

Electrochemical stability and transformations of fluorinated poly(2,6-dimethyl-1,4-phenylene oxide)

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Abstract

Fluorination of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) leads to narrowing of its window of electrochemical stability in a cathodic range of potentials. It is found this is connected with appearance of both perfluorinated and incompletely fluorinated units in the polymer. The former units are liable to electrochemical reduction (at potentials < -2.0 V) followed by elimination of fluorine anions and the latter react with basic products (generated at potentials < -1.8 V) of electrochemical reduction of the background solution. In the both cases this results in appearance of conjugated multiple bonds in the fluorinated macromolecules. Quantities of these units in fluorinated PPO were determined with a help of direct and indirect electrochemical reductive degradation techniques. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Probably the most important reasons, stimulating investigations of electrochemically initiated transformations and degradation of polymers, are both the necessity to predict their stability in different electrochemical systems (e.g. membranes, coatings, polymer binders for electrodes, conducting polymers for corrosion protection, electrodes, polymer electrolytes, sensors or electrocatalysts, battery cases, etc.) and the possibility of their electrochemical modification. At present, it is shown for many hetero- and carbochain polymers that their electrochemical and subsequent chemical reactions lead to major changes of their properties and chemical composition, to cross-linking and/or even to chain breaking [1–4]. These destructive transformations running at a cathode were defined as electrochemical reductive degradation (ECRD) of polymers [1–3,6].

Specifically, for perfluorinated polymers in particular for PTFE or other polymers with perfluorinated units it was shown that they could be electrochemically reduced

at medium cathodic potentials (~ -1.5 to -2.0 V) with splitting off fluorine anions and formation of polyconjugated multiple bonds [2,3,5–7]. This way of polymer transformations as a result of their electrochemical reactions was defined earlier as direct ECRD [2].

Polymers with hydrogenfluoro-containing (incompletely fluorinated) units, such as poly(vinylidene fluoride) (PVDF) and poly(vinyl fluoride) (PVF), are not electrochemically active but can be transformed by the action of reactive basic products of electrochemical reduction of the background solution (tetraalkylammonium salt in aprotic solvent) at platinum or steel electrodes at potentials < -1.8 V [2,3]. Specifically, it was shown recently [8] that such products in dimethylformamide (DMF) solutions are both hydroxyl ions formed due to reduction of residual water and the intermediate charged complex DMF-OH^- . In acetonitrile solutions the intermediates of the solvent hydrolysis CH_2CN^- , $\text{CH}_3\text{-C(OH)=N}^-$ could serve as such products. As a result of such the action the polymers eliminate hydrogen fluoride and polyconjugated multiple bonds are formed. This way of electrochemically induced polymer transformations was defined earlier as indirect ECRD [2].

The known data suggested that use of the fluorination technique, which imparts to common polymers new

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specific properties [9,10], could result in changes of their stability in some electrochemical systems. Specifically, recently it was confirmed for fluorinated poly(vinyl trimethylsilane) that its surface layers after fluorination contained mainly perfluorinated units and some quantity of incompletely fluorinated units, which were transformed by mechanisms of both direct and indirect ECRD [11].

On the whole this means that electrochemical properties and stability of fluorinated polymer materials should be taken into account either before making a decision on their usage in electrochemical systems or at least when finding limitations for this case.

In this regard our work is devoted to investigation of electrochemical transformations and stability of new advanced polymer membrane materials which were formed by direct fluorination of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The precise functional composition of the fluorinated PPO (FPPO) has not been established yet but it has been found that due to deep fluorination it contains mainly perfluorinated units (perfluoro-2,6-dimethylcyclohexane) divided by oxygen atoms [9]. However, it can be supposed obviously that the FPPO films must have a distribution of fluorination degree resulting in the presence of incompletely fluorinated (hydrogenfluoro-containing) units (e.g. hexafluorocyclohexane with partly fluorinated methyl groups etc.) in the macromolecules at least in a transition zone between the perfluorinated and virgin layers. These suggest that FPPO may have electrochemical properties similar to those of fluorinated polymers.

2. Experimental

Virgin PPO and FPPO films (produced by the technique of direct fluorination at different duration [9,10], Table 1) were investigated.

As solvents for background solutions we used acetonitrile AN (MERCK, for chromatography) as received and dimethylformamide (DMF) (Ukraine) reagent grade purified by the technique of [12]. Tetrabutylammonium (TBA) perchlorate (0.05 M) was used as supporting electrolyte. It was synthesized by the reaction of TBAOH with HClO_4 with a subsequent recrystallization from ethyl acetate + hexane (1:1 v/v) mixture.

Previous tests showed that the virgin PPO was insoluble in both solvents but swelled up to ~4 wt.% for

30 min. However, most of the fluorinated layers of the samples dissolved fast in both solvents. Therefore, sensitivity of the virgin PPO to electrochemical reduction or oxidation was studied using in-house techniques for an investigation of electrochemical properties of solid phase polymers [1,13]. Electrochemical properties of the FPPO samples were investigated in solutions of their dissolved fluorinated parts.

Indirect ECRD of the polymers was investigated in the following way [11]. The background solution (working volume 8.5 ml) was reduced at the platinum electrode in a galvanostatic mode at current density 1.15 mA/cm² ensuring the potentials of formation of the reactive basic products (−1.8 to −2.4 V, see Section 1). Then the portions of the freshly reduced electrolyte were added to the solutions of the FPPO fluorinated parts with fixed weight concentrations placed into the cuvettes for UV–vis spectroscopy.

Cyclic voltammetry (CV) and preparative electrolysis of the polymers and background solutions were performed with a help of a potentiostat PI-50-1.1 (Byelorussia) under an argon atmosphere in a two compartment cell described in [1,13]. Potentials were measured vs aqueous saturated calomel electrode.

UV–vis spectroscopy (spectrophotometer M-40), IR spectroscopy in a transmission mode for KBr crystal covered with films of the FPPO soluble fluorinated part and of its dehydrofluorination products (spectrophotometer M-80) were used to monitor changes in the polymer.

3. Results and discussion

We found that the virgin PPO is electrochemically inactive and stable in a wide range of potentials (−2.8 V to 2.9 V), which is limited only by the cathodic and anodic breakdowns of the aprotic background solutions used. This means that the real electrochemical stability window of potentials of this polymer is even wider than this range. However, it differs from Beck and Pruss [14] data for oxidation of PPO (mixed with carbon) in other conditions — in concentrated strong water acids (8–18 M). For these conditions they showed that PPO was partly decomposed to 2,6-dimethylquinone by oxidation at 0.4 V (vs $\text{Hg}/\text{Hg}_2\text{SO}_4/1 \text{ M H}_2\text{SO}_4$ reference electrode).

The fluorination sharply changed the direct and indirect electrochemical reactivity of PPO. An investigation

Table 1
Characteristics of the bilaterally fluorinated film samples of PPO. Treatment with undiluted fluorine ($p_{\text{F}} = 58.8 \text{ Torr}$)

Sample number	Treatment duration (min)	Treatment temperature (K)	Thickness of fluorinated layer (μm)
FPPO1	33	290.5	0.89
FPPO2	62	290.5	1.22

of electrochemical properties of the dissolved fluorinated parts of the both samples in wide anodic and cathodic potential ranges has shown that they are able to accept electrons and cannot be oxidized. Specifically, their cyclic voltammograms obtained at a glass carbon electrode in DMF solutions contain two irreversible cathodic peaks ($E_p^I = -2.22$ V and $E_p^{II} = -2.73$ V) (Fig. 1). In AN solutions only the first peak, shifted a little to $E_p^I = -2.25$ V can be observed (Fig. 2). The second one is probably hidden by the cathodic breakdown of the AN background solution because of the lower working potential window of the AN used. But the two corresponding poorly resolved peaks at the anodic backward (Fig. 2) confirmed the presence of the both cathodic peaks. Such peaks are also observed in the DMF case. In all cases these anodic peaks were of less height than

corresponding cathodic ones and highly shifted into the anodic potential region, which demonstrates a considerable irreversibility of electrochemical reduction of FPPO. The irreversibility can probably be assigned to subsequent chemical stages of the electrochemical process. This agrees with the known electrochemical behaviour of perfluorinated polymers [2,3,6]. On the whole, the obtained CV data and the fact that electrochemical reduction of fluorinated polymers can be connected only with perfluorinated units [2,3] allow us to suppose that the peaks in the cyclic voltammograms correspond to such units appearing in PPO due to its fluorination.

Naturally, there is a difference in quantity of these units in the samples used. Indeed, we normalized the concentration of the dissolved fluorinated samples and found that the heights of the peaks are higher in the case

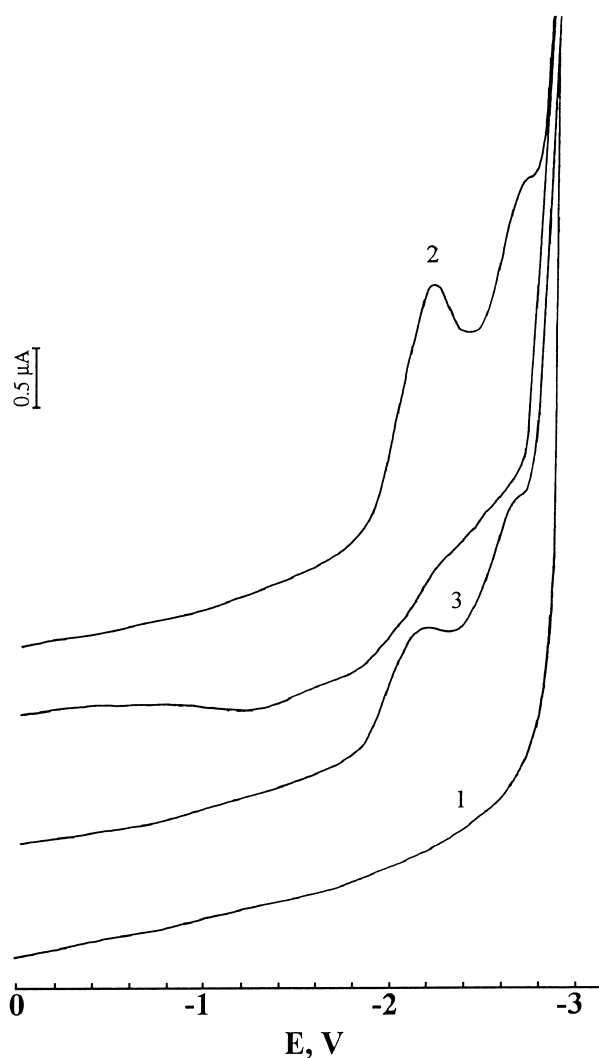


Fig. 1. Typical cyclic voltammograms of the dissolved FPPO part ($C = 2.1 \times 10^{-4}$ g/ml) in 0.05 M $N(C_4H_9)_4ClO_4$ in DMF: 1, background solution; 2, the dissolved FPPO part before electrolysis; 3, cathodic branch of the cyclic voltammogram of this solution after the first electrolysis at $i = 0.17$ mA/cm², $t_1 = 15$ min.

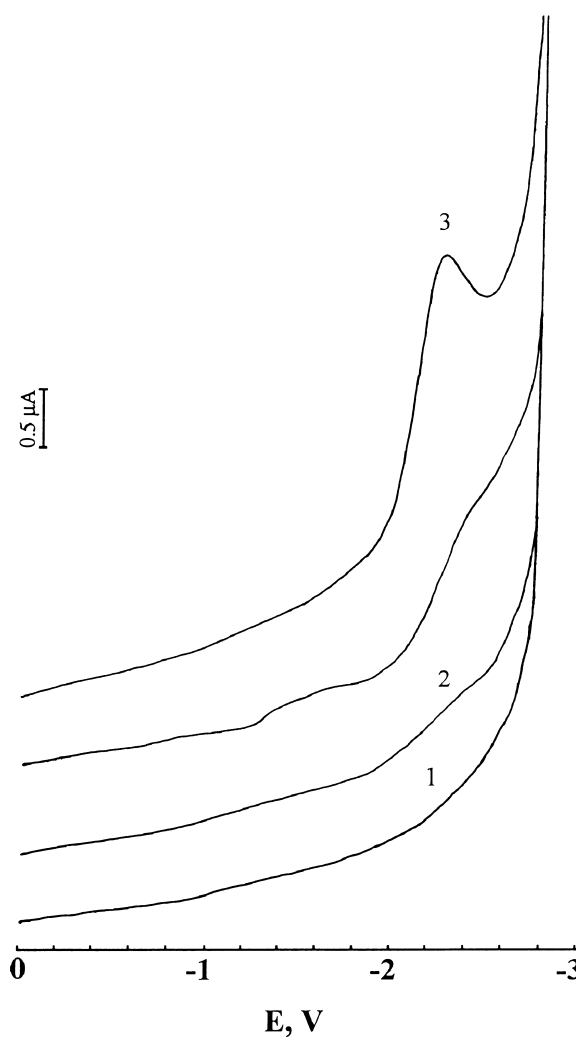


Fig. 2. Typical cyclic voltammograms of the dissolved FPPO part ($C = 5.5 \times 10^{-4}$ g/ml) in 0.05 M $N(C_4H_9)_4ClO_4$ in AN: 1, background solution; 2, the dissolved FPPO part before electrolysis; 3, cathodic branch of the cyclic voltammogram of this solution after the electrolysis at $i = 0.2$ mA/cm², $t = 50$ min.

of FPPO2. This testifies that this sample contains more perfluorinated units than FPPO1, which agrees with the treatment time of the samples (Table 1).

The presence of perfluorinated units in the samples was also confirmed by the preparative electrolysis of the FPPO solutions at the peak potentials at the glass carbon cathode. These resulted in brown colouring of the catholytes and in an appearance in their UV-Vis spectra of a wide, structureless absorption (Figs. 3 and 4, curve 1), which could obviously be assigned to conjugated double bonds originating from the electrochemically

reduced dissolved macromolecules. In compliance with the known behaviour of fluorinated polymers, these bonds are formed due to electrochemical reduction and splitting of C–F bonds in the perfluorinated units of the polymers [2,3].

It should be noticed that preparative electrolysis of the FPPO samples in a galvanostatic mode ensuring potentials close to the beginning of the first peak (~ -2.0 to -2.2 V) led to a decrease of this peak and then to its disappearing. But the height of the second peak was practically constant (in the DMF solutions,

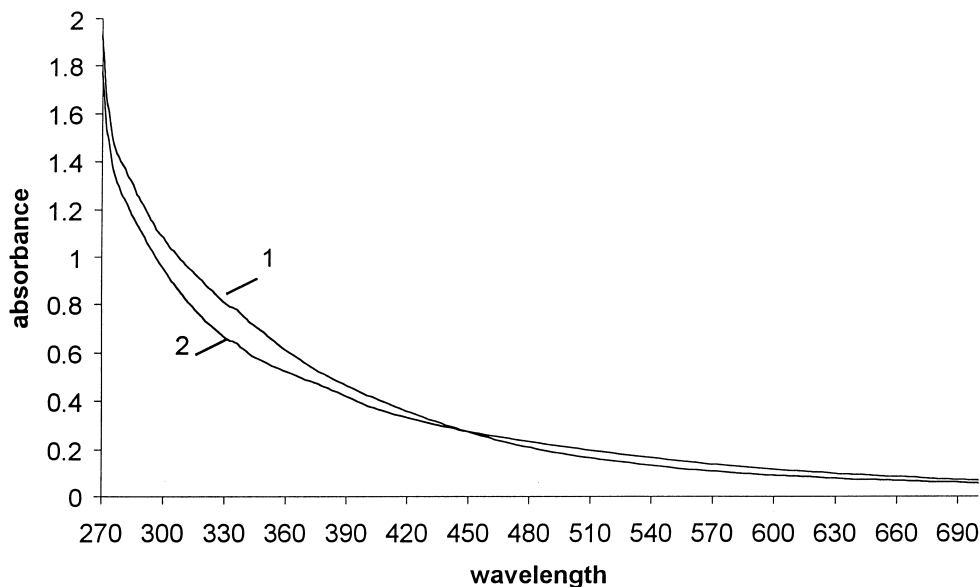


Fig. 3. Typical UV-vis spectra of the solutions of the dissolved FPPO part after direct (1) and indirect (2) ECRD in DMF. Concentration of the dissolved FPPO part = 3.7×10^{-4} g/ml (1) and 7×10^{-5} g/ml (2); of $\text{Nu}^- = 4.5 \times 10^{-3}$ mol/l.

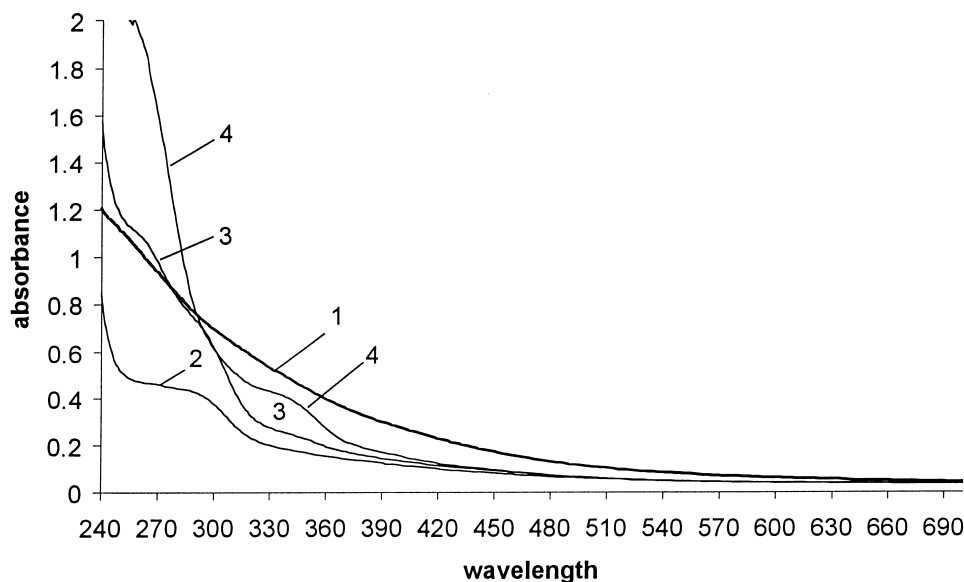


Fig. 4. Typical UV-vis spectra of the solutions of the dissolved FPPO part after direct (1) and indirect (2–4) ECRD in AN: 2, the reaction time $t = 1$ min; 3, $t = 13$ min; 4, $t = 50$ min (final). Concentration of the dissolved fluorinated PPO = 6.5×10^{-4} g/ml (1) and 5×10^{-5} g/ml (2–4); of $\text{Nu}^- = 4.5 \times 10^{-3}$ mol/l.

Fig. 1). This suggests that both peaks correspond to different kinds of electrochemically active groups. Specifically, the first peak, if judged by its potentials that are very close to those of perfluorinated polymers [2,3,6], is responsible for the reduction of the units similar to $-\text{CF}_2-\text{CF}_2-$. However, the second one, located at more cathodic potentials, can be probably assigned to units with less electron affinity. Taking into account the structure of the virgin PPO and the fact that the fluorination technique leads to saturation of aromatic rings and even to breakdown of the chains [9,10], one can suppose that probably the groups like $-\text{CF}_2-\text{CF}_2\text{O}-$ can serve as such the units.

Since the CV method turned out selective to the perfluorinated units [2,3] we tried to estimate their quantity in the fractions of the FPPO samples dissolved in the AN background solution. To this end short electrolyses of the FPPO solutions were performed in galvanostatic mode at the first peak potentials. Then the changes of the first peak height, which should be proportional to changes of concentration of the electroactive species (in our case — perfluorinated units) in the solution [15], were set proportional to a quantity of electricity (in moles) passed through the solution. Based on the known fact that splitting of one C–Halogen bond in vicinal halogen-containing compounds consumes one electron [16], we found the number of moles of C–F bonds corresponding to an accepted quantity of electrons. It was determined that the FPPO1 fraction dissolved in AN contained 5.6×10^{-6} mol of these fragments per mg. For the FPPO2 sample this value was higher -9.7×10^{-6} mol/mg.

Based on the previous experience [2,3], we may postulate that isolated C–F bonds can be electrochemically reduced only if they are in perfluorinated units like $-\text{CF}_2-\text{CF}_2-$ (in which at least two such the bonds can be split to form one double bond). As a consequence, the quantity of the units in the dissolved parts of the FPPO samples will be 2.8×10^{-6} mol/mg and 4.85×10^{-6} mol/mg correspondingly. It is very likely these values are averaged because they are determined for the solutions formed due to dissolution of the fluorinated layers containing macromolecules with inhomogeneous degree of fluorination.

The FPPO samples are also able to participate in indirect ECRD reactions. Thus, addition of previously electrochemically reduced AN or DMF background solutions to cuvettes with solutions of the fluorinated parts of the samples resulted in brown colouring of the reaction solutions. The intensity of colouring of both solutions increased during the reaction. In the UV-Vis spectra of these solutions (Figs. 3 and 4) we observed an absorption assigned in accord with [2,3] to conjugated double bonds, which appeared in the dehydrofluorinated (degraded) macromolecules.

This agrees also with IR spectra of the untreated and treated FPPO dissolved parts, which were separated

from the solution. Specifically, the IR spectrum of the untreated one showed weak, poorly resolved bands that could be assigned to C–H vibrations of CH_3 (2960 cm^{-1}), CH_2 (2915 cm^{-1} and 2840 cm^{-1}) groups and strong overlapping diffuse bands ($900\text{--}1400 \text{ cm}^{-1}$) attributed to C–F vibrations [17]. Dehydrofluorination of FPPO in the conditions under investigation (in the AN medium) resulted in a decrease of C–F band intensity and in an appearance of a strong wide poor resolved absorption band with maximum at 1650 cm^{-1} and shoulder at 1600 cm^{-1} which probably can be assigned to conjugated double bonds [17].

It should be noted that judging by the shape of the UV-Vis spectra of the indirect ECRD products (Figs. 3 and 4) there is a difference between those produced in the DMF and AN media. These distinctions can be caused probably by a different nature of active species generated in both cases (see Section 1).

On the whole, comparing such transformations to known data for polymers with hydrogenfluorine-containing units {poly(vinylidene fluoride), poly(vinyl fluoride), etc.} [2,3], one can suppose that we observed dehydrofluorination of the incompletely fluorinated units in the dissolved part of the FPPO under the action of the basic products of electrochemical reduction of the background solution. In fact, the technique of indirect ECRD confirmed the above supposition that the FPPO films have a gradient of fluorination degree (see Section 1) resulting in a presence of such units at least in the dissolved part.

The solubility of the fluorinated parts of the samples under investigation and the selectivity of the indirect ECRD reactions, affecting only incompletely fluorinated units [2,3,18], allowed us to perform some quantitative measurements. Specifically, we used the integral intensity of the absorption at the UV-Vis spectra of the dehydrofluorinated soluble parts of the samples to compare with the quantity of electrochemically generated reactive basic products (Nu^-). The latter was calculated by Faraday's law. This approach gave the possibility to investigate the kinetics of the indirect dehydrofluorination reaction in the AN background solution. It was found that the reaction in the solutions had the first order both in the Nu^- and in the soluble fluorinated polymers. As could be expected, the rate constants for both the fluorinated samples were close: for the FPPO1 $-72.5 \text{ l mol}^{-1} \text{ min}^{-1}$; for the FPPO2 $-62.2 \text{ l mol}^{-1} \text{ min}^{-1}$.

Unfortunately, at present we could not determine these values for the DMF solutions because in these conditions the reaction is too fast to be measured. Probably, this difference in the kinetics in DMF and AN media is connected with different nature of the reactive basic products (Nu^-) of electrochemical reduction of the background solutions (see Section 1 and [8]).

Basing on the kinetic data for the dehydrofluorination reaction in the AN solutions, we found that FPPO1 contains 1×10^{-5} mol/mg of the incompletely fluorinated units and FPPO2 contains about half as many -4.6×10^{-6} mol/mg.

Comparing the calculated quantities of perfluorinated and the incompletely fluorinated units in the samples under investigation we can say that, practically, FPPO2 is more extensively (about twice) fluorinated than FPPO1. This matches with the fact that FPPO2 is produced with about twice longer fluorination treatment of parent PPO than FPPO1 (Table 1). On the whole, the data obtained testify that the techniques of direct and indirect ECRD not only allow distinguishing of perfluorinated and incompletely fluorinated units but also give information on the quantitative composition of a fluorinated polymer.

It should be noted that even if the formation of conjugated double bonds in FPPO is well confirmed by the spectral data for both the direct and indirect ECRD cases, it is still unclear why they are able to absorb in the visible region. It is known that this demands the presence of enough long polyene sequence (not less than 5) or other chromophore group [19]. In its turn, formation of such sequences is likely only in the case of a long carbon chains (at least of 10 carbon atoms), which are absent in the parent PPO. This suggests an appearance of long carbon sequences in PPO after its fluorination. It is possible probably due to both cross-linking reactions (e.g. of methyl substituents) and breaks of macromolecular chains in places of C–O bonds followed by recombination of macroradicals formed. However, cross-linking can lead to insolubility of the fluorinated layer. Therefore, it can be dissolved only in the case of a small quantity of cross-links. Another way of appearance of chromophore groups could be defluorination (the direct ECRD case) or dehydrofluorination (the indirect ECRD case) of end groups, with formation of quinoid-like structures.

However, the data obtained are not enough to make a precise conclusion on real structures, which appear in FPPO due to its electrochemically initiated transformations. This will be the topic of separate investigations.

4. Conclusion

Virgin PPO has a wide potential window of electrochemical stability (-2.8 V to 2.9 V, vs saturated calomel electrode) in aprotic media. Its fluorination leads to narrowing of this window in the cathodic range of potentials to ~ -1.8 V to 2.9 V. It is connected with ability both of the FPPO perfluorinated units to participate in direct electrochemical reactions with elimination of fluorine anions (the direct ECRD process) and of the FPPO incompletely fluorinated units to react with basic products of electrochemical reduction of the

background solution (the indirect ECRD process). In both cases this results in appearance of conjugated multiple bonds in the fluorinated macromolecules.

Selectivity of the perfluorinated and incompletely fluorinated units in reactions of the direct and indirect transformations (ECRD) correspondingly allowed determining the quantity of these units in the fluorinated samples and, on this basis, judging on degree of fluorination of PPO.

In fact the results obtained testified that the simple electrochemical techniques not only can be used to determine and to distinguish these units in fluorinated polymers but also are an additional way to study a composition of such polymers.

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