with the polymer surface (organic media), thereby locally increasing the activity of hydroxide. This increases the reaction rates between the hydroxide and PVdF polymer chains. After reacting the PTC attaches to another hydroxide from the aqueous solution and thus acts as a true catalyst.

(b) Elimination
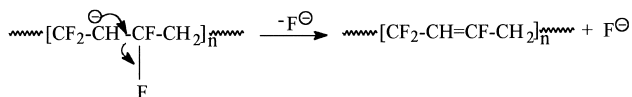
The above chain fragment can rearrange as shown, to yield the in chain C=C double bond, this is known as an elimination reaction. The F^- ion is stable as the reaction occurs in aqueous solution and the driving force is the formation of a carbon–carbon double bond. This process then, continues to yield a conjugated structure containing up to nine carbon double bonds.

Steps (a) and (b) may also occur simultaneously via an E2 (elimination, bimolecular) in chain reaction.
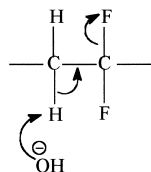

However, this is unlikely as it is part of a long polymer chain and will thus experience high steric hindrance. Again, in this case the hydroxide ion is associated with the phosphonium ion or ammonium ion in question.

(c) Hydroxylation
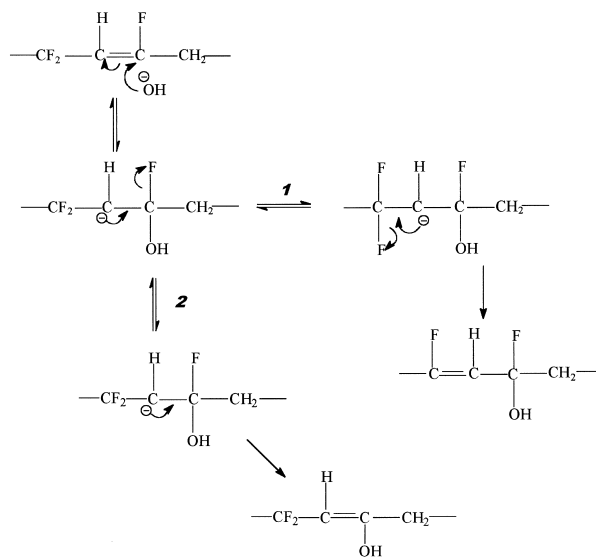
All analytical data presented in the paper indicates that there is HO–C–F in the treated PVdF surface, however there is no CF_2 remaining. It is concluded therefore, that step (c) occurs slower than steps (a) and (b) so that all the CF_2 is removed but HO–C–F remains, as shown above. This is a result of the steric hindrance observed, the attacking hydroxide is associated with a quaternary onium cation. The HO–C–F group can also be an intermediate group leading to the formation of hydroxide groups as shown above.

(d) Carbonyl Formation
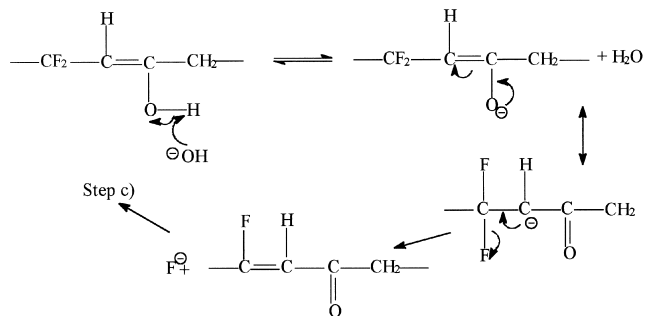
In the presence of an alkaline environment, deprotonisation of the incorporated hydroxide will occur. The resultant structure is resonance stabilised as shown, and will lose fluoride, which is stable in aqueous solutions. Again, the driving force is the formation of a carbon–carbon double bond.

Deeper into the surface layers, the polyene structures of 8–9 double bonds are formed by the continuation of step (b). The double bond formed, encourages the hydrogen on the neighbouring carbon atom to leave, forming another

Table 9
.Average percentages after the different treatments

Treatment	Elemental percentage						
	C	O	F	Na	P	N	Br
No Catalyst (12 M NaOH)[a]	69.1	15.4	13.7	0.5	0	1.3	0
TBPB (4 M NaOH)[b]	72.6	18.6	3.4	3.5	1.2	0.3	0.5
TBAHS (4 M NaOH)[b]	73.1	18.6	3.3	4.0	0.0	0.7	0.0

[a] Actual concentration for 48 h treatment.
[b] Average concentration for samples treated between 1 and 24 h.

double bond and therefore removing the next fluorine atom in the path. This procedure leads to the formation of the polyene chain. The propagation terminates at 8–9 double bonds in length, possibly as a result of the optimum energy of the fermi level. The authors note that these mechanism proposals are speculative, as they are based on the examination of the film surfaces alone.

7. Conclusions

The conclusions can be summarised as follows:

- Defluorination and oxygenation occurs on treatment with sodium hydroxide. The presence of PTCs greatly increases the rate of the defluorination reaction, in an alkaline environment, so that the surface reaction is complete within 1 h.
- The XPS results indicate that no CF_2 groups remain following 1 h of treatment. Fluorine remains in the form of HO–C–F and =CF groups, but is always less than 4% of the overall product. This phenomenon is explained by the proposed reaction mechanism.
- With the use of PTCs the concentration of sodium hydroxide can be reduced three-fold, whilst still increasing the rate of reaction.
- At the Raman analysis depth, the maximum number of conjugated chains is reached after 4 h treatment, all the polyene chains formed are between 8 and 9 double bonds long.
- It is proposed that the reaction mechanism involves an initial fluorine elimination step, followed by substitution of oxygen. This is supported by the fact that there is no evidence of oxygen inclusion at the Raman analysis depth.

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