

# Surface modification of poly(vinylidene fluoride) by alkaline treatment

## 1. The degradation mechanism

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### Abstract

A detailed study of the alkaline degradation of PVdF has been carried out by X-ray photoelectron spectroscopy, secondary ion mass spectrometry and Raman spectroscopy to determine the composition of the modified layer. The study indicates the formation of a surface layer consisting of conjugated C=C bonds and the inclusion of oxygen functionalities on treatment. A mechanism for this degradation process is proposed. This includes the formation of the polyene structure followed by hydroxide attack to yield hydroxyl and carbonyl groups. © 1999 Elsevier Science Ltd. All rights reserved.

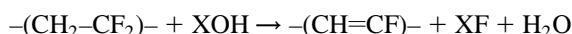
**Keywords:** Poly(vinylidene fluoride); Degradation; Time-of-flight secondary ion mass spectrometry

### 1. Introduction

Interest in fluorinated polymers is largely a result of the excellent resistance they possess to harsh chemical, thermal, ultraviolet weathering, oxidising and high energy radiation environments. Poly(vinylidene fluoride) (PVdF) is essentially as inert as fully fluorinated polymers, yet has the advantage of being processable by the standard routes used for thermoplastics. It is also a tough engineering plastic that can withstand temperatures between  $-60$  and  $150^{\circ}\text{C}$ .

Although PVdF is highly chemically resistant, it is still susceptible to attack from concentrated sodium hydroxide. Commercially it is known that the resistance to such alkaline environments can be improved by “flashing” the PVdF in caustic solutions of very high pH (e.g. 14) producing a surface layer that is chemically resistant to attack in less aggressive solutions.

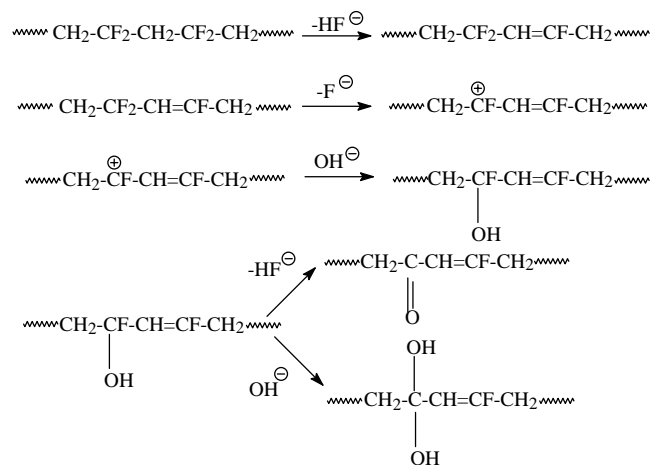
Previous investigations [1–7] of the composition of such surface layers formed as a result of alkaline degradation of PVdF all conclude that the following reaction occurs:



where X = Li or Na.

This mechanism is generally accepted, but has been generated on the basis of a rather modest set of experimental data from several research groups. The main aim of past

investigations has been, by and large, towards the development of a process to surface engineer PVdF to provide the appropriate properties, e.g. printability and adhesion, the development of a mechanistic model, generally, being of secondary importance. Brewis et al. [2] and Kise and Ogata [6] did however expand this mechanism to include the formation of hydroxide and carbonyl groups on the polyene chain. The mechanisms proposed by Brewis et al. are shown below:



Many of the investigations of the alkaline degradation of PVdF [2–6] have involved the use of phase transfer catalysts (PTCs) which may be expected to alter the mechanism

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of degradation, this has been investigated and is to be discussed in a forthcoming communication. Other differences between past work and the current investigations are the type and concentration of alkali, the temperature of the experiments and the cover gas composition. The aim of the current paper is to provide a mechanistic model of the alkaline degradation of PVdF on the basis of chemical analysis obtained by XPS (X-ray photoelectron spectroscopy), ToF-SIMS (time-of-flight secondary ion mass spectrometry) and Raman spectroscopy data. ToF-SIMS and XPS are surface chemical analysis techniques that complement each other well, particularly for the analysis of organic polymers.

XPS provides chemical state information as well as a quantitative surface chemical analysis. Shifts in the peaks obtained represent differences in the chemical structure of the sample. The technique itself involves bombarding the sample with soft X-rays in ultra high vacuum (UHV). The X-rays cause the sample to emit photoelectrons whose energies are then analysed to yield the XPS spectrum. Electrostatic charging occurs during analysis of insulators such as PVdF and must be taken into account when interpreting the spectra. The characteristic depth of analysis is 2–5 nm.

ToF-SIMS is a surface mass spectrometry, which provides chemical information of surfaces by the detection of sputtered ionised molecular fragments. SIMS can detect hydrogen and distinguish between different isotopes. ToF-SIMS can rapidly collect mass spectra, by parallel acquisition over the mass range selected. The depth of analyses of SIMS is 1–2 monolayers, more surface specific than XPS, and it is now generally accepted that the elemental ions have a larger analysis depth than molecular fragments. The SIMS process itself involves the sample in UHV being bombarded with a beam of positively charged ions ( $^{69}\text{Ga}^+$ ), and ions and neutrals are sputtered from the top monolayers. The main emission process in SIMS is where surface atoms or clusters are ejected as a result of the collision cascade, which occurs after the primary ion enters the polymer surface. The fragments that are charged secondary ions are accelerated by a high voltage into the flight tube of the mass analyser. Mass spectra are obtained in either the negative or the positive mode.

The exact mass (more strictly  $m/z$ ) of the ions produced by the sputtering process is determined in SIMS analysis. This mass can represent one or more types of ion. XPS provides the chemical state of the elements, but does not indicate molecular size. Use of these two techniques in parallel provides a method to identify the sample being analysed. The techniques concentrate on different depths in the sample, if the sample is not identical at both of these depths the information must be used separately, possibly with other techniques (e.g. Rutherford backscattering spectrometry) to provide a depth profile.

FT-IR was complemented by Raman spectroscopy because of the latter technique's unique ability to estimate the extent of conjugation within the modified layer.

## 2. Experimental

Two types of PVdF were used, injection moulded samples (3–4 mm) and film samples (25, 50 and 100  $\mu\text{m}$ ). The as moulded PVdF was scraped with a scalpel and wiped with isopropanol to remove any contamination and then rinsed in ultra clean water (milli Q water,  $0.056 \text{ S cm}^{-1}$ ). The film samples 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 then wiped with isopropanol followed by a milli Q water rinse. The samples were treated with 12 M NaOH (analar grade NaOH in milli Q water) at  $80^\circ\text{C}$  in a shaking waterbath, for between 1 and 256 h. The waterbath was set at a mixing speed of 111 rpm. On removal from the solution, the samples were rinsed in milli Q water to quench the reaction.

The analyses were carried out by XPS, ToF-SIMS, FT-IRS and Raman spectroscopy.

### 2.1. X-ray photoelectron spectroscopy

A VG Scientific ESCALAB MKII spectrometer was used at an operating pressure of  $10^{-9}$  for the analysis with a twin anode X-ray source supplying either Mg K $\alpha$  or Al K $\alpha$  radiation. All samples were recorded at a  $45^\circ$  take off angle, using an analyser pass energy of 20 eV for high resolution spectra and 50 eV for survey spectra. Data analysis, and curve fitting were performed by a VGS 5000S data system based on a DEC PDP 11/73 computer.

It is well known that the presence of fluorine in an organic polymer leads to large chemical shifts of the carbon 1s electrons as a result of the electronegativity of the halogen atom. The interpretation of these shifts is quite straightforward for bulk homopolymers such as PTFE (polytetrafluoroethylene) and PVdF [8] however, as indicated elsewhere [9] such shifts become more complex in the case of treatments that bring about surface fluorination (or indeed defluorination).

Further XPS spectra were acquired on a Scienta ESCA 300 at RUSTI, CLRC, Daresbury, this equipment produces spectra with greater resolution. The spectrometer utilises a monochromatic Al K $\alpha$  source with a rotating aluminium anode, quartz crystal monochromator, high transmission/imaging lens, hemispherical analyser and multichannel detector [8]. Survey and high resolution spectra were acquired, at a pass energy of 150 eV with a slit width of 1.9 or 0.8 mm. All samples were recorded at a  $45^\circ$  take off angle, an electron flood gun was used for surface charge management. The film samples were mounted on stainless steel stubs and secured with a stainless steel ring. Quantitative surface analyses were obtained from three sets of samples, these were quantified and peak fitted using the Scienta software [8].

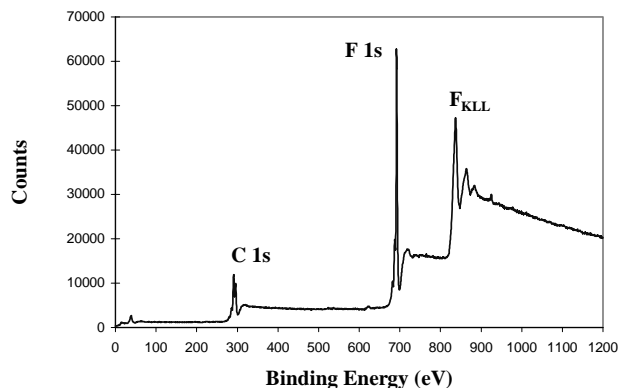


Fig. 1. XPS survey spectra of PVdF after scraping and isopropanol wipe from Al X-rays.

## 2.2. Raman spectroscopy

The Raman spectra of the samples were recorded in back-scattering geometry on a DILOR XY multichannel spectrometer using an excitation line at either 632 nm (out of resonance) of the He–Ne model 207B Spectra Physics laser (25 mW power at the laser head) or at 514.53 nm (resonance conditions) of a Ar<sup>+</sup> model 165 Spectra Physics laser (power less than 50 mW). Briefly the spectrometer consists of a triple monochromator used in subtractive mode to select a given spectral range followed by the spectrograph to complete the dispersion, and a Jobi-Yvon CCD (Charge Coupled Device) matrix thermoelectrically cooled. Using 200  $\mu\text{m}$  slit widths, the spectral resolution was always better than 5  $\text{cm}^{-1}$ .

## 2.3. Time-of-flight secondary ion mass spectrometry

The ToF-SIMS spectra were obtained using a VG Scientific type 23 system equipped with a Poschenrieder time-of-flight system and a MIG300PB pulsed liquid ion source. Static SIMS conditions were employed, using a pulsed (5 KHz and 40 ns) 20 KeV <sup>69</sup>Ga<sup>+</sup> primary ion beam rastered over a frame area of 0.5  $\times$  0.5  $\text{mm}^2$ . SIMS spectra were

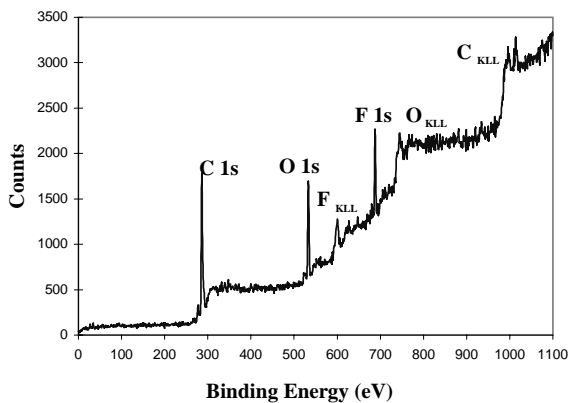


Fig. 2. XPS survey spectra of PVdF after 48 h treatment with 12 M NaOH at 80°C from Mg X-rays.

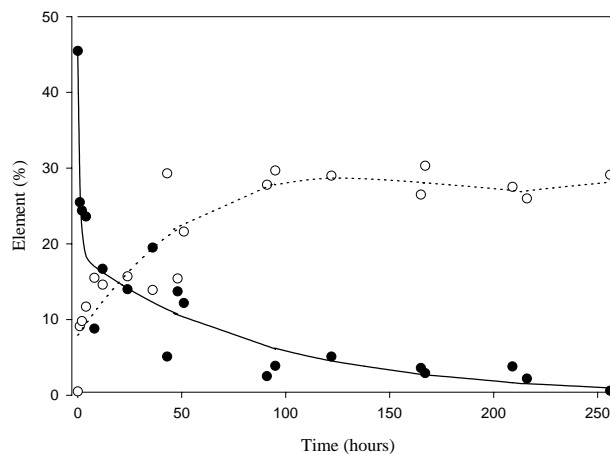


Fig. 3. Changes in XPS elemental percentages of fluorine and oxygen with treatment time (●, Fluorine; ○, Oxygen).

acquired over a mass range of  $m/z$  5–600 in both positive and negative ion modes.

## 2.4. Infrared spectroscopy

A Perkin–Elmer IR spectrometer was used with an ATR (attenuated total reflection) crystal; 20 scans were taken between wavenumbers 400–4000  $\text{cm}^{-1}$ . Good contact between the samples and the ATR crystal was achieved by applying 9 N force.

## 3. Results

### 3.1. XPS spectra

The XPS survey spectrum of untreated PVdF is shown in Fig. 1, and that of PVdF after 48 h treatment in 12 M NaOH at 80°C is shown in Fig. 2. The spectrum of the treated material has a higher level of noise; this phenomenon is a result of the change in surface roughness produced on treatment as a result of the formation of a new topography. A reduction in fluorine intensity occurs together with an increase in oxygen intensity and relative increase in the carbon. In Fig. 2, a steep rise in the background after the fluorine peak at 686 eV is observed; this represents a buried layer of fluorine, adding to the evidence of defluorination and providing an indication of the depth to which the process has occurred. The decrease in fluorine concentration and increase in oxygen concentration with time is shown in Fig. 3. The quantitative data indicates that the majority of defluorination on the surface layer (>5 nm), probed by XPS, occurs within the first hour of treatment, after which the rate slows down substantially. The formation of oxygen containing functional groups appears to be completed after 50 h of treatment. The oxygen does not appear to completely replace the fluorine as it never reaches the same surface concentration as the initial concentration of fluorine (45 at.%) but remains at a lower value of 30 at.%.

Table 1  
Carbon peak assignments for PVdF after treatment with 12 M NaOH at 80°C

Peak	Binding energy	Full width at half maximum	Assignment
1	285.0	1.2	CH–CH
2	286.3	1.5	CH–CF <sub>2</sub> /COH
3	287.7	1.6	C=O
4	289.1	1.3	COF
5	290.8	1.1	CF <sub>2</sub>

The C1s spectra indicate that carbon is present in the form of C–F<sub>2</sub>, C–H, O–C–F, C–OH and C=O, the assignments used in this work are presented in Table 1. The chemical state of the elements involved cannot be unambiguously resolved with the spectra obtained with standard XPS because the spectral resolution is not sufficient to distinguish between some of the fluorine and oxygen groups. The spectra obtained using monochromated Al K $\alpha$  XPS are of greater resolution enabling certain groups to be readily distinguished. Samples analysed by this method were treated between 0–48 h only, and Fig. 4 shows the evolution of the carbon 1s spectra with time. The peaks can be resolved to show that the oxygen is present in the form of carbonyl and hydroxyl groups. Fluorine is mainly present as CF<sub>2</sub>. There is a peak attributed to either C–F or C=O, this peak is much smaller than the amount of converted C–F<sub>2</sub>. The fluorine spectra yields only one component; fluorine from CF<sub>2</sub> groups, and no contribution from the C–F groups which would be at least 1 eV lower (see Fig. 4). Therefore the “C–F or C=O” peak can be assigned to C=O. In the carbon spectra there is also a peak shifted by 4.1 eV which can be interpreted as a C–OF contribution, the fluorine peak for this component will appear in the same position as the C–F<sub>2</sub> fluorine 1s component and therefore only one peak will be observed in the fluorine spectra. The change in components as a function of treatment time in terms of elemental surface composition, the various contributions to the C1s spectra, and the surface concentration of these species, is shown in Tables 2–4 respectively. In Table 4, the data is presented as surface concentration of the carbon

Table 2  
Atomic percentage of elements of PVdF on treatment with 12 M NaOH at 80°C

Time (h)	Element (at.%)			Others [N and Na]
	Carbon	Oxygen	Fluorine	
1	63.5	9.1	25.5	1.9
2	64.2	9.8	24.4	1.6
4	64.1	11.7	23.6	0.6
8	74.3	15.5	8.8	1.4
12	67.5	14.6	16.7	1.2
24	68.3	15.7	14.0	1.9
36	65.4	13.9	19.5	1.1
48	69.1	15.4	13.7	1.8

Table 3  
Results of peak fitting of C1s spectra for PVdF treated with 12 M NaOH at 80°C as a function of time.

Time (h)	Relative intensity of C1s spectra (%)				
	1	2	3	4	5
1	27.2	41.3	7.2	1.6	22.7
2	30.6	37.6	7.6	1.6	22.6
4	30.4	35.7	9.5	3.6	20.7
8	55.5	25.8	8.5	3.5	6.7
12	38.4	36.4	7.9	4.5	12.9
24	40.5	29.2	13.6	5.6	11.1
36	32.3	36.1	11.3	4.4	15.9
48	41.8	30.1	11.3	5.3	11.6

functionalities. This is achieved by combining the results of peak fitting of the C1s spectra in Table 3 with the integral carbon component of Table 2.

The presence of a CF<sub>2</sub> group will lead to the expected C1s shift, and will also give rise to a secondary shift on the adjacent methylene carbon. In PVdF the relative intensity of CF<sub>2</sub> and CH<sub>2</sub>–CF<sub>2</sub> will be the same as a result of the ABAB arrangement of these groups. Once treated however this regularity is destroyed, as shown in our mechanistic degradation scheme below, and the methylene groups are no longer in the ABAB arrangement with CF<sub>2</sub> as a result of defluorination. The “methylene type” carbon may now be adjacent to other groups, such as oxygen containing moieties, which will also give rise to a secondary shift. Thus, as indicated in Table 1, the component at 286.3 eV represents a contribution from the secondary shift experienced by the CH<sub>2</sub> groups that are adjacent to CF<sub>2</sub>, primary C–OH groups, and perhaps secondary shifts from the other oxygen and fluorine containing functionalities. As noted in Table 1 the FWHM of this component is slightly greater than expected, indicating several components within this spectral envelope. The shift on the methylene carbon, as a result of the electronegative species attached to adjacent carbons, is similar to the shift as a result of carbon attached to hydroxyl groups, these components form the CH–CF/ C–OH (Peak 2) assignment of Table 3. As the surface

Table 4  
Surface composition, with respect to carbon functionalities for PVdF treated in 12 M NaOH at 80°C as a function of time

Time (h)	Surface concentration of carbon functionalities (atomic %)					
	CH <sub>2</sub>	CH–CF <sub>2</sub>	COH	C=O	COF	CF <sub>2</sub>
1	17.3	24.4	3.5	4.6	1	14.4
2	19.6	22.6	3.9	4.9	1	14.5
4	19.5	21.1	3.3	6.1	2.3	13.3
8	41.2	13.2	6.6	6.3	2.6	5
12	25.9	18.7	6.3	5.3	3	8.7
24	27.6	18.0	2.6	9.3	3.8	7.6
36	21.1	20.7	3.6	7.4	2.9	10.4
48	28.9	18.0	3.9	7.8	3.7	8

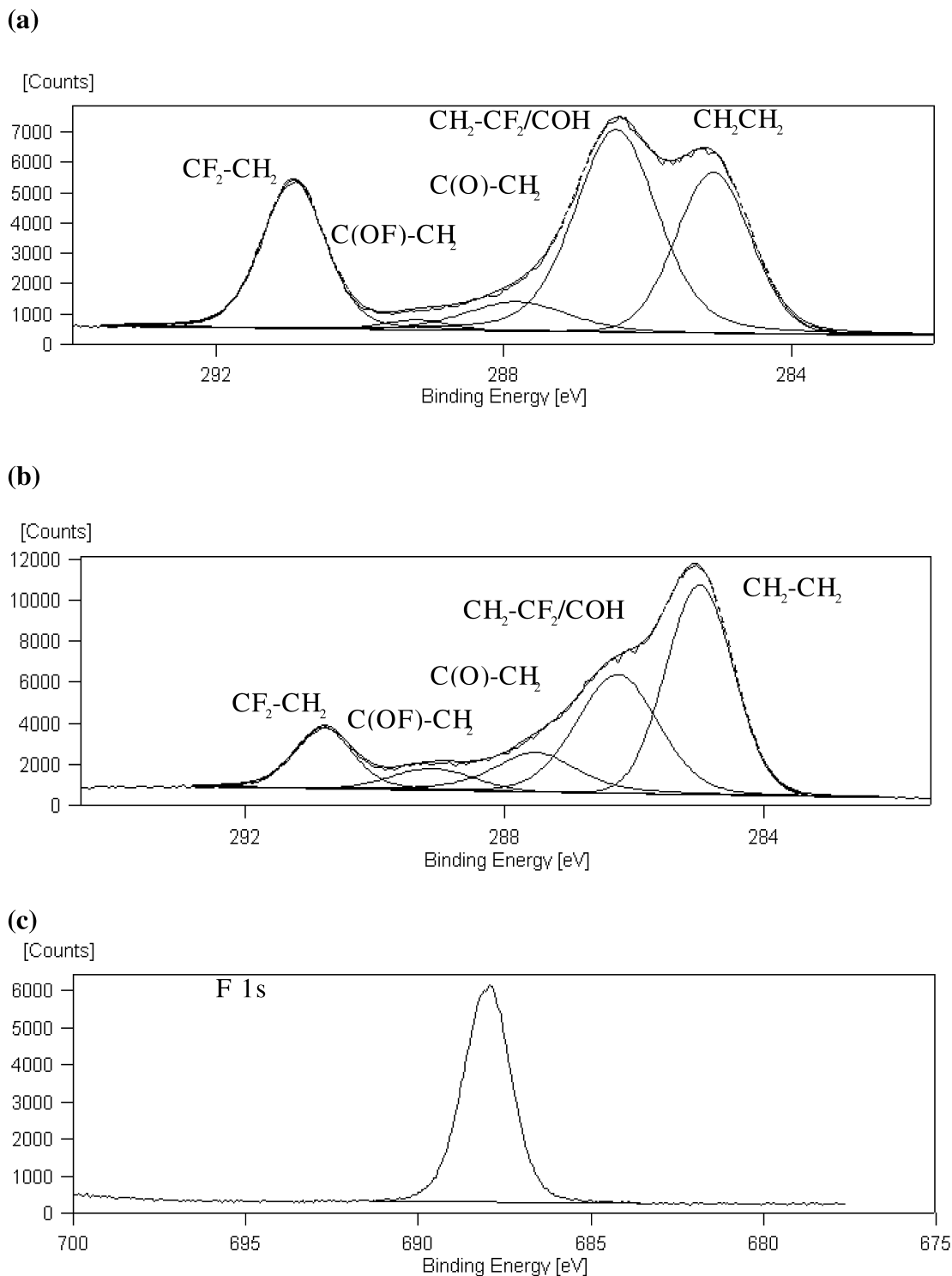


Fig. 4. Monochromated AlK $\alpha$  XPS spectra of PVdF: (a) C1s, after 1 h treatment; (b) C1s, after 48 h treatment; (c) F1s, after 1 h treatment in 12 M NaOH at 80°C.

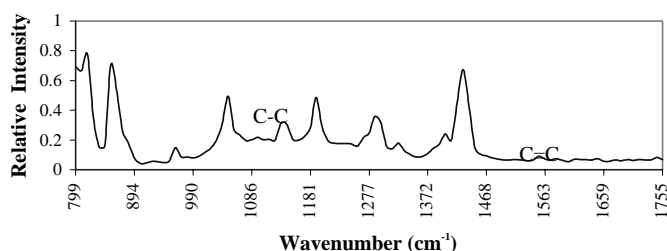
concentration of oxygen is known (Table 2), the hydroxyl concentration can be estimated, quite simply by subtracting the sum of the known oxygen species (C=O and C–OF, peaks 3 and 4 (Table 3)) in the carbon spectra from the total oxygen concentration of Table 2. Having established the contribution of the C–OH groups to the convolution of

[C–OH + CH<sub>2</sub>–CF<sub>2</sub>] it is a simple matter to evaluate [CH<sub>2</sub>–CF<sub>2</sub>], which yields the data of Table 4.

### 3.2. Raman spectra

The Raman spectra of untreated and treated PVdF are

(a) Raman conditions: green laser, 514.53nm, power 200mW over a wavenumber range of 830-1700cm<sup>-1</sup>.



(b) Raman conditions: green laser, power 2mW over a wavenumber range 750-1600cm<sup>-1</sup>.

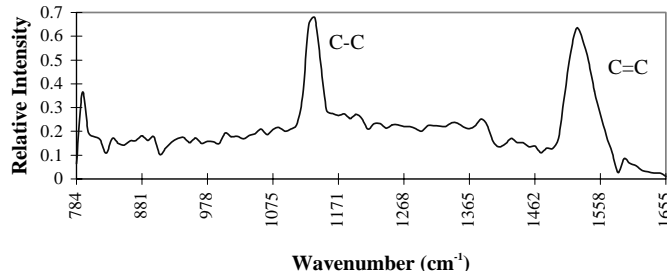


Fig. 5. Raman spectra of PVdF: (a) untreated (conditions: green laser, 514.53 nm, power 200 mW over a wavenumber range of 830–1700 cm<sup>-1</sup>); (b) after 1 h treatment with 12 M NaOH at 80°C (conditions: green laser, power 2 mW over a wavenumber range 750–1600 cm<sup>-1</sup>).

shown in Figs. 5(a) and (b). After 1 h treatment the spectra is completely different from the original spectra indicating a complete change in the chemical nature of the surface. The peaks at 1129 and 1525 cm<sup>-1</sup> are representative of the C–C and C=C respectively. The spectra are similar to that of polyacetylene shown in Fig. 6 [10]. Polyacetylene has a conjugated carbon double bond structure, the length of which can be estimated from the distance between the C–C bond peak and the C=C bond peak in the Raman spectra. Mathematical models that show this relationship can be found in the literature for polyacetylene [11–16]. After treatment there is no indication in the spectra of the presence of oxygen or fluorine groups, whilst fluorine is present, as expected, in the untreated spectra. The Raman spectra of the polyene structures formed are not unlike those obtained by Owen and Shah [11] who treated PVC with NaOH at 70°C with a catalyst. Owen and Shah used a mathematical relationship to calculate the length of the conjugated chain of their polyene, which they calculated as 10 C=C units. The estimation of the conjugated chain length and the polydispersity of the polyene can be obtained from the wavenumber of the C=C band (around 1527 cm<sup>-1</sup>). The linear decrease of the Raman shift occurs with the inverse of the conjugation length. Schaffer et al. [12] investigated the Raman shift of the C–C and C=C peak for different length polyenes between 3–12 C=C bonds in length. Two mathematical methods were discussed in Schaffer's paper; the amplitude model (AM) and an equation based on their experimental results. The AM model did not appear to fit

the experimental data well while their empirical model had no theoretical basis. The data of C–C ( $R_1$ ) and C=C ( $R_4$ ) peak separation were taken from Schaffer's paper and plotted against polyene length. The data produced are shown in Fig. 7. A logarithm equation produces a best fit line that utilises positions of both peaks unlike the equation obtained in Schaffer's paper. By use of the graph an estimation of conjugation length from our Raman results can be obtained. A separation of 399 cm<sup>-1</sup> of the two Raman peaks represents a polyene with 8–9 C=C bonds present.

### 3.3. ToF-SIMS spectra

Positive SIMS spectra of the untreated and treated PVdF samples are shown in Fig. 8. In the negative SIMS spectra the fluoride intensity decreases with treatment time, defluorination occurs on treatment. It is, perhaps, surprising that the level of fluorine does not drop to zero, as one would expect if the defluorination reaction proceeds to completion.

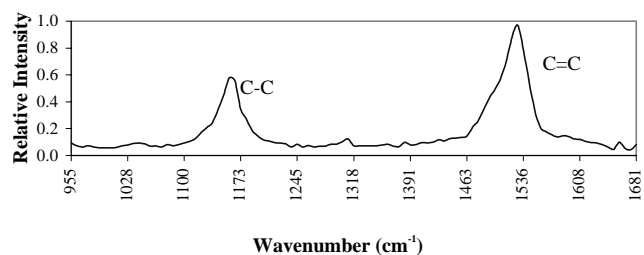


Fig. 6. Raman spectra of polyacetylene from Ref. [10].

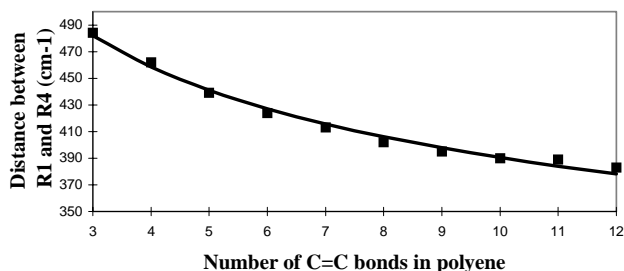


Fig. 7. Raman peak separation ( $R_1$  and  $R_4$ ), of polyene structures between 3–12 C=C bonds in length, from Ref. [12].

Bearing in mind that the SIMS is more sensitive as an analytical technique than XPS (which has a detection limit of 0.1 at.%) the results from the two surface analysis techniques are in broad agreement with each other. This indicates that 5–10% of the fluorine atoms at the surface remain intact following the defluorination treatment. This point is considered further in the next section. Oxygen intensity increases with treatment time indicating inclusion of oxygen into the surface. Small carbon fragments increase with treatment time.

Fig. 9(a) shows the excellent consistency of the SIMS results, the positive SIMS spectra show masses that are 14 mass units apart (14 represents a  $\text{CH}_2$  group (Table 5)).

Fig. 9(b) shows the increase in oxygen intensity and a complementary decrease in fluorine intensity in the negative spectra with treatment time. In the positive SIMS spectra there are peaks whose intensities increase with time, Fig. 9(c), and those which decrease with treatment time, Fig. 9(d). From the XPS results it is clear that the fluorine components are decreasing with treatment time whilst the oxygen components are increasing with treatment time. Therefore, it is logical to assign peaks that increase with treatment time to oxygen containing species and those that are decreasing with treatment to fluorine containing species (as shown in Table 5). The Raman spectroscopy results indicate that conjugated carbon double bonds are also forming on treatment, therefore the increasing counts may also be attributed to this type of structure, Fig. 9(e), Table 5. In the positive SIMS spectra the smaller  $\text{CH}_x$  ( $x = 0-3$ ) fragments are decreasing. The initial increase in intensity relating to conjugated structures in Fig. 9 indicates that most of the reaction up to 1 nm in depth has occurred within the first 50 h of treatment. After 200 h there is a second step increase in characteristic ions, indicating that a new stage of the reaction may be taking place at the surface. The same pattern is observed for the oxygen containing species.

There are many species indicated that could be attributed to groups containing CHF and CF groups. The ToF-SIMS data complements the Raman data that indicates the

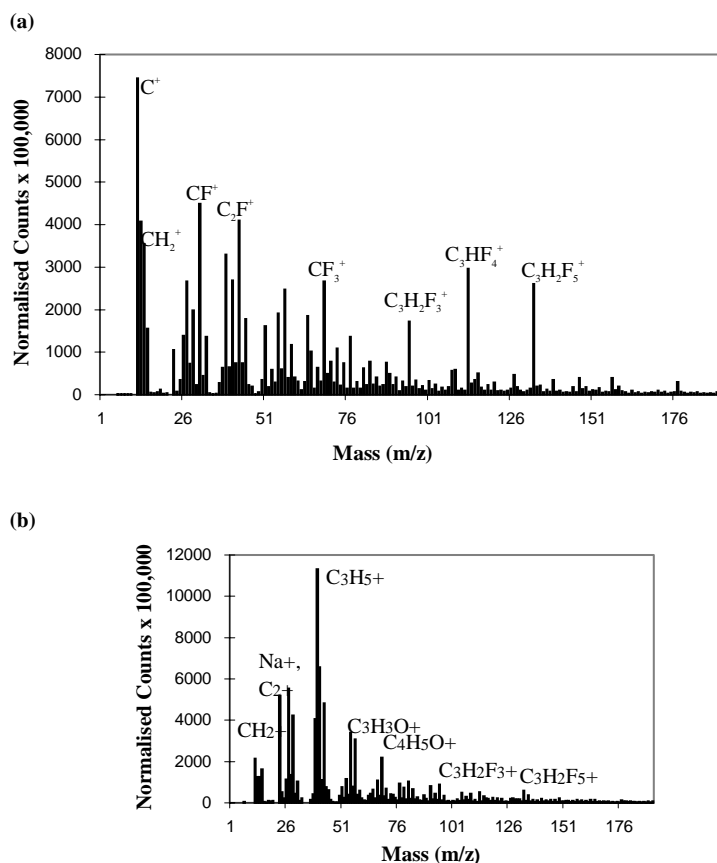


Fig. 8. Positive ToF-SIMS spectra of: (a) untreated PVdF; and (b) PVdF after 43 h treatment in 12 M NaOH at 80°C.

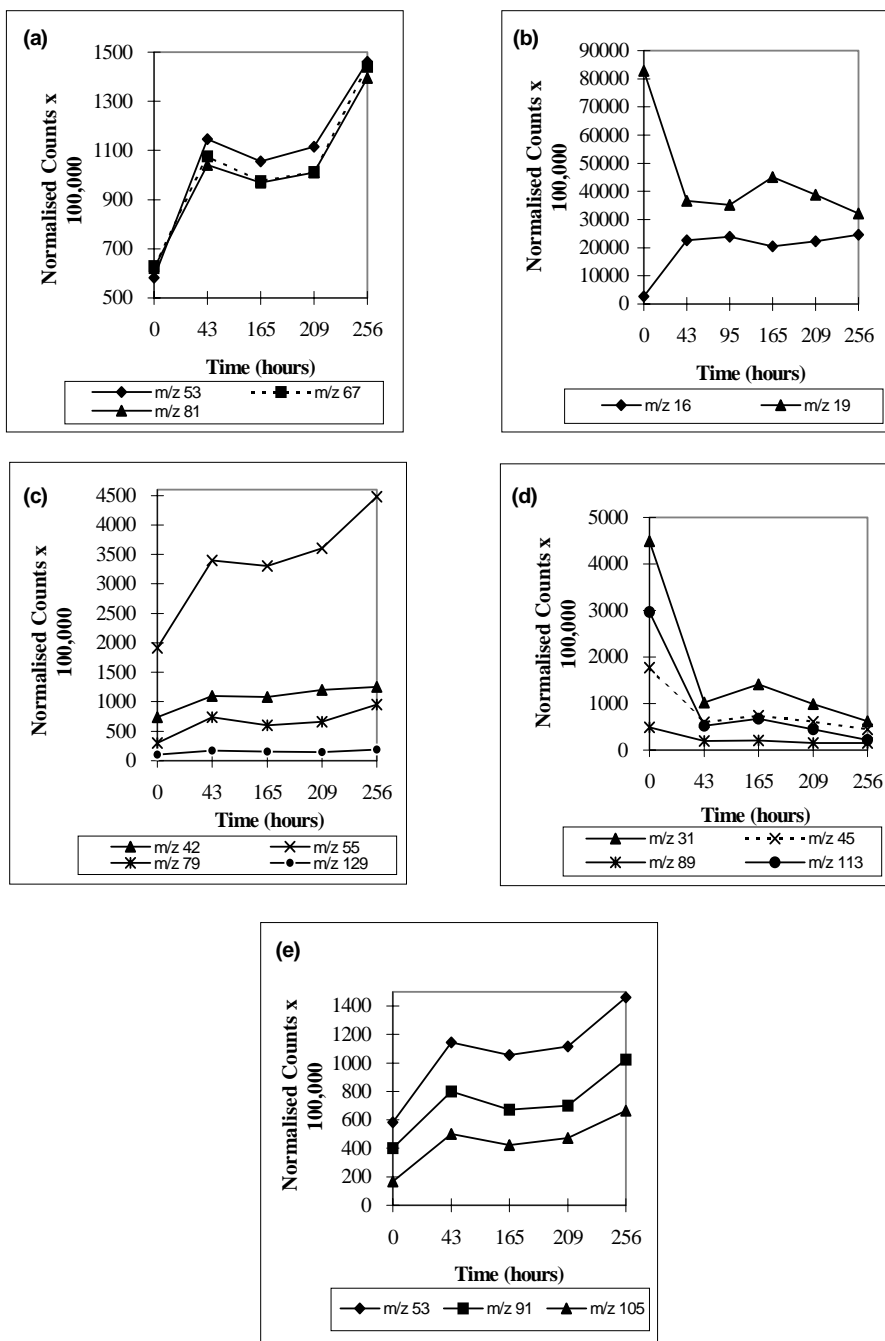


Fig. 9. SIMS counts of PVdF with treatment time showing: (a) reproducibility of data; (b) increasing oxygen counts, and decreasing fluorine counts with treatment time; (c) increasing counts with treatment time that are consistent with oxygen containing/hydrocarbon structures; (d) decreasing counts with treatment time consistent with fluorine containing hydrocarbons; (e) possible conjugated structures, increasing with treatment time.

formation of conjugated sequences. The ToF-SIMS data also confirms the XPS data, which indicates that C–F groups do not remain within the conjugated structure as indicated by the low surface concentration of fluorine present. XPS and ToF-SIMS both indicate oxygenation on treatment as well as partial defluorination of the polymer. The presence of the conjugated structures cannot be detected by XPS as the chemical shift between  $(-\text{CH}=\text{CH}-)_n$  and  $(-\text{CH}_2-\text{CH}_2-)_n$  is negligible. However the whole XP spectrum can shift as a result

of the increased conductivity that occurs on conjugation. This is shown in the samples that are analysed using the ESCALAB where the whole spectrum shifts down by 3 eV. Here the carbon line is 1 eV higher than the value for a conducting sample and 3 eV lower than that of an insulating sample of PVdF. This observation leads to the rather tantalising possibility that the modified layer on the PVdF may possess intrinsic conductivity. Attempts to measure the surface conductivity were inconclusive, but if



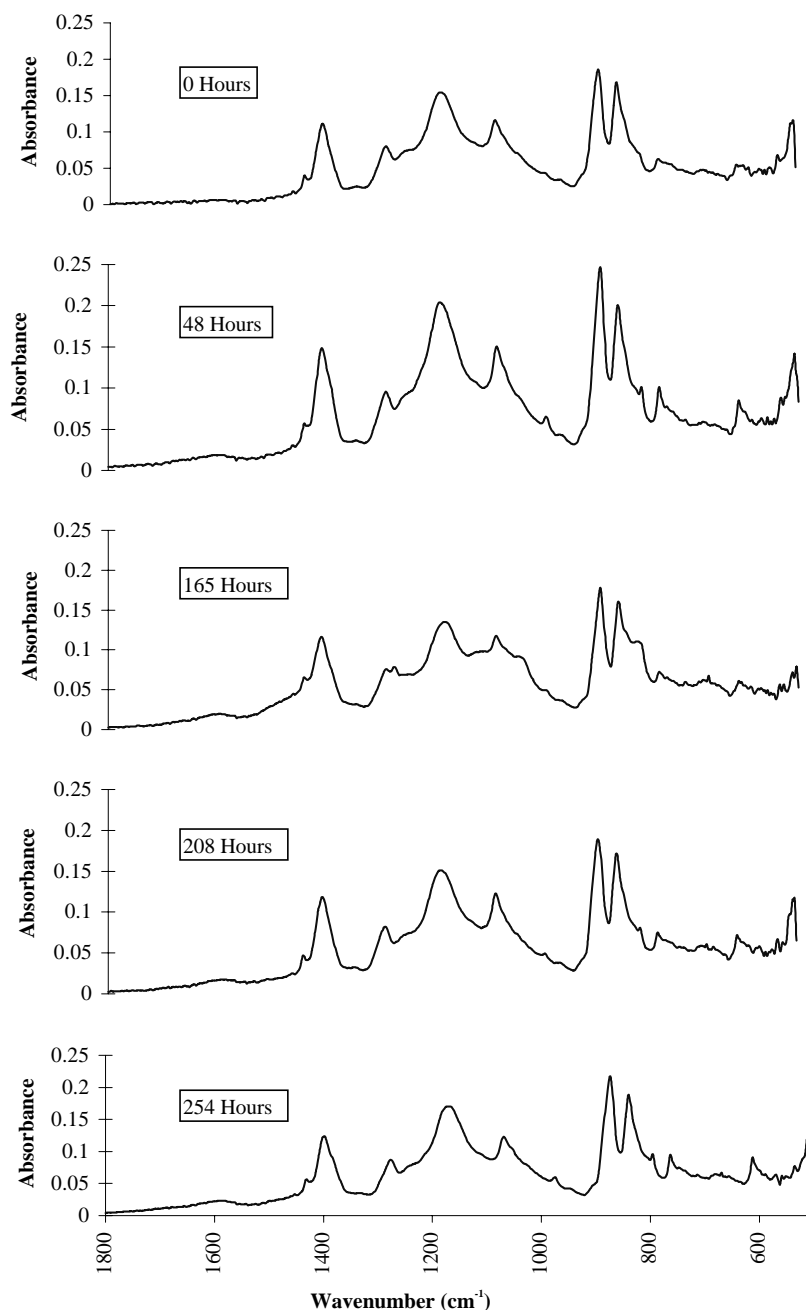


Fig. 10. ATR FT-IR after treatment with 12 M NaOH at 80°C.

the layer formed is indeed an intrinsically conducting polymer the conductivity is low ( $<10^5 \Omega \text{ cm}^{-2}$ ).

### 3.4. Infrared spectra

The infrared spectra in Fig. 10 show PVdF prior to and after treatment. The spectra indicate formation of carbon double bond groups ( $1600 \text{ cm}^{-1}$ ) on treatment with a change in the fluorocarbon groups ( $1000\text{--}1250 \text{ cm}^{-1}$ ). The absorbance at  $1600 \text{ cm}^{-1}$  is weak as a result of the fact that the C=C bond is inactive in infrared (normally conjugated structures are not active in the infrared but are

Raman active). Complex changes occur in the fluorocarbon stretching frequencies ( $1250\text{--}1000 \text{ cm}^{-1}$ ) in the fingerprint region of the spectrum, indicating that the fluorine groups change with treatment. The hydrocarbon deformations  $1350\text{--}1450$  and  $800\text{--}900 \text{ cm}^{-1}$  do not change significantly with treatment. There is no indication of oxygen present in the infrared spectra.

### 4. Discussion

Defluorination, oxygenation and formation of a conjugated carbon double bond structure is shown to occur on

Table 5  
Assignment of major peaks in the ToF-SIMS spectra of Fig. 9.

$m/z$	Structure
(a)	
53	CH <sub>2</sub> -CH=CH-CH
67	CH <sub>2</sub> -CH=CH-CH-CH <sub>2</sub>
81	CH <sub>2</sub> -CH <sub>2</sub> -CH=CH-CH-CH <sub>2</sub>
(b)	
16	Oxygen
19	Fluorine
(c)	
42	CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> and/or CH-COH
55	CH <sub>2</sub> -CH <sub>2</sub> -CH-CH <sub>2</sub> and/or CH=CH-COH
79	CH=CH-CH=CH-CH=CH <sub>2</sub>
129	CHOH-CH-CHOH-CH=CH-CHOH
(d)	
31	CF
45	CH=CHF
89	CHF-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>
113	CF <sub>2</sub> -CH-CF <sub>2</sub>
(e)	
53	CH=CH-CH=CH <sub>2</sub>
91	CH=CH-CH=CH-CH=CH-CH
105	CH=CH-CH=CH-CH=CH-CH=CH <sub>2</sub>

treatment with sodium hydroxide (pH 14). XPS analysis indicates that the oxygen present is mainly in the form of carbonyl and hydroxyl groups; however some small percentage of O-C-F groups are also present. From the XPS and Raman results, it is evident that no significant amounts of CF groups remain after treatment. Although SIMS indicates the presence of CF groups in the spectra, the intensity of these groups does decrease with treatment, which indicates that they are an intermediate species present during the reaction. If the majority of these CF groups did not react further, much higher intensities of CF ions would be expected to account for all the CF<sub>2</sub> groups that were defluorinated.

The SIMS process is a result of collisions caused by the impact of gallium ions at the surface. These collisions can lead to a cascade of secondary collisions where small parts of the substrate are sputtered and the ions are accelerated towards the analyser. This leads to most of the masses detected being fragments of the original molecules. Therefore, it is not conclusive that all the CF ions produced are present on the original surface as they could originate from a CF<sub>2</sub> containing fragment on the surface. This is supported by the fact that there are high CF counts from untreated PVdF which does not contain CF species but only CF<sub>2</sub> species and CH<sub>2</sub> species. XPS indicates the presence of CF<sub>2</sub> but not CF species. In the SIMS spectra the CF fragments are decreasing on treatment, if the end product of defluorination was CF species, then an increase of CF species would be expected on treatment which is not the case. The ToF-SIMS spectra also indicate the formation of conjugated carbon double bond structures that do not

contain CF species. All these factors suggest that once one fluoride ion is removed from the CF<sub>2</sub> species the second fluorine is removed rapidly and replaced by either a proton, a hydroxyl ion or a carbonyl group. Previously all published mechanisms suggest that CF is formed on treatment, in our case it is present as an intermediate. The residual fluorine is present as COF species and CF<sub>2</sub> after treatment, indicating that total defluorination does not occur. The remaining CF<sub>2</sub> species are only a small percentage of the initial concentration of fluorine (5–10%, that is 2–4.5% of the end product) and may be attributed to crystalline parts of the polymer that are difficult to penetrate. This possibility must be investigated further.

The reduction in the smaller carbon masses in the positive ToF-SIMS spectra may be a result of a more stable conjugated double bond system making it less likely for the smaller masses to separate from the main chain. Small carbon fragments are more likely to appear in the negative spectra due to the odd electron ions created during the break up of a conjugated double bond system.

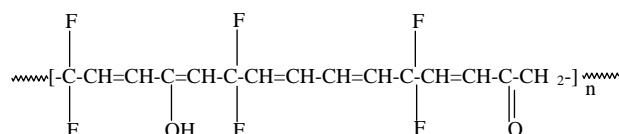
The ToF-SIMS and XPS spectra both indicate the formation of C-OH, COF and C=O groups. Mechanisms for oxygen inclusion in the form of hydroxyl groups and carbonyl groups have been suggested by Brewis et al. [2]. The mechanisms they proposed included the formation of CF groups as indicated in the introduction, our results clearly indicate that CF groups are not present in the final product. Also these mechanisms do not account for the presence of COF groups, therefore a different mechanism must be considered.

Infrared spectroscopy indicates the formation of a carbon double bond structure, but no oxygen is present in the spectra. Raman indicates that a polyacetylene type structure is formed but there is no evidence of fluorine or oxygen groups in the Raman spectra. The ToF-SIMS spectra indicate that

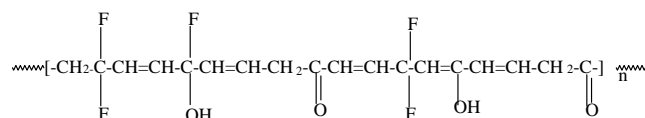
Table 6  
Change in oxygen functionalities with treatment time

Treatment time (h)	C/O	C/F	C-OH/C=O	Structure number
1	7	2.5	1	1 <sup>a</sup>
48	4.5	5	1	2 <sup>b</sup>

<sup>a</sup> Structure 1:



<sup>b</sup> Structure 2:



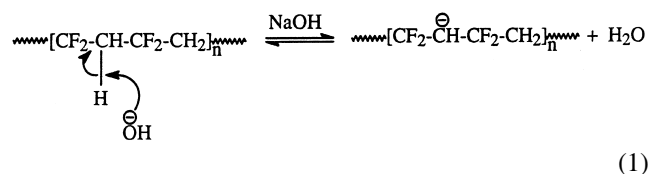
the oxygen is present mainly in the forms of hydroxyl and carbonyl groups and attached to conjugated carbon double bond structures. The XP spectra indicate oxygen is present in three forms—hydroxyl, carbonyl and COF groups. From the XPS results, a typical chain structure can be estimated, but XPS does not account for hydrogen, which must be included where appropriate. Table 6 shows the change in oxygen functionalities over treatment time.

The quantitative XPS data indicate that the final conjugation length could not exceed two double bonds. The Raman spectroscopy indicates a conjugation length of eight double bonds for a polyacetylene structure with a similar Raman spectra, whilst this is of the same order it cannot be described as being in good agreement. The difference is believed to result from the discrepancy in analysis depths between the two techniques, indicating compositional changes in the near surface region. The variation of composition with depth, on the micrometer scale, is to be investigated by the use of Rutherford backscattering spectrometry. The carbonyl and COF groups disrupt the conjugation chain length therefore a longer chain length is unlikely with the observed concentration of oxygen.

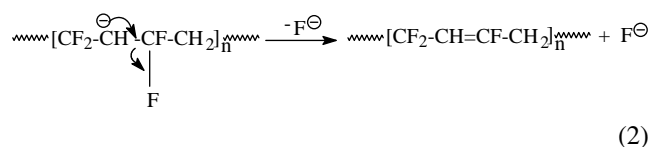
Raman and infrared spectroscopy probe deeper into the surface (micrometers) than that of ToF-SIMS and XPS. The vibrational spectroscopies indicate that deeper into the sample oxygen is not being incorporated into the structure, therefore permitting a longer conjugation length.

#### 4.1. The degradation mechanism

A possible mechanism of defluorination in an aqueous solution is shown below:

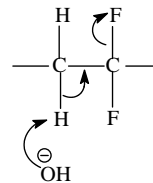


As a result of the high alkalinity of the aqueous solution and high temperature, deprotonisation of CH<sub>2</sub> group in the chain will occur quite readily to achieve the above equilibrium. The resulting anion is stabilised by the presence of four electron withdrawing atoms, i.e. fluorine:

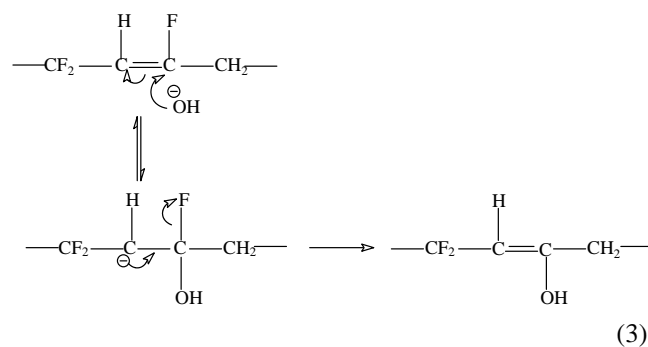


The above chain fragment can rearrange as shown to yield the in chain C=C double bond, this is known as an elimination reaction. The F<sup>−</sup> ion is stable as the reaction occurs in an aqueous solution and the driving force is the formation of a carbon to carbon double bond. Steps 1 and 2 may occur simultaneously via an E2 (elimination, bimolecular) in

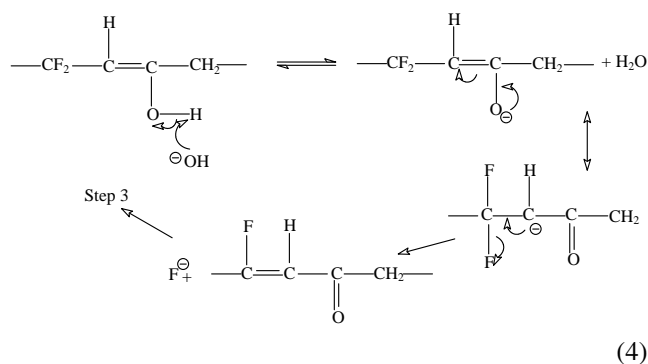
chain reaction:



However, this is unlikely as it is part of a long polymer chain and will thus experience high steric hindrance:



The C=C double bond formation involves the creation of a C–F bond. All analytical data presented in the paper indicate that there is no C–F in the treated PVdF surface. It is concluded therefore that step (3) occurs very rapidly on the production of the C=C double bond in step (2). The fluorine not the hydroxide breaks because of the high activity of hydroxide in solution. The above reaction thus reduces the activity of hydroxide in solution:

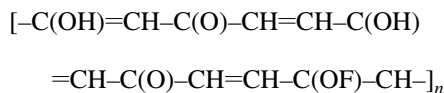


In the presence of an alkaline environment deprotonisation of the unincorporated hydroxide will occur. The resultant structure is resonance stabilised, as shown, and will lose fluoride which is stable in aqueous solutions. Again, the driving force is the formation of a carbon–carbon double bond.

## 5. Conclusions

Defluorination and oxygenation occur on treatment. The formation of conjugated double bond structures on treatment are indicated by ToF-SIMS, Raman spectroscopy and FT-IR, whilst the chemical changes of the process can be followed by XPS. Raman, XPS and ToF-SIMS also

indicate that the removal of fluorine occurs in such a manner that CF groups are present as an intermediate group only. The XPS results also indicate that the oxygen present in the near surface region is mainly in the form of hydroxyl and carbonyl groups but also to a lesser extent in the form of COF groups. On completion of the reaction the product in the near surface region is of the form:



The proposed reaction mechanism entails a number of steps which are energetically unfavourable and highly unlikely to occur under normal conditions, e.g. substitution of fluorine by hydroxide. However the material is exposed to 12 M NaOH at 80°C which, as expected, is a very aggressive environment. The presence of such high activities of hydroxide transforms unfavourable reactions because they result in a reduction in the hydroxide concentration. These reactions still require the presence of  $\beta$  hydrogens which are not present in fully fluorinated polymers and are thus stable in alkaline environments. Deeper in the polymer the oxygen is not incorporated into the polymer during the treatment and a polyene structure of eight double carbon bonds in length, not unlike that of polyacetylene, is created.

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