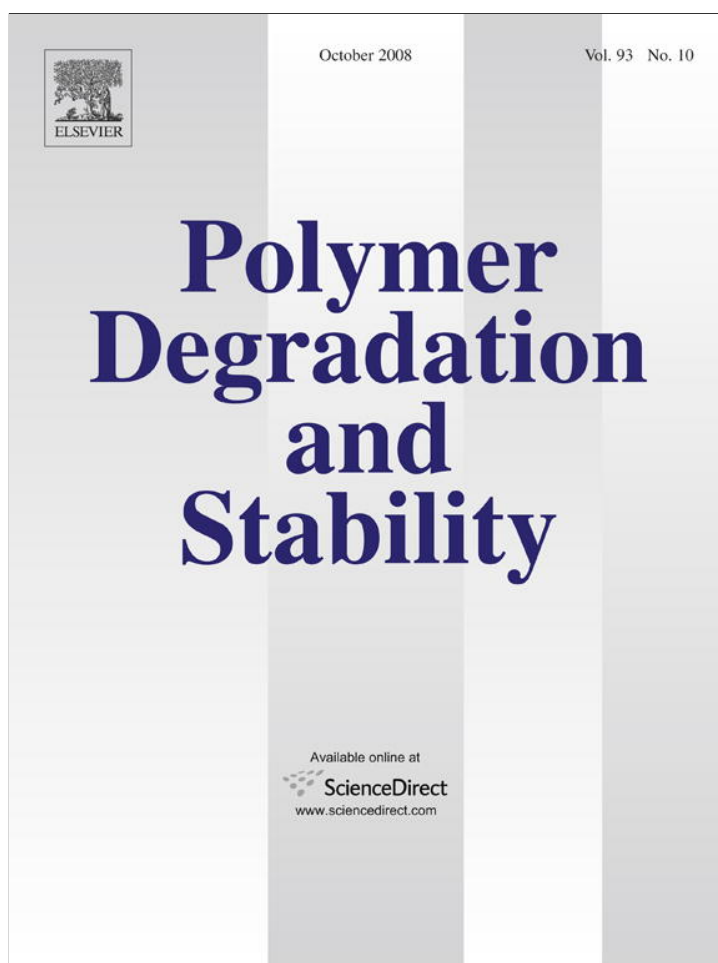


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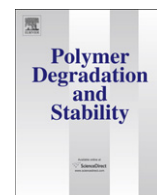
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Kinetics of radiation-induced carbonization of poly(vinylidene fluoride) film surface

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ABSTRACT

The kinetics of radiation-induced carbonization of PVDF surfaces aiming at carbyne (one-dimensional carbon allotrope) synthesis have been studied. A sample of poly(vinylidene fluoride) film was exposed to Mg K α radiation ($h\nu = 1253.6$ eV) in an ESCALAB Mk II spectrometer for 14 h with the aim of surface carbonization. Some 221 spectra of C 1s electrons were measured and expanded using 7 Gaussian curves to reveal and identify species being created on the film surface during its carbonization. A decrease in the content of CF₂ groups, the emergence of CF species in two different states, and growth of a number of fluorine-free carbon atoms have been detected. Simultaneous variations of CH/CH₂, CF and CF₂ peaks suggest elimination of H and F atoms as HF. A proposed model shows three probabilistic factors affecting the rate of degradation, one of which remains uncertain.

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1. Introduction

Radiation-induced carbonization of halogenated polymers offers promise as an approach for synthesizing the linear carbon allotrope – carbyne [1]. X-ray photoelectron spectroscopy (XPS) provides an opportunity for gradual surface modification by elevating irradiation doses in ultra-high vacuum and for simultaneous *in situ* monitoring of chemical reactions involved in the overall modification, e.g. using valence states of carbon atoms. Poly(vinylidene fluoride) (PVDF) appears to be one of the most appropriate precursors for carbynoid structures due to the fact that elimination of carbon atoms is not observed *via* analysis of residual gases in ultra-high vacuum chamber during radiative treatment [2]. The carbonization of PVDF is extremely interesting not only in a pure academic aspect. Carbonized derivatives of PVDF are promising materials for a lot of medical and technological applications [3]. Although numerous studies involving X-ray [4,5], electron [6,7] or ion [7–10] irradiation of PVDF have been carried out since the mid 1980s, a microscopic mechanism of elimination and carbonization processes is not fully understood so far.

The photoelectron spectrum of C 1s electrons in PVDF has two well resolved peaks separated by about 4.5 eV (286.5 and 290.9 eV

[4]). The first peak at lower binding energy is related to carbon atoms bonded to hydrogen (methylene groups), and the second peak is associated with difluoromethylene CF₂ groups [5]. The latter peak decreases under irradiation along with the total fluorine content in the sample. The defluorination process of PVDF has in most studies been considered to occur in two steps CF₂ → CF → C [4,6,7]. So there should exist and vary an additional C 1s peak related to fluoromethine CF groups in the spectra of irradiated samples. This feature has never been observed as an isolated peak because of insufficient energy resolution but is proposed in some studies in order to interpret the modification of spectra during irradiation [4,8].

Voinkova et al. assumed elimination of equal amounts of fluorine and hydrogen with simultaneous formation of hydrogen fluoride [6]. A mathematical model was proposed for the carbonization involving two steps with two probabilistic factors for each. However, no detailed mechanism consistent with this model is known yet.

The aim of this study was to reveal and identify species being formed on the surface of the PVDF film as well as to obtain information about the direction and rate of the evolution of carbon–carbon bonds during soft X-ray irradiation. The nature and properties of a carbonized layer would provide an idea about the behaviour of modified material in various environments thus suggesting its potential applications. One can expect such materials to

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possess unique electronic properties. The deposition of the PVDF layer onto various carbon substrates (e.g. diamond, graphite, glassy carbon) followed by its controlled carbonization could open up promising ways towards the creation of new hetero-structures for carbon-based electronics [11–15] called C-tronics, and the present study is one of the first steps in this direction.

2. Experimental

The XPS study was carried out using a round (16 mm in diameter) sample of partially crystalline PVDF Kynar film (type 720, thickness 50 μm). The film was kindly donated by Atofina, France. The sample was exposed to a Mg K α radiation ($h\nu = 1253.6$ eV) in an ESCALAB Mk II spectrometer during ca. 14 h using an X-ray source in a permanent working mode (12 kV, 20 mA). The measurements were performed with 90° take-off angle in a constant analyzer energy mode at passing energy of 20 eV. The residual gas pressure did not exceed 2.7×10^{-7} Pa. Some 221 spectra of C 1s electrons were scanned without any breaks in a 278–300 eV binding energy range with a 0.1 eV pitch and exposition of 1 s/dot. The registration of each spectrum took 226 s including the 'dead' time between scans.

3. Results and discussion

3.1. Spectral line-shape and expansion approach

The spectrum of pristine PVDF is quite similar to those obtained earlier in numerous studies [4–10]. Apart from two sharp peaks attributable to CH₂ and CF₂ groups there also exist two additional weak features. The first is probably caused by residual hydrocarbon surface contaminants and/or processing additives in the commercial PVDF film. It is shifted by 6.2 eV towards lower binding energies from C 1s peak of difluoromethylene CF₂ groups and is seen as a shoulder on the methylene peak. Its intensity decreases during irradiation, becoming negligible at the end of the experiment. The other small feature is shifted by 1 and 2 eV higher from C 1s peak of CF₂ groups. Its nature is not clear, but it can presumably be associated with tetrafluoroethylene CF₂–CF₂ groupings, which are 'head-to-head' defects [16,17] in the polymer chains. The intensity of this feature is low and varies from one spectrum to other considerably but irregularly, and thus no tendency of its variation could be revealed. However, this feature is necessary for the spectral shape fitting.

During XPS measurements both CH₂ and CF₂ peaks were monotonously and to the same extent shifting towards lower binding energy values. One can suggest this shift to be due to decrease of electrostatic charging as it has previously been interpreted by Duca et al. [4]. The full width half maximum (FWHM) for CF₂ peak was estimated to be 1.2 eV and represents instrumental resolution at the applied passing energy.

To eliminate the charge influence we will consider all energy positions in terms of relative binding energy, with reference to the CF₂ peak.

The C 1s spectra at the beginning and at the end of irradiation are shown in Fig. 1. Analyzing changes in the line-shape, one can notice that the intensity of the high energy peak decreases and the low energy peak becomes broader. Suggesting its complicated nature, we should assume it to consist of several peaks. According to earlier studies [4,7], such variations in spectral shape are caused by stepwise carbonization of PVDF surface. The feature emerging at the higher energy side of the dominant peak (see for example a shoulder between 285.5 and 288.0 eV on the spectrum of irradiated sample shown in Fig. 1) was reliably detected in this study and has never been observed before in such an obvious way. After the subtraction of the linear background all spectra were expanded

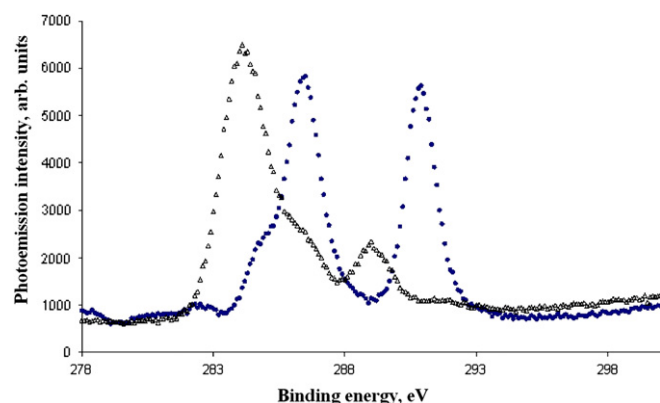


Fig. 1. XPS line-shape in the beginning (solid circles) and at the end (triangles) of irradiation.

into 7 Gaussian peaks of equal widths (FWHM 1.2 eV) as shown in Fig. 2. Each describes a specific functional group or a state of carbon atoms. Temporal variations of the intensity ratio of each individual peak normalized to the whole spectrum intensity were studied. Naturally this ratio is equal to the relative content of a chemical group associated with a certain peak.

Positions of peaks 1–5 were fixed with reference to the peak 6 at -6.2 , -5.4 , -4.5 , -3.1 and -2.0 eV, respectively. For better fitting only 0.2 eV variations of binding energy were allowed for peaks 1–5. Peak 7 simulates the above-mentioned weak feature at higher binding energy. Its position was estimated to fit spectral shape and amounted to $+1$ – 2 eV. Peak 1 corresponds to the low energy feature attributable to hydrocarbon contaminants as discussed above.

3.2. Assignment of peaks and kinetics of their intensity variation

The peaks are recognized using temporal variations of their intensity fractions (Fig. 3) and specific values of their chemical shifts. According to all previous XPS studies [4,6–10], peak 6 can be unambiguously attributed to CF₂ groups. Briggs and Seach [18] reported direct and secondary chemical shifts of core-level energy for carbon bonded with fluorine to be $+2.9$ and $+0.7$ eV/bond, respectively. They also postulated that binding with hydrogen does not lead to any shift in carbon core-level. But 'direct' simulation of spectrum for PVDF and derivatives of its partial carbonization containing CH₂, CF₂, CH, CF and $=C=$ species in various combinations does not bring about values of chemical shifts correlating with experimental data. Peak 3 should be assigned to CH₂ groups due to the fact that its original fraction is over 40% (Fig. 3) (ideal

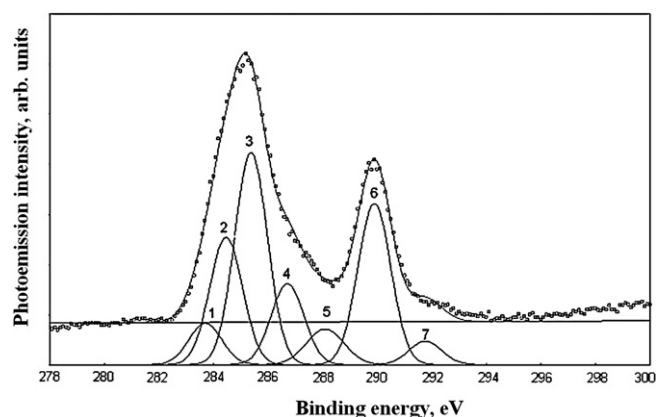


Fig. 2. An example of expansion for the spectrum obtained after 157 min of irradiation. The straight line simulates a linear background.

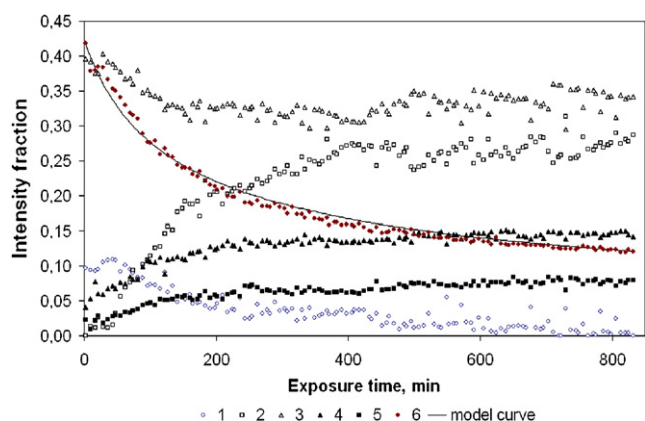


Fig. 3. Variation of normalized intensity of Gaussians 1 (○), 2 (□), 3 (△), 4 (▲), 5 (■) and 6 (●) during irradiation. The model curve (solid line) representing a mathematical simulation of peak 6 variation is discussed in Section 3.3.

PVDF should have 50% of carbon atoms in CH₂ groups). That very position of CH₂ peak is also given by Beamson and Briggs [18] and Le Moël et al. [7–10].

When searching for a peak attributable to CF groups we were unable to describe spectral line-shape between CF₂ and CH₂/CH peaks by 1 Gaussian of the same width, and thus the existence of two peaks (4 and 5) was proposed. Their intensities vary proportionally to each other during irradiation, and thus they may presumably be attributed to the same functional group. Surprisingly, the proportionality factor is close to 2 (see Fig. 3). We consider peak 5 to be C 1s photoelectrons of CF groups. Its position (−2.0 eV) is intermediate between that given by Le Moël (−1.7 to −1.3 eV) [8] and Duca (−2.6 eV) [4]. *Ab initio* calculations of C 1s energy in PVDF and in its partially carbonized derivatives performed *via* routine similar to that used by Morikawa et al. [2] show the position of CF peak to be quite close to that of peak 5 in experimental spectra.

Peak 4 (−3.1 eV) has been revealed in this study for the first time. Its nature is not clear yet. One can suppose it to be created by photoelectrons emitted from unsaturated excited CF* groups, which had already lost a fluorine atom, but did not form an additional π-bond in polymeric chain or a σ-crosslink. Alternatively, the difference in energy positions between peaks 4 and 5 may be an effect of secondary shift in crosslinks formed by adjacent chains: C 1s electrons in CF group crosslinked with other CF group should undergo a secondary shift, whereas in CF group crosslinked with CH one this effect should not occur.

Considering variations of peaks 2 and 3, one can note that their combined fraction within the latter part of the irradiation time amounts to 60% and over, whereas even in pristine PVDF only 50% of carbon atoms are bonded with hydrogen. This means that peak 2 can be at least partially attributed to the yield of carbon atoms not bonded with fluorine or hydrogen. Relative content of carbon atoms bonded with fluorine (N_F) both in CF and CF₂ groups can be calculated by summing over fractions of peaks 4–6: $N_F = N_4 + N_5 + N_6$. The decrease of this value during irradiation is $-\Delta N_F(t) = N_F(0) - N_F(t)$, where $N_F(0)$ is the fraction of atoms bonded with fluorine at the outset of exposition. Hence, the difference $-\Delta N_F(t)$ shows the fraction of carbon atoms rid of bonding with both fluorine atoms. As is seen in Fig. 4, the intensity fraction of peak 2 is quite close to $2\Delta N_F$ at any exposition dose. Another surprising fact is that the decrease in the combined intensity of peaks 1 and 3 makes up nearly the same fraction. This leads to the following assumptions:

1. Hydrogen is being eliminated in the same amount as fluorine and, most probably, coupled with fluorine.

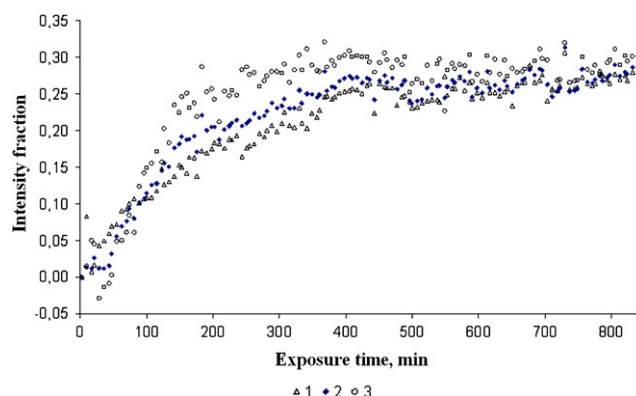


Fig. 4. Increase in content of fluorine-free carbon atoms, multiplied by factor 2 (1, empty triangles); intensity growth of peak 2 (2, solid rhombs) and decrease in combined intensity of peaks 1 and 3, multiplied by factor 2 (3, empty circles).

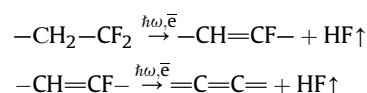
2. Peak 2 is attributable to carbon atoms not bonded with fluorine or hydrogen. These ones may be yielded not only from carbon atoms previously bonded with fluorine (peaks 4, 5 and 6) and hydrogen (peak 3) but also from hydrocarbon fragments of surface contaminations or processing additives initially not included in the main polymer chains (peak 1). However, we can only suggest the types of carbonic structure forming in the latter case, but this process undoubtedly makes products of carbonization much more various by hybridization type.

The elimination of hydrogen leads to the formation of chain fragments like CF–CH–CF or CF₂–CH–CF in which hydrogen-bonded carbon atom should undergo a weaker secondary shift compared to that in original polymer chain CF₂–CH₂–CF₂. This effect is expected to elicit two additional C 1s peaks. But actually these do not appear in experimental spectra thus suggesting that secondary shifts produced by vicinity of CF₂ and CF groups are nearly the same. This might be due to the bond shortening in the case of fluoromethine groups: although the number of fluorine atoms in the nearest proximity of CH_x group decreases, they are spaced closer, thus elevating the secondary shift. Nevertheless such an exact compensation seems to be rather doubtful.

The assignment of XPS peaks is summarized in Table 1.

3.3. A model for decomposition of CF₂ groups

The previously proposed model [6] was taken as the starting point. The carbonization process is considered within this model as two consecutive elimination acts of HF molecules:



In this study we consider only the first step of carbonization. The rate of the second step has been shown to be sufficiently lower [6]. Furthermore, the processes occurring during the second step may

Table 1
Assignment of C1s XPS peaks

Peak No.	Position relative to CF ₂ , eV	Assignment
1	−6.2	CH ₂ or CH (surface contamination)
2	−5.4	=C= (or −C≡)
3	−4.5	CH ₂ or CH (PVDF)
4	−3.1	CF*
5	−2.0	CF
6	0	CF ₂
7	+1 to +2	CF ₂ –CF ₂ ('head-to-head' defect)

be more complicated. The decomposition rate of CF_2 groups was previously [6] determined as:

$$\frac{dN}{dt} = -kN^2 \quad (1)$$

where N is the content of CF_2 groups, and factor k shows the ionization probability of CF_2 group by an X-ray photon.

The initial condition for solving Eq. (1) is a certain amount of CF_2 groups at the beginning of the process:

$$N(0) = N_0 = \text{const.} \quad (2)$$

Solving Eq. (1) with regard to the initial condition (2) brings about:

$$N(t) = \frac{N_0}{1 + kN_0t} \quad (3)$$

The fact that N is taken to the second power can be explained by probabilistic considerations. The probability of photo-ionization is proportional to the content of objects being ionized, i.e. atoms, molecules or functional groups. Simultaneous elimination of fluorine and hydrogen in terms of a probability theory is a compound event, the probability of which is equal to the product of probabilities of single events it comprises. The elimination of HF is possible if an ionized CF_2 group has an adjacent CH_2 group [6]. The number of excited CF_2 groups is proportional to their content N . Since the decomposition of CH_2 groups occurs simultaneously and to the same extent, its content is N as well. Hence, the rate of carbonization should be proportional to N^2 .

So, each power of N in Eq. (1) can be considered as probabilistic factor necessary for the decomposition of CF_2 groups.

However, Eq. (3) is inconsistent with experimental data. In order to get better fitting, the model was modified by including integer parameter $n > 1$, which shows the number of probabilistic factors for a unit act of decay. Kinetic equation for the decomposition of CF_2 groups in this case becomes the following:

$$\frac{dN}{dt} = -kN^n \quad (4)$$

Solving Eq. (4) with regard to the initial condition (2) gives:

$$N(t) = \sqrt[n-1]{\frac{(n-1)N_0^{n-1}}{n-1 + kN_0^{n-1}t}} \quad (5)$$

The best fitting of Eq. (5) (model curve in Fig. 3) with the experimental data occurs if $n = 3$ and $k = 0.569$. Hence, the carbonization process is governed by three probabilistic factors, two of which are discussed above.

The origin of the third factor is not clear yet. One can assume that the ionization rate of $\text{CF}_2\text{-CH}_2$ difluoroethylene fragments in polymer chains decreases in the environment of CH=CF fluorovinylene fragments due to the experimentally observed fact [6] that the latter structures are noticeably more stable under irradiation than the former ones. Such an influence of environment can be characterized by proportionality of the ionization rate to one more N . However, this interpretation is extremely tentative and needs a proper discussion and further experimental studies.

4. Conclusions

During radiation-induced carbonization of PVDF the line-shape of C 1s XPS spectra varies greatly and shows the presence of CF_2 , CF , CH_2 , CH , and C=C species in the sample. These variations point to a stepwise fashion of the carbonization process. The existence of two peaks between $\text{CH}_2\text{-}$ and $\text{CF}_2\text{-}$ peaks shows that CF groups can be created in two distinct states.

Simultaneous elimination of hydrogen and fluorine as an HF molecule was expected and experimentally supported by the fact that only a half of 'naked' carbon atoms were originally bonded with fluorine (Fig. 4). Carbonization of surface contamination or processing additives with carbon atoms in the main polymer chains was suggested.

A mathematical model of the first step of carbonization shows that a single act of HF elimination depends on three probabilistic factors, which are presumably associated with the presence of neighbouring CF_2 and CH_2 groups, and distinctions between PVDF and its carbonized derivatives concerning their stability against soft X-ray radiation.

Further studies should be done with increased irradiation time in order to achieve higher degree of carbonization. Interpretation of the third probabilistic factor for CF_2 groups decay needs additional both experimental and theoretical efforts.

The third probabilistic factor for the decomposition of CF_2 groups cannot be unambiguously interpreted and has yet to be dealt with.

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