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Poly[1-(trimethylsilyl)-1-propyne] as chromatographic adsorbent and prospects of its application in packed and capillary columns

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Abstract

The application of film-forming organic polymers, which are in common use in membrane technology, as chromatographic adsorbents for packed and capillary columns has been suggested. The chromatographic characteristics of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) as an adsorbent were studied. The film-forming properties of PTMSP simplify manufacturing of capillary and packed gas–solid columns. It was shown that separation of C_1 – C_4 hydrocarbon gases on the columns with PTMSP is of practical interest. In the authors' opinion, PTMSP is also promising for the separation of inorganic gases. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The nature of the stationary phase has a great influence on such important characteristics of a chromatographic column as selectivity and efficiency.

During the last 10 years, new types of adsorbents such as organic polymers have been introduced more efficiently into the practice of gas–solid chromatography (GSC). Hollis [1,2] was the first to suggest and develop the adsorbents which are now promising and actively used.

The use of organic polymers in gas chromatography (GC) has expanded recently due to the following favourable characteristics: (1) the polymers have uniform surface, and therefore, symmetric chromatographic zones of compounds to be separated; (2)

they have a hydrophobic surface for hydrocarbon adsorbents (this makes chromatographic determination of water and other polar compounds possible); (3) it is possible to vary the main chromatographic characteristics by changing polymer nature, its structure and specific surface; (4) it is possible to obtain adsorbents of high capacity.

Many well-known researchers emphasised the importance of porous organic polymers for analytical GC [3–5]. The development of new polymer adsorbents and their application for packed [6] and capillary [7] columns persists today. But many polymer adsorbents used in chromatography are characterised by some limitations as well. In our opinion, the complicated procedure for manufacturing capillary columns and lack of effective adsorbents for packed columns on the basis of conventional organic polymers are one of the major limitations since the known polymer adsorbents are insoluble in solvents.

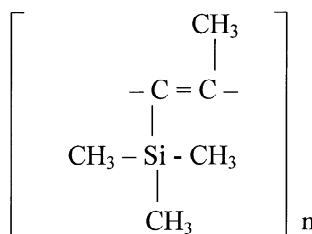
To extend the number of polymers used in gas

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chromatography, we recently suggested a new approach for selection and broadening of polymer adsorbents [8]. It is based on application of film-forming glassy polymers as adsorbents. Note that polymers of this type are in common use as permeable membranes in membrane technology. Suggesting application of the polymers as chromatographic adsorbents, we supposed that selectively-permeable polymers for membrane separation should have a developed porous network and, therefore, the internal surface should be significant. We found it reasonable to use literature data on penetrability and glass transition temperature for selection of the first specific polymer among those used in membrane technology.

Table 1 [9] shows the data on penetrability and glass transition temperature for some membrane polymers regarding O_2 and N_2 . As seen, poly[1-(trimethylsilyl)-1-propine] (PTMSP) is characterised by the highest penetrability regarding O_2 (penetrability for PTMSP is 270 times greater than that for poly(4-methylpenten-1), the polymer which has the second highest penetrability. Regarding N_2 , penetrability for PTMSP is 760 times greater than that for poly(4-methylpenten-1), which again is the polymer which has the second highest penetrability. It can be seen that PTMSP is a unique polymer with a glass transition temperature of $\sim 300^\circ\text{C}$. Therefore, first of all it was of interest to study PTMSP as a chromatographic adsorbent. The chemical structure of the polymer is shown below:



High penetrability of PTMSP deals with its high unconfined space which can be explained by the following peculiarities of the polymer: (1) rigid main chain ($-\text{C}=\text{C}-$) and (2) volumetric side group [$-\text{Si}(\text{CH}_3)_3$]. This polymer has very low density (0.7 g/cm^3) and, therefore, an unusually high portion of unconfined space ($\sim 20\%$) [10].

The results of unconfined space study by sound techniques allows to conclude that this polymer has unusually high values of radius of free micro-elements (micro-volumes) [11,12]. According to the data on PTMSP study by positron annihilation method, the unconfined space in the polymer is characterised by a bimodal distribution according to volumes, large micro-volumes (diameter $\sim 11\text{--}14 \text{ \AA}$, concentration $6 \times 10^{19} \text{ cavity/cm}^3$) [13] predominate in the distribution. Note that the diameter of micro-volumes is $\sim 3\text{--}6 \text{ \AA}$ for polymers, which are not used in membrane technology. In the thesis [13], the micro-heterogeneous structure of PTMS was studied by physical methods and it was found that micropores of $10\text{--}15 \text{ \AA}$ diameter and submicro-pores of $3\text{--}5 \text{ \AA}$ predominate in the polymer.

Table 1

Penetrability and glass transition temperature (T_{gt}) of some polymers regarding oxygen and nitrogen [9]

Polymer	T_{gt} ($^\circ\text{C}$)	$P(O_2)$ (bars)	$P(N_2)$ (bars)
Polyphenylenoxide	210	16.8	3.8
Polytrimethylsilylpropine	~ 300	10 040	6745
Ethylcellulose	43	11.2	3.3
Poly(4-methylpentene-1)	29	37.2	8.9
Polypropylene	-10	1.6	0.3
Polychloroprene	-73	4.0	1.2
Polyethylene of low density	-73	2.9	1.0
Polyethylene of high density	-23	0.4	0.14

Comments: As known [9], the flow of compound J through a membrane can be expressed as: $J = DS (\Delta P_i/l)$ or $J = P(\Delta P_i/l)$ where $P = DS$ is the penetrability, D is the diffusion coefficient of a compound in membrane, S is the solubility coefficient ($S = c/P_g$, c is the concentration, P_g partial gas pressure), l is the thickness of membrane, ΔP_i is the membrane pressure difference.

Thus, taking into account all the published data, we concluded that PTMSP was the most promising chromatographic adsorbent among well known membrane materials.

The purpose of the present research was to study the new class of organic solid-phase glassy-state film-forming polymers as chromatographic adsorbents in packed and capillary columns using PTMSP as an example. We hoped that study of the polymers is of interest both for theory and practice of gas–solid chromatography since they are characterized by unique properties.

Note that Tennikova et al. [14] were the first to apply membrane materials as adsorbents for HPLC.

2. Results and discussion

2.1. Gas chromatography of liquid hydrocarbons on a capillary column with PTMSP

A fused silica capillary column 15 m×0.24 mm with PTMSP (film thickness 1.4 μm) was used in experiments. Capillary columns were dynamically coated with PTMSP using 5% solution of the polymer in chloroform. The relative retention of various hydrocarbons was studied both on PTMSP and on polydimethylsiloxane (PDMS), the conventional stationary liquid phase SPL, at 150 °C.

Unusual selectivity of PTMSP as adsorbent appears in separation of liquid hydrocarbons. For example, benzene eluted much earlier than hexane,

toluene did before heptane, naphthalene before *n*-decane. Let us point out that earlier such elution order was not observed for any stationary phase.

The data on retention indices of hydrocarbons are listed in Table 2 [8]. As seen, relative retention of hydrocarbons expressed as Kovats' indexes is much higher (100–200 IU) on the column with PDMS than that on the column with PTMSP. Isooctane is the only exception: it is characterised by greater retention on PTMSP than on PDMS.

To characterise selectivity of the new phase, we compared the retention of hydrocarbons both on PTMSP and on non-polar phase (for example, SE-30). For this purpose, we considered the following linear dependence for the above-mentioned phases (see e.g. [15])

$$\log k = a + bT_b \quad (1)$$

where k is the retention factor, T_b is boiling point (°C), and a and b are constants.

The dependences of the logarithm of the retention factor on boiling points of compounds to be chromatographed for two stationary phases (PTMSP and SE-30) at 150 °C are shown in Fig. 1. As seen, there are two different linear dependences (1) for *n*-alkanes and aromatic compounds on the column with PTMSP (Fig. 1a). Note that PTMSP has specific sorption properties for some organic compounds (see, isooctane, cyclohexane, decaline and naphthalene), which is evidence of high individual selectivity of the polymer. Analogous dependence (see Eq. (1))

Table 2

Retention indices (I) of some liquid hydrocarbons obtained on open capillary columns coated with PTMSP and polydimethylsiloxane (PDMS) with helium as carrier gas at 150 °C

Solute	T_b (°C)	Retention index, I (IU)		$\Delta I = I(\text{PDMS}) - I(\text{PTMSP})$
		PTMSP (adsorbent)	PDMS (liquid phase)	
Benzene	80.1	553.36	670.45	117.09
Toluene	110.6	659.89	773.24	113.35
Isooctane	99.3	744.33	700	-44.3
Ethylbenzene	136.2	754.70	866.85	112.15
<i>p</i> -Xylene	138.3	765.13	874.28	109.15
<i>o</i> -Xylene	144.4	774.57	900	125.43
Naphthalene	218	972.59	1180.61	208.02

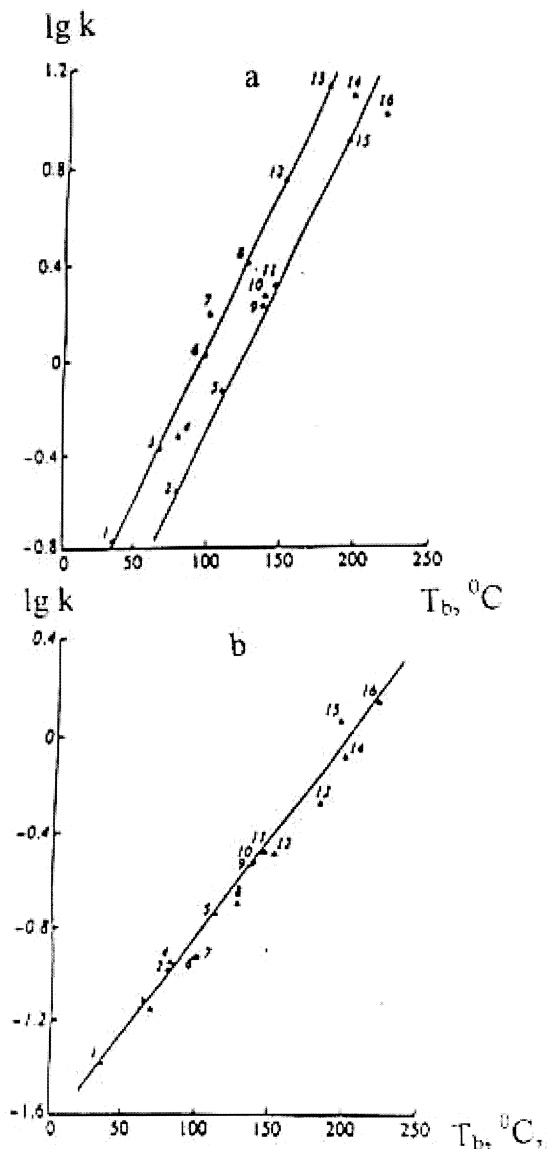


Fig. 1. Dependence of logarithm of retention factor (k) on boiling points of solutes (T_b , °C) for PTMSP (a) and polydimethylsiloxane SE-30 (b) at 150 °C. Solutes: 1, *n*-pentane; 2, benzene; 3, *n*-hexane; 4, cyclohexane; 5, toluene; 6, *n*-heptane; 7, isooctane; 8, *n*-octane; 9, ethylbenzene; 10, *p*-xylene; 11, *o*-xylene; 12, *n*-nonane; 13, *n*-decane; 14, decaline; 15, dimethylaniline; 16, naphthalene.

is shown in Fig. 1b. As follows, SE-30 is not a selective phase, nearly all hydrocarbons of different structure are characterised by the same general linear dependence. Therefore, PTMSP shows selective retention for hydrocarbons.

No doubt, the retention mechanism of organic compounds on PTMSP is determined by many processes, but, in our opinion, it makes sense to suppose that molecular-sieve effects arise as a result of correspondence (or misfit) of some adsorbent microcavities with dimensions of molecules to be adsorbed. In general, the results show that molecules of greater volumetric structure (and greater diameter) are characterised by less retention than *n*-alkanes, which are able to adsorb in most microcavities.

The closeness of increments of differential adsorption heat of methene-group CH_2 IQ for *n*-alkanes on various adsorbents indicates molecular-sieve properties relative to *n*-alkanes (Table 3). As follows, IQ values for classic inorganic molecular sieves 13X and organic adsorbent PTMSP are the same, and differ from adsorbents of other types.

The concept of molecular-sieve retention mechanism of solutes on PTMSP correlates with the data on band-broadening of organic compounds on capillary columns with the adsorbent.

As a rule, resistance to mass transfer contributes appreciably into height equivalent to a theoretical plate (HETP). This term deals with the kinetics of mass transfer in the system gas-adsorbent and, especially, in the stationary phase.

Dependence of HETP on carrier gas velocity for isooctane and *n*-octane is shown in Fig. 2. As seen, band-broadening for branched (volumetric) isomers is much greater than that for corresponding *n*-alkane. For example, HETP for isooctane is 17 times greater than that for *n*-octane.

Poorer kinetic characteristics for iso-alkanes than

Table 3
Increments of differential adsorption heat of methene-group IQ for *n*-alkane series on various adsorbents

Adsorbent	IQ (kcal/mol)
Graphitized carbon black [18]	1.3
Chromosorb 101 (copolymer of styrene and divinylbenzene) [18]	1.4
Molecular sieves 13X [19]	2.3
PTMSP (the present study)	2.3

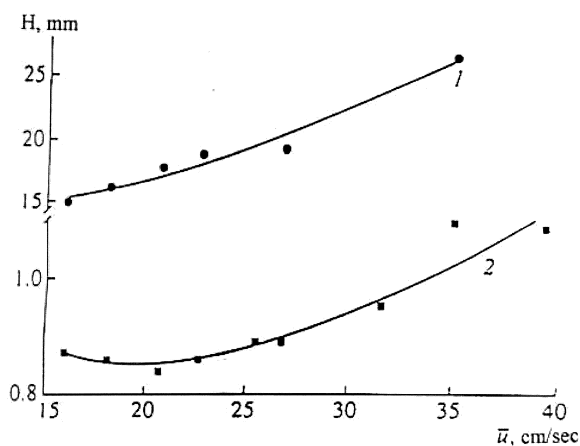


Fig. 2. Dependence of height equivalent to one theoretical plate (HETP) on carrier gas velocity (helium) u for isooctane (1) and *n*-octane (2). Experimental conditions: column 15 m \times 0.24 mm, adsorbent PTMSP, film thickness 1.4 μ m, temperature 150 $^{\circ}$ C.

for *n*-alkanes can be attributed to the presence of such cavities (channels), whose geometric sizes create great resistance to mass transfer of solutes of greater volumetric structure.

In conclusion, let us note that the studies performed showed that PTMSP is a selective adsorbent, first, and chromatography of hydrocarbons on this adsorbent demonstrates molecular-sieve effects.

2.2. PTMSP as adsorbent for separation of hydrocarbon gases on packed and capillary columns

Separation of hydrocarbon gases is of great practical interest. Great attention has been paid to this problem (see, e.g. Refs. [6,15]). Thus it seemed reasonable to consider the possibility of PTMSP application for separation of hydrocarbon gases taking into account molecules of hydrocarbon gases.

Note that PTMSP can be used in packed columns as well. PTMSP was dissolved in chloroform and then Chromosorb W (80–100 mesh) coated with the solution by the well-known technique (see, e.g. Ref. [16]). Then stainless-steel column 6 m \times 3 mm was filled with the adsorbent.

Chromatograms of C_1 – C_4 hydrocarbon gases obtained at various temperatures on packed and capillary columns are shown in Fig. 3. In our

opinion, the results obtained are of analytical interest.

As follows from the chromatograms, PTMSP as adsorbent for gas chromatography is characterised by the following peculiarities of hydrocarbon gases retention: (1) the group separation can be seen: C_2 -group, C_3 -group and C_4 -group; (2) within the group, first unsaturated and branched hydrocarbons elute from a column, then the corresponding *n*-alkane.

Note that C_2 hydrocarbon gases elute as follows: acetylene < ethylene < ethane. The same elution order is listed in the “Alltech” catalogue—separation of C_2 hydrocarbons on packed column with carbon molecular sieve Carbosphere [17]. We would like to point out that columns with PTMSP are characterised by some advantages in comparison with commercially available columns. Although the elution order of C_2 hydrocarbons is the same both on PTMSP and on Carbosphere, the analysis on the columns with Carbosphere is performed at much higher temperature (225 $^{\circ}$ C) than on columns with PTMSP (65 $^{\circ}$ C), the duration of the analysis being the same. This is of great importance for determination of ethylene contamination (Fig. 4).

In our opinion, specific analytical characteristics of C_1 – C_4 hydrocarbon gases to be separated on PTMSP can be improved after optimisation of the techniques.

Adsorption heat of solutes is an important characteristic of hydrocarbon gas adsorption on specific adsorbent. Table 4 shows adsorption heats (Q , kcal/mol) for hydrocarbon gases both on PTMSP and graphitized carbon black [18,19].

When comparing adsorption heats on these adsorbents the following regularity is observed: adsorption heats for C_2 hydrocarbons on PTMSP are less than those on graphitized carbon black, adsorption heats for C_3 – C_4 hydrocarbons are greater on the adsorbent we suggested. Buten-1 is the only exception from the regularity, with adsorption heat much greater on graphitized carbon black (for 1.05 kcal/mol). As seen from Table 4, for C_2 – C_3 hydrocarbons, the greatest adsorption heat is observed for saturated hydrocarbons (ethane and propane) in comparison with unsaturated ones (ethylene and propylene).

Many processes contribute to the retention mecha-

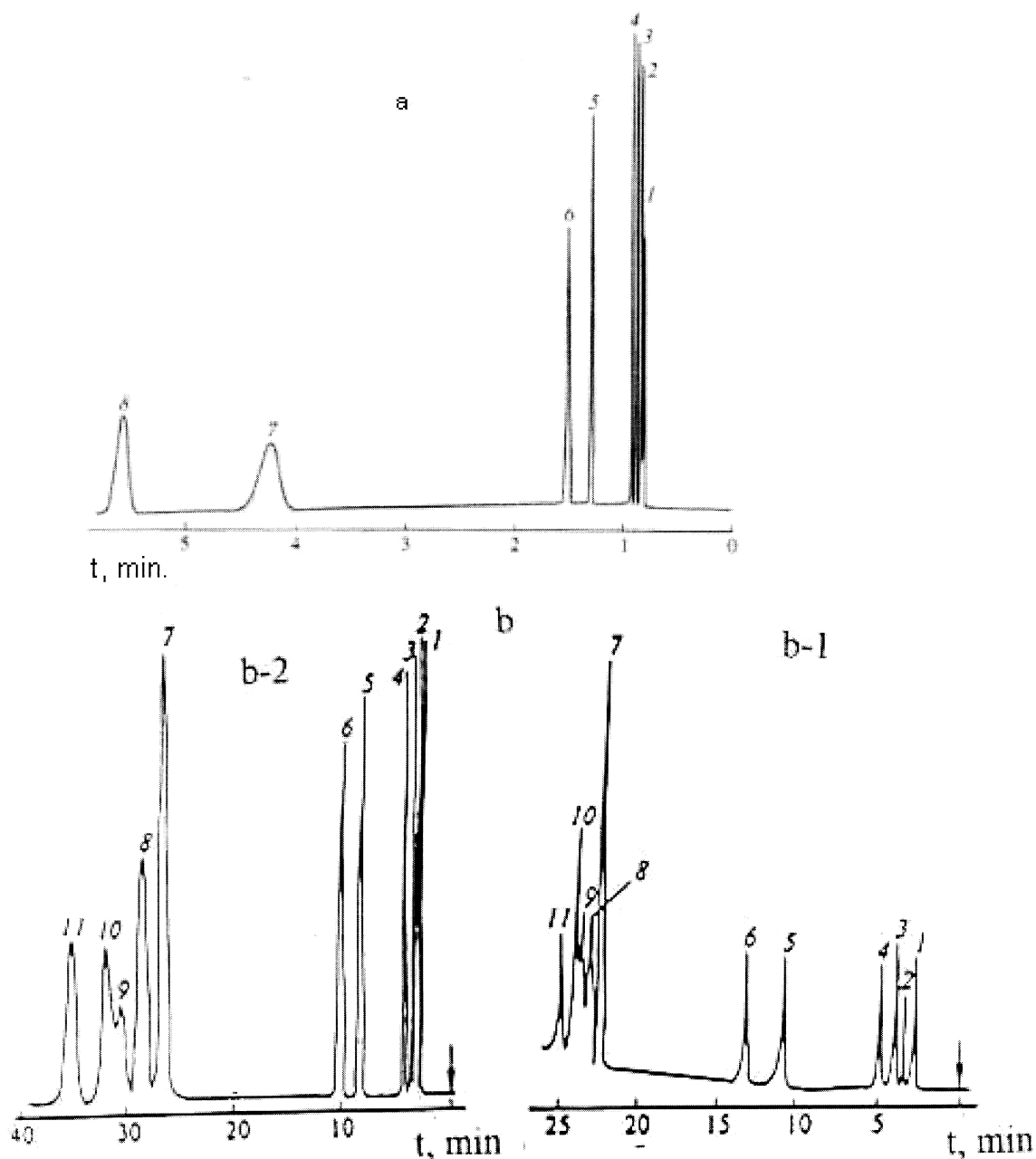


Fig. 3. Chromatograms of hydrocarbon gases obtained on capillary (a) and packed (b) columns. Experimental conditions: (a) capillary column 15 m \times 0.24 mm; adsorbent PTMSP (film thickness 1.4 μ m); oven temperature 27.5 $^{\circ}$ C; carrier gas, helium. Solutes: 1, methane; 2, acetylene; 3, ethylene; 4, ethane; 5, propylene; 6, propane; 7, isobutane; 8, *n*-butane. (b) Packed column 6 m \times 3 mm; adsorbent, 10% PTMSP on Chromosorb W; carrier gas, helium; flow-rate, 35 ml/min. Solutes: 1, methane; 2, acetylene; 3, ethylene; 4, ethane; 5, propylene; 6, propane; 7, buten-1; 8, isobutane; 9, isobutylene; 10, *trans*-buten-1; 11, *n*-butane. Oven temperature program: b-1, Isothermal at 55 $^{\circ}$ C (6 min), rate 4 $^{\circ}$ C/min, final temperature = 155 $^{\circ}$ C; b-2, Isothermal at +75 $^{\circ}$ C.

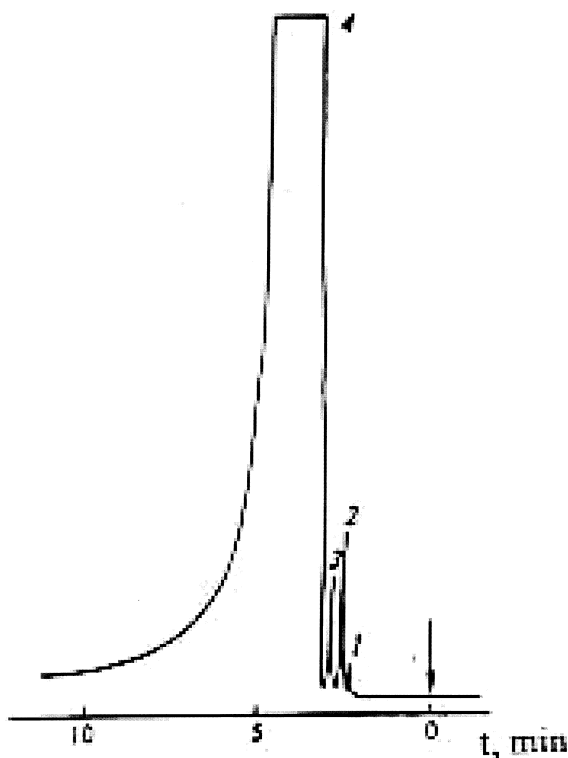


Fig. 4. Chromatogram of acetylene traces in ethylene. Experimental conditions: stainless steel packed column 6 m×3 mm; sorbent, 10% PTMSP on Chromosorb W (80–100 mesh); temperature, 65 °C; flow-rate of helium, 35 ml/min. Solutes: 1, methane; 2, acetylene; 3, unidentified admixture; 4, ethylene.

Table 4
Adsorption heat of C₁–C₄ hydrocarbon gases

Solute	$Q/(\text{kcal/mol})^{-1}$		$\Delta Q = (Q_{\text{PTMSP}} - Q_{\text{gcb}})$
	I	II	
Acetylene	3.4	4.23	−0.83
Ethylene	3.8	4.30	−0.50
Ethane	4.3	4.53	−0.23
Propylene	5.7	–	–
Propane	6.2	5.93	0.27
Butene-1	5.9	6.95	−1.05
Isobutane	7.6	6.95	0.65
Isobutene	8.0	–	–
<i>trans</i> -Butene-2	7.9	7.29	0.61
<i>n</i> -Butane	7.8	7.21	0.59

Adsorbents: I, 10% PTMSP on Chromosorb W; II, graphitized carbon black [20].

nism of hydrocarbon gases (as well as liquid hydrocarbons) on PTMSP. The experimental data we obtained shows that molecules with more volumetric structure are characterised by less retention than *n*-alkanes which can be adsorbed in most microcavities. The concept of certain role of molecular-sieve retention mechanism for PTMSP stated earlier correlates with the data on band-broadening of organic compounds on capillary columns with the adsorbent.

In gas–solid chromatography, resistance to mass transfer in the stationary phase contributes much into HETP (H) [20]. The dependence of HETP on carrier gas velocity for isobutane and *n*-butane on capillary column is shown in Fig. 5. Band-broadening is much greater for branched isobutane than for the corresponding *n*-alkane.

Kinetic characteristics disimprove for iso-alkanes with PTMSP. Most likely, it deals with the presence of such cavities (channels), whose geometry creates great resistance to mass transfer of the more volumetric solutes.

As is known, carrier gas nature and its average column pressure have an influence on the relative retention in gas–solid chromatography [21]. Dependence of relative retention of propylene (1), isobutane (2) and *n*-butane on average column pressure

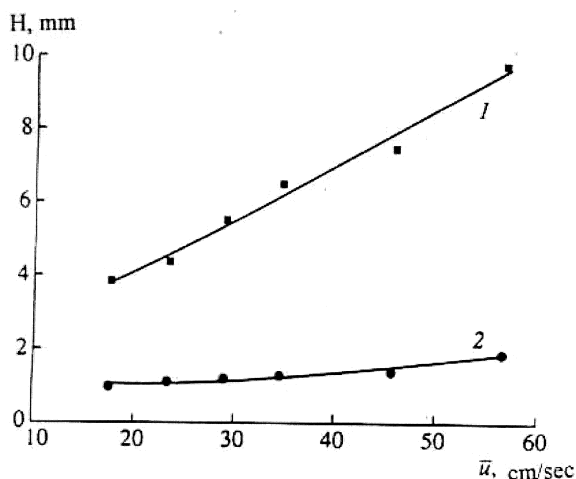


Fig. 5. Dependence of HETP on carrier gas velocity (helium) u for isobutane (1) and *n*-butane (2). Experimental conditions: capillary column, 15 m×0.24 mm; adsorbent PTMSP; film thickness, 1.4 μm ; temperature, 27.5 °C; carrier gas, helium.

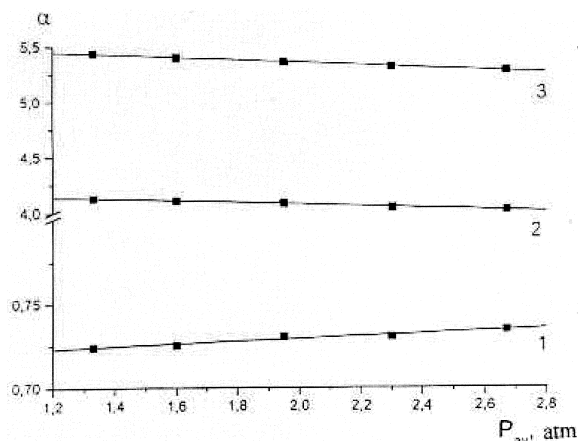


Fig. 6. Linear dependence of relative retention on average column pressure of helium as carrier gas for propylene (1), propane (2) and *n*-butane (3). Experimental conditions: 25 m×0.22 mm; adsorbent PTMSP; film thickness, 1.4 μ m; temperature, 31 °C.

is shown in Fig. 6. As seen, relative retention is linearly dependent on average column pressure. Note that in this figure, the changes in relative retention are indicated for a small pressure variation of 1.3 atm. The data presented in the given study justify the view that carrier gas can be used as a means for improvement of separation, as was shown earlier (see, e.g. Ref. [22]).

3. Conclusion

In our opinion, the results obtained show the prospects for PTMSP application in capillary and packed gas-adsorption columns. This polymer adsorbent is of special interest for separation of inorganic and organic gases.

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