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# Chemical modification of Hyflon® AD copolymer end groups by means of physical and chemical treatments. A joint spectroscopic and quantum chemical investigation

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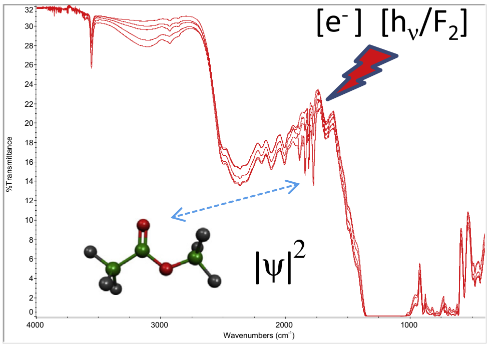
## HIGHLIGHTS

- Chemical modifications occurring in a class of amorphous fluorinated polymers have been investigated.
- The adopted experimental tool is Vibrational Spectroscopy.
- Quantum chemical calculations allowed to rationalize experimental data.
- The joint experimental and theoretical approach shed light on the physico-chemical phenomena occurring.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper is presented a study on the effects of physical treatments, namely electron beam irradiation or fluorination, on a perfluoropolymer copolymer of tetrafluoroethylene with 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (Hyflon® AD copolymer). The analysis has been carried out by means of IR spectroscopy and quantum chemical modeling based on density functional theory; this combined experimental/theoretical approach has proven effective for the interpretation of previously unassigned IR bands, which are associated to functional groups generated by polymer degradation and chain scission. We performed a systematic screening of chemical groups and structures compatible with degradation pathways that are possible from the chemical point of view: the chemical mechanisms and the correlation with the spectroscopic experimental data (both frequency and intensity) provide guidelines in understanding the phenomena. Moreover, the spectroscopic experimental/theoretical and chemical approaches allowed us to identify some chemical structures responsible for the unassigned IR bands in the C=O stretching frequency region above 1800 $cm^{-1}$, which is typical for carbonyl groups in fluorinated systems.

## Introduction

Recent technologies related to the development of communication devices, electronics and optics also require new materials with outstanding chemical, optical and mechanical properties. Among the organic polymers the materials based on perfluoropolymers provide ultimate resistance to hostile chemical environments and high working temperatures. In this paper, we deal with a family of copolymers of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), known commercially as Hyflon® AD copolymer; these copolymers are amorphous and have

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a glass transition temperature (Tg) significantly higher than room temperature, while their thermal decomposition temperature exceeds 400 °C [1–5]. Depending on their composition, such copolymers span a refractive index range from 1.32 to 1.331, making them suitable for many optical applications. These peculiar properties make this class of amorphous materials a candidate for state of the art technology in different fields like optics, photonics, electronics, membrane science, biotechnology, nanotechnology.

An important aspect to consider in case of optical applications is the almost complete absence of end groups [6], which may affect both optical and surface properties. Therefore we will show the effects of two different polymer treatments capable of generating or of removing end groups, namely:

- *Electron beam irradiation*, which results in chain scissions, generating a great number of ionic end groups and bringing to an effective reduction of molecular weight and, in some cases, of the chemical/thermal stability [7].
- *Chemical fluorination*, which aims at eliminating the ionic end groups, replacing them with perfluorinated structures.

Many papers have dealt in the past with the effects of gamma radiation and electron beam irradiation in PTFE-like polymers and copolymers [8–10]: the main effects observed are chain scission, formation of ionic end groups as carboxylic acids and acyl fluorides. Also, chain branching, variation of the conformational order/disorder parameter or of the crystallinity degree are expected [11–13]. More recently, similar studies have been conducted on amorphous perfluoropolymers as well [14,15].

In this paper we present a detailed spectroscopic study, in conjunction with quantum chemical modeling based on density functional theory (DFT) calculations for several model systems, aimed at understanding and detecting chemical modifications induced by physical and chemical treatment on Hyflon® AD copolymer. It was indeed demonstrated in previous papers [15–20] that such a joint experimental/computational investigation allows to obtain an in-depth description of the structural and vibrational properties of perfluorinated polymers, unraveling both the intra- and intermolecular phenomena which are responsible for their physicochemical properties.

## Experimental and computational details

### Polymer treatments

*Electron beam irradiation*: the irradiation dose varied from 20 to 80 KGy.

*Fluorination*: According to Ref. [6] the fluorination of Hyflon® AD copolymer is carried out in presence of UV radiation (the spectrum of the UV source employed, a high pressure mercury lamp, is reported in SI).

A solution of the polymer (6%wt.) in a perfluorinated solvent (e.g. Galden® LS165 PFPE, a perfluoropolyether having a bp = 165 °C) is loaded into a photochemical glass reactor equipped with a mechanical stirrer and the UV immersion lamp described above. Nitrogen is fed for 1 h into the solution to purge the solubilized oxygen, and then a 1:1 by volume mixture of nitrogen/fluorine is fed in the presence of the UV radiation for 40 h at 25 °C. Eventually the reaction fluorine is removed by purging the solution with nitrogen. Different samples are taken at different times during the fluorination procedure, in order to obtain an evaluation of the kinetics of the reaction. The concentration of end-groups (carboxylic acid and acyl fluorides) is determined by means of FTIR analysis on the dry polymer after solvent removal, according to Ref. [6].

### Spectroscopy

Powders of samples (few mg) before and after irradiation were pressed at room temperature, making pellet dies (5 mm diameter) suitable for transmission analysis. IR spectral data were collected with a Thermo Nicolet Nexus instrument, averaging 256 scans at a resolution of 2 $cm^{-1}$.

FT-Raman spectra have been collected on powders using a Nicolet Nexus 870 spectrometer with FT-Raman module which provided a laser line at 1064 nm with a power at sample of about 300 mW. The acquisition parameters were: 8 $cm^{-1}$ of resolution and 1024 scans.

### Computational details

Model molecules of various possible degradation products were investigated by means of DFT computations. For each of them we carried out geometry optimization and IR spectra calculation runs. In the case of systems possessing a flexible backbone, the conformational space was explored as successfully done in the past [15–19] on similar systems, in order to take into account the contribution of all the relevant conformers. The resulting average values of frequency and IR intensity were calculated and reported in Table 1. For all DFT calculations the hybrid exchange–correlation functional B3LYP [21] and the 6-311++G(d,p) basis set were used: as seen in a previous paper [17], this combination gives a quite accurate description of the spectral pattern (i.e. frequency and IR intensities) of fluorinated molecules in different environments, in good agreement with the available experimental data. For all the calculations the Gaussian09 code was used [22]. Frequency values have been scaled by 0.9711 for all the model systems: this scaling factor was determined by comparing the well-known [23] experimental C═O stretching frequency of the acyl fluoride group, with the result obtained for the model system $CF_3—CF_2—CF_2—C(F)═O$ (model 1 in Table 1).

## Experimental results and discussions

### Irradiation

In Fig. 1 the IR spectra of irradiated and non-irradiated powders are reported. The overall spectral pattern is similar, while two components in the OH stretching region clearly increase with the irradiation dose: these features are a sharp peak at 3557 $cm^{-1}$ and a broad band in the range 3400–2800 $cm^{-1}$, which are due to the O—H stretching in carboxylic acid end groups [23]. A complex pattern, whose intensity increases with the irradiation dose, is also visible in the region 2000–1600 $cm^{-1}$.

The spectrum in Fig. 1, in absorbance units, is plotted in a limited range (4000–1500 $cm^{-1}$), in order to better appreciate the components that arise and grow with irradiation dose; the whole vibrational spectrum (recorded in transmittance) is reported in the Supplementary Data, Fig. SD1. Three bands at 1884 $cm^{-1}$, 1813 $cm^{-1}$ and 1775 $cm^{-1}$ can be clearly detected: they have been already observed in the IR spectra of other TFE based polymers and are commonly assigned to $R_f$-COF and $R_f$-COOH groups respectively [13,23,24]; in addition, at higher irradiation doses we observe two components that are not usually present in PTFE like polymers. These two bands, at 1860 $cm^{-1}$ and 1841 $cm^{-1}$, which were so far unassigned, suggest that irradiation can generate some different degradation products, aside from acids and acyl fluorides. It is very important that all the features observed in the spectra are assigned in detail, whenever the spectroscopic data are used for analytical purposes: for this reason we decided to carry out a wide computational investigation on the vibrational properties of