Surface modification of polymers by direct fluorination: A convenient approach to improve commercial properties of polymeric articles*

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Abstract: The fundamental features and industrial applications of the direct fluorination of polymers are reviewed. Direct fluorination of polymers (i.e., treatment of a polymer surface with gaseous fluorine mixtures) proceeds spontaneously at room temperature and is a surface modification process. More than 25 polymers have been studied with the aid of a variety of analytical and spectroscopic techniques. The fundamental features of the direct fluorination, such as influence of treatment conditions (composition of the fluorinating mixture, fluorine partial pressure, temperature, and fluorination duration) on the rate of formation, chemical composition, density, refraction index, and surface energy of the fluorinated layer, kinetics of formation of radicals during fluorination and their termination, texture of fluorinated layer, etc. were studied. It was demonstrated experimentally that direct fluorination can be effectively used to enhance commercial properties of polymer articles, such as barrier properties of polymer vessels, bottles, and packaging films and envelopes; gas-separation properties of polymer membranes; adhesion and printability properties of polymer articles; and mechanical properties of polymer-based composites.

Keywords: surface modification; direct fluorination; polymers; barrier properties; polymer membranes; gas separation and purification; adhesion; printability; reinforcement of polymer composites.

INTRODUCTION

Commonly used polymers have many advantages, such as low cost and processability, but they have also a lot of disadvantages (often poor adhesion, poor printability and barrier properties, low chemical resistance, etc.). It is possible to fabricate the whole article from specialty polymers (e.g., fluorine-containing polymers) that have improved commercial properties. Fluorinated polymers have a set of unique properties such as enhanced chemical stability, thermal stability, good barrier properties, etc. [1–15]. However, practical use of specially synthesized polymers, such as fluorine-containing polymers, is restricted due to their high cost and complexity of synthesis. But very often, application properties of polymer goods are defined mainly by their surface properties. Hence, it is not necessary to fabricate articles from fluoropolymers but simpler, cheaper, and more convenient to apply a surface treatment of articles made from commonly used polymers. In this case, direct fluorination can be effectively used...
Direct fluorination of polymers is a heterogeneous reaction of gaseous F\textsubscript{2} and its mixtures with a polymer surface. This is a method of surface modification: for the majority of glassy polymers, only the upper surface layer is modified (~0.01–10 \(\mu\)m in thickness), but the bulk properties remain unchanged. Since fluorination is one of the most effective chemical methods to modify and control physicochemical properties of polymers over a wide range, this process has become an important tool of great interest. Direct fluorination has many advantages when used in industry. Due to the high exothermicity of the main elementary stages, fluorination proceeds spontaneously at room temperature with a sufficient rate for industrial applications. Direct fluorination is a dry technology. Polymer articles of any shape can be treated. There are safe and reliable methods to neutralize (by converting into the solid phase) unused F\textsubscript{2} and the end-product HF. These features of direct fluorination initiated wide industrial utilization for enhancement of the barrier properties of automotive polymer fuel tanks and vessels for storage of toxic and volatile liquids [2–16]. Gas-separation properties of polymer membranes can also be highly enhanced by direct fluorination [2,4–9,16]. Adhesion properties of polymer articles of any shape can be substantially improved [2–9,13–15]. Also, the coefficient of friction can be reduced, and antibacterial properties and chemical resistance can be improved [2,4–7,9,16].

MATERIALS AND METHODS

The following polymers were investigated: high- and low-density polyethylene (HDPE, 6 varieties, and LDPE, 2 varieties), polyvinylfluoride (PVF), polyvinylidenefluoride (PVDF), polystyrene (PS), poly(ethylene terephthalate) (PET), polymethylmethacrylate (PMMA), pol(phenylene oxide) (PPO, 2 varieties), polyimide Matrimid\textsuperscript{®} 5218 (PI), poly(4-methyl-pentene-1) (PMP), polypropylene (PP), sulfonated polyetheretherketone (SPEEK), block copolymer of sulfone and butadiene (Seragel\textsuperscript{®} S3760/3), polyvinyltrimethylsilane (PVTMS), polycarbonatesiloxane Carbosil\textsuperscript{®} (PCS), polysulfone Udel 3500 (PSU), polyvinylalcohol (PVA), epoxy resin (ER) (see also [6,7]). Fluorine contained less than 0.1 % of admixtures (mainly oxygen). He, Ar, N\textsubscript{2}, and O\textsubscript{2} were of 99.999–99.99 % purity.

A large variety of common experimental methods, such as Fourier transform infrared (FTIR), visible and near-UV spectroscopy, electron spin resonance (ESR) spectroscopy, refractometry, electron microscopy, surface energy measurement, gas-chromatographic and volumetric methods, measurement of permeability of liquids through polymer materials, etc. were applied. Two original methods were also especially elaborated: (1) laser interference spectroscopic method to measure the dependence of the thickness of the fluorinated layer on the fluorination duration “in situ” and (2) a method to measure the density of thin fluorinated layers (over 0.5–10 \(\mu\)m range) formed on the surface of fluorinated polymers. Those methods are described below.

The majority of research in the field of direct fluorination of polymers has until recently been concerned with practical applications of direct fluorination, and only a limited number of investigators have focused upon the fundamental aspects of the direct fluorination of polyethylene. In addition, there seems to be a number of discrepancies between the various findings as reported in the literature.

CHEMICAL COMPOSITION OF THE FLUORINATED LAYER

It is known that a direct fluorination of hydrogen–carbon-based polymers during a sufficiently long period of time results in a practically total disruption of C–H and C–OH bonds and saturation of double (conjugated) bonds followed by a formation of C–F, C–F\textsubscript{2}, and C–F\textsubscript{3} groups due to the fact that the bond energy of C–F bonds is much higher as compared with C–H and C–OH bonds [1,2,4–9,16–18]. Also, C=O-containing groups are formed. There is no clear certainty concerning the composition of the fluorinated layer for the case of PE. The formation of a totally fluorinated polymer having Teflon-like structure (\(\text{CF}_{2}-\text{CF}_{2}\))\(_n\) needs a duration exceeding several weeks or even months [1,17–19] at conditions far from industrially acceptable. When the treatment conditions are close to industrially acceptable (the duration does not exceed 1–2 h, fluorine pressure does not exceed 0.1 bar and the temperature...
is over 20–60 °C) F/C value (mainly measured by X-ray photoelectron spectroscopy, XPS) is varied from 0.5 to 1.69 \[2,4,18\] and the maximum theoretical ratio \(\text{F/C} = 2\) is never achieved. For other polymers, the literature data indicate a large discrepancy in the F/C ratio \[5–7\]. That fact can be due to the following reasons: insufficient fluorination duration, low fluorine pressure, formation of cross-links, and formation of \(-\text{COF}\) groups (initiated by oxygen admixtures).

The presence of oxygen (common technological admixtures in fluorine or inserted admixture) results in a formation of \(-\text{COF}\) groups, which are transformed into \(-\text{COOH}\) groups under atmospheric moisture action. Concentration of \(-\text{COF}\) group in fluorinated LDPE can reach \(1.8 \times 10^{-2}\) mole\(\cdot\)g\(^{-1}\) \[1\].

Changes of chemical composition can be demonstrated for the case of PS and LDPE \[2,4,28\]. The case of PPO, PI, PVTMS, PMMA, and other polymers is described in details in \[2,4–8,27\].

For the case of PS, fluorination results in a substantial change of the polymer chemical composition (Fig. 1): all the bands corresponding to \(\text{C–H}\) and \(\text{C–H}_2\) bonds and double \(\text{C=H}\) bonds disappear. Thin PS film (10.2 \(\mu\)m in thickness) was placed inside a reaction vessel equipped with two optical ZnSe windows. To remove HF emitted during the fluorination, NaF pellet was inserted inside the reaction vessel \([\text{HF} + \text{NaF} = \text{NaHF}_2\) (solid)]\). Then the reactor was evacuated and filled with 0.1 bar fluorine pressure at 24 °C. The fluorine consumption at the end of fluorination did not exceed 7 %, so the fluorine pressure could be regarded as constant. The reaction vessel was placed in the FTIR spectrometer and IR spectra were continuously monitored. The evolution of \(\text{CH}_2\) bonds at 2924 and 2890 cm\(^{-1}\), \(\text{C–H}\) bonds in a phenyl ring at 1493, 1451, 757 and 699 cm\(^{-1}\) and a very broad diffuse band over 870–1450 cm\(^{-1}\) \((\text{C–F, C–F}_2\) and \(\text{C–F}_3\) bonds) \[21,22\] was continuously monitored. Computer simulation was used to separate overlapping bands and calculate the area \(S\) (cm\(^{-1}\)) under those bands in “absorbance” mode, because the total amount of separate groups is proportional to the area of corresponding groups. Decrease of the relative amount \(N/N_0\) \((N\) and \(N_0\) are the amount of groups of a polymer chain at a moment \(t\) and in a virgin polymer, respectively) and \(S\) value for the band over 870–1450 cm\(^{-1}\) with square root of fluorination duration \(t\) is shown in Fig. 2. Square root of \(t\) was used as a horizontal axis because the thickness \(\delta F\) of a fluorinated layer is proportional just to \(t^{0.5}\) \(\text{(see [20])}\). An \(S\) value (i.e., the total concentration of \(\text{C–F, C–F}_2\), and \(\text{C–F}_3\) bonds) is proportional to \(t^{0.5}\) or, respectively, is proportional to the \(\delta F\) value. \(N/N_0\) values for all the \(\text{C–H}\) and \(\text{C–H}_2\) bonds decrease with increase of \(\delta F\) value practically simultaneously. It means that the amount of \(\text{C–H}\) and \(\text{C–H}_2\) bonds is decreased simultaneously with an increase of the total amount of \(\text{C–F, C–F}_2\), and \(\text{C–F}_3\) bonds.

Fig. 1 IR spectra of virgin (1) and fluorinated through all its thickness (2) PS film, cast onto ZnSe support. Treatment conditions were as follows: fluorine pressure 0.2 bar, temperature 295 K. Spectra 2 was measured in 3 min after removal of the fluorinated film from the reaction vessel. (3) Spectra of the same film treated (hydrolyzed) with air during 15 h.
According to the IR data, no hydrogen was observed in totally fluorinated PS films. Chemical analysis indicated the following chemical formula of a monomeric unit of PS, treated with undiluted fluorine: $C_8F_{12} \pm 0.5$ \cite{20}. The formula of untreated PS monomeric unit is $C_8H_8$, and fluorinated PS still containing conjugated bonds would be $C_8F_8$. Would all the conjugated bonds be saturated with fluorine, the content would be $C_8F_{14}$. It is known that under the action of fluorine, both breakdown (disruption) and cross-linking take place \cite{1,23–25}, hence, the discrepancy between the above-mentioned formulae ($C_8F_{12}$, $C_8F_8$, and $C_8F_{14}$) can be attributed to simultaneous breakdown and cross-linking of polymer chains and the number of cross-links (or additional C–C bonds) per each monomeric unit is 2 units more than the number of scissions. It is necessary to mention that our results do not agree with data for the chemical composition of fluorinated PS by other authors: $C_8F_{14}$ \cite{18} and $C_8F_{9.1}$ \cite{26}.

The spectra of virgin and fluorinated LDPE (density 0.926 g cm$^{-3}$) are shown in Fig. 3 \cite{2,4,28}. It is pertinent to note that the spectra shown in Fig. 3 were measured in several hours after the stop of fluorination (i.e., all the samples were in contact with atmospheric air for several hours and were thus subjected to hydrolysis). The action of fluorine substantially changes the IR spectrum of the virgin LDPE films. Moreover, it was clear from the changes in the IR spectra that the oxygen admixture in the fluorinating mixture influenced the chemical composition of a fluorinated surface layer. The main feature in the IR spectra of LDPE treated with undiluted fluorine is a very broad diffuse band over the 1000–1300 cm$^{-1}$ region. Two maxima within that band located at ~1183 and ~1148 cm$^{-1}$ are due to the absorption of C–F, CF$_2$, and CF$_3$ groups. This means that a substantial quantity of partially fluorinated groups (e.g., –CHF–) is present in a fluorinated polymer. The intensity of the diffuse band increases with the thickness of the fluorinated layer. The spectrum of LDPE treated with an oxygen-containing F$_2$/He mixture substantially differs from the spectrum of LDPE treated with undiluted, pure fluorine. At first, the absorption maximum of the previously mentioned diffuse band system shifts to ~1093 cm$^{-1}$. The shift can be associated with the preferred formation of monofluorinated compounds such as –CHF– and –C(O)F–. The formation of C=O bonds is evident from the appearance of the bands between 1600–1900 cm$^{-1}$. The amount $N_{C=O}$ of C=O-containing groups per each monomeric unit of fluorinated PE is rather high ($N_{C=O}$ = 0.04–0.06) even when undiluted fluorine is used. Insertion of 2–3 % of oxygen in the fluorinating mixture increases $N_{C=O}$ value up to 0.5–0.7 \cite{2,4,7,28}. © 2009 IUPAC, Pure and Applied Chemistry 81, 451–471

\[ N/N_0 \text{ vs. } t^{0.5} \text{ minute} \]

**Fig. 2** Relative amount $N/N_0$ ($N$ and $N_0$ - amount of groups of a polymer chain at a moment $t$ and in a virgin polymer, respectively) (curves 1–5) and $S$ value (curve 6) on a square root of fluorination duration $t$ for the case of treatment of PS film with fluorine (fluorine pressure 0.1 bar, temperature 24 °C). Curves 1–5 refer to the bands at 1493, 1451, 757, 699 cm$^{-1}$ and for a sum of 2924 and 2890 cm$^{-1}$ bands, respectively. Curve 6 refers to the broad diffuse band over 870–1450 cm$^{-1}$. 

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To separate overlapping bands, computer simulation was applied. It was clearly evident that in freshly oxyfluorinated samples (i.e., treated with mixtures of $F_2/O_2$), four bands at 1853, 1762, 1741, and 1622 cm$^{-1}$ arose. The absorption at 1853 cm$^{-1}$ can be attributed to a carbonyl vibration in a $\text{–C(O)F}$ group. The band at 1762 cm$^{-1}$ can be assigned to the $\text{C=O}$ vibration in the $\alpha$-fluoroketone $\text{–CHF–(CO)–CHF–}$ while the band at 1741 cm$^{-1}$ can be attributed to the $\text{C=O}$ vibration in the $\alpha$-fluoroester $\text{–CHF–(CO)–O–}$ or the $\alpha$-fluoroketone $\text{–CHF–(CO)–OH–}$ or the double bond $\text{C=C}$ (e.g., $\text{–FC=CH–}$) stretching vibration. After hydrolysis (reaction with atmospheric moisture), three new absorptions at 1736, 1653, and 1623 cm$^{-1}$ arose, while the band at 1853 cm$^{-1}$ disappeared as a result of the acid fluoride hydrolysis: $\text{–COF + H}_2\text{O} \rightarrow \text{COOH + HF}$. The 1736 cm$^{-1}$ band is probably the $\text{C=O}$ vibration in either $\text{–CHF–(CO)OH–}$, the $\alpha$-fluoroester $\text{–CHF–(CO)–O–}$, the $\alpha$-fluoroaldehyde $\text{–CHF–(CO)H}$, or the $\alpha$-fluoroketone $\text{–CHF–(CO)–CHF–}$. Newly formed $\text{C=C}$ bonds were most likely responsible for the absorption at 1653 cm$^{-1}$. The band at 1623 cm$^{-1}$ can be assigned to both the $\text{C=O}$ vibration of the enol form of the $\beta$-diketones $\text{–(CO)–CF=C(OH)–}$ or the double bond $\text{C=C}$ (e.g., $\text{–FC=CH–}$) stretching vibration. All the assignments were made on the basis of [22].

**KINETICS OF FORMATION OF THE FLUORINATED LAYER**

**Evidence of a layered structure of fluorine-treated polymers:** Monitoring the rate of formation of the fluorinated layer

Investigations of the kinetics of growth of the thickness $\delta_F$ of fluorinated layer were performed by several researches, but there is no data in the available literature on “in situ” measurements (excluding kinetics of the mass increase during fluorination of PE [19]). To measure the $\delta_F$ value, the fluorination was interrupted. Thickness $\delta_F$ of the fluorinated layer was found to be proportional to $t$ (HDPE and PP [30]), $(p_F)0.5$ (PE [31]), (PS, polycarbonate, and PMMA [26]), $t$ (polymethylpentene [32]). At the initial stage, the mass increase of PE was not constant and tended to increase, but in several min the mass of the film was increased proportionally to $t^{0.5}$ [19]. Unfortunately, calculated in [19], the activation energy of the rate of fluorination is not valid, because the mathematical model only took into account the diffusion of fluorine through the fluorinated layer to the untreated one, but the consumption of fluorine.

inside the reaction zone between fluorinated and untreated layers was not taken into account. In [33], the mass increase of LDPE, HDPE, PVF, PVDF, PP, and ethylene–propylene (EP) copolymer was very small at the initial stage (1–2 min), but then the mass of the film was increased proportionally to $t^{0.5}$.

No reaction was observed for the case of PVDF at 50 °C during 1 h. The fluorination rate increased in the sequence LDPE-PVF-HDPE-(EP copolymer)-PP [33] and in the sequence HDPE-LDPE-PP [34]. Oxygen inhibits the fluorination rate: an increase of fluorine content from 0.1 to 1 % resulted in an almost 10-fold decrease of the rate of fluorination of PE [34].

A reported estimate, in excess of several tens of microns, for the thickness of the transient layer between fluorinated and untreated layers [26] seems unrealistically high. The unreliability of those results becomes evident, taking into account that the thickness of the fluorinated layers did not exceed several microns. Direct visualization (by electron microscopy) of the existence of the sharp boundary between fluorinated and untreated layers of PMP and block copolymer of PSU and polybutadiene (Seragel) can be found in [35], for the case of PVTMS in [2,4,6,7]. Visible region transmittance spectra of fluorine-treated films exhibit interference features and consist of a set of equidistant (in wavenumber scale) maxima and minima (Fig. 4) [2,4,6,7,27,29], due to the following reason: fluorine-treated polymers represent a layered structure and consist of a substantially (in many cases, mainly fluorinated) fluorinated layer (LDPE, HDPE, and PVF are exceptions of the rule) and a virgin (unmodified) layer, which are separated by a very narrow transient reaction zone. The thickness of the boundary layer $\delta_b << 0.1 \mu m$. The main chemical conversion processes proceed inside that reaction zone. But the main chemical composition changes may be followed by several minor post-reactions inside the fluorinated layer. The rate of formation of the fluorinated layer is limited by the rate of penetration of fluorine through the fluorinated layer to the untreated one. This is valid when $\delta_F$ exceeds ~0.1 $\mu m$.

To study the kinetics of formation of the fluorinated layer on the surface of both optically transparent and deposited onto nontransparent supports “in situ” (i.e., the fluorination was not interrupted to carry out a single measurement of $\delta_F$), an original nondestructive method was developed by our research group [2,4,6,7,16,20,36,37]. Such a method can be applied when $\delta_F \geq 0.1–0.12 \mu m$. In some experiments, $\delta_F$ was monitored up to 50 $\mu m$. Another method can be applied to measure the $\delta_F$ value. The

![Transmittance T (%) of the fluorine-treated PI film vs. wavenumber $\nu$ (cm$^{-1}$).](image)

**Fig. 4** Transmittance $T$ (%) of the fluorine-treated PI film (cast and fluorinated on a sapphire substrate) vs. wavenumber $\nu$ (cm$^{-1}$). Thickness $\delta_F$ of fluorinated layer $\delta_F = 2.14 \mu m$. Film was not fluorinated through all its thickness.
transition (or absorption) spectra of fluorinated polymer films in the visible and near-UV spectral regions have interference features and consist of a set of equidistant minima and maxima when frequency $\nu$ is measured in cm$^{-1}$ (Fig. 4) and the $\delta_F$ value can be calculated by the following formula: $\delta_F = (2 \cdot n_F \cdot \Delta \nu)^{-1}$, where $\Delta \nu$ (cm$^{-1}$) is the distance between two neighboring interference spectrum maxims (minima) and $n_F$ is the refraction index of fluorinated polymer. Experimentally measured $n_F$ values are listed in Table 1. The main disadvantage of this method is that fluorination must be interrupted to carry out each measurement.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$n_D^V$</th>
<th>$n_D^F$</th>
<th>$\rho_V$, g cm$^{-3}$</th>
<th>$\rho_F$, g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1.59</td>
<td>1.366</td>
<td>1.05</td>
<td>2.05</td>
</tr>
<tr>
<td>PET</td>
<td>1.655</td>
<td>1.38</td>
<td>1.46</td>
<td>1.75</td>
</tr>
<tr>
<td>PI</td>
<td>1.63</td>
<td>1.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPO (M.W. = 34 000)</td>
<td></td>
<td>1.3730</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPO (M.W. = 244 000)</td>
<td></td>
<td>1.3808</td>
<td>1.07</td>
<td>1.72</td>
</tr>
<tr>
<td>PVTM</td>
<td>1.4915</td>
<td>1.376</td>
<td>0.85</td>
<td>1.73</td>
</tr>
<tr>
<td>PTFE</td>
<td>1.35–1.38</td>
<td></td>
<td>–</td>
<td>2.12–2.28</td>
</tr>
</tbody>
</table>

**Dependence of the rate of fluorinated layer formation on the fluorinating mixture composition**

In all the experiments (excluding the study of the influence of HF, emitted during the fluorination, on the kinetics of fluorination), a pellet of NaF was inserted into the reaction vessel to remove HF via the following reaction: $\text{NaF} + \text{HF} \rightarrow \text{NaHF}_2$ (solid). For all the studied polymers, it was shown that layers of fluorinated and unmodified polymer are separated by a very thin boundary layer (much less than 0.1 µm in thickness) when thickness $\delta_F$ of fluorinated layer exceeds 0.1 µm [2,4,6,7,16,20,27,28,36–38]. For all the studied polymers (excluding composite membranes based on PCS [64]) and all the used fluorinating mixtures, the $\delta_F$ value was proportional to the square root of fluorination duration $t$

$$\delta_F = A \cdot r^n + \text{const} = B \cdot (p_F)^k \cdot t^{0.5} + \text{const}$$

where the value of $A$ depends on $p_F$, $p_{He}$, $p_N$, and $p_{HF}$—partial pressures of F$_2$, O$_2$, He, N$_2$, and HF. “const” value in eq. 1 can be neglected for all the studied polymers, excluding LDPE, HDPE, and PVF. For all the studied polymers, $n$ value was equal to $n = 0.50 \pm 0.03$ [2,4,6,7]. $B$ and $k$ values for different polymers can be found in [2,4,6,7]. The treatment duration necessary to form the thickness of fluorinated layer $\delta_F = 1$ µm depends on a polymer nature and varies from ~20 min to ~10 h when fluorine partial pressure is equal to 0.1 bar and treatment is carried out at room temperature (Fig. 5). The rate of fluorination is increased with temperature [1,2,4,6,7].

To minimize possible formation of defects (polymer chain scissions, macro- and microdefects, and caverns), so-called “mild” treatment conditions are used in industry: fluorine is diluted with N$_2$, He, Ar, CO$_2$, etc. The concentration of F$_2$ is usually around 1–20 vol %. The square root dependence of $\delta_F$ on $t$ is valid even when fluorine concentration is equal to 1 %. Diluents such as N$_2$, He, Ar, and CO$_2$ slightly influence the rate of fluorination [2,4,6,7].
Oxygen inhibits the process of fluorination of polymers, but the degree of inhibition depends on the nature of the polymer. The influence of O\textsubscript{2} on A value (eq. 1) is shown in Fig. 6. Increase of an O\textsubscript{2} concentration results in a decrease of A value. O\textsubscript{2} concentration has the prevailing meaning, but some influence of fluorine partial pressure (when O\textsubscript{2} concentration is constant) was observed [2,4,6,7]. It was shown above that treatment of polymers with F\textsubscript{2}–O\textsubscript{2} mixtures (so-called oxyfluorination) resulted in a formation of C=O-containing groups. It is known [39] that introduction of C=O groups in a polymer structure results in a substantial drop of permeability of different gases (e.g., N\textsubscript{2} and O\textsubscript{2}). It is reasonable to propose that introduction of C=O groups into the fluorinated polymer structure decreases the permeability of F\textsubscript{2} through the fluorinated layer and hence results in a decrease of the fluorination rate.

Fig. 5 Treatment duration t necessary to form thickness of fluorinated layer $\delta_{F} = 1 \mu m$ when fluorine partial pressure is equal to 0.1 bar and treatment is carried out at room temperature.

Fig. 6 $A/A_0$ value vs. concentration of oxygen [O\textsubscript{2}] in F\textsubscript{2}–O\textsubscript{2} mixture. $A_0$ is A value for the case when [O\textsubscript{2}] = 0. Designations: ■ - PCS, ● - PI, ▲ - PPO, ▼ - PMMA, ○ - PET. The fluorine pressure was maintained constant for each polymer: 0.35 bar (PMMA), 0.1 bar (PCS), 0.2 bar (PPO, M.W. 244000), 0.28 bar (PET), 0.1 bar (PI).
As mentioned above, in the majority of experiments, a NaF pellet was inserted into the reaction vessel to remove emitted HF. But some experiments were carried out to study the influence of HF on the fluorination rate \([2,4,6,7]\). It was shown that insertion of 3 vol % of HF to fluorine results in a decrease of \(A\) value (eq. 1) by a factor of 1.4. For the case of the copolymer of PSU and PCS, inhibiting action of HF exhibits nonmonotonic behavior \([38]\).

The influence of the treatment temperature on the fluorination rate was studied for LDPE (density 0.918 g cm\(^{-3}\)) and HDPE (density 0.945 and 0.949 g cm\(^{-3}\)) over 293–338 K temperature range when F–N blends with 10 % fluorine concentration were used. Dependence of \(A\) value on temperature \(T\) can be represented as \(A \sim A_0 \exp(-E_{\text{act}}/RT)\). \(E_{\text{act}}\) values are equal (within accuracy \(\sim 10 \%\)) to 13.4 kJ/mol for LDPE (density 0.918 g cm\(^{-3}\)), 28.1 kJ/mol for HDPE (density 0.945 g cm\(^{-3}\)), and 34.2 kJ/mol for HDPE (density 0.949 g cm\(^{-3}\)) \([28]\).

Fluorination results in a replacement of “light” H-atoms for “heavier” F-atoms, so the density of fluorinated polymers should be greater as compared with the density of virgin polymers. There is a single paper in the available literature on the direct measurement of density of fluorinated PE \([31]\), where the fluorinated layer was separated in boiling xylene. The density was measured by an ordinary method “buried-emerged” and was evaluated as slightly greater than 2.0 g cm\(^{-3}\). Another direct nondestructive method was proposed by our research group \([2,4,6,7,27]\). Polymer films were cast on a solid support of sapphire and then removed from it. Only flat-parallel films (i.e., films having a uniform thickness with an accuracy \(\sim 0.1 \mu\text{m}\) over its surface) were selected. Those films were treated with fluorine from both sides. The transmission spectrum of those films in the visible region of spectra exhibited interference features due to a formation of a three-layered structure, fluorinated layer–virgin layer–fluorinated layer. By applying fast Fourier transformation to those spectra, the thickness of the virgin and fluorinated layers can be calculated. The above-mentioned laser interference method was applied to monitor the thickness of the fluorinated layer \(\delta_F\) independently. Simultaneously with measurement of thicknesses \(\delta_V\) and \(\delta_F\), each sample was weighed after each fluorination stage. The sample area was not changed in the course of treatment. Calculated on the basis of obtained data of an average density, \(\rho_F\) of fluorinated layer is listed in Table 1. For the films fabricated from PS, PET, and PPO, the \(\rho_F\) values did not depend on \(\delta_F\). But for the case of PI, \(\rho_F\) values depended on \(\delta_F\). It can be explained by the assumption that the chemical transformation of PI Matrimid 5218 proceeds via two stages. During the first stage (when the \(\delta_F\) value reaches \(\sim 1–2 \mu\text{m}\)), the majority of chemical conversions take place inside the boundary reaction zone followed by a step decrease of refractive index and increase of a polymer density increase from 1.24 to \(\sim 1.6–1.7 \text{ g cm}^{-3}\). Further increase of a polymer density to \(\sim 1.9 \text{ g cm}^{-3}\) proceeds rather due to (a) post-reactions with fluorine resulting in chemical composition change or (b) formation of cross-links via termination of two adjacent radicals without change of chemical composition, resulting in an increase of the polymer density.

**KINETICS OF FORMATION AND TERMINATION OF RADICALS**

At present, the majority of research \([1,17,19,34,40,41]\) considers the process of the direct fluorination of polymers as a radical-chain one. But such an affirmation was based only on the fact that long-life radicals were detected in the fluorine-treated polymers, but no radicals taking part in the processes of chain initiation and propagation were detected except by research carried out by our group \([2,4,6,7,41–43]\). Authors of \([1,23,24,44,45]\) detected long-lived radicals in fluorinated (at room temperature and up to 55 °C) PE, PS, PVC, PVDC, etc. ESR spectra represented a mixture of peroxy RO\(_2\) radicals and an unidentified very broad component, which was tentatively assigned to metal fluorides with altering valency \([23]\). The concentration of radicals was varied over \(10^{16}–10^{19}\) radicals per 1 g of a total mass of a polymer. But it is necessary to emphasize that the above value does not represent a real concentration of radicals inside the fluorinated layer because polymers were not fluorinated through all their thickness and the thickness of a fluorinated layer was not measured. The origin of superimposed broad (8 mT in width) and narrow (0.9 mT in width) lines in fluorinated poly(paraphenylene) was attrib-
ated to a “dangling” carbon bond having localized spin and, probably, to another type of “dangling” carbon bond (defects with different neighbors) [46]. An attempt to describe the mechanism of direct fluorination of PE on the basis of ESCA data on the chemical composition of thick upper fluorinated layer (~5 nm in thickness) has been made in [41], but no detection of radicals has been carried out.

The kinetics of radical formation for the case of fluorination of LDPE and HDPE was studied by our research group [2,4,6,7,28,42,43] at 77 K and at room temperature. Fluorination of LDPE (density 0.918 g cm−3) in the form of cotton wool was carried out in a quartz reaction vial at 77 K, and ESR spectra were monitored as fluorination proceeded. The spectra reveal the instantaneous (in just 2 min after the insertion of fluorine) formation of both fluoroalkyl and peroxy radicals. The formation of peroxy radicals is due to oxygen traces in fluorine or to a formation of an oxygen in reactions of fluorine with absorbed water. The shape of the ESR spectra was not practically changed during fluorination (Fig. 7, spectrum 1). The spectra represented a superposition of an asymmetric singlet of peroxy RO\textsubscript{2}• radicals and a spectrum of at least one radical. The total width of the spectrum was around 16–17 mT. The concentration of the radicals soon reached a maximum concentration of ~10\textsuperscript{17} radicals per 1 g of the total sample mass in 7–8 min, and then the radical formation was stopped. Spectrum 1 (Fig. 7) was measured in a fluorine environment in 20 min after the beginning of fluorination. Then the vial was evacuated and filled with air, i.e., subjected to oxidation. Spectra 2 and 3 of an oxidized sample (Fig. 7) were measured at 77 and 293 K, respectively. It is evident that all the primary formed radicals were transformed into peroxy RO\textsubscript{2}• ones under oxygen action.

On the basis of the above presented data, it is possible to make a conclusion concerning the initiation stage of the direct fluorination of polymers. Fluorination proceeds even at a temperature of 77 K. This means that the initiation proceeds with a zero activation energy. Usually, a process of molecular fluorine dissociation \( \text{F}_2 \rightarrow \text{F}^- + \text{F}^+ \) is regarded as the initiation process of the fluorination of polymers [1,3,17], but that reaction is highly endothermic (\( \Delta H = -163.4 \text{ kJ/mol at 298 K} \) [1–4]). But there are several exothermic reactions that can be regarded as initiation processes.

Fig. 7: ESR spectrum of a LDPE sample in the form of “cotton wool” as measured 20 min after the insertion of fluorine into the reaction vessel. The reaction was carried out at \( T = 77 \text{ K} \). 2 and 3: spectra of the same sample which was evacuated after fluorination and oxidized by air. 4 and 5: spectra of LDPE films fluorinated at room temperature. Treatment conditions: undiluted fluorine, \( p_F = 0.072 \text{ bar} \), fluorination time \( t = 100 \text{ min} \) at \( T = 293 \text{ K} \). Spectra 4 and 5 were measured at 77 and 293 K, respectively. 6: DPPH spectrum (\( g = 2.0036 \)). Spectra were corrected with respect to the absorption of the sample before fluorination. Spectra 1, 2, and 4 were measured at 77 K, spectra 3 and 5 at 293 K.

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\[ \text{F}_2 + \text{–CH}_2 \rightarrow \text{F}^* + \text{–CH}^* + \text{HF} \]
\[ \text{F}_2 + \text{–CH}_2\text{–CH}=\text{CH–CH}_2 \rightarrow \text{F}^* + \text{–CH}_2\text{–CH}=\text{CH}^* + \text{CH}_2^* + \text{HF} \]
\[ \text{F}_2 + \text{–CH}_2\text{–CH}_2\text{–C(=CH}_2\text{)}\text{–CH}_2 \rightarrow \text{F}^* + \text{–CH}_2\text{–CH}^* + \text{C(=CH}_2\text{)}\text{–CH}_2^* + \text{HF} \]
\[ \text{F}_2 + \text{–CH}=\text{CH–} \rightarrow \text{–CHF–CH}^* + \text{F}^* \]

Similar results were obtained for flat LDPE films treated with an undiluted fluorine for \( t = 100 \) min at \( T = 293 \text{ K} \) and \( 0.072 \) bar fluorine partial pressure (Fig. 7). The spectra were measured immediately after fluorination. The asymmetric singlet (g-factor: \( g_\perp = 2.0022, g_\parallel = 2.0356 \)) corresponds again to the RO\(_2^*\) radical superimposed on a fluororadical spectrum. Radical formation and termination for the case of other polymers is described in detail in [2,4–8].

The kinetics of radical termination at and above room temperature was studied for LDPE (density 0.918 and 0.926 g cm\(^{-3}\)) and HDPE (density 0.945, 0.946, 0.947, 0.948, and 0.949 g cm\(^{-3}\)) (Fig. 8). Both peroxy RO\(_2^*\) and perfluoroalkyl radicals were detected, but the majority of the radicals (80–95 \%) were found to be the peroxy type. It is evident that the direct fluorination of LDPE generates a relatively high concentration of long-lifetime radicals, up to \( (3–5)\times10^{19} \) radicals per cm\(^3\) of fluorinated polymer. A very rough estimate indicates that \(~0.3\%\) of monomeric units of fluorinated LDPE contain radicals and the majority of the radicals are peroxy RO\(_2^*\) ones. The concentration of radicals is decreased by a factor of 2 over an interval of between 4 and 6 h at room temperature, and therefore the radicals can be considered as long-lifetime. A decrease of both fluorine partial pressure and treatment time results in a small decline in concentration of the long-lifetime radicals, although this decline was not particularly dramatic.

The kinetics of radical termination at \( T = 293 \text{ K} \) can be represented as follows:

\[ \frac{[R]}{[R_0]} = \frac{1}{(1 + a \cdot t)} \]  
(2)

It looks like the termination kinetics of radicals \( R^* \) can be described by a bimolecular reaction

\[ R^* + R^* \rightarrow R_2 \]  
(3)

where \( k_2 \) is the rate constant, then

\[ \frac{[R]}{[R_0]} = (1 + 2k_2[RO^*]_0 \cdot t)^{-1} \]  
(4)

Fig. 8 Ratio \([R]/[R_0]\) (\([R]\): concentration of radicals at time \( t \), \([R_0]\): concentration of radicals 12 min after completion of fluorination) vs. storage time \( t \) for the case of LDPE of density 0.918 g cm\(^{-3}\). Circles, squares, and triangles correspond to the samples treated at fluorine pressure 73.5 Torr during 15, 30, and 60 min, respectively.
For the case of LDPE of density 0.918 g cm\(^{-3}\), rate constants \(k_2\) are equal to \((0.36 \pm 0.04) \times 10^{-24}\), \((0.75 \pm 0.04) \times 10^{-24}\), and \((1.11 \pm 0.14) \times 10^{-24}\) cm\(^3\) s\(^{-1}\) for the samples treated at fluorine pressure 73.5 Torr during 15, 30, and 60 min, respectively, at room temperature. Average \(k_2\) value is equal to \((0.74 \pm 0.25) \times 10^{-24}\) cm\(^3\) s\(^{-1}\).

For the case of fluorinated PI and PPO, concentration of radicals inside fluorinated layer depends on treatment conditions and is over \((2.3–5.4) \times 10^{19}\) cm\(^{-3}\). Termination kinetics can be described by a two-step mechanism. During the first step (storage duration less than 2 h), termination proceeds similarly to the LDPE case via a bimolecular reaction (3) and average \(k_2\) values, calculated similarly to the case of LDPE, are equal to \((2.4 \pm 0.54) \times 10^{-24}\) and \((1.1 \pm 0.2) \times 10^{-24}\) cm\(^3\) s\(^{-1}\) for PI and PPO, respectively. During the second stage (above 5 h for PI and 20 h for PPO), the termination can be approximated as follows: \(\text{Ln}[R] = a_1 - a_2 t\) or \([R] = b_1 \exp(-a_2 t)\). Such a dependence indicates that the termination became monomolecular \(R^* \rightarrow A\) with rate constant \(k_1 = a_2\). \(k_1\) is equal to \((2.7 \pm 0.1) \times 10^{-6}\) s\(^{-1}\) and \((2.0 \pm 0.01) \times 10^{-6}\) s\(^{-1}\) for PI and PPO, respectively.

To measure the kinetics of accumulation of radicals during fluorination, PS film was placed inside a Teflon vial, which was inserted inside the resonator of an ESR spectrometer [2,4,6,7,42]. Then, a mixture of 80 % F\(_2\) + 20 % O\(_2\) composition at total pressure 0.24 bar at 22 °C temperature was inserted into the vial and ESR spectra were monitored “in situ”. Radicals originate just after insertion of fluorinating mixture into the vial, but at an initial stage there is no linear dependence of radicals amount on \(\delta_F\) value. Some time (4–5 min, which corresponds to a formation of a fluorinated layer 0.3–0.4 \(\mu\)m in thickness) is needed to reach the linear dependence.

**PRACTICAL APPLICATIONS OF DIRECT FLUORINATION**

**Improvement of barrier properties**

At present, one of the most commercially significant applications of direct fluorination of polymeric goods is the enhancement of their barrier properties [2–10,28,47–65]. In the United States and Europe, a significant amount of automotive fuel tanks, vessels for storage of toxic and volatile liquids, and pipes for transfer of liquids are fabricated from polymers, mainly from PE and PP. PE (HDPE and LDPE) is a cheap and well-processed polymer, but it has relatively large (for some applications) permeability, which results in too large a loss of liquids stored inside polymer vessels. Direct fluorination creates a barrier to permeation of multiatomic molecules (e.g., hydrocarbons) for the following reasons. Fluorination results in a remarkable increase of the specific gravity [2,4,6–8,27], the free volume is decreased, and hence the permeability of fluorinated polymers should be decreased. Also, direct fluorination leads to the cross-linking of polymers [1,5–7,23–25]. Such an effect results in a suppressing of the swelling and plasticization effects under the action of hydrocarbons and a permeability value decreases. Also, the surface energy of fluorine-treated polymer surfaces in many cases is increased and hence the solubility (also, permeability) of low-polarity organic liquids in fluorinated polymers is decreased.

The direct fluorination of the interior of polymeric automotive fuel tanks prevents nonpolar or low-polar substance (e.g., hydrocarbons) emission and reduces air pollution. According to [3], the permeability value of fluorine-treated HDPE is around \(10^{-13}–10^{-14}\) (cc(STP) cm cm\(^{-2}\) s\(^{-1}\)) and is 6–7 orders of magnitude lower than one of an untreated HDPE. Investigators paid most attention to PE (especially HDPE) [3,47,48,57–69]. The loss of gasoline from automotive polymer fuel tanks can be reduced upon the direct fluorination by a factor of 100 [3,61] and 70 [62]. Spread in the above data may be due to several reasons: different treatment conditions (composition of fluorinating mixture, duration of treatment), variations in chemical structure of polyethylene, etc. The leakage of a mixture of petrol and alcohol can be reduced under fluorination by a factor of 18 [3,71]. Fluorination results in a decrease
of the loss of petrol from HDPE pipes, used between reservoirs and pumps at filling stations, by a factor of 80 [63]. Direct fluorination of polymer containers for packaging of industrial and consumer chemicals decreases the loss of liquids which are stored inside the containers. Carstens [63] has shown that the loss of chemicals such as creosote, paints, polishes, hand cleaners, etc. from HDPE containers can be reduced by the direct fluorination by a factor of 10–100. Leakage of toluene from HDPE containers can be also reduced by a factor of 100 [64], 50–60 [59], and 15 [65], and leakage of pentane by a factor of 100 [66]. Direct fluorination of HDPE decreases the permeability of nonpolar liquids (C7H16, C6H6, C12H26, CCl4 [47]) but slightly influences the permeability of highly polar CH3OH [47]. The barrier properties of LDPE can be also improved under the direct fluorination: the loss of n-heptane and pentane can be reduced by a factor of 100 [66]. Direct fluorination was shown to decrease permeability of PVC, thermosetting resins, natural and synthetic fibers [67], polyurethane [3], LDPE, PP, and PET [63]. The addition of oxygen to fluorinating mixtures can provide better barrier properties for nonpolar liquids as compared to fluorinating mixtures without oxygen [2,3,66]. Direct fluorination inhibits the migration of plasticizers from polymers and improves thermal aging resistance [68]. Rubber sheets used in sealing electrolytic capacitors become impermeable to paste and gas upon fluorination [69,70].

Toughening of the pollution limitations and use in alcohol as admixture to the petrol to enhance ignition resulted in a strong need to improve the fluorination procedure. Permeability of petrol–alcohol mixtures through the walls of the fluorinated automotive polymer fuel tank is increased as compared with permeability of an undiluted petrol [71]. The indispensable presence of oxygen in a fluorinating mixture and in the reaction vessel results in a formation of polar groups such as –COF and –COOH and peroxy radicals on the polymer surface. Oxygen is a technology admixture in fluorine and is solved in the polymer bulk and absorbed on the polymer surface. Another source of oxygen is an absorbed water which reacts with fluorine and provides oxygen. Peroxy radicals may participate in the post-reactions inside the fluorinated layer, which lead to a scission of polymer chains and a formation of highly polar groups. All the mentioned factors result in worsening of polymer barrier properties when petrol–alcohol mixtures are used. In industrial applications, the temperature of fuel tanks (usually fabricated from HDPE) at the end of fluorination is around 55–65 °C; due to technology limitations, the time available for termination of radicals cannot exceed 15–20 min and a treatment technology should be a “dry” one. Concentration of radicals in fluorinated HDPE reaches sufficiently high values (up to 2.4·10^20 radicals per cm^3 of the fluorinated layer) and remarkably exceeds an appropriate value for the case of LDPE. ESR spectra consist of at least two types of radicals: peroxy type (~8 mT in width) and very broad spectrum (~25 mT in width) which can be attributed to fluoro-containing radicals. It was proposed that treatment of freshly fluorinated HDPE with gases (to provide dry technology), reacting very quickly with radicals, may result in enhancement of barrier properties of fluorinated HDPE. The kinetics of self-terminations of long-lived radicals and of the reactions of long-lived radicals with several gases have been studied at room temperature and at 55–65 °C for five varieties of industrially available HDPEs [2,4,6,7,10–12,28]. At 20–22 °C, radical concentration is decreased by a factor of 2 in 5–8 h after removing fluorine from the reaction vessel. It means that even in several hours after the end of fluorination, peroxy radicals can take part in reactions which may result in polymer-chain scissions and formation of highly polar groups. Those reactions definitely worsen the barrier properties of HDPE. An increase of temperature up to 60–65 °C results in a significant increase of the termination rate: the half-termination time of radicals is decreased to ~15 min. It was found that the post-treatment with triethylamine and NO at 60–65 °C resulted in a more than 10-fold decrease of the radicals concentration in 15 and 2–3 min, respectively. Permeability of undiluted petrol (grade “CEC-RF-02-99 Oxy 08-1.2” from “Haltermann”, Germany) and mixtures (5 % methanol + 95 % petrol) and (10 % ethanol + 90 % petrol) was studied for (a) virgin HDPE, (b) fluorinated only HDPE, and (c) fluorinated HDPE and post-treated with triethylamine and NO. The post-treatment of fluorinated HDPE with triethylamine or NO practically eliminates the negative influence of alcohol on the barrier properties of HDPE. It means that the permeability of HDPE films fluorinated and post-treated with triethylamine or NO does not depend
on the presence of methanol or ethanol in the petrol. Moreover, there is one additional advantage of the proposed method. As mentioned above, oxygen admixture in used fluorine provides negative influence on the barrier properties of fluorinated polymers via formation of peroxy radicals and highly polar groups. So it is necessary to purify fluorine from oxygen and to remove very carefully oxygen traces from the reaction vessel. The proposed method does not permit careful removal of oxygen from fluorine and from the reaction vessel, because the peroxy radicals can be terminated very quickly and those radicals will not take part in post-reactions. The method described above was patented [10–12].

**Improvement of the separation properties of polymer membranes**

Polymeric membranes can be used for the separation of gas mixtures such as He–CH₄, H₂–CH₄, H₂–CO₂, CO₂–CH₄, H₂–N₂, O₂–N₂, CO₂–H₂S, CH₄–CO₂–H₂–He, etc. There is, however, a common problem in a gas separation if a polymeric membrane is used: membranes with high gas permeability often have low gas-separation factor and, on the contrary, membranes with high separation factor have low permeability factors (Fig. 9). Direct fluorination results in a significant decrease of permeability of multiatomic gases (CH₄, C₂H₄, etc.) as compared to diatomic and monoatomic ones (H₂, He, etc.). So direct fluorination can be used to enhance the separation factor value α of polymeric membranes without significant reduction of the permeability value of small gases (He, H₂, etc.). Direct fluorination was used to enhance gas-separation properties of polymer membranes by some research. Authors of [72] fluorinated LDPE films and succeeded in an increase of the He/CH₄ separation factor from 2 to 100. Fluorination of poly(1-trimethylsilylpropyne) (PTMSP) and poly(1-trimethylgermylpropyne) resulted in an increase of a selectivity of He/CH₄ separation factor from 0.41 to 248 [73–75]. Fluorination of membranes fabricated from PSU, PS, PE, polyarylate, PC, etc. resulted in increase of O₂/N₂, N₂/CH₄, and CO₂/CH₄ separation selectivity by a factor of 2 to 3 [76]. The α value for H₂/CH₄ and CO₂/CH₄ pairs for aromatic PI membranes can be increased by factors of 23 and 3.3, respectively, under fluorine treatment, whereas permeability values of H₂ and CO₂ are decreased by factors of 3 and 21, respectively [77]. For PSU/polybutadiene block copolymer homogeneous membrane α value for CO₂/CH₄ mixture continuously increases from α = 7 (starting membrane) to 54 when the δₕ value increases from
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0 to 1.6 µm and goes down with δF when the latter is increased, whereas the permeability value of CO2 is decreased by a factor of 2.5–3 only when the α value reaches the maximum value [35]. Fluorination results in increase of O2/N2 selectivity for polytrimethylsilylpropyne (from 1.5 to 4.9) [73,74], polytrimethylgermylpropyne [75] and for Seragel (from 3 to 7.2) [35].

Fluorination of PSU ultrafiltration membranes results in an increase of the flux and decrease of the membrane fouling rate [78]. Direct fluorination improves the chemical resistance of polymers. Fluorinated PS and polyethylene terephthalate cannot be dissolved in those solvents where virgin polymers can be dissolved [2,4,6–9]. So direct fluorination of polymer membranes for separation of aggressive liquids and vapors should improve their durability.

As mentioned above, there is a common problem in gas separation when polymeric membranes are used: membranes with high gas permeability often have a low gas-separation factor, and, on the contrary, membranes with high separation factor have low permeability value (Fig. 9). The best membrane materials should lie at the upper right corner of Fig. 9, but at present, no materials, placed above the straight line in Fig. 9, were synthesized. So the following solution should be provided: to fluorinate commercially available membrane which possesses high permeability but low selectivity. Direct fluorination results in a significant decrease of permeability of large-size gases (CH4, C2H6, CO2, etc.) as compared with those of small size (H2, He, etc.). The selectivity of the membrane for (large and small size) pairs of gases will be enhanced without significant reduction of the permeability value with respect to small-size molecules. The selectivity values for He/CH4 mixture separation are shown in the Fig. 9 for virgin and fluorinated membranes and modules. It is evident that selectivity values for fluorinated membranes are placed above the straight line. Moreover, the decrease of He permeability after fluorination is relatively small.

We have studied the influence of direct fluorination on gas-separation properties of PI Matrimid hollow-fiber modules and PVTMS membranes [2,4,6–9,16,79]. It is necessary to emphasize that the degree of improvement of the separation selectivity depends on the quality of the starting fibers (uniformity of the upper separation layer, etc.). As mentioned above, direct fluorination results in a more significant decrease of permeability of large-size gases (CH4, C2H6, CO2, etc.) as compared with those of small size (H2, He, etc.). Fluorination of hollow-fiber PI membrane modules resulted in a significant—by a factor of up to 47 and 7, respectively—increase of selectivity of separation for He/CH4 and CO2/CH4 mixtures (Figs. 9 and 10). The permeability of He was not practically changed in that case.

The case of PVTMS influence of fluorination on selectivity is shown in Fig. 11. The effect of fluorination is most remarkable for the case of the He–CH4 pair. Selectivity of separation of the He/CH4 mixture depended on the treatment conditions and increased by a factor of 100 when the F2–O2 mixture was used for the treatment. In all the cases, the loss of He permeability did not exceed 40 % with respect to the virgin membrane. Selectivity of separation of the CO2–CH4 mixture can be increased by a factor of 5.4 (treatment with 33 % F2 + 67 % He mixture) and 7 (treatment with 60 % F2 + 40 % O2 mixture), but permeability of CO2 is decreased by a factor of 2.2 and 29, respectively. A summary of data for separation of the CO2–CH4 mixture is shown in Fig. 10. It becomes evident that direct fluorination results in a significant improvement of the CO2–CH4 selectivity, but a decrease of the CO2 permeability is more remarkable than in the case of He–CH4 selectivity. Hence, direct fluorination of PVTMS membranes and PI Matrimid 5218 hollow-fiber modules provides the possibility to “overjump” the so-called “Robeson boundary” (straight line in Fig. 9, corresponding to the highest level of permeability/selectivity for most investigated homopolymers, including PIs). It can be concluded that direct fluorination of flat membranes and hollow-fiber modules can be successfully used to enhance their gas-separation properties.

To demonstrate the effect of fluorination on the separation properties of real membranes, a computer simulation (software developed at the Topchiev Institute of Petrochemical Syntheses has been used) has been provided for the case of separation of the H2/CH4 = 20:80 mixture by Matrimid 5218 flat membrane (feed 1000 l/h, membrane productivity 100 l/(m2 h bar), pressure up 10 bar, pressure down 0.1 bar, membrane area 0.1 m2). For the case of virgin membrane, permeate composition is
94.8 % H₂ + 5.2 % CH₄, whereas fluorinated membrane exhibits a much better degree of separation: permeate composition is 99.3 % H₂ + 0.7 % CH₄.

Fluorinated polymer membranes can be successfully used to enhance the purification of natural gas from CO₂, purification of hydrogen from CO, and further use of purified hydrogen in fuel cells, correction of H₂/CO in a syngas (synthesized from methane or methanol) for further synthesis, separation of biogas components, separation of hydrogen and helium from the natural gas, separation of hydrogen and...
from the exhaust gases of the petroleum-chemistry industry and in ethylene synthesis, etc. In the metallurgy industry, fluorine-treated polymer membranes can be used as a cheaper alternative for the neon separation from the exhaust gases.

### Adhesion and printability properties: Reinforcement of polymer composites

One of the main disadvantages of polyolefins and some other polymers is a low adhesion, which is due to a very low total surface energy \( \gamma \) and low polarity of the polymer surface (i.e., the polar component \( \gamma^p \) is close to zero). Upon direct fluorination, the polar component of the surface energy can be greatly increased [82,83]. For example, the \( \gamma^p \) value for PE can be increased up to 40–43 mJ m\(^{-2}\) when oxygen is introduced into the fluorinating mixture [83]. Direct fluorination was shown to improve adhesion of polyolefins (HDPE) [63,84–86], LDPE [85], ethylenevinyl acetate copolymers [87], rubber [88], PP [63,89], polymers of aliphatic mono-1-olefins and elastomeric, resinous polymers of conjugated dienes and vinyl-substituted aromatic compounds [90], poly(arylene sulfide) [91], polyamides, polyethers [92], butadiene-styrene copolymer, PE-vinylacetate copolymer [86], and other polymers [93]. Wettability (printability), hydrophilicity, and hydrophobicity of polymers can also be modified [15,92,94,95,101].

The possible commercial applications of the enhancement of adhesion are as follows: enhancement of adhesion of polymer fibers and fabric to rubber, improvement of dye ability of polymer goods, reinforcement of polymer composites, increased resistance to delamination in coated flexible films [2,3,63]. Direct fluorination of fibrous plastics was used to strengthen and reinforce composite materials, such as cementitious and metal components [13,96,97]. Adhesive bonding of various polymers, such as PP, polybutyleneterephthalate and its blends, and polyetheretherketone [99,100] can be improved by fluorination. Oxyfluorination (treatment with \( F_2-O_2 \) mixtures) results in a higher (as compared with a treatment with oxygen-free fluorinating mixtures) adhesion of PP, and such an effect is a long-lasting one [14].

The influence of fluorination of one of the components of polymer-fiber composites can be demonstrated by the following example. Short-fiber reinforced polymeric composites are important due to the advantages in outstanding mechanical properties, low cost and processing. \( P \)-Phenylene terephthalamide (i.e., Kevlar\(^{\text{®}} \)) is a well-known synthetic polymeric fiber for high-performance composite applications due to its high specific strength, high modulus, high thermal and chemical resistance, and low electrical conductivity when compared to metallic or carbon glass fibers. However, a poor interfacial adhesion affects the chemical and thermal properties of the composites. Thermal and mechanical properties of composites fabricated from Kevlar fiber, modified by direct fluorination and oxyfluorination, and EP copolymer were studied in [102]. It was shown, that the thermal and mechanical properties of composite material based on EP copolymer reinforced with 1.4 % of Kevlar fibers can be markedly enhanced under oxyfluorination of Kevlar fibers: the first decomposition temperature of the composite material is increased by 36 °C, tensile strength is increased by 22 %, and tensile modulus by 89 % [102]. For the case of composite (PP + 2.5 % Twaron\(^{\text{®}} \) fibers) fluorination of fibers resulted in an increase of the composite tensile strength by 38 % [103]. A more pronounced effect was obtained for the case of a composite on the base of LDPE and 10 % (wt) of ultra-high-molecular-weight polyethylene fibers. Fluorination of fibers resulted in an increase of the composite tensile strength by a factor of ~2 and tensile modulus by a factor of ~1.5 [104].

### CONCLUSION

The fluorination of all the studied polymers is a diffusion-controlled process. This indicates that the rate of formation of a fluorinated layer is limited by the rate of penetration of fluorine \( F_2 \) through the fluorinated polymer layer into the untreated layer. The fluorinated and untreated polymer layers are separated by a very thin transient boundary layer where the majority of the chemical reaction takes place.
The direct fluorination of H–C-based polymers during a sufficiently long period of time results in a practically total disruption of C–H, C–OH, and C–Si bonds and saturation of double (conjugated) bonds followed by a formation of C–F, C–F₂, and C–F₃. Also, C=O-containing groups are formed.

The dependence of the fluorinated layer thickness $\delta_F$ on fluorination time $t$ and fluorine partial pressure $p_F$ is described by the following formula: $\delta_F = \frac{B}{k^{0.5}} + \text{const}$, where $\text{const}$ value can be neglected for all the studied polymers except HDPE, LDPE, and PVF. $B$ and $k$ values were measured. The rate of formation of a fluorinated layer increases with fluorine partial pressure and temperature and is slightly affected by the presence of He and/or N₂ and Ar in the fluorinating mixture. O₂ and HF inhibit the fluorination rate.

Fluorination results in a decrease of the refraction index of polymers. The density of fluorinated layer substantially exceeds the density of the virgin polymer.

The fluorination of studied polymers is a chain-radical process. Initiation of the reaction takes places via exothermic reaction of molecular fluorine with C–H or C=C bond and not via the dissociation of molecular fluorine. Peroxy RO₂• and fluororadicals are present in the fluorinated polymers in a relatively large concentration. Those radicals are long-life radicals: their amount is decreased by a factor of 2 in several hours. Termination of those radicals can be highly accelerated when several gases are in contact with a fluorinated polymer.

Direct fluorination improves to a great extent the barrier properties of polymer vessels, bottles, and packaging films and envelopes; gas-separation properties of polymer membranes; adhesion and printability properties of polymer articles; and mechanical properties of polymer-based composite materials.

REFERENCES

Surface modification of polymers by fluorination

