

## Electrochemical reductive carbonization of polymers derived from hexafluoropropene

L. Kavan, F. P. Dousek

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Dolejškova 3, CS-182 23 Prague 8 (CSFR)*

and K. Doblhofer

*Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-W-1000 Berlin 33 (Germany)*

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### Abstract

Poly(tetrafluoroethylene-co-hexafluoropropene) reacts with lithium amalgam even at room temperature to form n-doped elemental carbon and lithium fluoride. The reaction is governed by an electrochemical corrosion mechanism as for other perfluorinated polymers. The same reaction with plasma-polymerized hexafluoropropene is considerably hindered. The difference is explained by the existence of non-reducible crosslinked sites in the plasma-polymerized hexafluoropropene. These block the formation of an electrically conductive carbon skeleton, which is essential for propagation of the electrochemical reaction into the bulk of the polymer.

### Introduction

Polymers of hexafluoropropene can be prepared either by chemical or plasma polymerization. The chemical homopolymerization of hexafluoropropene (HFP) has only limited practical significance [1]. On the other hand, the homopolymerization of hexafluoropropene in plasma enables the preparation of well-defined thin polymeric films with prospective applications for coatings, dielectrics, sensors, etc. [2–8].

Although the process of plasma polymerization is rather complex and far from being understood, it can be used to prepare films with a homogeneous thickness of as low as *ca.* 100 nm [6, 7]. These films are suitable for modelling support/film degradation effects, *e.g.* the corrosion of painted metals [5]. From this point of view, studies of the intrinsic chemical and electrochemical stability of plasma-polymerized monomers in comparison with that of chemically polymerized ones should provide useful information.

Perfluorinated polymers can be reduced electrochemically at potentials of  $-1.8$  to  $-2.3$  V *vs.* SHE to fluorides mixed with n-doped elemental carbon. The reaction proceeds in cells with aprotic liquid or solid electrolytes or during the reaction of fluoropolymers with alkali metal amalgams [9].

The reductive carbonization is controlled in all cases by charge transport (both electrons [10] and electrolyte cations [11]) in the product mixture.

There are two main arguments against considering the reaction of alkali metal amalgams with perfluorinated molecules as being a purely chemical process: (1) the reaction rate is almost independent of the amalgam concentration and (2) the solid product is a perfectly uniform layer impermeable to the amalgam, *i.e.* it separates both reactants immediately after their initial contact [9, 11].

The reaction of alkali metal amalgams with fluoropolymers (and also small molecules such as hexafluorobenzene and tetradecafluorohexane [12]) can, however, be understood in terms of the self-discharge of a galvanic corrosion cell, with an alkali metal amalgam anode and the fluoropolymer functioning as the depolariser of a carbon cathode:

$\text{Me(Hg)}|\text{C-MeF}|C$ , fluoropolymer

(Me is an alkali metal and C-MeF denotes the product [a mixture of *n*-doped elemental carbon and alkali metal fluoride]) [9]. The reaction rate is controlled by the cation conductivity of the product. This is not particularly dependent on the fluoropolymer type, but decreases substantially in the sequence Me = Li, Na, K, *i.e.* the most rapid system is that with lithium amalgam.

The formation of an electron/cation conductive product is readily achieved only with perfluorinated polymers (with a limited number of heteroatoms such as Cl, O or S); partly fluorinated polymers [*e.g.* poly(vinylidene fluoride)] are stable towards this treatment because of the presence of non-reducible C-H bonds [9, 11]. This paper deals with the Li(Hg) carbonization of plasma-polymerized hexafluoropropene in comparison with that of common, chemically polymerized fluoropolymers.

## Experimental

The plasma-polymerization of hexafluoropropene was effected via an AC glow discharge (450 V, 10  $\mu\text{A}$ , 20 kHz) (see also ref. 5) in a 1:1 (by volume) mixture of HFP and Ar (pressure 40 Pa, flow rate 10 ml  $\text{min}^{-1}$ ). The polymeric film was deposited on Pt or Ag supports at the rate of *ca.* 7  $\mu\text{g cm}^{-2} \text{min}^{-1}$ . The deposited polymer was weighed on a Sartorius ultramicrobalance (precision  $\pm 0.1 \mu\text{g}$ ). For some studies, the polymer films were stripped from the metal support after heating to 100 °C followed by fast cooling with water or methanol. FEP foil (Asahi Chemical), 50  $\mu\text{m}$  thick, containing 20% of hexafluoropropene and 80% of tetrafluoroethylene units, was cleaned with an  $\text{Na}_3\text{PO}_4$ -NaOH mixture and outgassed at 150 °C/1 mPa [11].

The concentration of Li amalgam was *ca.* 400 ppm by weight (limited by the low solubility of Li in mercury at room temperature). The reaction of Li(Hg) with polymers was performed in an all-glass vacuum apparatus. The stoichiometric consumption of reactants was determined from acidimetric

titration of amalgam aliquots, fluoropolymer mass differences, and spectrophotometric or potentiometric determination of the fluoride content in the product [11].

UV-VIS spectra of plasma polymerized films were recorded in transmission or reflective modes using a Perkin-Elmer Lambda 9 instrument. In the latter case, the plasma-polymerized HFP films were prepared on optical quality Ag sheets or vacuum-deposited Pt layers on a glass support. X-Ray photoelectron spectra were recorded on an ESCA 3 Mk II apparatus (VG Scientific) with an Al  $K\alpha$  source. Quantitative surface analysis involved corrections for the Scofield cross-section and kinetic energy [13, 14]. The charging effect was corrected using a vacuum-deposited silver sub-monolayer (Ag  $3d_{5/2}$ , 368.27 eV; Ag/C=0.1-0.3). The impedance of plasma-polymerized HFP was measured using 30-5000 Hz, 10 mV AC voltage, a Philips PM 2554 high-frequency millivoltmeter and a Hewlett-Packard 3557A gain phase meter.

## Results and discussion

### *Characterization of the plasma-polymerized hexafluoropropene*

Plasma-polymerized hexafluoropropene (PP-HFP) films of suitable thickness show typical interference effects in their UV-VIS spectra (Fig. 1).

Assuming a refractive index for PP-HFP equal to 1.39 [6], one can calculate the film thickness from the shift in the interference maxima. The film thickness thus obtained combined with the known film mass per unit area gave a density of 1.4-1.8 g cm<sup>-3</sup> (increasing systematically with increasing film thickness) [5]. The strong optical absorption of PP-HFP in the UV and near-UV regions (responsible for the yellowish colouration of the films) is explained by the presence of unsaturation and fluorine-deficient sites [6]. These are formed by the action of high-energy particles during plasma

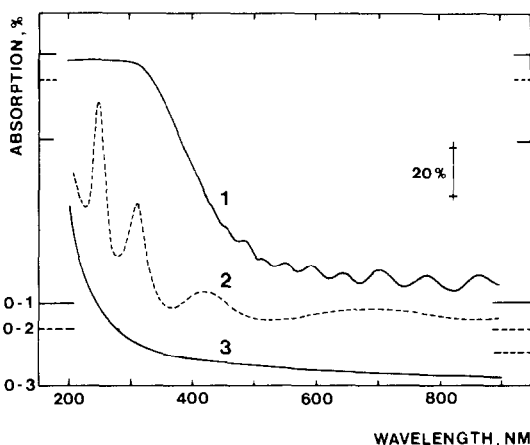


Fig. 1. UV-VIS transmission (solid line) or reflection (dashed line) spectra. (1) PP-HFP, 490  $\mu\text{g cm}^{-2}$ ; (2) Pt-supported PP-HFP, 35  $\mu\text{g cm}^{-2}$ ; (3) FEP foil 10.5  $\mu\text{g cm}^{-2}$ .

polymerization; hence, chemically polymerized fluorocarbons with a regular structure show considerably less UV absorption (*cf.* Fig. 1).

The film thickness can also be calculated from its AC impedance. The PP-HFP films deposited on the cross-section of a Pt cylinder were immersed in mercury to study the impedance of the metal/dielectric/metal configuration (see the inset in Fig. 2). The measured impedance was purely capacitive (phase shift  $-88^\circ$  to  $-90^\circ$ ). Figure 2 presents these derived capacitances per unit area of the film, together with a curve calculated on the basis of the parallel-plate capacitor equation:

$$C = \frac{\epsilon\epsilon_0}{d} = \frac{\rho\epsilon\epsilon_0}{m} \quad (1)$$

where  $\epsilon$  is the dielectric constant of the film,  $\epsilon_0$  the vacuum permittivity,  $d$  the film thickness,  $\rho$  its density, and  $m$  the mass per unit area of the film. For the purposes of calculation, literature values for poly(tetrafluoroethylene) (PTFE) or poly(tetrafluoroethylene-co-hexafluoropropene) (FEP) were used, *i.e.*  $\epsilon=2.1$ ,  $\rho=2.1 \text{ g cm}^{-3}$  [1]. The experimental  $C$  values are lower than the calculated ones; thus, even for optically determined densities ( $1.4\text{--}1.8 \text{ g cm}^{-3}$ ) the dielectric constants were found to lie in the range  $1.5\text{--}1.9$ . The lower dielectric constant of plasma-polymerized fluorocarbons in comparison with that of chemically polymerized monomers has been attributed to the presence of oxygen impurities and the corresponding C–O orientation effects in the plasma-polymerized dielectrics [8]. Oxygen is attached to the plasma-polymerized skeleton by radical oxidation upon air exposure [8], which is demonstrated by infrared absorption bands corresponding to C–O and C=O bonds [5].

Air oxidation of plasma-polymerized HFP is also evidenced by X-ray photoelectron spectroscopy: the O 1s peak (binding energy 533.0 eV) corresponds to the atomic ratio O/C=0.12 (FEP exhibits a negligible O 1s signal). The C 1s peaks of PP-HFP (Fig. 3, curve 1) can be assigned to  $\text{CF}_3$  (292.8 eV) and  $\text{CF}/\text{CF}_2$  (290.5 eV). The envelope at 288–286 eV corresponds

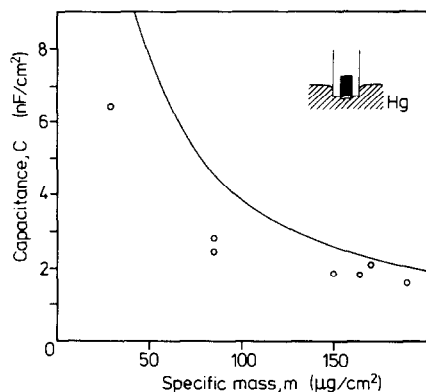


Fig. 2. Dielectric capacitance of PP-HFP films on Pt.

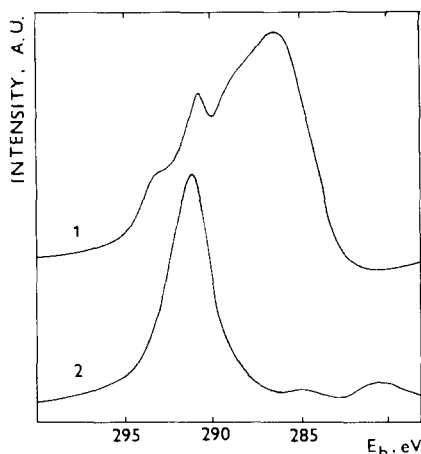


Fig. 3. The C 1s XPS spectrum of (1) PP-HFP and (2) FEP.

to C–O and C=O species, as well as to C–C bonds in the crosslinked polymer skeleton of PP-HFP. On the other hand, the regular FEP polymer (Fig. 3, curve 2) exhibits virtually only the C 1s band of the CF<sub>2</sub> species (291.1 eV). This is due to the fact that the expected chemically shifted peaks of CF/CF<sub>3</sub> would have 10-times lower intensity, *i.e.* they are completely masked by the overlapping CF<sub>2</sub> peak. (The content of hexafluoropropene units in FEP is 20 mol%, see experimental section).

#### *Reaction of hexafluoropropene polymers with Li amalgam*

A FEP foil reacts, as expected, with Li amalgam even at room temperature with the formation of an uniform carbonized layer C–LiF. The thickness of the carbonized polymer,  $d$ , depends on the reaction time,  $t$ :

$$d = k \cdot t^{1/2} \quad (2)$$

where the rate constant,  $k$ , was determined (following the procedure described in [11]) as 47 nm s<sup>-1/2</sup> at 25 °C. This value compares well with that for PTFE and other fluoropolymers [9, 11]. The observed composition of the C–LiF product was CLi<sub>0.2</sub>(LiF)<sub>2</sub>, *i.e.* the carbonization is complete and the consumption of Li corresponds to 110% of the stoichiometric amount equivalent to the fluorine content in the starting polymer. By analogy with other electrochemical carbonizations of fluoropolymers [9, 11], this indicates that the carbon produced is not pure elemental carbon, but an n-doped one in which the 'superstoichiometric' Li<sup>+</sup> compensates the negative charge of the carbon skeleton.

The carbonization process of metal-supported, thin PP-HFP film was conveniently followed by the measurement of the DC electrical conductivity of a Pt/PP-HFP/Li(Hg) sandwich, employing a set-up similar to that shown in Fig. 2. The PP-HFP films which had been exposed to air before reaction with Li(Hg) gave contradictory data: some films reacted with Li(Hg) forming

a black, electrically conductive product, but others remained intact even after several days of exposure at elevated temperatures (up to 100 °C). The poorly defined air oxidation of the PP-HFP films might possibly be responsible for this lack of reproducibility, although it is known that the presence of oxygen in the fluoropolymer skeleton does not necessarily block the carbonization reaction, *e.g.* the oxidized analogue of the polymer studied in this work, poly(perfluoropropene oxide), and also poly(tetrafluoroethylene-co-perfluoropropylvinylether) or Nafion, react quantitatively with Li(Hg) with the reaction kinetics being well defined [11].

The *in situ* carbonization of PP-HFP films, *i.e.* the Li(Hg) treatment of PP-HFP films without previous air exposure, proceeds reproducibly without the above complications; however, the electrical conductivity of the product was still far removed from that of carbonized bulk fluoropolymer (PTFE, FEP). Figure 4 depicts the experimental DC conductivity of a PP-HFP film ( $m=140 \mu\text{g cm}^{-2}$ ;  $d=780 \text{ nm}$ ) in contact with Li(Hg) at 25 °C.

The DC conductivity was measured using a low DC voltage, typically 50 mV, in order to prevent the electrical breakdown of the ultrathin film (for a dielectric strength  $\approx 10^6 \text{ V m}^{-1}$  the critical polymer thickness is  $\approx 50 \text{ nm}$  at 50 mV). The above-mentioned film thickness of 780 nm, according to eqn. (1) corresponds to the reaction time for total carbonization ( $t=275 \text{ s}$ ) at 25 °C.

Indeed, Fig. 4 shows that some electronic conductivity is observed at about that time, but its value is three to four orders of magnitude less than expected for a perfectly carbonized C–LiF mixture (from PTFE). The latter is indicated by a dashed curve in Fig. 4, this being based on data from ref. 10 for  $t=297 \text{ s}$ ,  $d=819 \text{ nm}$  (the dotted curve is an extrapolation). The

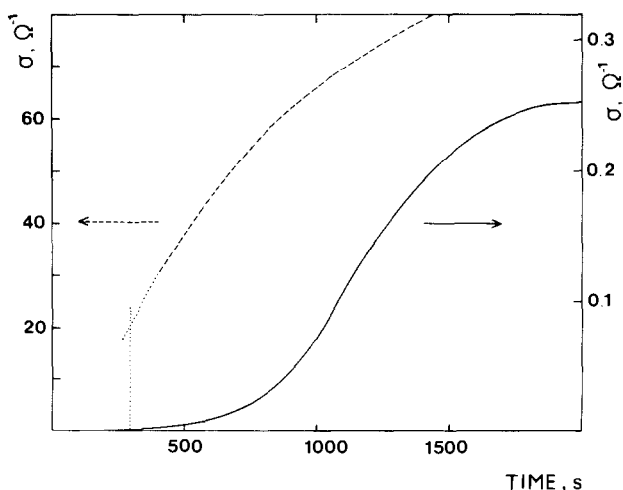
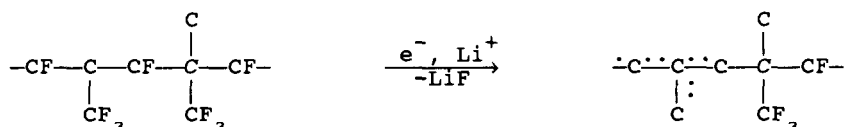


Fig. 4. The DC conductance of carbonized PP-HFP at 25 °C (solid line); sample area  $0.28 \text{ cm}^2$ ;  $t$  = time, measured from the start of Li(Hg)/PP-HFP contact. Dashed line: the expected dependence for pure C–LiF.

increase in conductivity of C–LiF with time is due to the solid-state crosslinking of the carbon skeleton, as discussed elsewhere [10]. The discussion of the conductivity/time dependence for carbonized PP-HFP is less straightforward since incomplete carbonization presumably dominates here (see below).

On washing carbonized PP-HFP films (after 1–5 days contact with Li(Hg)) with water, the LiF is extracted while the insoluble remainder disintegrates into flakes. Analysis of the water extract for fluoride gave only about 30–40% of the stoichiometrically expected F content for complete carbonization. Microscopic inspection of the flakes clearly demonstrated incomplete carbonization of PP-HFP: the plasma-polymerized film contained carbonized fibrous areas surrounded by the intact polymer (Fig. 5).

Non-uniform carbonization is a characteristic of plasma-polymerized films; the bulk, chemically polymerized FEP and other perfluorinated polymers always carbonize quantitatively [9, 11]. The different structure of PP-HFP is apparently responsible for this effect. Besides regular perfluorinated chains [ideally  $-\text{CF}_2-\text{CF}(\text{CF}_3)-$ ], the PP-HFP skeleton also contains various fluorine-deficient and crosslinked sites. Since the C–C bond (similar to C–H bond [11]) is presumably stable against electrochemical reductive splitting [9, 15], the crosslinked site (C) might be a centre at which reaction propagation stops:



The same effect has also been observed with poly(vinylidene fluoride), polyethylene and poly(vinyl chloride), where the non-reducible  $-\text{CH}_2-$  sites in the polymer chain present a perfect barrier against the formation of a  $\pi$ -conjugated conductive carbon chain, which would allow reaction propagation

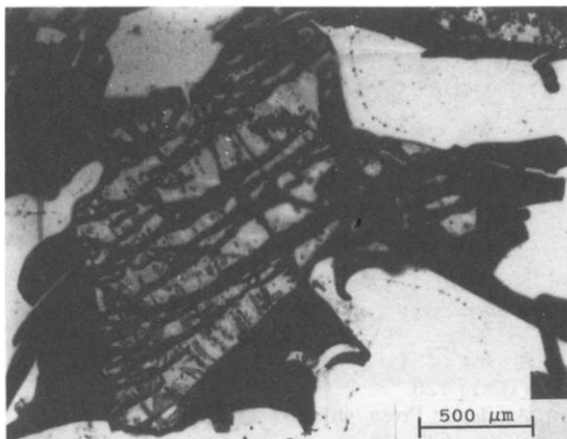


Fig. 5. Flakes of carbonized PP-HFP after extraction with  $\text{H}_2\text{O}$ .

via charge transfer into the bulk of the polymer [9, 11]. (This 'CH<sub>2</sub> blocking' is only effective for electrochemical carbonization; chemical carbonization of, for example, poly(vinylidene fluoride) by dehydrofluorination is possible [16].)

The inhomogeneous reductive carbonization of PP-HFP resembles the anisotropic reduction of oriented poly(tetrafluoroethylene): the PTFE foil, oriented by stretching, shows preferential carbonization along aligned fluorocarbon chains [17]. Carbonization of PP-HFP proceeds exclusively along regular fluorocarbon chains in the plasma-polymerized skeleton. Figure 4 demonstrates that some conductive paths leading through the PP-HFP film, and corresponding to these reducible chains, are gradually formed, as can be expected for the carbonization of an ideal perfluorinated chain (PTFE). Note that the first conductive channels are formed in a time which is more or less equal to the carbonization time of a PTFE layer of the same thickness. (According to eqn. (2) and with  $k_{\text{PTFE}} = 47.5 \text{ nm s}^{-1/2}$  [11], the 780-nm thick PTFE layer is completely carbonized in 270 s at 25 °C.) The carbonization rate is, however, not controlled by the electronic conductivity of the carbonaceous chain formed, but by its conductivity for Li<sup>+</sup> cations [11].

## Conclusions

Reaction of hexafluoropropene polymers with lithium amalgam allows chemically polymerized materials with a regular chain structure to be distinguished from plasma-polymerized materials which have a more complicated structure. Although the electrochemical carbonization of fluoropolymers results in complete defluorination of the precursor and subsequent crosslinking of the carbonaceous chains produced, the partly defluorinated and crosslinked precursor (PP-HFP) does not exhibit any enhanced ability towards carbonization.

This surprising fact may, however, be understood in terms of an electrochemical mechanism: the formation of an electrically conductive carbonaceous product from PP-HFP is confined to residues of the regular perfluorinated chains in the PP-HFP structure.

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