

Direct fluorination of polystyrene films

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Abstract

Kinetics of fluorinated layer formation in polystyrene (PS) were investigated for various fluorine and oxygen partial pressures and temperatures. The PS direct fluorination process was shown to be diffusion-limited, i.e., the rate of the process is limited by fluorine penetration through the fluorinated layer. Dependence of fluorine permeability value and concentration of carbonyl groups in treated polymer on F_2 - O_2 mixture composition were investigated. The inhibiting action of oxygen is due to C=O groups formation. A scheme of elementary stages of the direct fluorination is proposed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Fluorination; Polystyrene films; Fluorine permeability; Oxygen inhibition

1. Introduction

Direct fluorination is a well known method for the surface modification of polymers [1,2]. This paper continues our investigations on the direct fluorination of polymers. Earlier we described the kinetic interference spectroscopy method to monitor the thickness of the fluorinated polymer layer during the direct fluorination, kinetics of the direct fluorination of a set of polymers and the kinetics of accumulation of free radicals during the direct fluorination of polystyrene (PS) [3–10].

2. Experimental

Atactic amorphous PS was produced at the Kuskovo's plant (Russia) by a bulk heat polymerization followed by washing out the monomer. No catalyst or plasticizer were used. Average-viscosity molecular weight was equal to 199 000. Two types of polymer films were used: free films (thickness 20–25 μm) and films deposited onto sapphire or zinc selenide transparent substrates (film thicknesses were 1 to 5 μm). The dimensions of the films were usually $5 \times 5 \text{ mm}^2$. Hydrogen fluoride HF generated during the direct fluorination process inhibits reaction so NaF was used as chemical adsorber of HF. The amount of impurities (mainly oxygen) in fluorine was less than 0.1 vol % (analysis by mass-spectrometry). Also O_2 , N_2 , He, Ar and CO_2 with impurities less

than 0.01 vol % were used. Fluorination was carried out in closed metal vessels. The fluorine pressure was 44 to 441 Torr. Fluorine consumption did not exceed 5% so the fluorine pressure was considered to be constant during the fluorination.

We used the following methods of investigations: IR, UV and visible spectroscopy (IFS-113v ('Bruker', Germany) and 'Spekord UV-VIS' ('Karl Zeiss Jena', Germany) spectrometers were used, the original method of the interference spectroscopy in the visible region of spectra (equipment was described in [3–7]), elemental chemical analysis, refractometry (refractometer RF-454B, USSR), weighing, ESR (electron spin resonance) spectrometry (EPR-21, USSR) [3–10].

3. Results and discussion

The IR spectra of totally fluorinated PS (the film was treated with undiluted fluorine, i.e., no admixtures were inserted into the fluorine; fluorination time was sufficient to modify the sample through all its thickness), and untreated PS (Fig. 1) differ substantially from each other. In fluorine treated PS all the IR bands of CH, CH_2 and phenyl groups are absent, i.e., all the hydrogen atoms are substituted by fluorine and also all the phenyl group conjugated bonds are saturated by fluorine. A weak diffuse band around 3022 cm^{-1} is due to an absorption of $(HF)_n$ associates which tend to form hydrogen bonds [10]. The most characteristic spectral features of PS treated by undiluted fluorine are a strong sys-

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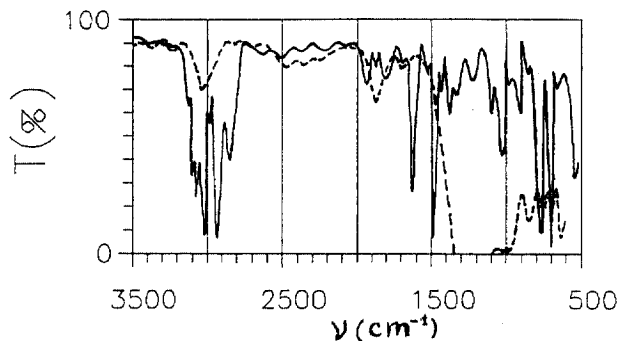


Fig. 1. IR spectra of untreated (curve 1) and totally fluorinated (curve 2) PS films. Thicknesses of the films are equal to 20 and 30 μm respectively.

tem of diffuse C–F bands in the 1400–800 cm^{-1} region [1] and a set of very weak unidentified bands near 900–400 cm^{-1} . Spectral features of PS treated by F_2 – O_2 mixtures will be described below. According to the elemental chemical analysis data no hydrogen was observed and in totally fluorinated PS the chemical formula of a molecular unit of fluorinated (with undiluted fluorine) PS is $\text{C}_8\text{F}_{12\pm 0.5}$. The formula of untreated PS monomeric unit is C_8H_8 and fluorinated PS still containing conjugated bonds would be C_8F_8 . If all the conjugated bonds are saturated by fluorine the content would be C_8F_{14} . It is known that under the action of fluorine both breakdown and crosslinking take place [1,11–13] hence the discrepancy between the above mentioned formulae (C_8F_{12} , C_8F_8 and C_8F_{14}) can be attributed to breakdown (destruction) and crosslinking of polymer chains and the number of crosslinks or additional C–C bonds per each monomeric unit is 2 units more than the number of scissions. The concentration of crosslinks is therefore equal to 1 per each monomeric unit of fluorinated PS. Fluorinated PS cannot be dissolved in Freons-62, -63, -112, -113. Our results do not agree with data for the chemical composition of fluorinated PS by other authors: C_8F_{14} [14] and $\text{C}_8\text{F}_{9.1}$ [15].

An new method of kinetic interference spectroscopy using visible light developed by us was used to investigate the direct fluorination process of polymers [3–7]. In our experiments we used very flat films having good reflectance ('shining' surface). If the untreated and fluorinated polymer layers are separated by a very thin transition (boundary) layer (Fig. 2; thickness of this boundary layer must be much smaller than $\lambda/4$, where λ is the wavelength of the probe beam transmitted through the polymer film) and this boundary is parallel to

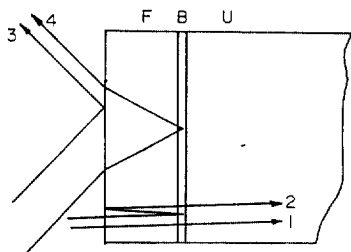


Fig. 2. Cross-section of partially fluorinated PS film. 'U', 'F' and 'B' are untreated, fluorinated and boundary layers respectively.

external surface of polymer (i.e., the fluorinated layer thickness is uniform across the polymer surface), the intensity I of light (at fixed wavelength λ) transmitted through the vessel in which polymer film is treated by fluorine has interference features (see Fig. 3 in our previous paper [3]), i.e., the intensity of light depends on time and consists of a series of maxima and minima. These interference features are due to the interference of the light beam transmitted through the polymer film without reflections (beam 1, Fig. 2) and the light beam double reflected from the fluorinated polymer–virgin polymer boundary and fluorinated polymer–gaseous phase boundary (beam 2, Fig. 2). The first maximum corresponds to the thickness of the antireflecting layer (fluorinated layer thickness $\delta_F = (1/4) \lambda/n_F$ where n_F is the refractive index of the fluorinated polymer, the first minimum corresponds to $\delta_F = (1/2) \lambda/n_F$ and so on. The sensitivity φ of this method is defined by the oscillation of the light intensity and hence depends on the relation $\varphi = (I_{\text{max}} - I_{\text{min}})/I_{\text{min}}$, where I_{max} and I_{min} are the maximum and minimum values of intensity I . The φ value usually does not exceed 0.03–0.1 because the intensity of the double reflected light beam is much smaller than the intensity of transmitted light. To increase φ the method of light monitoring was modified [5–7] (Figs. 2 and 3). The polymer film surface was oriented at 45° with respect to the incident light beam and reflected light was monitored. The interference features (Fig. 3) of the reflected light beam intensity are due to the interference of two beams reflected from boundaries fluorinated polymer–gaseous phase (beam 3, Fig. 2) and fluorinated polymer–untreated polymer (beam 4, Fig. 2); hence the φ value is enhanced up to $\varphi \sim 1$. This method of interference spectroscopy allows measurement of the minimum value of the fluorinated layer thickness $\delta_F \sim 0.1 \mu\text{m}$ for $\lambda = 0.6328 \mu\text{m}$ (He–Ne laser was used as light source); the upper limit of the δ_F value is greater than 50 μm . The main advantage of this method is that the time dependence of the δ_F is monitored during the fluorination process.

Another method can be applied to measure the δ_F value. The transition (or absorption) spectra of fluorinated polymer

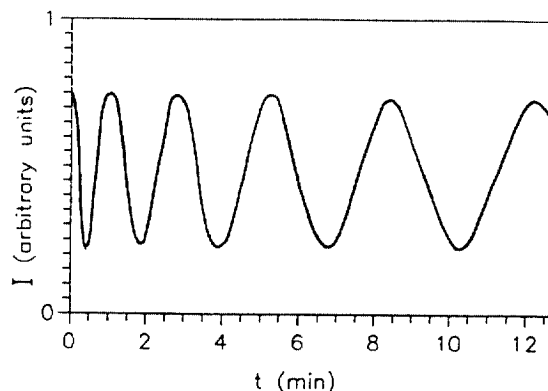


Fig. 3. Reflected light beam intensity I (arbitrary units) monitored at $\lambda = 0.6328 \mu\text{m}$ vs. time t (min) for free PS film treated with undiluted F_2 ($p_F = 147$ Torr). The film was treated from both sides. Fluorine injection was started at $t = 0$.

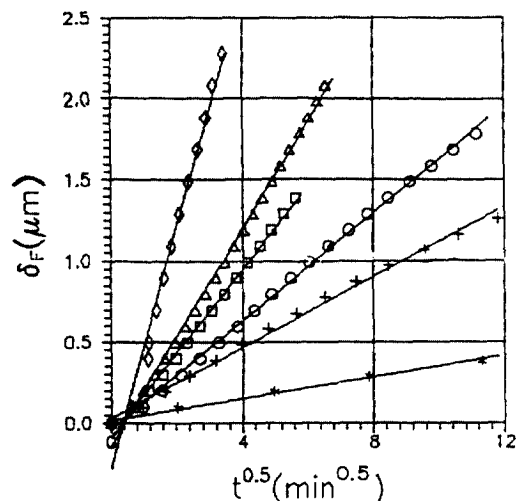


Fig. 4. The dependence of the thickness of the fluorinated layer δ_F (μm) on the fluorination duration t (min). The experimental conditions were as follows (figures in brackets are equal to the fluorine partial pressure p_F and the oxygen partial pressure p_O respectively): \circ (44; 0), \square (88; 0), \triangle (147; 0), \diamond (441; 0), $+$ (147; 37), $*$ (147; 147). Treatment temperature 293 ± 1 K.

films in the visible and near UV spectral regions have interference features and consist of a set of equidistant minima and maxima when frequency ν is measured in cm^{-1} (see Fig. 1 from Ref. [3]) and the δ_F value can be calculated by the formula: $\delta_F = (2n_F \Delta\nu)^{-1}$, where $\Delta\nu$ (cm^{-1}) is the distance between two neighbouring interference spectrum maxima (minima). This method was used in [15] to investigate the fluorination of PS. The main disadvantage of this method is that fluorination must be interrupted to carry out each measurement.

Taking into account the above data we came to the conclusion that fluorinated and untreated polymer layers are separated by a very sharp boundary layer (the thickness of this boundary layer is designated as δ_b). Practically all the elementary chemical reactions between fluorine and polymer occur only inside this boundary layer (Fig. 2). We have shown also (see Fig. 4 below) that the fluorinated layer thickness is proportional to the square root of the fluorination duration. On the basis of these facts we conclude that the limiting stage of direct fluorination process is fluorine penetration through the fluorinated layer to the untreated polymer. The same conclusion has been made in our earlier paper [4] for fluorination of poly(ethylene terephthalate). Intensity of the light beam I decreases with treatment time. This behaviour can be attributed to several reasons. For example increase of δ_b can result in intensity I decrease. The dependence of I on δ_F during PS fluorination is similar to Fig. 2 from our earlier paper [4]. In our earlier work [3] we have shown that the finite δ_b value results in a decrease of the ratio I/I_0 by a $[1 + \pi^2(n + n_F)^2 \lambda^{-2} \delta_b^{-2}]$ factor, where I_0 corresponds to the value $\delta_b = 0$ (i.e., I_0 is the first peak intensity in Fig. 3 from Ref. [3]) and n is the refractive index of virgin PS. The refractive index $n(z)$ value dependence on coordinate z (directed inside the film surface) has been written as

Table 1

Influence of composition of fluorinating mixture on properties of resulting polymer

Fluorinated (oxyfluorinated) PS				Untreated PS
R	$> 10^3$	4	0.33	–
N_C	~ 0	0.63	1.34	0
n_F^D	1.366	1.416	1.457	1.59

N_C corresponds to the number of C=O groups per monomer unit of fluorinated PS, n_F^D —refractive index measured at D-line of Na.

$n(z) = n - 0.5(n - n_F) \exp(-2z/\delta_b)$. At the point $z=0$ the refractive index $n(0)$ value is equal to the half-sum of the refractive indexes of the fluorinated and untreated polymer. For example the upper limit of δ_b values for fluorinated PS is described by the following equation:

$$\delta_b \leq 4 \cdot 10^{-3} \delta_F \text{ for } \delta_F \geq 1 \mu\text{m} \text{ and} \quad (1)$$

$$\delta_b \ll 0.1 \mu\text{m} \text{ for } \delta_b \leq 1 \mu\text{m}$$

Lagow and Margrave [14] estimated the δ_b value for fluorinated PS as greater than a few tens of μm . This estimate seems unreal because interference spectroscopy cannot be used in that case.

The refractive index $n_F^D = 1.366$ (at D-line of Na, $\lambda = 0.593 \mu\text{m}$) of fluorinated (by undiluted fluorine) PS is substantially smaller than the corresponding value ($n^D = 1.59$) of untreated PS. The influence of oxygen content on n value will be presented below (Table 1).

As mentioned above the limiting stage of the direct fluorination is fluorine penetration through fluorinated layer to the untreated polymer, i.e., the direct fluorination process is diffusion-limited and can be characterized by fluorine permeability \bar{P} through the fluorinated PS layer. The balance between the amount of fluorine consumed in the reaction zone and the amount of fluorine passed through the fluorinated layer can be expressed by the following relation:

$$B(d\delta_F/dt) = D(dc_F/dx) \quad (2)$$

where D is the diffusion coefficient of fluorine for the fluorinated polymer; c_F is the concentration of fluorine in the fluorinated polymer; axis x is directed into the film perpendicular to its surface (on the film surface $x=0$); and the experimentally determined coefficient B is the amount of fluorine (cm^3 under standard conditions) necessary to form 1 cm^3 of the fluorinated polymer divided by 1 cm^3 of the fluorinated polymer. For fluorinated PS we have obtained experimentally (similarly to our previous paper [4]; an experimentally measured density of PS treated with undiluted fluorine equal to $2.05 \pm 0.1 \text{ g cm}^{-3}$) $B = 1440$, within an infinitely reaction zone (that is $\delta_b \ll \delta_F$) $c_F(x = \delta_F) \ll c_F(x = 0)$. When the physico-chemical properties of the fluorinated layer are constant along the axis x then

$$B(d\delta_F/dt) = D[c_F(0)/\delta_F] = DS(p_F/\delta_F) = \bar{P}(p_F/\delta_F) \quad (3)$$

where S is the solubility coefficient of fluorine in fluorinated polymer and \bar{P} is the permeability coefficient for fluorine in fluorinated polymer ($c_F(x=0) = S \cdot p_F$ and $\bar{P} = D \cdot S$). If the partial fluorine pressure is constant during fluorination and \bar{P} remains unchanged during fluorination, then

$$\delta_F = (2/B)(\bar{P} \cdot p_F \cdot t)^{0.5} = A \cdot t^{0.5} \quad (4)$$

The dependence of the fluorinated layer thickness δ_F on the treatment duration t for various fluorine partial pressures p_F are represented in Fig. 4. Coefficient A dependence on p_F is represented in Fig. 5. According to Figs. 4 and 5 δ_F (μm) depends on p_F (Torr) and t (s) as follows ($T = 293 \pm 1$ K):

$$\begin{aligned} \delta_F &= 1.68 \cdot 10^{-3} p_F^{0.67} t^{0.5} + b \\ &= 1.68 \cdot 10^{-3} \left[p_F^{0.34} (p_F t) \right]^{0.5} + b \end{aligned} \quad (5)$$

The second term b in Eq. (5) is much smaller than the first one for our experimental conditions and is probably due to finite time of fluorine injection into the reaction vessel and b can therefore be neglected. Injection time was increased from ~ 5 s at $p_F = 44$ Torr up to ~ 0.5 min at $p_F = 441$ Torr because a smaller injection time could result in a polymer film ignition. Comparison of formulae (4) and (5) permit us to come to the conclusion that the fluorine permeability \bar{P} value ($\text{cm}^3(\text{normal conditions}) \text{cm}^{-1} \text{Torr}^{-1} \text{s}^{-1}$) through fluorinated PS is constant during a single fluorination set and depends slightly on fluorine partial pressure as follows ($T = 293 \pm 1$ K):

$$\bar{P} = 2.1 \cdot 10^{-11} p_F^{0.34} \quad (6)$$

Nitrogen, helium, argon and carbon dioxide do not affect the rate of the direct fluorination even when the partial pressures of these gases in the fluorinating mixture are 7 times greater than the fluorine partial pressure.

The activation energy E for the permeability \bar{P} for fluorinated (by undiluted fluorine) PS is equal to $7.2 \text{ kcal mole}^{-1}$ in the 205–300 K temperature range, changes stepwise at $T \cong 300$ K and is equal to $4.4 \text{ kcal mole}^{-1}$ in the 300–343 K

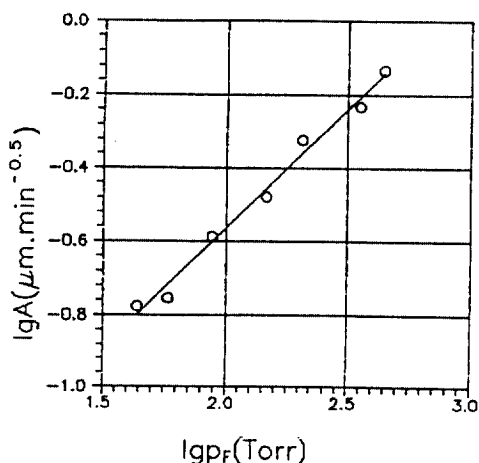


Fig. 5. Coefficient A ($\mu\text{m} \text{min}^{-0.5}$) vs. fluorine partial pressure p_F (Torr).

temperature range. The drop of the E value at $T \cong 300$ K can be related to a phase transition in the fluorinated polymer that occurs during fluorination.

According to our estimates, in which we neglected turbulence of the gas medium arising when fluorine is introduced, heating of polymer films at the beginning of the reaction did not exceed 5 K. Considering the experimental activation energies dependence (6) can, therefore hardly be explained by a film heating. One possible explanation of the dependence (6) is the suggestion that the number of crosslinks decreases with increasing p_F .

Oxygen acts as an inhibitor of direct fluorination: the rate of the formation of the fluorinated layer decreases when concentration of oxygen is increased. The rate of the formation of the fluorinated layer is limited by permeability \bar{P} . In the case of treatment with $\text{F}_2\text{-O}_2$ mixtures fluorinated and untreated layers are also separated by a very thin transition zone and $\delta_F \sim t^{0.5}$ even when the fluorine permeability \bar{P} through the layer of oxyfluorinated (i.e., treated with a $\text{F}_2\text{-O}_2$ mixture) PS decreases 200–300 times from its value for PS treated with pure (undiluted) fluorine. The fluorinated layer thickness dependence on treatment time fits an equation of type (4) and so \bar{P} values for oxyfluorinated PS can be calculated from Eq. (4) (see also Fig. 4). \bar{P} dependence on the ratio R of partial pressures p_F and p_{O} ($R = p_F/p_{\text{O}}$) is seen from Fig. 6 and satisfactorily fits the equation:

$$\bar{P} = \bar{P}_0 \exp[-7.45(1+0.64R)^{-1}] \quad (7)$$

where the \bar{P} value is the permeability value for the case $R > 1000$ (treatment by undiluted fluorine). The \bar{P} value depends on the fluorine partial pressure p_F (Eq. (6)). To take into account the influence of fluorinating mixture composition on the refractive index of oxyfluorinated (i.e., treated with $\text{F}_2\text{-O}_2$ mixtures) polymers which are used to calculate δ_F values, we have measured them by a refractometer. Refractive indexes are listed in Table 1.

Oxygen content in a fluorinating mixture (Fig. 6) changes fluorine permeability through oxyfluorinated PS by more than

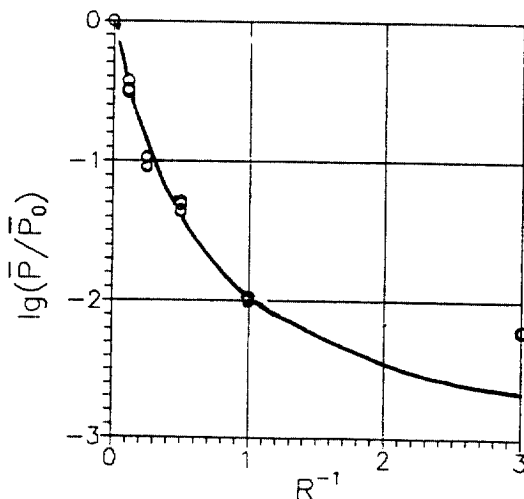


Fig. 6. Plot of the ratio P/P_0 vs. the reciprocal value of R .

two orders of magnitude. To explain such a strong oxygen influence we used results of Salame [16] who had shown that the polymer permeability \bar{P} is a function of the polymer chemical structure. The most marked spectroscopic features of oxyfluorinated PS are C=O ($-\text{COF}$) 1875 and 1790 cm^{-1} bands which are transformed into a broad 1750 cm^{-1} band by atmospheric moisture which also gives strong diffuse OH bands (plausible explanation of this fact is [1,17]: $\text{COF} + \text{H}_2\text{O} \Rightarrow -\text{COOH} + \text{HF}$). The origin of C=O groups in the course of polymer fluorination was noted in [1,17,18]. Absorption by C=O bands is also present in the near UV spectrum. The R^{-1} value ($R = p_F/p_O$) increase leads to C=O bands intensity growth, moreover the 1790 cm^{-1} band intensity rises more rapidly than the 1875 cm^{-1} . The R value decrease results in a shift of the maximum of a very broad C-F_x band to lower frequencies. To verify the suggestion that C=O groups formation results in a \bar{P} decrease we have measured C=O concentrations in oxyfluorinated PS.

Standard methods of C=O groups determination do not apply to oxyfluorinated PS due to its insolubility and atmospheric hydrolysis so we used IR spectroscopy. To avoid the influence of atmospheric moisture on IR spectra a reaction vessel with ZnSe optical windows was used and IR spectra were recorded in vacuum. We could not find quantitative data in the literature on absorption coefficients of carbonyl groups in fluorinated PS. To measure absorption coefficients we have used thin flat-parallel PMMA (polymethylmethacrylate) films (thickness 1 to 5 μm) cast onto ZnSe optical substrates (rather stable to fluorine action and transparent up to 500 cm^{-1}) and treated by fluorine. It should be noted that C=O groups are also present in an untreated PMMA (one group per monomer unit). Thicknesses of untreated and fluorinated layers were measured by the above mentioned interference spectroscopy method [3–7]. The C=O groups extinction coefficients σ of oxyfluorinated PMMA [$\sigma(\nu) = \delta_F^{-1} \cdot \log(T_{\text{background}}/T(\nu))$] versus frequency ν are shown in Fig. 7. We have made two assumptions in our analysis: (i) the concentrations of C=O groups in untreated and fluorinated PMMA are equal to each other being one carbonyl group per monomer unit; and (ii) the values of $\int \sigma(\nu) d\nu$ for fluorinated PMMA and PS are coincident ($\int \sigma(\nu) d\nu$ value is proportional to the C=O groups concentration). The difference between the $\int \sigma(\nu) d\nu$ values for untreated and fluorinated PMMA was less than 20%.

The $\int \sigma(\nu) d\nu$ value is shown to be proportional to δ_F and hence the concentration N_C of C=O groups is fixed during the course of treatment. The concentration of C=O groups depends very weakly on p_F ($N_C \sim p_F^{-0.14}$) on treatment with a mixture of fixed R value.

Extinction coefficient σ values of C=O groups vs. ν are shown in Fig. 7. The number N_C of C=O groups per monomer unit of fluorinated PS depends on the R value as follows (Fig. 8):

$$N_C = 1.53(1 + 0.29R)^{-1} \quad (8)$$

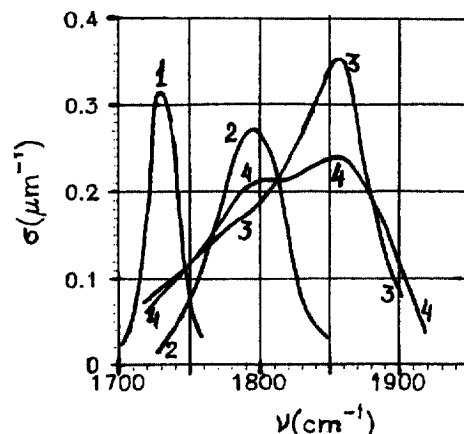


Fig. 7. Plot of the extinction coefficient $\sigma(\mu\text{m}^{-1})$ of C=O groups in untreated PMMA (curve 1), PMMA treated with undiluted fluorine (curve 2), treated with a fluorine–oxygen mixtures ($R=4$) PS (curve 3) and treated with a fluorine–oxygen mixture ($R=0.33$) PS (curve 4) vs. frequency $\nu(\text{cm}^{-1})$.

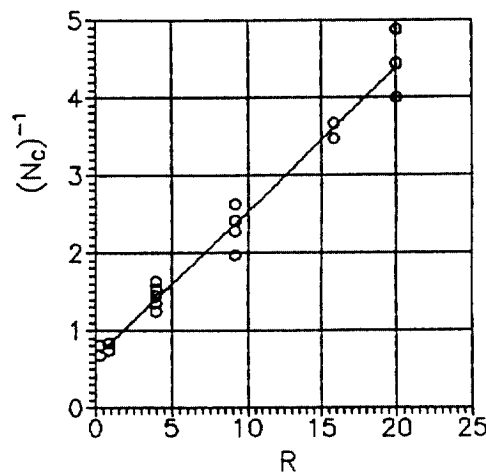


Fig. 8. Plot of the number N_C of C=O groups per monomer unit for oxyfluorinated PS vs. the ratio R of fluorine to oxygen partial pressures.

From Eq. (8) the value of N_C reaches its maximum at ca. 1.5 when $R \rightarrow 0$, i.e., when oxygen concentration is increased.

The difference between the permeability \bar{P} values of untreated and oxyfluorinated (by a mixture with a high oxygen concentration, i.e., when $R \rightarrow 0$) can exceed more than two orders in magnitude (see Fig. 6). According to [16] introduction of highly polar groups (such as hydroxyl OH and carbonyl C=O) into polymer structures results in a large decrease of \bar{P} . For example, on comparing two polymers, polyethylene ($-\text{CH}_2-\text{CH}_2-$)_n and polyvinylalcohol ($-\text{CH}_2-\text{CHOH}-$)_n, the difference between \bar{P} values for these polymers is found to exceed six orders of magnitude. So the strong C=O group influence on the \bar{P} value is not surprising (the maximum number of C=O groups per monomer unit of fluorinated PS reaches a value of $N_C \sim 1.5$).

Not only formation of C=O groups can result in \bar{P} value decrease. The same effect can also arise due to a formation of crosslinks such as 'oxygen bridges' $-\text{C}-\text{O}-\text{C}-$. Unfortunately standard methods of crosslinking determination (e.g.,

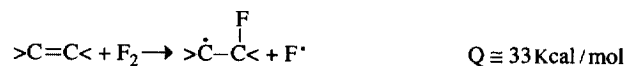
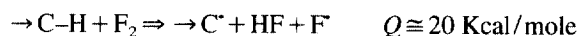
swelling method) cannot be used. IR spectroscopy cannot be applied to detect $-C-O-C-$ groups because the absorption bands of these groups are usually situated near 1100–1300 cm^{-1} and are masked by a very strong absorption of carbon-fluorine bonds.

The nature of the chain carriers of the direct fluorination of polymers was only little investigated. Only long-living stable peroxy RO_2^\cdot and thermostable fluorocarbon radicals which are the end products of the direct fluorination of polymers have been detected previously [11,19]. According to our data [9] the concentration of RO_2^\cdot radicals increases with oxygen concentration and can be as large as $\sim 10^{20}$ per 1 g of the fluorinated polymer layer. All attempts to detect active shortlife radicals (chain carriers) in thick polymer films (thickness $\sim 10\text{--}20\ \mu\text{m}$) were not successful because almost all the chain carriers are present inside the very thin boundary layer between fluorinated and untreated polymer layers (see Fig. 1; almost all the chemical reactions of fluorine with polymer are located inside this boundary layer) and active radicals are masked by peroxy radicals (the total amount of peroxy radicals is much greater than the total amount of chain carriers). To enhance the amount of chain carriers with respect to peroxy radicals we designed the following new experimental procedure [9,20]. Very thin polymer films in a form of a cotton wool were used. The average thickness of such a PS films was $\sim 0.01\ \mu\text{m}$. Undiluted fluorine was used in these experiments. The fluorine amount inserted inside the reaction vessel was less than the fluorine amount needed for the total transformation of an untreated polymer into the totally fluorinated polymer. Here chain carriers were not masked by peroxy radicals. To reduce the rate of the direct fluorination the samples were treated at a liquid nitrogen temperature ($T=77\ \text{K}$). A special nonmagnetic reaction vessel was used to monitor the kinetics of radical accumulation during the treatment. The total concentration of active radicals in fluorinated PS reached $(2\text{--}5)10^{18}\ \text{g}^{-1}$ at $T=77\ \text{K}$. We have observed the six types of radicals. Identification of these radicals is in progress.

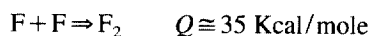
We have established that the direct fluorination is a diffusion-limited process. It means that the chemical composition and structure (also concentration of additional C–C bonds which are formed during the treatment) of fluorinated polymer do not depend on time. The concentration of fluorine and the rates of chemical reactions inside the reaction zone decrease when the reaction zone moves into the polymer bulk hence the relative rates of various chemical reactions does not depend on time. These processes known [21,22] to take place for the branched chain processes. Total or energy branching does not occur but so-called stimulated chain branching through an intermediate product (C=C double bonds) is rather liked. For energy reasons we consider that the rate of fluorine reaction with C=C bonds substantially exceeds the rate of fluorine reaction with initial polymer fragments. The scheme of the chain fluorination process is shown below. Only treatment with undiluted fluorine was considered and the influence of oxygen admixture was neglected.

3.1. Initiation stages

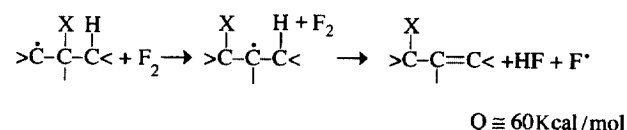
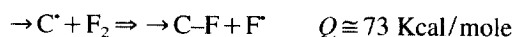
The thermal dissociation of molecular fluorine is usually regarded as a source of fluorine atoms [1,23]: $\text{F}_2 \Rightarrow 2\text{F}$. But this reaction is highly endothermic: heat absorption is ~ 35 kcal/mole. Therefore this reaction will be negligible at 77 K (but we did observe [9,20] the direct fluorination of a set of polymers at 77 K) and is hardly to occur even at room temperature. There are some much more feasible exothermic reactions such as the reaction of molecular fluorine with tertiary hydrogen and with double bonds which always exist in polymers as technology admixtures:



(1). Reactions of atomic fluorine.



(2). Reactions of macroradicals with molecular fluorine.

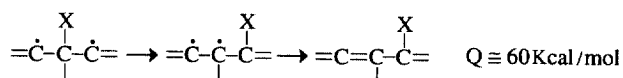
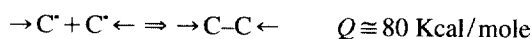


where X = H, F.

(3). Reactions of macroradicals with double bonds.



(4). Recombination of macroradicals.



(5). Reactions of HF.



(R-macroradical).

The main simplification of the above scheme is as follows: we do not take into account the differences in the neighbours of C–H bonds and hence we are using an ‘unificated’ macroradical. But even this simplified scheme allowed us to come to the following conclusions: quasi-state concentrations of double bonds and macroradicals are proportional to the fluorine pressure; the formation rate of additional C–C bonds (also the formation rates of HF and different bonds in the polymer chain) divided by the rate of F consumption do not depend on fluorine pressure.

In our paper [24] we have examined the influence of the opposite flows of F₂ (to the reaction zone) and HF (from the reaction zone) on the fluorination process. We have shown that in that case when (a) HF is removed from the gas phase and (b) the chemical composition and structure of the fluorinated polymer do not depend on fluorine pressure inside the reaction zone the fluorination layer thickness depends on time as a square root.

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