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Reactions and stability of fluorinated poly(vinyl trimethylsilane) in electrochemical systems

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Abstract

Fluorinated poly(vinyl trimethylsilane) (FPVTMS) unlike virgin PVTMS is able to participate in electrochemical reactions and undergoes direct and indirect electrochemical reductive degradation. Specifically, its perfluorinated units are reduced irreversibly at a glass carbon electrode in a 0.05-M $(C_4H_9)_4ClO_4$ solution in dimethylformamide with subsequent splitting of C–F bonds and formation of conjugated double bonds in macromolecules at the polymer surface. On the other hand, the incompletely fluorinated units at the FPVTMS surface interact with the previously electrochemically reduced background solution to be dehydrofluorinated. This is accompanied by the formation of conjugated double bonds and dissolution of the dehydrofluorinated layer also. The data obtained allowed distinguishing the incompletely fluorinated units from the perfluorinated ones in the fluorinated layer of FPVTMS. Moreover, the quantity of the incompletely fluorinated units in FPVTMS can be determined. It was found that the strengthening of fluorination conditions led to an enhancement of the electrochemically induced FPVTMS transformations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorinated poly(vinyl trimethylsilane); Electrochemical properties; Degradation

1. Introduction

For the last few decades we have been observing an expansion of polymer applications in different electrochemical systems (e.g. polymer insulating and paint coatings, conducting polymers for corrosion protection, electrodes, polymer binders for electrodes in batteries, polymer electrolytes, sensors or electrocatalysts, membranes, battery cases, etc.). Naturally, this has resulted in the appearance of new polymer requirements, one of the most important of which is the electrochemical stability of polymer materials under service conditions. Indeed, irreversible electrochemical reactions of a polymer or its interaction with other electrochemically transformed components of the system lead to its degradation and even to a failure much earlier than expected by traditional evaluations of polymer stability [1,2].

From our point of view, the electrochemical stability of polymer materials is so important that it should be taken into account either before making a decision on the usage of one or the other polymer in electrochemical systems or at least when finding limitations for this case. On this basis, the main objective of our work was an investigation of the electrochemical stability of new advanced polymer membrane materials, which were formed by fluorination of poly(vinyl trimethylsilane) (PVTMS). These materials consisted of two fluorinated layers divided by one of virgin PVTMS [3]. The precise functional composition of the layers has not been established yet but it has been found that their surface contained mainly perfluorinated units like those of PTFE [3]. On the other hand, it can obviously be supposed that a gradation in the degree of fluorination of PVTMS should exist in the fluorinated layers resulting in the presence of incompletely fluorinated (hydrogenfluorocontaining) units in the macromolecules at least in a transition zone between the perfluorinated and virgin layers. The availability of both kinds of unit suggests that the fluorinated PVTMS (FPVTMS) can have electrochemical properties close to those of fluorinated polyolefins. Specifically,

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Table 1
Conditions of the PVTMS direct fluorination to form the FPVTMS polymers

Sample number	Composition of fluorinating mixture	Fluorine partial pressure (Torr)	Fluorination duration (min)	Treatment temperature (K)
FPVTMS1	33.3% F_2 + 66.7% He	58.8	21	294.5
FPVTMS2	33.3% F_2 + 66.7% He	58.8	80	294.5
FPVTMS3	2% F_2 + 98% He	4.2	1440	294.5
FPVTMS4	33.3% F_2 + 66.7% He	58.8	80	291.5
FPVTMS5	10% F_2 + 90% He	58.8	40	293

according to known data [4–8], perfluorinated units of FPVTMS like those of perfluorinated polymers (e.g. of PTFE) could be electrochemically reduced at cathodic potentials that are not very low (~ -1.5 to -2.0 V) with splitting off of fluorine anions and formation of polyconjugated multiple bonds. This process was defined earlier as direct electrochemical reductive degradation (direct ECRD) [1,9].

Incompletely fluorinated units of FPVTMS can probably be transformed in a similar manner to VDF and VF hydrogenfluoro-containing units of PVDF and PVF, which are not electrochemically active but can react with basic products of the electrochemical reduction of a background solution at a platinum cathode. This leads to elimination of hydrogen fluoride and to formation of polyconjugated multiple bonds in their macromolecules [1,10] much in the same way as electrochemically induced polymer transformations was defined earlier as indirect ECRD [1]. This deep mechanistic difference between both types of electrochemically induced polymer transformation is probably the basis for solving the inverse problem — distinguishing incompletely fluorinated units from perfluorinated ones in fluorinated polymers.

2. Experimental

2.1. Reagents

We investigated six samples: the first one was the virgin PVTMS (thickness 15 μm) and the other five were FPVTMS samples produced from the virgin PVTMS by the technique of direct fluorination [3,11,12] under different conditions (Table 1). As solvents, we used acetonitrile (AN) (MERCK, for chromatography) and dimethylformamide (DMF) (Ukraine) reagent grade purified by the technique described elsewhere [13]. To prepare background solutions with these solvents, we used 0.05-M $(C_4H_9)_4ClO_4$, which was synthesized by the reaction of TBAOH with $HClO_4$ followed by recrystallization from the ethyl acetate + hexane (1:1 v/v) mixture as a supporting electrolyte tetrabutylammonium perchlorate. Residual water content of the background solutions was 0.02 wt% (by a Fischer titration method).

2.2. Direct ECRD

Previous tests have shown that the virgin PVTMS and all the FPVTMS samples were insoluble in both solvents but swelled up to only 2–4 wt% for 30 min. As a consequence, their ability to undergo electrochemical reduction or oxidation was studied in a solid phase state. To realize this, the polymer films were either perforated and pressed to a working glass carbon electrode with the assistance of a cotton thread before the experiments (Fig. 1) or were pressed to a platinum mesh electrode in accordance with domestic techniques published elsewhere [14,15]. These allowed creation of a three-phase interface (TI) “polymer–electrode–solution” where electrochemical reactions of solid phase polymers could be realized (Fig. 2) [1,13,14].

Because of difficulties in determination of a size of the TI [1] this electrode set (Fig. 1) was used only for the determination of potentials of reduction of the polymers under investigation and for the preparative electrolysis to qualitatively transform the polymer surface.

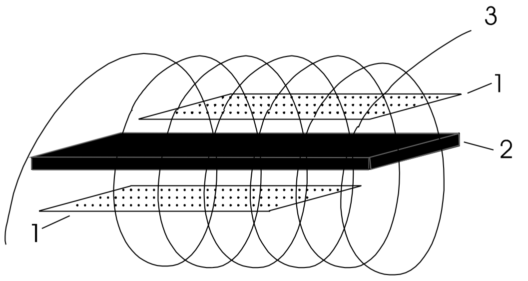

Fig. 1. A scheme of the electrode set for the cyclic voltammetry measurements: (1) perforated FPVTMS films; (2) a glass carbon cathode; and (3) cotton thread for the film fixation.

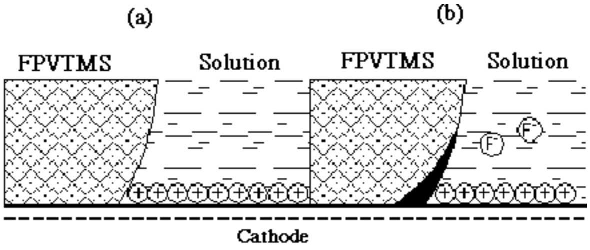

Fig. 2. A scheme for the three-phase interface “FPVTMS–cathode–solution”: (a) the starting condition; (b) after electrochemical reduction of the polymer.

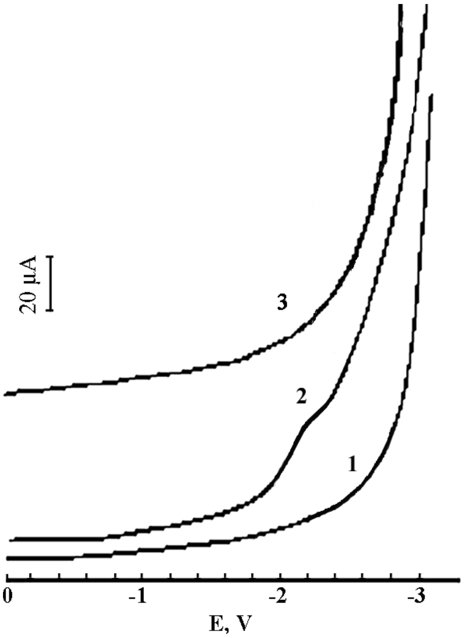

Fig. 3. Cathodic branches of FPVTMS typical cyclic voltammograms obtained at a glass carbon electrode: (1) the background solution (0.05-M $(C_4H_9)_4ClO_4$ in DMF); (2) FPVTMS; and (3) FPVTMS after the preparative electrolysis.

2.3. Indirect ECRD

Indirect ECRD of the polymers was investigated in the following way. Through the cell with working volume of 8.5 ml of the cathodic space, electricity was passed at current density 1.15 mA/cm^2 (ensuring potentials of $-1,8$ to -2.4 V) to create in the catholyte the necessary concentration of active basic products of electrochemical reduction of the background solution. In this case, we used a platinum cathode with a working area of 7.8 cm^2. Then the portions of the freshly reduced catholyte were added to the polymer films (with fixed area 0.5×2 cm^2) placed inside cuvettes (thickness 1 cm) for conducting UV–Vis spectroscopy measurements.

The role of platinum as a cathode material for an intensive indirect ECRD process should be emphasized here. This is connected with the fact that the cathodic limit in aprotic medium at platinum having low hydrogen overpotential is at $\backsim -1.8$ V because of reduction of residual water to hydroxyl anions. The last and/or charged intermediates of the solvent hydrolysis are the active agents of indirect ECRD [16]. In turn, the glass carbon has the cathodic limit at $\backsim -2.8$ V for the background solutions used and correspondingly allows excluding the effect of residual water reduction on direct polymer electrochemical reactions up to this potential.

For IR investigations, the soluble products of these FPVTMS transformations were separated from the reaction solutions. To this end, the solvent was removed by vacuum distillation, then dry residues were divided on a chromatographic column filled with silica gel 30–60 mesh (Aldrich). This allowed the separation of the products from the background electrolyte.

2.4. Instruments

Cyclic voltammetry (CV) and preparative electrolysis of the polymers and background solutions were performed with the help of the potentiostat PI-50-1.1 (Byelorussia) under argon atmosphere in a two-compartment cell with electrode spaces separated by a glass filter. Potentials were measured versus an aqueous saturated calomel electrode separated from the working solution with an electrolytic bridge.

UV–Vis spectroscopy (spectrophotometer M-40), IR-spectroscopy in internal reflection mode for the films and in a transmission mode for pellets of KBr with FPVTMS transformation products (BRUKER IFS66 spectrometer and spectrophotometer UR-20) and gravimetry were used to control changes in the polymers and solutions.

3. Results and discussion

3.1. Electrochemical reactions and direct ECRD of the perfluorinated units

It appears that the virgin PVTMS is unable to accept or to dispose of electrons within the wide range of potentials -2.8 to $+2.9$ V (in AN or DMF media), which agrees with literature data for low molecular silanes R_4Si [17]. However, the fluorination treatment dramatically changed the electrochemical activity of this polymer at cathodic potentials. Specifically, all the fluorinated samples were able to electrochemically reduce at a glass carbon cathode, but not in a simple way. Thus, we found that the ability of FPVTMS to electrochemically reduce depends strongly on the aprotic solvent nature. When AN was used as a solvent, all the samples were unable to accept electrons in the working potential range up to the cathodic limit at -2.8 V. Moreover, it turned out that in the AN medium, even electrochemically active PTFE begins to reduce at the potential -2.4 V, although this value was equal to -2.0 V in the case of DMF [7]. It seems that the solvents strongly affect the condition along the TI “FPVTMS–cathode–solution” (Fig. 2), where the solid polymer electrochemical reactions occur [1,18]. In particular, such a shift could be assigned to the different surface activities of both solvents. This suggestion agreed with the data of electrochemical reduction of PTFE in the DMF solutions of various tetraalkylammonium salts having diverse surface activity [1,19] and necessitated the study of electrochemical responses of FPVTMS in DMF medium also.

This resulted in the fact that all the FPVTMS samples could display their ability to undergo electrochemical reduction in the DMF background solution. Cathodic branches of their cyclic voltammograms exhibited a single distinct

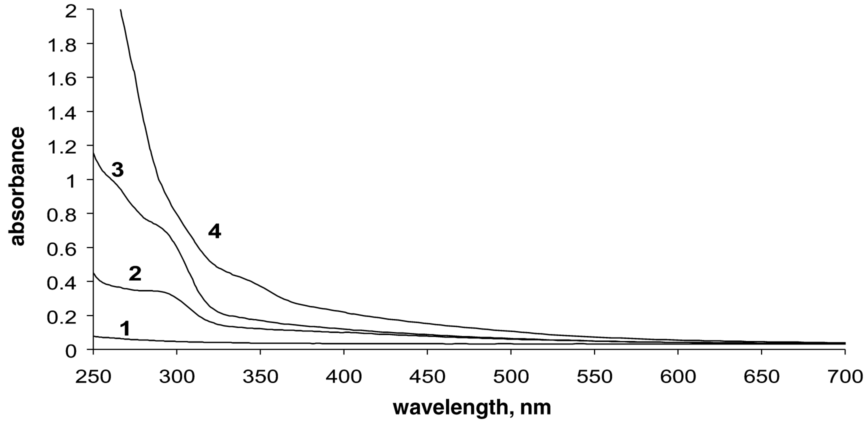

Fig. 4. Typical UV–Vis spectra of 0.05-M $(C_4H_9)_4ClO_4$ in AN (1) and of the solution of the dissolved dehydrofluorinated part of the FPVTMS film scanned during its indirect ECRD in this background solution at time of electrolysis for 1 (2), 15 (3) and 35 min (4). Concentration of the reactive basic products of electrochemical reduction of the background solution calculated by Faraday's law was equal to 4.5×10^{-3} mol/l.

irreversible wave with a half-wave potential $E_{1/2} = -2.1$ V (Fig. 3). This indicated the appearance of electrochemically active groups in PVTMS after its fluorination. Taking into account the above-mentioned fact, that electrochemical activity of fluorinated polymers exists only because of perfluorinated units, one may suppose that the wave at the cyclic voltammograms corresponds to the electrochemical reduction of the units in the FPVTMS samples. The presence of perfluorinated units matches also with earlier IR data [11,12] for the completely fluorinated PVTMS.

The results of electrochemical reduction at a glass carbon of all the FPVTMS samples in the DMF background solution at the wave potentials confirmed this supposition. Thus, electrolysis of the polymer films at -2.2 V for 30 min resulted in brown coloring of their surface along the TI (Fig. 2). In the UV–Vis spectra of the treated films, a structureless absorption appeared in the visible region, which was characteristic of conjugated double bonds [10]. In accordance with the PTFE case [1,5–7], this can be explained probably through electrochemical reduction and subsequent splitting of C–F bonds in perfluorinated units of FPVTMS. After the electrolysis, the wave in the voltammograms of all the reduced FPVTMS samples disappeared (Fig. 3), which testified to the fact that defluorinated units in the degraded samples did not have electrochemical activity.

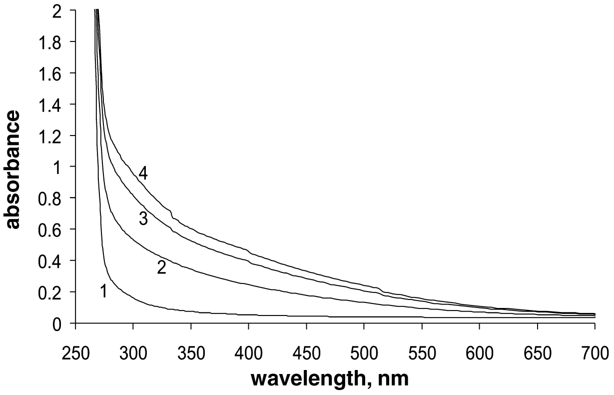

Fig. 5. Typical UV–Vis spectra of 0.05-M $(C_4H_9)_4ClO_4$ in DMF (1) and of the solution of the dissolved dehydrofluorinated part of the FPVTMS film scanned during its indirect ECRD in this background solution at time of electrolysis for 1 (2), 15 (3) and 35 min (4). Concentration of the reactive basic products of electrochemical reduction of the background solution calculated by Faraday's law was equal to 4.5×10^{-3} mol/l.

It should be noticed that at this time we could not evaluate the quantity of perfluorinated units in the samples from electrochemical data to be compared because of an equivocation of sizes of the polymer interface with the cathode. However, from visual and spectral observations of the reduced sample surfaces, we can say qualitatively that their transformation degree increased with increasing strength of fluorinating treatment.

3.2. Indirect ECRD of the incompletely fluorinated units

The technique of indirect ECRD [1,10] was used to verify the suggestion that the fluorinated layers should have a gradient of fluorination degree of PVTMS (see Section 1) resulting in the presence of some quantity of hydrogen-fluoro-containing units. Specifically, when we added the previously electrochemically reduced background solution (independently on the solvent nature) to all the FPVTMS films (placed inside UV–Vis cuvettes), both the films and the reaction solutions became brown. The intensity of the solution coloring increased during the reaction in both DMF and AN media by visual and spectral observations. At the end of the reaction, almost only PVTMS parts of the films were left undissolved (by FTIR data). Their surfaces were light brown tinted only but the reaction solutions became dark brown. This testified to a solubility of the major part of the FPVTMS transformed fluorinated layer (unlike the untreated FPVTMS) in the reaction medium. The virgin PVTMS was quite resistive in these conditions as in the case of direct ECRD (see above).

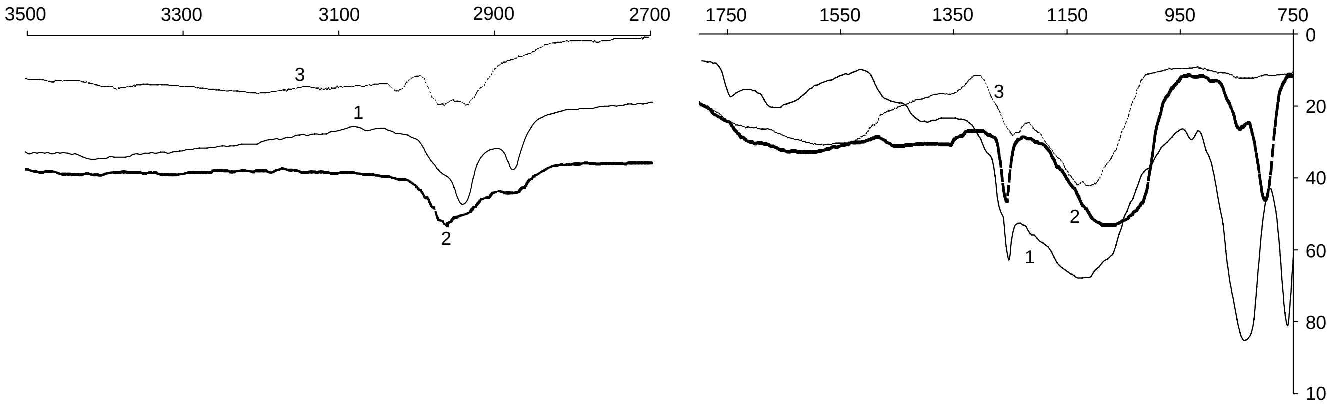

Fig. 6. Typical IR-spectra of FPVTMS (1) and products from its indirect ECRD separated from the AN medium (2) and the DMF one (3).

Such transformations proved the presence of the incompletely fluorinated units in FPVTMS and suggested their dehydrofluorination with a formation of conjugated multiple bonds in the surface layers of FPVTMS under conditions of indirect ECRD, as was shown earlier for fluorinated polyolefins [1,10]. Indeed, in the UV–Vis spectra of the dark brown solutions (in both the solvents) (Figs. 4 and 5) an absorption is observed, seemingly corresponding to the presence of conjugated multiple bonds [1,10] in the dissolved products of the FPVTMS transformations. This also agrees with IR-spectroscopy data. Specifically, in the IR-spectra of these products (Fig. 6, curves 2 and 3) a wide absorption band (differing in shape and intensity for the DMF and AN medium) emerged in the range of 1600 cm^{-1}, which is assigned to conjugated double bond vibrations in accordance with Refs. [1,20]. Moreover, dehydrofluorination of FPVTMS is also corroborated by a decrease of intensities of C–H and C–F (950–1200 cm^{-1}) vibrations in both media.

It should be emphasized that the spectral data not only confirmed dehydrofluorination of FPVTMS under the indirect ECRD conditions but also displayed a noticeable difference in the intensity of its transformations depending on the medium used. Specifically, even from the UV range of the UV–Vis spectra (Figs. 4 and 5) one can see a structural difference between the products produced in the AN and DMF media. Furthermore, judging by IR-spectroscopy data (Fig. 6) in the AN medium FPVTMS undergo comparatively small transformations: a shallow dehydrofluorination (see above) is observed; and besides, it conserves $Si–CH_3$ groups (bands at 843 and 1256 cm^{-1} [20]). However, a new band emerges at 799 cm^{-1} and the band at 759 cm^{-1} (Si–C stretching or methyl rocking vibrations [20]) disappears. At the same time, the possibility that the band at 799 cm^{-1} corresponds to the 759 cm^{-1} band shifted to a higher-frequency region owing to a change of surroundings cannot be excluded.

It should be noticed that the band at 843 cm^{-1} could correspond to bands both of $Si–CH_3$ and of Si–OH vibrations [20], i.e. it could be a superposition of these bands. Therefore, its decrease to the level observed might be explained through a removal of silanol groups in the course of the indirect ECRD reactions. On the other hand, its decrease resulting from splitting of Si–C bonds in the AN medium is less plausible because the characteristic band of $Si–CH_3$ vibrations at 1256 cm^{-1} is left practically unchanged.

The IR-spectrum of the transformation products of FPVTMS in the DMF medium testified to its much deeper and different changes in comparison with those of the AN medium (Fig. 6). Thus, the bands of C–F vibrations became less intense and of different shape than those in the AN medium. The bands of Si–C vibrations practically disappeared. The bands of C–H stretching vibrations decreased [20] and at 3030 cm^{-1} a new band appeared. The last could probably be assigned to =CH absorption [20]. Furthermore, the strong wide band resulting from conjugated double bonds emerged at the spectrum in the range of 1600 cm^{-1} (Fig. 6, curve 3).

The spectral data suggested that the deep distinctions observed between the products formed in the AN and DMF media could be caused by different active species generated in both the electrochemically reduced background solutions. Indeed, it was proposed recently that in the AN medium the charged intermediates CH_2CN^-, $CH_3–C(OH)=N^-$ could act as such species [16]. In the DMF case the species were found to be hydroxyl anions OH^- or their labile complex with DMF molecules [16], which were able to dehydrohalogenate polyvinylchloride or poly(vinylidene fluoride). Judging by the IR-spectroscopy data, the species in the DMF medium are more active, demonstrated by the ability to split the sufficiently strong Si–C bonds (activated in comparison with virgin PVTMS) in FPVTMS. This suggestion agrees with the disappearance of the bands of Si–C vibrations (759, 843, 1256 cm^{-1}) in the IR-spectrum of the products (Fig. 6). Instead, in the place of Si bonds in the lattice, new C–H bonds were formed. Specifically, this corresponds with the appearance of =CH absorption at the IR-spectrum.

As in the above-mentioned direct ECRD case, we

Table 2
The spectra integral intensities and the weight losses during indirect ECRD of fluorinated PVTMS in AN solution. Conditions of the galvanostatic electrolysis of the background solution at the Pt cathode: $Q = 4.8$ C ($E = -1.8$ to -2.4 V), integral limits: $\lambda_1 = 333$ nm, $\lambda_2 = 828$ nm

FPVTMS	**I**	Weight loss (wt%)
FPVTMS1	35.9	5.9
FPVTMS3	59.3	6.1
FPVTMS2(4)	86.5	15
FPVTMS5	18	2.2

observed that the transformation degree of the FPVTMS samples under indirect ECRD differed according to the conditions of the fluorination of PVTMS. Specifically, this was confirmed by calculation of integral intensities (**I**) of the optical spectra of the cuvettes containing both the transformed films and brown solutions as well as by the weight losses of the FPVTMS films with the fixed areas handled by the reduced background AN solution (Table 2).

As one can see from Tables 1 and 2 (comparing samples FPVTMS1 and FPVTMS2(4)), the 3.8-fold increase of the fluorination duration, but at the same concentration of fluorine (33.3%) in the fluorinating mixture, resulted in more than twice (2.54) the augmentation of the quantity of the transformed FPVTMS dissolved in the solution. At first glance, the result is excessive and this augmentation should be less. Specifically, this follows from the known fact [11] that the fluorination of PVTMS is diffusion-limited. As a consequence, both the thickness of the fluorinated layer and the quantity of the transformed FPVTMS dissolved should be multiplied in this case by the square root of the fluorination duration increase (of 3.8), i.e. only by the value of 1.95. However, this contradiction can probably be resolved if we accept that the specific gravity of the fluorinated polymers is higher than that of virgin PVTMS [11]. As a consequence, the more fluorinated sample gives the excessive result.

On the other hand, the increase of the fluorination duration led also to the augmentation of **I** value, which corresponded to the amount of dehydrofluorinated units in the dissolved products. This augmentation was almost proportional to the change of the weight losses (compare FPVTMS1 and FPVTMS2(4) samples) (Table 2). Taking into account these and the above-mentioned fact that a fluorinated layer of FPVTMS is dissolved because of dehydrofluorination of its incompletely fluorinated units, it is possible to suppose that the weight loss is proportional to their amount in these samples also.

It should be emphasized that under milder conditions (2% concentration of fluorine in the fluorinating mixture) but at very long fluorination, the FPVTMS3 sample was obtained which, after indirect ECRD, gave the ratio of **I** to the weight loss as differing from that of other samples (Table 2). Specifically, if these values are compared with those of FPVTMS1 having a similar weight loss, one can see that the dissolved products of FPVTMS3 transformations contain more dehydrofluorinated units. Obviously, this difference is connected with the greater number of incompletely fluorinated units in the fluorinated layer of FPVTMS3 in comparison with FPVTMS1.

On the whole, the interrelation observed allows evaluating this amount for any sample of FPVTMS. Specifically, when comparing the **I** value with the weight loss and consumed electricity, we determined the quantity of incompletely fluorinated units on the example of FPVTMS5. This was equal to 4.4×10^{-6} mol/mg.

4. Conclusions

The data obtained prove that the virgin PVTMS is electrochemically inactive and stable in the wide working potential window (-2.8 to $+2.9$ V versus saturated calomel electrode) in aprotic media. The fluorination of PVTMS dramatically changes its electrochemical activity and leads to narrowing this window to the range -1.8 to $+2.9$ V. Specifically, the fluorinated layer of FPVTMS formed participates both in direct electrochemical reactions with elimination of fluorine anions, which are characteristic for perfluorinated units in the macromolecules, and in indirect electrochemical ones with elimination of HF through the reaction with products of electrochemical reduction of the background solution. The latter is characteristic for the hydrogenfluoro-containing units in the macromolecules. The intensity of the indirect transformations increases with strengthening of the fluorination conditions.

On the whole, the ability of FPVTMS to undergo direct and indirect ECRD means that its fluorinated layer contains both perfluorinated and incompletely fluorinated units. However, the possibility that in the very surface of the layer there are only perfluorinated units and in the sublayer there is a gradation in the degree of fluorination cannot be excluded. As a consequence, in the indirect case the reaction medium penetrates through the perfluorinated surface and dehydrofluorinates the sublayers.

Acknowledgements

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