



## Research Paper

## Gas Selective Properties of Poly(4-Methyl-1-Pentene) Modified by Gas Phase Fluorination

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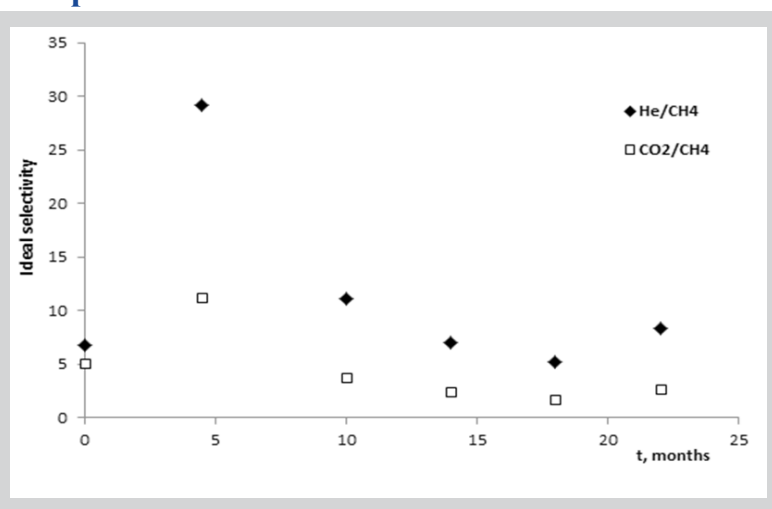
## Keywords

Poly(4-methyl-1-pentene)  
 Fluorination  
 Gas permeability  
 Stability with time

## Highlights

- PMP fluorinated possesses an increased selectivity of He/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub>.
- P values of CO<sub>2</sub> and CH<sub>4</sub> are decreased during a few months and then returned.
- Modified PMP demonstrates a good C<sub>1</sub>-C<sub>4</sub> alkanes and He selectivity.

## Graphical abstract



## Abstract

Fluorine-containing polymers have a number of valuable physical and chemical properties, such as high chemical and heat resistance, high mechanical strength and highly selective gas separation characteristics. One of the ways to produce fluoropolymer membranes is through surface fluorination. The modification of commercial polymers with membrane properties, poly(4-methyl-1-pentene) (PMP) in particular, is of special interest. PMP is widely used in the creation of protective coatings in microelectronics and it is used in membrane oxygenation. This paper presents new results for the gas-phase fluorination of PMP films with improved gas separation characteristics. The fluorination is confirmed by infrared (IR) spectroscopy. It is shown that such modification of PMP under "soft" conditions leads to an increase in the ideal selectivity of He/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> by up to 2.0 and 4.3 times, respectively, which is in contrast to data described in the available literature. Gas separation properties of PMP films were monitored for 22 months. It is shown that the permeability coefficients of CO<sub>2</sub> and CH<sub>4</sub> after 5 months decrease by 2.7 and 6.0 times, respectively, and then return to values below those for virgin PMP films. The permeability coefficients of He pass through a minimum as well and then return at values higher than the initial ones. The permeability of C<sub>1</sub>-C<sub>4</sub> alkanes in fluorinated PMP was estimated by using the correlation approach. It is shown that modified PMP has a practical application in the separation of the He from natural gas and for the separation of lower hydrocarbons as its components.

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## 1. Introduction

Fluorine-containing polymers are a class of materials that attract the attention of researchers due to a combination of such properties as: high chemical resistance over a wide range of temperatures, excellent dielectric properties, high resistance to ultraviolet destruction, and exceptional optical, electrical and surface properties. These materials are resistant to many chemicals, including acids, bases, organic solvents, oils and strong oxidants. These properties led to the commercial use of fluorine-containing polymers in numerous fields including electronics, space exploration, chemical,

medical and other industries [1]. Due to a variety of valuable physical and chemical properties, as well as high separation characteristics, many fluorine-containing polymers are of interest in membrane technology.

One representative group of fluorine-containing polymers is the perfluorinated polymers. As an example, membranes based on polyvinylidene fluoride and polytetrafluoroethylene are used in processes such as ultra and microfiltration, membrane distillation and pervaporation etc. [2]. In membrane gas separation, perfluoropolymers such as Teflon® AF [3],

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Cytop™ [4] and Hyflon® AD [5] are used because of their relatively high gas permeability, for example oxygen permeability at room temperature for Teflon AF 2400 is 1140 Barrer [6, 7], Hyflon AD60 is 69 Barrer and Cytop 69 is 16 Barrer [1]. Membranes based on these polymers are resistant to the plasticisation effects caused by the solubility of hydrocarbons in polymers [2, 8]. Recently, new perfluorinated polymers that can be used as membrane materials have been synthesised. These polymers combine relatively high gas permeability and high selectivity for some gas pairs including He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, N<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/CH<sub>4</sub> etc. compared with commercial perfluoropolymers [8, 9]. However, the practical use of specially synthesised fluorine-containing polymers is limited due to their high cost and complexity of synthesis. It should be noted that the required membrane properties of polymers are often determined by their surface properties [10]. Therefore, it is easier, cheaper and much more convenient to carry out controlled surface treatment of frequently used polymers. One of the ways of surface modification of polymers is direct gas phase fluorination. Surface fluorination involves sorption and diffusion of fluorine in the polymer and subsequent chemical reactions. The practical application of direct gas phase fluorination in membrane gas separation makes it possible to improve the separation properties of polymeric membranes and to increase their chemical stability [11]. Moreover, direct gas phase fluorination can be used to modify polymer films and membranes of any shape as well as membrane modules. In particular, the gas phase fluorination of membrane polymers is directed to increasing the selectivity of He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation [12-17]. It should be noted that the modified membranes for gas separation processes are actively developed up to now [18-20].

Of special interest is the modification of commercially available polymers with membrane properties, in particular poly(4-methyl-1-pentene) (PMP). PMP is widely used in the creation of protective coatings in microelectronics and it is used in membrane oxygenation (membranes in the form of hollow fibres) [21-24]. Mohr et al. [17] investigated the process of PMP direct gas phase fluorination to improve the gas separation properties of polymeric membranes based on it. Two-sided gas phase fluorination was carried out for TPX™ films and composite membranes with a selective PMP layer (PMP was cast from the solution in cyclohexane). It was shown that PMP is difficult to use to create a fluorinated polymer: the gas phase modification takes several tens of hours. The gas separation characteristics were improved after fluorination but it transpired that fluorine contained an inhibitor (oxygen impurity) [17]. The modification conditions did not correspond to the optimal ones.

This paper presents the results of gas phase fluorination, without any inhibitor impurity, in order to estimate the actual potential of surface fluorination as well as improve the gas separation characteristics of PMP membranes. Poly(4-methyl-1-pentene) is a semi-crystalline polymer with a

glass-transition temperature of approximately 30°C and it has similar densities in the crystalline and amorphous phases. PMP has average values of gas permeability and selectivity [22, 25, 26]. PMP hollow fibre membranes are obtained by a reagent-less extrusion method, which is a valuable ecology friendly membrane preparation method [21]. It should be emphasised that the fluorination effect can be unstable over time [17]. In this respect, the aim of the present work was the systematic study of the direct gas phase fluorination of the semi-crystalline membrane polymer with a permeable crystalline phase and the study of the gas separation properties of modified membranes over time.

## 2. Experimental

### 2.1. Material and methods

Polymeric films (both virgin and fluorinated) based on PMP were used in this work. The film thickness was  $50 \pm 1 \mu\text{m}$ . PMP was obtained by suspension polymerisation of 4-methyl-1-pentene in the presence of catalytic systems based on a titanium-magnesium catalyst and organic aluminium compounds in an organometallic catalysis laboratory (A. V. Topchiev Institute of petrochemical synthesis RAS) [27]. The structural formula of the PMP monomer unit is shown in Figure 1. PMP films were obtained by heating the pellets to a temperature of 523 K followed by pressing the melt to obtain a flat work-piece that is then rolled between rollers with a fixed gap in order to produce a sample with the desired thickness. A differential scanning calorimetric (DSC) thermogram of the virgin PMP film (see Figure 2) shows that  $T_g = 30^\circ\text{C}$ ,  $T_m = 233^\circ\text{C}$  and the degree of crystallinity is 69%.

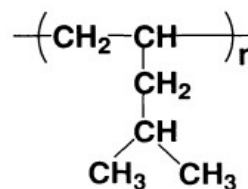


Fig.1. Structural formula of PMP monomer unit.

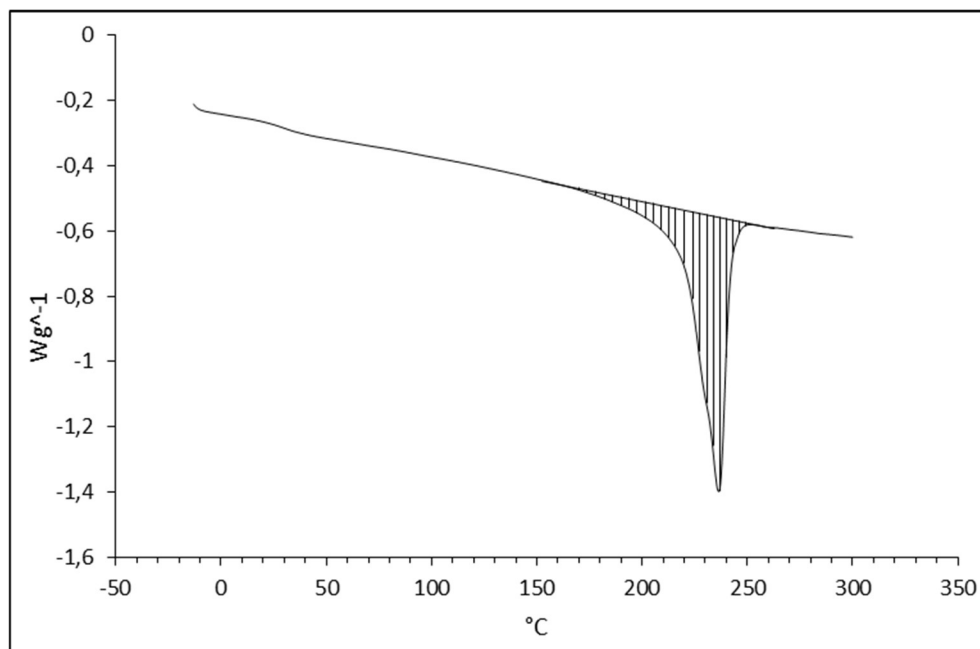


Fig. 2. DSC thermogram of the virgin PMP film

One-sided gas phase fluorination in static conditions was used to modify the PMP films. The amount of impurities (mainly oxygen) in fluorine was less than 0.1 vol. % [28]. The polymeric films were placed in a closed reactor which was pumped to a residual pressure of  $10^{-1}$ - $10^{-2}$  Torr. The reactor was filled with fluorine or its mixtures. The fluorine consumption in the reactor did not exceed 5%. The experimental configuration for gas phase fluorination is shown in Figure 3.

Preliminary experiments of gas phase fluorination were carried out and the results lead to the following fluorination conditions being chosen: a composition mixture of 10%  $F_2$  + 90%  $N_2$ , a fluorination time of 1 and 4 hours exposure at temperature of 26°C. After the fluorination process the samples were removed, vacuum pumped during one day and stored on air.

## 2.2. Chemical structure analysis

The chemical structure analysis of fluorinated films was carried out by IR spectroscopy (using an IR microscope Hyperion 2000) conjugated with an IR Fourier spectrometer (Brucker IFS-66 v/s) using a spectral range of 4000 to 600  $cm^{-1}$  and a resolution of 2  $cm^{-1}$ . The reflection spectra from the surface of the initial film were measured before and after fluorination on both sides. The mathematical processing of the spectra was carried out in the OPUS-7 software package and the IR spectra of the initial and modified PMP films are shown in Figure 4.

It was shown that the gas phase fluorination of PMP requires "hard" process conditions in comparison with other conventional polymers: according to IR spectroscopy fluorination most of it fully occurs within 1 to 4 hours. All the spectra of the modified films contain bands from the initial PMP from stretching vibrations of C-H bonds (in the 2970-2840  $cm^{-1}$  region), from deformation vibrations of methyl and methylene groups (at 1462  $cm^{-1}$  and 1380-1365  $cm^{-1}$ ), from skeletal vibrations of C-C bonds (at 921  $cm^{-1}$ ) and very intense bands from C-F bonds (in the range of 1250-1000  $cm^{-1}$ ). It should be noted that as the fluorination time increases, the intensity of the band of C-F bonds increases (similar to the data found in [29]). As we can see in Figure 4, for a sample fluorinated for one hour the difference in the intensity of the absorption bands of C-F bonds from the modified and unmodified sides is noticeable. In addition, all the spectra contain the bands of C=O groups and C=C bonds in the 1740  $cm^{-1}$  and 1640-1645  $cm^{-1}$  region, respectively, as well as the bands of -OH bonds in the 3500-3300  $cm^{-1}$  region;

this is indicative of the oxidation processes occurring to an insignificant degree in the polymer, upon modification. From the type of spectrum in the absorption region of C-F bonds (see Figure 5) it can be assumed that fluorination is not a selective process, since the  $R_3CF$  (1170  $cm^{-1}$ ),  $R_2CF_2$  (1150  $cm^{-1}$ ), and  $RCF_3$  (1105 and 1203  $cm^{-1}$ ) bands are present in the 1250-1000  $cm^{-1}$  region. Analysis of the spectra, shows that the 1170  $cm^{-1}$  band, from monofluorinated carbon atoms, is the most intensive in the sample with a shorter fluoridation time. Therefore, it is suggested that the fluorination of tertiary carbon atoms takes place first and then the secondary and primary carbon atoms after that (i.e. the main macrochain and the side group of the PMP monomer unit).

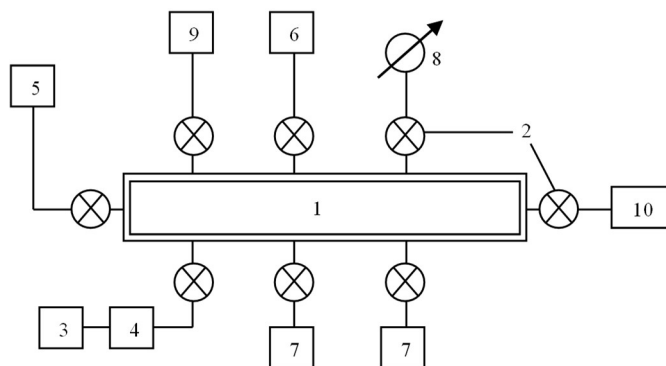


Fig. 3. Experimental configuration for gas phase fluorination: 1. Rationing block; 2. Gas valves; 3. Forevacuum pump; 4. Trap with silica gel and sodium fluoride; 5. Tank for the mixture preparation; 6. Fluorine storage tank; 7. Gas cylinder; 8. Vacuum meter standard; 9. Vacuum meter with ionizing thermocouple; 10. Reactor for gas phase fluorination.

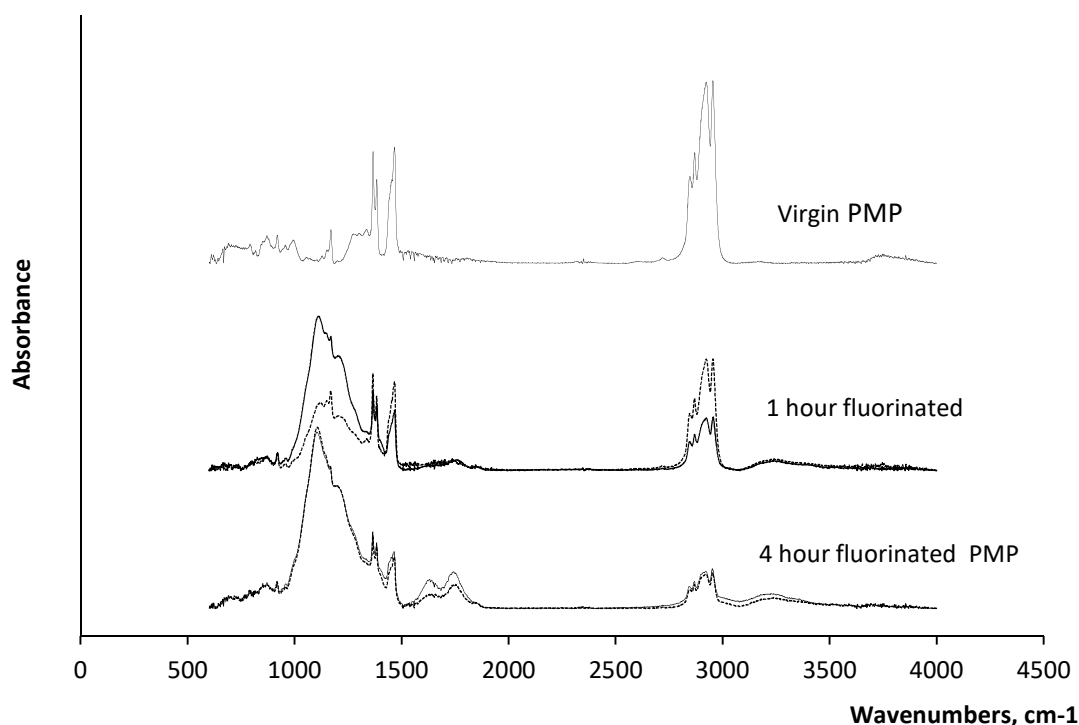


Fig. 4. IR spectra of virgin and fluorinated PMP films. Solid and dashed lines correspond to the modified and unmodified sides of the film, respectively.

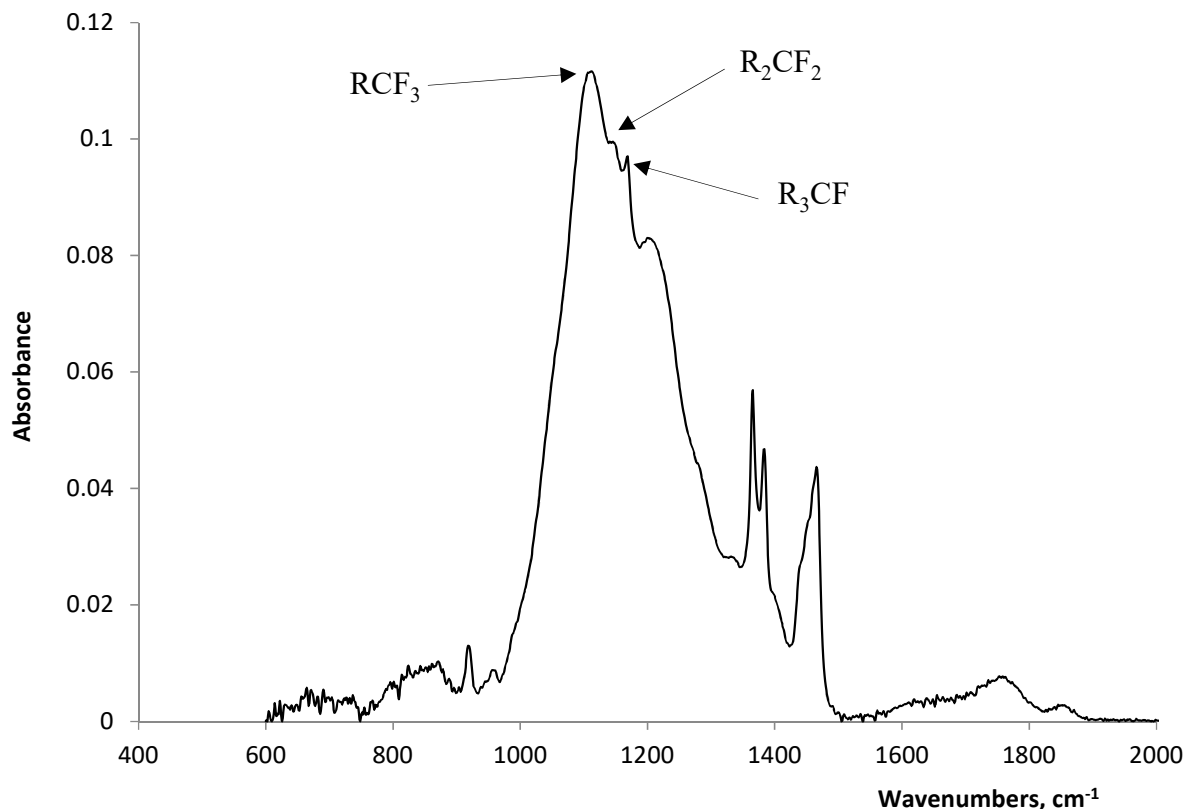


Fig. 5. IR spectrum in the absorption region of C-F bonds.

### 3. Results and discussion

#### 3.1. Gas permeability coefficients

The gas permeability of the He, CO<sub>2</sub>, and CH<sub>4</sub> for PMP films was measured by a differential method with gas-chromatography analysis. Gases (He, CH<sub>4</sub> and CO<sub>2</sub>) of purity > 99% were used without further purification. The experimental measurements were carried out with a partial drop pressure across the membrane of 1 bar in the temperature range of 22-25°C. Argon and helium were used as the gas carriers. The experimental apparatus for determination of gas transfer parameters is described in detail in [30]. The gas transfer parameters were measured from the modified and unmodified sides of the films in order to take into account the possible appearance of gas transfer anisotropy.

The permeability coefficients of the He, CH<sub>4</sub> and CO<sub>2</sub> for fluorinated PMP films were determined experimentally and the results are shown in Table 1.

Table 1  
Gas permeability coefficients for PMP films

Sample	Fluorination time, h	P, Barrer			Ideal selectivity	
		He	CO <sub>2</sub>	CH <sub>4</sub>	He/CH <sub>4</sub>	CO <sub>2</sub> /CH <sub>4</sub>
Virgin PMP	0	111.0	84.0	16.6	6.7	5.1
PMP ↑*	1	95.0	59.5	13.2	7.2	4.5
PMP ↓**	1	84.0	55.4	10.9	7.7	5.1
PMP ↑	4	81.8	33.0	2.1	39.0	15.7
PMP ↓	4	81.3	29.7	3.5	23.2	8.5

\* Permeability in direction from unmodified side of PMP; \*\* permeability in direction from modified side of PMP

Table 2  
Gas permeability coefficients of CH<sub>4</sub> for virgin and fluorinated polymeric films

Polymeric films	PMP (l=51 μm)	PMP* (l=50 μm)	PVTMS (l=33 μm)	PS* (l=76 μm)
P, Barrer (initial values)	16.6	18.5	17.0	0.28
Fluorination conditions	C <sub>F</sub> vol. = 10 %, treatment time - 240 min	C <sub>F</sub> vol. = 2 %, treatment time - 240 min	C <sub>F</sub> vol. = 1 %, treatment time - 10 min	C <sub>F</sub> vol. = 2 %, treatment time - 300 min
P, Barrer (after modification)	2.8	5.0	6.0	0.22
Ref.	Present paper	[17]	[31]	[32]

\* Methane gas permeability coefficients values for fluorinated PMP and PS films are taken from Figure 5 [17] and Figure 6 [32].

Table 2 presents the comparison of the methane permeability coefficients for the virgin and fluorinated films based on PMP, poly(vinyltrimethylsilane) (PVTMS) and polysulfone (PS). Data on methane are only available for this comparison. As can be seen from the Table 2 a decrease in the permeability coefficients of methane after fluorination is observed for all glassy polymers.

In general, it can be seen that the gas-phase fluorination of PMP films leads to a slight permeability decrease of helium, a greater permeability decrease of carbon dioxide and a significant decrease in the permeability of methane (Table 1). Thus, for the most fluorinated film, the helium permeability decreased by 26%, whilst for CO<sub>2</sub> and CH<sub>4</sub> it decreased by up to 2.7 and 6.0 times, respectively. It should also be noted that the values of the permeability coefficients obtained for the two sides of the films (modified and

unmodified) only differ insignificantly. The greatest difference was observed for methane. It was also noted in [17] that the gas phase fluorination of PMP films lead to a decrease in the permeability of hydrogen by approximately 15%, while the methane permeability decreased by 5.6 times. However, this effect was observed after 96 hours of fluorination. In our case, it was shown that gas phase fluorination initially leads to a significant improvement in the gas separating properties of PMP. So, the ideal selectivity for CO<sub>2</sub>/CH<sub>4</sub> and He/CH<sub>4</sub> pairs for the virgin PMP was 5.1 and 6.7, respectively. For the film fluorinated for 4 hours, the ideal selectivity for CO<sub>2</sub>/CH<sub>4</sub> and He/CH<sub>4</sub> was 11.2 and 29.1, respectively. The average permeability values obtained from both the modified and reverse sides of the films were used to evaluate the selectivity.

### 3.2. Gas diffusion coefficients

In the present work, the gas diffusion coefficients for fluorinated PMP films were determined for the first time. There are no published data of the gas diffusion coefficients for modified PMP samples. The procedure for the gas diffusion determination is described in [30, 33] and the results are presented in Table 2. From the data in Table 2, it can be seen that the gas diffusion coefficients obtained for fluorinated samples are lower than those for virgin PMP. Moreover, as the fluorination time increases, the diffusion coefficients decrease significantly.

**Table 2**  
Gas diffusion coefficients for PMP films

Sample	Fluorination time, h	D*10 <sup>7</sup> , cm <sup>2</sup> /c	
		CO <sub>2</sub>	CH <sub>4</sub>
Virgin PMP	0	3.40	2.50
PMP ↑	1	3.01	1.30
PMP ↓	1	2.97	1.48
PMP ↑	4	2.48	0.56
PMP ↓	4	1.72	0.47

Thus, fluorination of PMP leads to an improvement in the membrane gas separation properties, probably due to a dramatic decline in the diffusion mobility (for example, the methane diffusion coefficient decreases by a factor of 5). This effect could be associated with an increase in the sample density due to the replacement of hydrogen atoms by more "massive" fluorine atoms.

### 3.3. Stability of the gas separation properties of fluorinated PMP films over time

Despite the advantages of membrane gas phase fluorination, such modification methods do not find a wide application since the stability of fluorinated films over time is not known. In the present study, the stability of fluorinated films were determined for the samples fluorinated during 4 hours. The gas transfer parameters of fluorinated films were measured at regular intervals for 22 months. Figure 6 shows the change in the relative intensity of the absorption bands of C-F bonds. The band of C-C bonds was selected as an internal standard in the intensity change estimation, since the intensity of those bonds barely changed.

Figure 6 shows how the relative intensity of absorption bands of C-F bonds decreases with time. These changes with time might have several causes. Firstly, one might speculate that there is mechanical destruction of the sample when the densities of the fluorinated and non-fluorinated phases of the sample are significantly different. Secondly, there is some mechanism of chemical defluorination when interacting with moisture and oxygen in the air. The changes in the gas permeability coefficients of He, CH<sub>4</sub>, CO<sub>2</sub> for fluorinated PMP films as a function of time after fluorination are shown in Figure 7.

As could be observed in Figure 7, the gas permeability coefficients of all studied gases decrease for a few months after fluorination. However, further investigation showed that fluorination leads to an increase in the gas permeability coefficients. The permeability coefficients of CO<sub>2</sub> and CH<sub>4</sub>

decrease by 2.7 and 6.0 times, respectively, and then return to values below those for the virgin PMP films. The permeability coefficients of He pass through a minimum as well and then returned to values higher than the initial ones.

Figure 8 shows the change in the diffusion coefficients of CO<sub>2</sub> for the most fluorinated (4 hours) PMP films. As noted before, the diffusion coefficients of CO<sub>2</sub> decrease for a few months after fluorination. However, a slight increase in the diffusion coefficients can be observed, which is apparently caused by a change in the density of the sample.

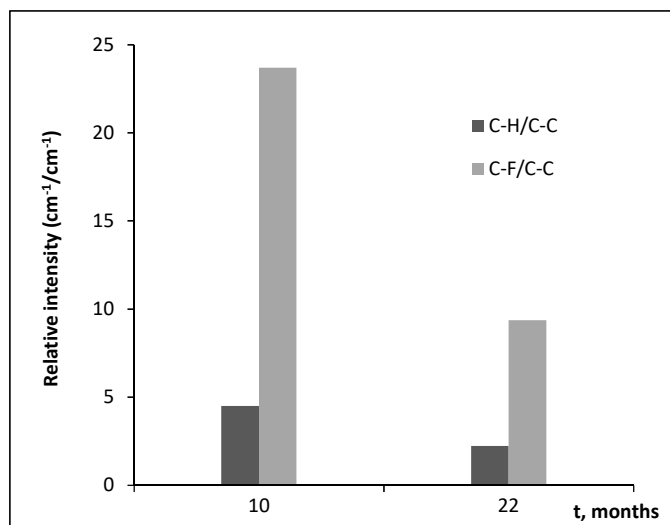


Fig. 6. Relative intensities of the bands in the fluorinated samples spectra.

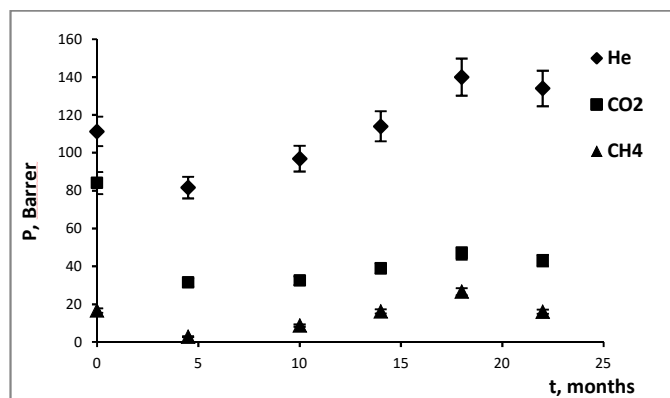


Fig. 7. Dependence of the gas permeability coefficients for fluorinated PMP films over time.

It should be noted that the increase in permeability leads to a decrease in the ideal selectivity for He/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> pairs with time (see Figure 9). Thus, the ideal selectivity for CO<sub>2</sub>/CH<sub>4</sub> decreases to 2.7 and for the He/CH<sub>4</sub> it decreases to 8.4 after 22 months from the moment of fluorination.

The defluorination of PMP is noted in [17] as well. However, it has been shown that for composite membranes the permeability of oxygen and methane decreases in the first month after fluorination, after which it begins to levelled off [17]. It can be noted that in our case, the change in methane permeability is insignificant over time.

### 3.4. The permeability estimation of C<sub>1</sub>-C<sub>4</sub> alkanes through fluorinated PMP films

It is known that PMP is resistant to the effects of lower hydrocarbons. As with other semi-crystalline polyolefins, there are no solvents which will dissolve PMP at room temperature [19]. It is experimentally difficult to determine the gas transfer parameters of C<sub>2</sub> + alkanes in fluorinated PMP. Therefore, attempts to estimate the gas permeability coefficients of lower hydrocarbons were made by using a correlation approach [34, 35] and available experimental data. Thus, the correlation of the diffusion coefficients D with the molecule cross section is known for the inert and a number of polyatomic gases and is described by equation (1):

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$$\log D_i = K_1 - K_2 d_{efi}^2 \quad (1)$$

The values of the gas solubility coefficients S increase exponentially with the Lennard-Jones constant (equation (2)):

$$\log S_i = K_3 + K_4 (\epsilon_i/k) \quad (2)$$

The general expression for estimating the gas permeability coefficient is described by equation (3):

$$\log P_i = \log D_i + \log S_i = K_1 - K_2 d_{efi}^2 + K_3 + K_4 (\epsilon_i/k) \quad (3)$$

The experimental data obtained in this work were used in a system of three linear equations (4) which combine the kinetic and thermodynamic components of the transport processes:

$$\begin{cases} \log P_{He} = K_1 + K_3 - K_2 d_{efHe}^2 + K_4 (\epsilon/k)_{He} \\ \log P_{CO_2} = K_1 + K_3 - K_2 d_{efCO_2}^2 + K_4 (\epsilon/k)_{CO_2} \\ \log P_{CH_4} = K_1 + K_3 - K_2 d_{efCH_4}^2 + K_4 (\epsilon/k)_{CH_4} \end{cases} \quad (4)$$

The solution of the system (4) and the use of data on the cross section and the Lennard-Jones constant for C<sub>1</sub>-C<sub>4</sub> alkanes made it possible to estimate the permeability and selectivity of modified PMP samples. The results are shown in Figures 10 and 11. As can be seen from the given data, the separation selectivity of helium-containing mixtures with C<sub>2</sub> + alkanes can reach values of 100 to 1500 units, which is of practical interest for the separation processes of helium from natural gas. In addition, the modified membranes can be efficiently used to separate mixtures of lower hydrocarbons.

The results obtained, based on the correlation analysis, are of potential interest for technologies involved in the separation and processing of natural gas components.

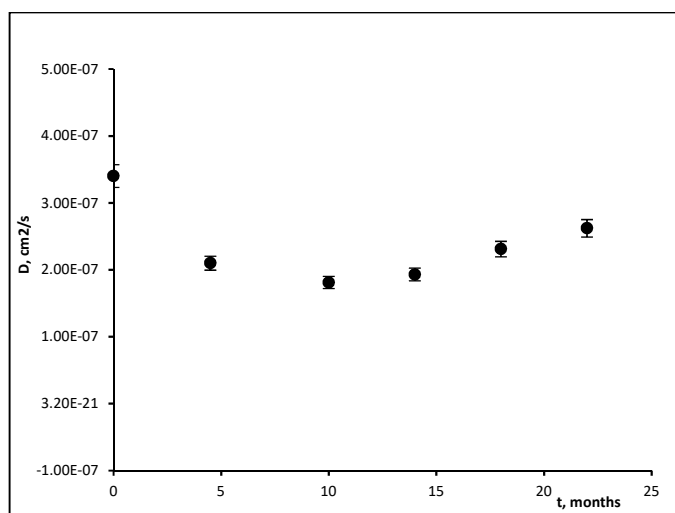


Fig. 8. Dependence of CO<sub>2</sub> diffusion coefficients for fluorinated PMP films with time.

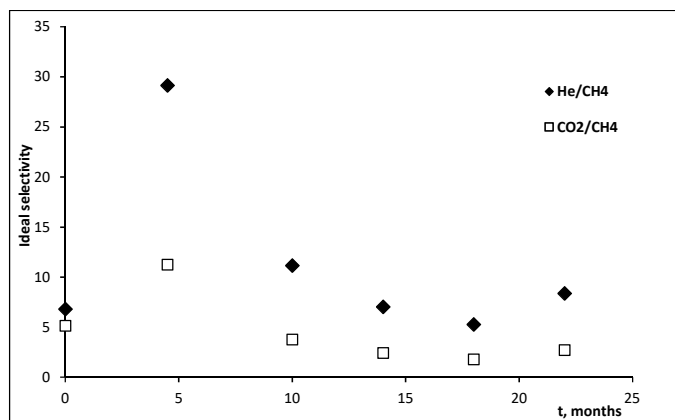


Fig. 9. Dependence of the ideal selectivity for fluorinated PMP films over time.

The defluorination of PMP is noted in [17] as well. However, it has been shown that for composite membranes the permeability of oxygen and methane decreases in the first month after fluorination, after which it begins to level off [17]. It can be noted that in our case, the change in methane permeability is insignificant over time.

### 3.4. The permeability estimation of C<sub>1</sub>-C<sub>4</sub> alkanes through fluorinated PMP films

It is known that PMP is resistant to the effects of lower hydrocarbons. As with other semi-crystalline polyolefins, there are no solvents which will dissolve PMP at room temperature [19]. It is experimentally difficult to

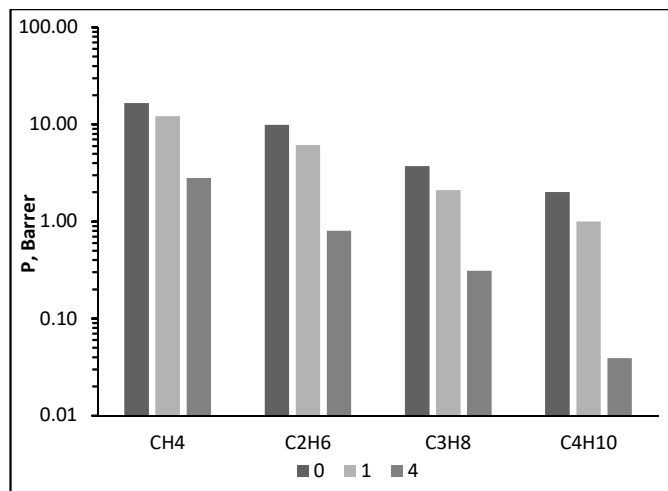


Fig. 10. Dependence of the gas permeability coefficients for the initial and fluorinated PMP: 0 – initial PMP, 1- one hour fluorination, 4 – four hours fluorination.

#### 4. Conclusions

In this paper, the results of gas phase fluorination of PMP films to improve gas separation characteristics are presented. The gas phase fluorination conditions were selected and it was shown that the gas phase fluorination of PMP under “soft” conditions (from 1 to 4 hours) leads to an increase in the ideal selectivity of He/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> by 2.0 and 4.3 times, respectively. This contrasts with the tens of hours for methods described in the existing literature. It was shown that fluorination leads to selectivity improvement of gas separation. Gas separation properties of PMP films were monitored for 22 months. The permeability coefficients of CO<sub>2</sub> and CH<sub>4</sub> decreased by 2.7 and 6.0 times, respectively, and then returned to values below those for the virgin PMP films. The permeability coefficients of He passed through a minimum as well and then returned to values higher than the initial values. These changes over time might be probably caused by partial defluorination of the samples. The permeability of C<sub>1</sub>-C<sub>4</sub> alkanes in fluorinated PMP was estimated by using the correlation approach. It has been shown that modified PMP can find practical applications in the separation of He from natural gas and for the separation of lower hydrocarbons into its component parts.

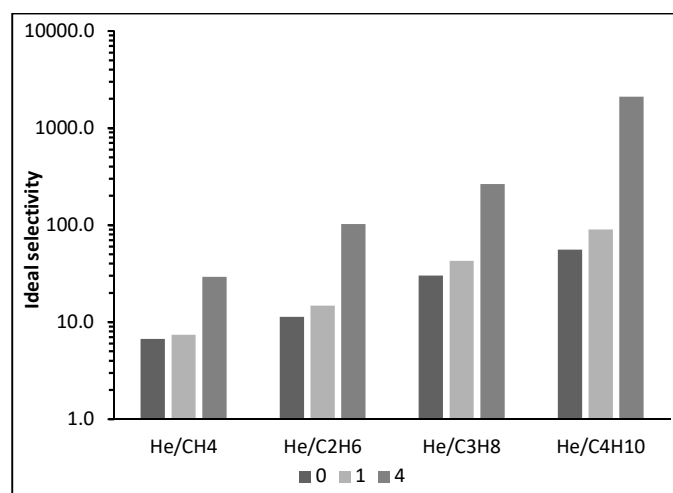


Fig. 11. Dependence of the ideal selectivity for the initial and fluorinated PMP: 0 – initial PMP, 1- one hour fluorination, 4 – four hours fluorination.

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#### References

- [1] T.C. Merkel, I. Pinnau, R. Prabhakar, B.D. Freeman, Gas and vapor transport of perfluoropolymers. Materials Science of Membranes for Gas and Vapor Separation, Wiley, Chichester, 2006.
- [2] Z. Cui, E. Drioli, Y.M. Lee, Recent progress in fluoropolymers for membranes, Prog. Polym. Sci. 39 (2014) 164-198.
- [3] Edward N. Squire, Glen Mills, Pa, Amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole, US Patent 4754009, 1988.
- [4] Masaru Nakamura, Isamu Kaneko, Kazuya Oharu, Gen Kojima, Masashi Matsuo, Shunichi Samejima, Motoi Kamba, Cyclic polymerization, US Patent 4910276, 1990.
- [5] Pasqua Colaianna, Giulio Brinati, Vincenzo Arcella, Amorphous perfluoropolymers, US Patent 5883177, 1999.
- [6] P.R. Resnick, W.H. Buck, In: Modern Fluoropolymers: High Performance Polymers for Diverse Applications. Ed. J. Scheirs, Wiley, Chichester (1997) 397.
- [7] A.Y. Alentiev, Y.P. Yampolskii, V.P. Shantarovich, S.M. Nemsr, N.A. Plate, High

- transport parameters and free volume of perfluorodioxole copolymers, J. Membr. Sci. 126 (1997) 123-132.
- [8] Y. Okamoto, H. Zhang, F. Mikes, Y. Koike, Z. He, T.C. Merkel, New perfluorodioxolane-based membranes for gas separations, J. Membr. Sci. 471 (2014) 412-419.
- [9] N.A. Belov, A.A. Zharov, A.V. Shashkin, M.Q. Shaikh, K. Raetzke, Y.P. Yampolskii, Gas transport and free volume in hexafluoropropylene polymers, J. Membr. Sci. 383 (2011) 70-77.
- [10] K.C. Khulbe, C. Feng, T. Matsuura, The art of surface modification of synthetic polymeric membranes, J. Appl. Polym. Sci. 115 (2010) 855-895.
- [11] A.P. Kharitonov, Direct fluorination of polymers – From fundamental research to industrial applications, Prog. Org. Coat. 61 (2008) 192-204.
- [12] J.D. Le Roux, D.R. Paul, J. Kampa, R.J. Lagow, Modification of asymmetric polysulfone membranes by mild surface fluorination. Part I. Transport properties, J. Membr. Sci. 94 (1994) 121-141.
- [13] J.M. Mohr, D.R. Paul, I. Pinnau, W.J. Koros, Surface fluorination of polysulfone asymmetric membranes and films, J. Membr. Sci. 56 (1991) 77-98.
- [14] J.D. Le Roux, V.V. Teplyakov, D.R. Paul, Gas transport properties of surface fluorinated poly(vinyltrimethylsilane) films and composite membranes, J. Membr. Sci. 90 (1994) 55-68.
- [15] M. Langsam, M. Anand, E.J. Karwacki, Substituted propyne polymers: In. Chemical surface modification of poly[1-(trimethylsilyl) propyne] for gas separation membranes, Gas Sep. Purif. 2 (1988) 162-170.
- [16] D.A. Syrsova, A.P. Kharitonov, V.V. Teplyakov, G.-H. Koops, Improving gas separation properties of polymeric membranes based on glassy polymers by gas phase fluorination, Desalination 163 (2004) 273-279.
- [17] J.M. Mohr, D.R. Paul, T.E. Mlsna, R.J. Lagow, Surface fluorination of composite membranes. Part I. Transport properties, J. Membr. Sci. 55 (1991) 131-148.
- [18] W.N.W. Salleh, A.F. Ismail, Carbon membranes for gas separation processes: Recent progress and future perspective, J. Membr. Sci. Res. 1 (2015) 2-15.
- [19] Ying Labreche, Functionalized Polymeric Membranes for CO<sub>2</sub> Capture, J. Membr. Sci. Res. 2 (2016) 59-65.
- [20] A. Sharif, Polymeric Gas Separation Membranes: What Makes them Industrially more Attractive?, J. Membr. Sci. Res. 4 (2018) 2-3.
- [21] [https://www.mitsuichemicals.com/tpx\\_pre.htm](https://www.mitsuichemicals.com/tpx_pre.htm) (30.07.2018).
- [22] L.C. Lopez, G.L. Wilkes, P.M. Stricklen, S.A. White, Synthesis, Structure, and Properties of Poly(4-Methyl-1-Pentene), J. Macromol. Sci. Part C. 32 (1992) 301-406.
- [23] US Patent № 4 421 529, 1983.
- [24] US Patent № 3 798 185, 1974.
- [25] T. Suzuuki, T. Tanaka, M. Nakajima, H. Yoshimizu, Y. Tsujita, Characterization of the Cavity in Poly(4-methyl-1-pentene) Crystal by Gas Permeation and <sup>129</sup>Xe NMR Measurements, Polym. J. 34 (2002) 891-896.
- [26] A.C. Puleo, D.R. Paul, P.K. Wong, Gas sorption and transport in semicrystalline poly(4-methyl-1-pentene), Polymer 30 (1989) 1357-1366.
- [27] V.I. Kleiner, S.M. Shishatskii, Y.P. Yampolskii, I.B. Kevdina, N.N. Kuz'min, B.A. Krentsel, Permeability of poly(4methylpentene-1) with different degrees of isotacticity, Vysokomolec. Soed. 35 (1993) 1679-1682.
- [28] A.P. Kharitonov, Y.L. Moskvina, Direct fluorination of polystyrene films, J. Fluorine Chem. 91 (1998) 87-93.
- [29] J.M. Mohr, D.R. Paul, Y. Taru, T.E. Mlsna, R.J. Lagow, Surface fluorination of composite membranes. Part II. Characterization of the fluorinated layer, J. Membr. Sci. 55 (1991) 149-171.
- [30] S.Y. Markova, N.M. Smirnova, V.V. Teplyakov, Gas Permeability through poly(4-Methyl-1-pentene) at temperatures above and below the glass transition point, Pet. Chem. 56 (2016) 948-955.
- [31] J.D. Le Roux, V.V. Teplyakov, D.R. Paul, Gas transport properties of surface fluorinated poly(vinyltrimethylsilane) films and composite membranes, J. Membr. Sci. 90 (1994) 55-68.
- [32] J. Mohr, D.R. Paul, I.Pinnau, W.J. Koros, Surface fluorination of polysulfone asymmetric membranes and films, J. Membr. Sci. 56 (1991) 77-98.
- [33] I.N. Beckman, V.V. Teplyakov, Selective gas transfer through binary polymeric systems based on block-copolymers, Adv. Colloid Interface Sci. 222 (2015) 70-78.
- [34] V. Teplyakov, P. Meares, Correlation aspects of the selective gas permeabilities of polymeric materials and membranes, Gas Sep. Purif. 4 (1990) 66-74.
- [35] O.V. Malykh, A.Y. Golub, V.V. Teplyakov, Polymeric membrane materials: New aspects of empirical approaches to prediction of gas permeability parameters in relation to permanent gases, linear lower hydrocarbons and some toxic gases, Adv. Colloid Interface Sci. 164 (2011) 89-99.