

## Chromatographic Adsorbents Based on Fluorinated Polyimides Supported on Diatomite

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### Abstract

New separation layers were obtained on the basis of fluorinated polyimides (PI) deposited on a diatomite support. The effect of thermal treatment of the separation layers on their texture and chromatographic characteristics was studied. The selectivity of chromatographic columns loaded with the new adsorbents was first evaluated. The adsorbent selectivity was found to depend on the pyrolysis temperatures in the range from 250 to 1100°C. The adsorbents prepared ensure the selective separation of permanent gases and hydrocarbons on their simultaneous presence.

### Keywords

Diatomite support; inorganic and organic gases; gas chromatography; hydrocarbons; polyimide (PI).

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### Introduction

Polyimides are ideal precursors for obtaining molecular-sieve membranes. It is well known that the precursors for producing porous carbonized membranes are phenolic resins, polyfurfuryl, alcohol resins, polyvinylidene chloride, condensed polycyclic aromatic compounds, and polyimides. Ceramic substrates are used as a support for carbonized layers.

Polymer materials, as well as their carbonized structures, are characterized by various specific surface areas with pore sizes from a few to tens of nanometers. The CF<sub>3</sub>- or CH<sub>3</sub>- substituted polyimides, because of their heat and chemical resistance, have shown promise as gas-separation membranes. Recent studies have demonstrated that both permeability and selectivity of glassy polymeric membranes can be enhanced by incorporation of bulky pendent groups into their structure, which makes their molecular structure rigid, inhibits efficient chain packing, and reduces local segmental mobility [1–7].

One way to control the selectivity and the permeability of membranes is to introduce fluorine atoms into the structure of the chain.

It is known that polyimides with the high content of fluorine atoms have lower packing density of

chains, and therefore they have higher transmission coefficients and larger free volumes. High permeability of membranes can also be achieved by thermal rearrangement of precursor polymers [8]. Pore dimensions and their distribution strongly depend not only on the chemical structure and pretreatment of polyimides but also on the choice of a pyrolysis protocol [9].

Polyimides have good thermal and chemical stability. The porous structure and the above properties make this material suitable for using it as electrodes, membranes, catalyst supports, but these properties may also be promising for the development of new, highly selective, chromatographic adsorbents.

The most important advantages of carbonized polyimides are the good yield and no deformation during carbonization. Carbon materials based on polyimides possess the properties of molecular sieves (zeolites A4, A5) and demonstrate high selectivity in gas separation [10].

The aim of this work was to study the formation of selective layers based on perfluorinated polyimides deposited onto Chromosorb P NAW diatomite support and to study their adsorptive and chromatographic characteristics.

## Experimental

**Reagents.** 2,2-Bis (30,40-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA, 99 %, Cas: 1107-00-2) was dried in a vacuum oven at 140 °C for 6 h. 2,4,6 – trimethyl-m-phenylenediamine (2,4,6-TMmPDA) (96 %, Cas: 3102-70-3, Product of Switzerland) was used as received.

2,7-Diaminohexafluoronaphthalene (2,7-DAHFN) was synthesized according to the published procedure [11]. N-methyl-2-pyrrolidone (NMP, Aldrich) was purified by distillation over P<sub>2</sub>O<sub>5</sub> under reduced pressure and stored over a CaA molecular sieve at a residual moisture <0.02 %. Diatomite of the type Chromosorb P NAW ( $S_{\text{BET}} = 4 \text{ m}^2/\text{g}$ , 80/100 mesh, Supelco) was used as an initial support. The structure of synthesized polyimides is shown in Fig. 1.

Polyimide PI-I was synthesized from 6FDA and 2,7-DAHFN according to a procedure described elsewhere [12]. Polyimide PI-II was synthesized from 6FDA and 2,4,6-TMmPDA by the following two-step method. Polyamic acids (PAA) were prepared by a stepwise addition of stoichiometric amounts of solid 6FDA to 2,4,6-TMmPDA dissolved in NMP.

The PAA solution was received at concentration of 20 wt%. Reaction mixtures were stirred in a nitrogen atmosphere at ambient temperature for 6 h. Then, dried PAA was thermally imidized in a nitrogen atmosphere using the following heating schedule: 1 h at 80 °C, 1 h at 150 °C, 1 h at 200 °C, 1 h at 250 °C, and 20 min at 300 °C. The inherent viscosity of obtained PI-II was 0.38 dL/g.

**Preparation of porous layers based on fluorinated polyimides supported on diatomite.** Modified samples of Chromosorb P NAW were prepared following the standard procedure [13]. The samples were impregnated with a solution of PI in dimethylacetamide in amount of 10 % of the Chromosorb P NAW weight. The suspension was transferred into a porcelain dish, and the solvent was removed at 90 °C under constant stirring until a constant weight of the residue. Separating layers based on Chromosorb P NAW and

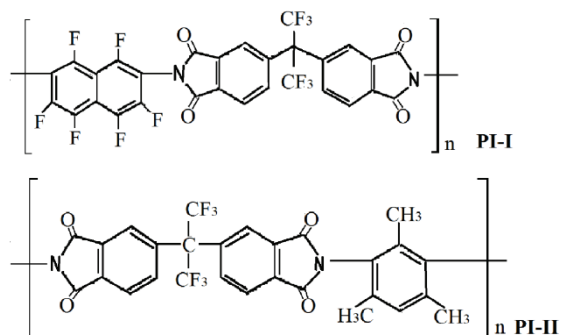


Fig. 1. Structure of polyimides synthesized from 6FDA and different diamines

fluorinated PIs were formed at specific temperatures ( $T = 250, 350, 700, 900,$  and  $1100 \text{ }^\circ\text{C}$ ). The adsorbents were individually loaded into a quartz reactor and thermally treated in an oven in a flow of argon.

Two types of the samples were prepared:

adsorbents PI-I were prepared from Chromosorb P NAW and 10 wt% PI-I ( $T_{\text{treatment}} = 250, 350,$  and  $700 \text{ }^\circ\text{C}$ );

adsorbents PI-II were prepared from Chromosorb P NAW and 10 wt% PI-II ( $T_{\text{treatment}} = 250, 350, 700, 900$  and  $1100 \text{ }^\circ\text{C}$ ).

**Methods.** Thermogravimetric analysis (TGA) of the samples was performed using an NETZSCH STA 409 instrument. The short-term thermal stability of PIs was estimated from the 5 % weight loss temperatures  $T_{5\%}$  with a heating rate of 10 °C/min in an inert (He) atmosphere. The elemental analysis was carried out using a Eurovector EA 3000 CHN analyzer. The fluorine content in the samples was determined by the spectrophotometric analysis. The inherent viscosities  $\eta_{\text{inh}}$  were determined using an Ubbelohde viscosimeter at a concentration 0.5 dL/g in DMA at 25 °C.

Adsorption properties of the samples were studied using an ASAP 2400 system (Micromeritics, USA): N<sub>2</sub> adsorption–desorption isotherms of the samples were recorded at 77 K after their treatment in vacuum at 150 °C. These isotherms were used to calculate the total accessible surface (by the Brunauer-Emmet-Teller (BET) method) and the specific surface. The pore volume distribution in the samples was determined from the desorption branch of the isotherms by the Langmuir method and by the Barrett–Joyner–Halenda method.

The samples were studied using high-resolution transmission electron microscopy (HRTEM) with a JEM-2010 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV and a resolution of 0.14 nm. The local elemental composition was analyzed with an energy-dispersive EDX spectrometer equipped with a Si (Li) detector with the energy resolution of 130 eV.

Chromatographic characteristics of the samples were tested in the separation of model mixtures containing inorganic and organic gases and saturated and unsaturated hydrocarbons. Column I and column II were loaded with the adsorbent PI-I and PI-II, respectively. A reference column (Column III) was filled with a conventional adsorbent (activated carbon AG-5). All the columns were 3 m × 2 mm in size.

The chromatographic characteristics of the adsorbents were studied using a Krystal 2000 system (Russia) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The thermostat temperature was maintained with a precision of  $\pm 0.5 \text{ }^\circ\text{C}$ . In the case of the FID, the flow

rate of the carrier gas (nitrogen) was 30 mL/min; the flow rates of hydrogen and air were 30 and 300 mL/min, respectively. When the TCD was used, the flow rate of the carrier gas (helium) was 30 mL/min. The model mixtures were separated under isothermal conditions or at programmed temperatures. Experimental chromatographic data were processed using the Netchrom software. To calibrate the experiment, mixtures of gases with known concentrations in argon were prepared in 10-L metal vessels using the volumetric (manometric) method. A mixture of C<sub>1</sub>–C<sub>2</sub> hydrocarbon gases was prepared in vessel 1. A mixture of C<sub>3</sub>–C<sub>4</sub> hydrocarbon gases was prepared in vessel 2. Liquid saturated and unsaturated C<sub>5</sub>–C<sub>10</sub> hydrocarbons were mixed in vials in arbitrary concentrations.

Model mixtures (hydrocarbon gases from the vessels or liquid hydrocarbons from the vials) were taken with a syringe and injected into the chromatographic detector.

## Results and discussion

*Thermal degradation of PIs.* The synthesized PIs demonstrated high thermal stability under pyrolysis in an inert atmosphere: their thermal decomposition started at temperatures above 400 °C. The pyrolysis at

higher temperatures (above 600°C) resulted in the formation of high yields of carbonated films (Table 1).

*The elemental analysis of PIs.* The chemical composition of the samples obtained at different temperatures is presented in Table 2. A universally accepted criterion for estimation of the carbonization of polymers is the amount of coke residues formed during the thermal treatment. According to the TGA data, after the pyrolysis at 1100 °C, the coke residues in PI-I and PI-II comprise 41.7 and 43.6 %, respectively, while a half of the weight is lost during the heating to 700 °C. As seen from Table 2, at 1100 °C the carbon content in the coke residue exceeds 90 %. The samples obtained under these conditions contain insignificant amounts of nitrogen and no hydrogen or fluorine. At that, the temperatures at which precursors lose atoms N, F, and H are different: fluorine atoms leave no trace at 700 °C, while hydrogen disappears above 900 °C.

*Low-temperature nitrogen adsorption of PIs.* To study the structure of the obtained adsorbents in detail, we analyzed their surface by the low-temperature adsorption of nitrogen with its subsequent thermal desorption. The results of the thermal desorption are presented in Table 3.

Table 1

**Thermal degradation of PIs in an inert atmosphere (TGA with the heating rate 10 °C/min)**

Polyimides	$T_{5\%}^a$ , °C	$R_{600}^b$ , %	$R_{700}^b$ , %	$R_{800}^b$ , %	$R_{900}^b$ , %	$R_{1000}^b$ , %	$R_{1100}^b$ , %
PI-I	506	68.8	57.2	51.7	47.1	42.8	42.3
PI-II	489	62.4	53.3	50.9	49.2	47.2	43.8

Note: <sup>a</sup>  $T_{5\%}$  is temperature at 5 % weight loss.

<sup>b</sup>  $R_{600}$ ,  $R_{700}$ ,  $R_{800}$ ,  $R_{900}$ ,  $R_{1000}$ , and  $R_{1100}$  are residual weights at 600, 700, 800, 900, 1000, and 1100 °C, respectively.

Table 2

**Results of the elemental analysis**

Polyimides	Temperature of treatment $T$ , °C	Time of treatment, $t$ (h)	Yield of coke residue, wt%	Elemental composition of PI film, %			
				C	H	N	F
PI-I	250	8	–	51.6	0.9	4.2	33.8
PI-I	350	4	–	51.5	0.9	4.2	33.7
PI-I	700	3	52.3	82.2	0.4	2.1	0
PI-I	1100	3	41.7	93.2	0	2.1	0
PI-II	250	8	–	60.2	0.3	5.0	20.4
PI-II	350	4	–	60.1	0.3	5.0	20.4
PI-II	700	2	49.6	88.1	1.0	5.5	0
PI-II	900	2	45.8	90.1	0.4	4.7	0
PI-II	1100	2	43.6	95.2	0	3.2	0

Textural characteristics of samples

Parameter <sup>a</sup>	Sample PI-I			Sample PI-II				
	250	350	700	250	350	700	900	1100
$T$ , °C	250	350	700	250	350	700	900	1100
$A_{\text{BET}}$ , m <sup>2</sup> /g	8.9	26.4	33.4	28.9	78.4	113.4	87.9	30.9
$A_{\mu}$ , m <sup>2</sup> /g	–	0.97	15.4	25.6	53.8	102.4	82.8	21.3
$V_{\mu}$ , cm <sup>3</sup> /g	–	0.001	0.007	0.011	0.026	0.048	0.038	0.010
$D_M$ , Å (on 4V/A by BET)	65.5	57.3	29.9	522.7*	46.7*	67.2*	74.2*	129.5*
$D_M$ , Å (Langmuir)	–	–	–	26.4	21.3	17.7	17.9	43.2

Note: <sup>a</sup>  $T$  is the temperature of the thermal treatment;  $A_{\text{BET}}$  is the specific surface area calculated by the BET method;  $A_{\mu}$  and  $V_{\mu}$  are the specific surface area and the specific volume of mesopores (i.e. pores with the volume below 1000 Å), respectively;  $D_M$  is the average pore diameter calculated from either BET or Langmuir isotherm.

\* the average pore diameter calculated for comparison by the Barrett–Joyner–Halenda method.

The analysis of textural characteristics of adsorbents PI-I and PI-II showed that an increase in the temperature of the thermal treatment leads to the change in their adsorption properties. In the temperature range from 250 to 700 °C, the specific surface  $A_{\text{BET}}$ , the specific surface and the specific volume of micropores of both adsorbents increased several times (Table 3). It led to a decrease in the average diameter of pores from 65 to 29.9 Å for the adsorbent PI-I and from 26.4 to 17.7 Å for the adsorbent PI-II.

The treatment at higher temperatures led to a decline in the textural characteristics of the adsorbents. For example, the specific surface, the surface and volume of micropores in the adsorbent PI-II after its treatment at 1100 °C became almost the same as the values obtained at 250 °C. Note, however, that the average diameter of pores after the treatment at 1100 °C increased almost twice: 26.4 Å at 250 °C and 43.2 Å at 1100 °C (Table 3).

The changes in the structure of polyimides synthesized on the basis of 6FDA occur in several stages in the temperature range of 200 to 1200 °C. The same behavior is typical of carbon molecular membranes obtained from this material. The polymeric precursor decomposes in the temperature range 500–700 °C with the formation of highly disordered carbon structures in the forms of micrographite crystals and noncrystalline areas. This form of carbon material possesses high permeability and low selectivity. Upon raising the temperature of pyrolysis, however, the volume of the noncrystalline areas diminishes, which leads to the formation of more ordered structures and to a decrease in the average diameter of pores [10].

The HRTEM micrographs of PIs. The changes in the structures of the adsorbents PI-I and PI-II as a result of their thermal treatment were confirmed by HRTEM [12]. According to HRTEM data, adsorbents

PI-I and PI-II treated at 250 and 350 °C have similar structures: they consist of particles with the different size (from 10 nm to 10 μm). The main part of the material is large particles of the micron size that consist of Si—O. The main feature of this material is the existence of large pores (from 100 nm to several μm) passing through the particle (Fig. 2, *a*, *b*).

At higher resolution, the micrographs demonstrate that the particle surface also contains small pores with the diameter from 1 to 20 nm. In addition, it is seen that the particle surface is covered with a carbon layer with the nanometer thickness. The adsorbent PI-II is amorphous material consisting of Si—O but inclusions of phases containing different elements (Mg, Al, K, Ca, Fe) can have a crystal structure.

According to the HRTEM data, the adsorbent PI-II treated at 700 °C is morphologically similar to the initial material. However, the particle surface of the sample is covered with a layer of amorphous carbon (Fig. 3), which consists of plate-like particles with the sizes of about 50 nm. Note, however, that the amorphous carbon layer is not uniform and covers the particle surface only partly.

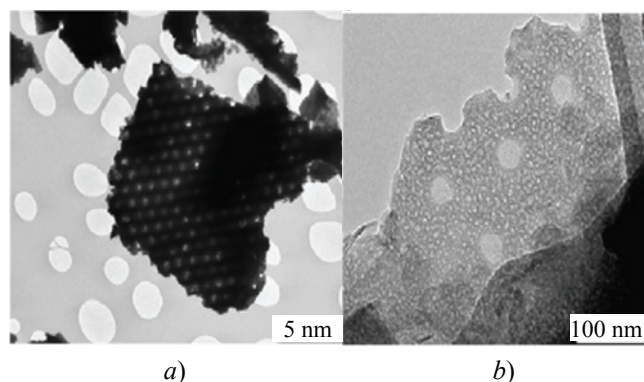


Fig. 2. HRTEM micrographs of adsorbent PI-II: *a* – Particle with large pores, *b* – microporous area



After the treatment at higher temperatures ( $T = 1100\text{ }^{\circ}\text{C}$ ), the adsorbent PI-II consists of two types of particles. The first type is similar to the initial material (Fig. 4 *a*). Particles of the second type are the result of the sintering of initial particles with the formation of massive nonporous structures of about a micron in size (Fig. 4 *b*) that are not covered with amorphous carbon.

Note that the carbon coating exists on some particles that saved their initial structure (Fig. 5 *a*). Moreover, there exists a different type of the carbon coating (Fig. 5 *b*), which morphologically consists of spherical carbon layers that were presumably formed because of combustion of inclusion phases.

*Chromatographic separation of permanent gases and hydrocarbons.* The changes in the textural characteristics of the adsorbent PI-I significantly affect its chromatographic properties. This is manifested by the change in the order of exit of adsorbates  $C_1$ – $C_4$ . On the adsorbent treated at  $250\text{ }^{\circ}\text{C}$ , hydrocarbons  $C_1$ – $C_2$  elute as one peak, whereas after the treatment at  $350\text{ }^{\circ}\text{C}$ , the adsorbent satisfactorily separates hydrocarbons  $C_1$ – $C_4$  with the exception of the unseparated pair of ethane and ethylene.

The behavior of adsorbates  $C_1$ – $C_4$  on the separation layer formed at  $700\text{ }^{\circ}\text{C}$  is similar to their chromatographic behavior on carbon molecular sieves and activated carbon AG-5, when acetylene elutes before ethane and ethylene. Permanent gases on the adsorbent PI-I elute as one peak (Fig. 6, *a*, *b*, *c*; Table 4).

The analysis of desorption curves obtained on the adsorbent PI-II showed that after the treatment at  $350\text{ }^{\circ}\text{C}$ , its surface provides the separation of hydrocarbons  $C_1$ – $C_{10}$  (Fig. 7, *a*). In contrast, the adsorbent PI-I cannot separate hydrocarbons from this group [13, 14]. The structure of the adsorbent PI-II formed at  $700\text{ }^{\circ}\text{C}$  is apparently characterized by a bimodal pore distribution.

On the one hand, the surface of the adsorbent contains micropores with the size that is negligibly higher than the size of pores of activated carbons (1.6 nm) with a very developed surface  $890\text{ m}^2/\text{g}$ . Such micropores allow one to separate hydrogen, oxygen+nitrogen, CO, and methane. On the other hand, the surface of the adsorbent contains mesopores that provide the selective elution of hydrocarbons  $C_2$ – $C_4$  with retention times that are lower than the retention times obtained on the activated charcoal AG-5 (Fig. 6, *b*, *c*; Fig. 7, *b*; Table 4).

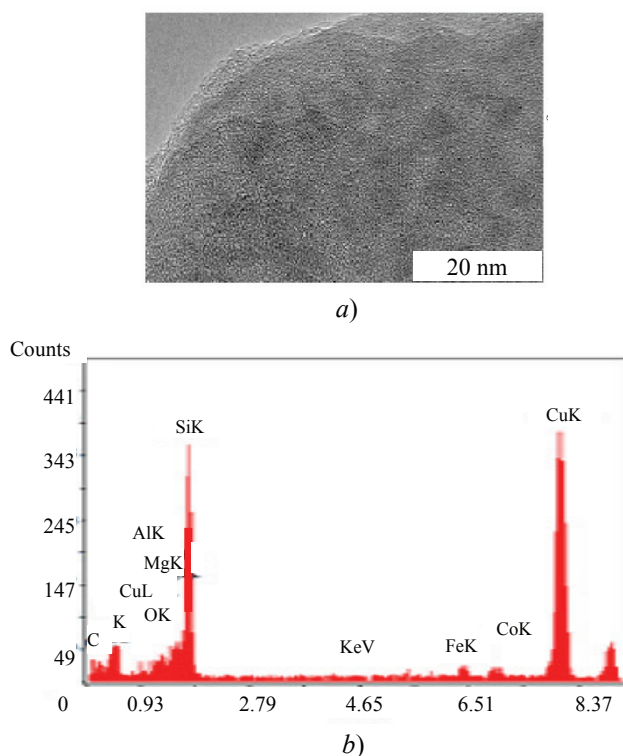


Fig. 3. HRTEM micrographs of the adsorbent PI-II treated at  $700\text{ }^{\circ}\text{C}$  (*a*); corresponding EDX spectrum (*b*)

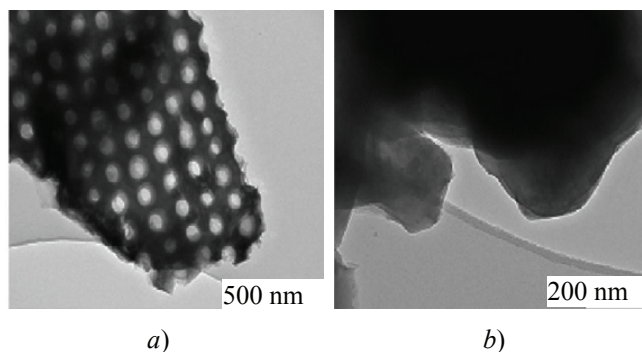


Fig. 4. HRTEM micrographs of the adsorbent PI-II treated at  $1100\text{ }^{\circ}\text{C}$ :

*a* – particle with large porous structure;  
*b* – particle without porous structure

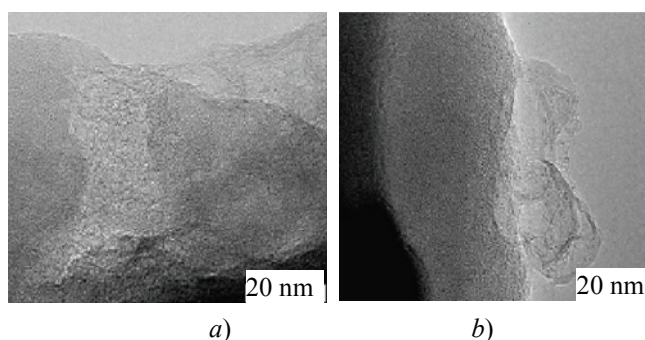


Fig. 5. HRTEM micrographs of carbon coatings on the surface of the adsorbent PI-II treated at  $1100\text{ }^{\circ}\text{C}$ :  
*a* – amorphous coating; *b* – globular carbon coating

Some characteristics and retention times ( $t_r$ , min) of compounds on columns loaded with adsorbents PI-I and PI-II

Component	Molecular weight	$T_{b,p}, ^\circ\text{C}$	$T_{\text{treatment}} = 350 ^\circ\text{C}$ ,	$T_{\text{treatment}} = 350 ^\circ\text{C}$ ,	$T_{\text{treatment}} = 700 ^\circ\text{C}$ ,	$T_{\text{treatment}} = 1100 ^\circ\text{C}$ ,
			PI-I <sup>a</sup>	PI-II <sup>a</sup>	PI-II <sup>b</sup>	PI-II <sup>b</sup>
H <sub>2</sub>	2	-252.7	0.84	1.01	0.93	1.06
N <sub>2</sub> +O <sub>2</sub>	29	-192	0.84	1.01	1.11	1.31
CO	28	-192	0.84	1.01	1.24	1.51
CH <sub>4</sub>	16	-161.6	0.92	1.13	2.01	2.57
CO <sub>2</sub>	44	-78.6 (0.52 MPa)	1.23	2.27	4.33	4.98
C <sub>2</sub> H <sub>2</sub>	26	-83.8	5.51	5.23	6.37	6.26
C <sub>2</sub> H <sub>4</sub>	28	-103.7	3.43	2.27	6.55	6.72
C <sub>2</sub> H <sub>6</sub>	30	-88.6	4.92	3.13	7.23	7.38
C <sub>3</sub> H <sub>6</sub>	42	-47.8	9.13	8.46	12.27	14.60
C <sub>3</sub> H <sub>8</sub>	44	-42.1	9.74	8.71	12.89	14.95
C <sub>4</sub> H <sub>10</sub>	58	-0.5	13.32	12.11	41.62	64.08
C <sub>4</sub> H <sub>6</sub>	54	-4.47	13.64	12.26	–	–
C <sub>5</sub> H <sub>12</sub>	72	36.1	14.52	13.87	–	–
C <sub>6</sub> H <sub>14</sub>	86	68.7	16.08	16.07	–	–
C <sub>7</sub> H <sub>16</sub>	100	98.4	17.76	17.76	–	–
C <sub>8</sub> H <sub>18</sub>	114	125.7	19.98	19.36	–	–
C <sub>9</sub> H <sub>20</sub>	128	150.8	22.43	21.40	–	–
C <sub>10</sub> H <sub>22</sub>	142	174.1	26.93	25.11	–	–

Note: <sup>a</sup> At 30 °C held for 4 min, followed by heating at the rate of 10 °C/min to 180 °C.

<sup>b</sup> at 30 °C held for 2 min, followed by heating at the rate of 20 °C/min to 180 °C.

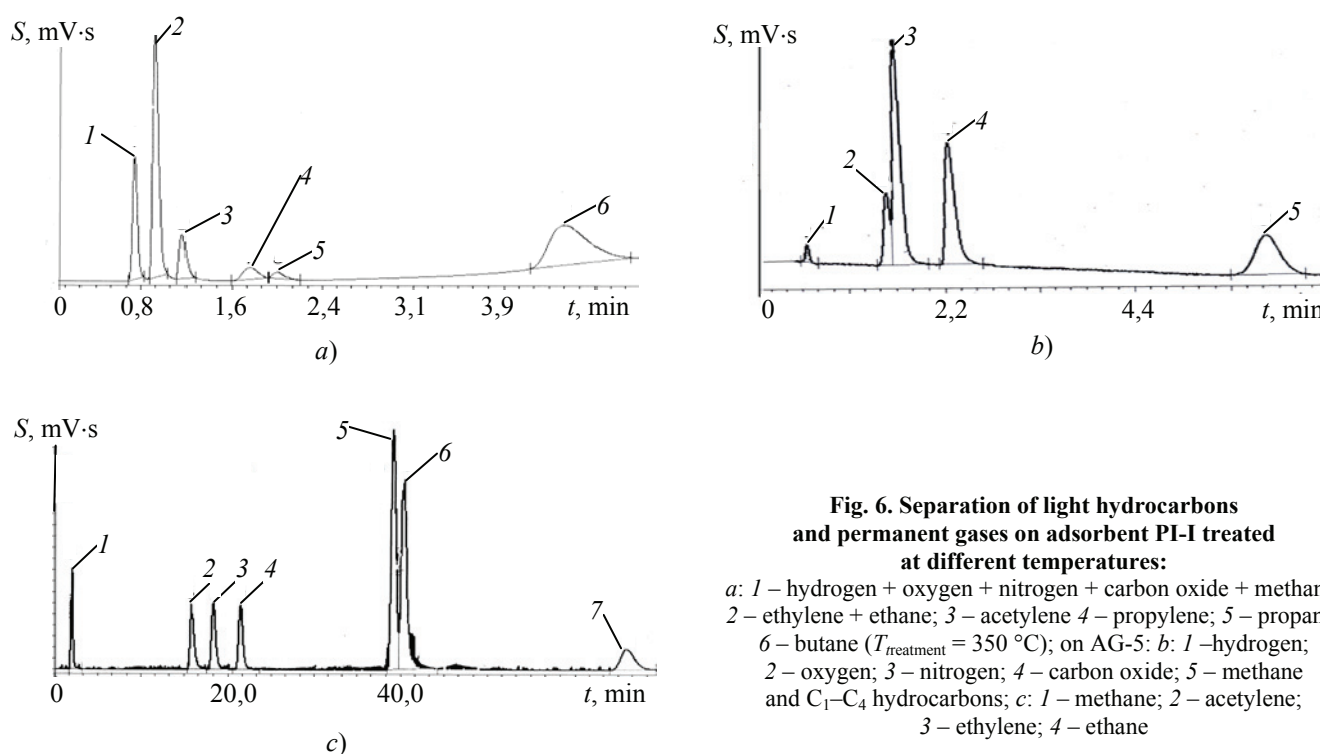
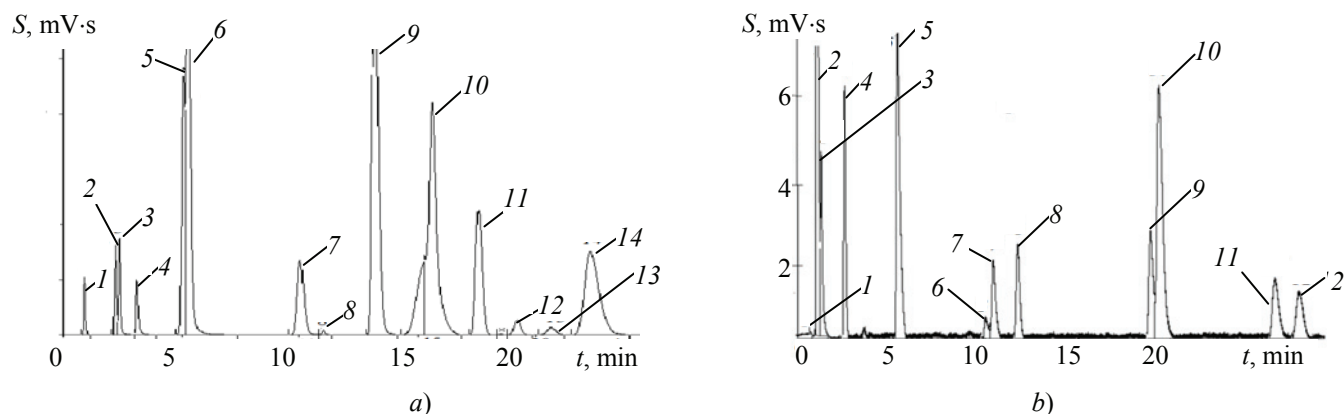


Fig. 6. Separation of light hydrocarbons and permanent gases on adsorbent PI-I treated at different temperatures:

*a*: 1 – hydrogen + oxygen + nitrogen + carbon oxide + methane; 2 – ethylene + ethane; 3 – acetylene 4 – propylene; 5 – propane; 6 – butane ( $T_{\text{treatment}} = 350 ^\circ\text{C}$ ); on AG-5: *b*: 1 – hydrogen; 2 – oxygen; 3 – nitrogen; 4 – carbon oxide; 5 – methane and C<sub>1</sub>–C<sub>4</sub> hydrocarbons; *c*: 1 – methane; 2 – acetylene; 3 – ethylene; 4 – ethane



**Fig. 7. Separation of permanent gases and hydrocarbons C<sub>1</sub>–C<sub>10</sub> on the adsorbent PI-II treated at different temperatures:**

*a:* 1 – hydrogen + oxygen + nitrogen + carbon oxide + methane; 2 – ethylene + CO<sub>2</sub>; 3 – ethane; 4 – acetylene; 5 – propylene; 6 – propane; 7 – butane; 8 – 1,3- butadiene; 9 – pentane; 10 – hexane; 11 – heptane; 12 – octane; 13 – nonane; 14 – decane ( $T_{\text{treatment}} = 350\text{ }^{\circ}\text{C}$ ); *b:* 1 – hydrogen; 2 – oxygen + nitrogen; 3 – carbon oxide; 4 – methane; 5 – CO<sub>2</sub>; 6 – acetylene; 7 – ethylene; 8 – ethane; 9 – propylene; 10 – propane; 11 – n – butane; 12 – i – butane ( $T_{\text{treatment}} = 700\text{ }^{\circ}\text{C}$ ).

## Conclusion

New chromatographic adsorbents were synthesized from polymeric fluorinated polyimide deposited on a Chromosorb P NAW diatomite support. The optimal composition and conditions of thermal treatment were selected to obtain the selective layers with the controlled pore size. The obtained adsorbents provide the separation of permanent gases and their mixtures with hydrocarbons C<sub>1</sub>–C<sub>10</sub>.

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