

Effects of Bulky Substituents on Transport Properties of Membrane Gas Separation Materials¹

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Abstract—In this review membrane gas separation properties of two groups of glassy polymers are considered and compared. The first group comprises highly permeable polymers with large free volume. They contain bulky substituents of the structure MR_3 , where $M = Si, Ge, C$, and $R = Me, Et, Ph$. The second group is represented by polycondensation materials (polyamides, polyimides etc.) with various bulky side groups. It was noted that introduction of such substituents into various main chains of polymers of both groups results in increases in gas permeability, free volume and diffusivity. Robeson diagrams for both cases are considered.

Keywords: highly permeable polymers, polycondensation materials, permeability, diffusion, solubility, selectivity of gas separation, free volume

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INTRODUCTION

Directed search for polymers with certain structure and desirable transport properties became recently an important direction of membrane science [1–3]. Different approaches are known today for variation of the polymer design in attempts to achieve the desirable results – high gas permeability in combination with great selectivity of gas separation and stability in separated mixtures. Let us summarize briefly some known features of design that can affect the resulting membrane properties.

1. Rigidity or flexibility of chains;
2. Role of intermolecular interactions (dipole-dipole, H-bonding etc.);
3. Cross-linking;
4. Configuration of side groups (chains);
 - 4.1 Bulky substituents attached directly to the main chains;
 - 4.2 Bulky substituents attached via spacers.

Different approaches are characterized by different efficiency. The strongest, popular and studied in detail is the approach 4.1. It results in obtaining of the most permeable membrane materials. However, in reality all of them work in combinations. For example, a bulky substituent (BS) can include polar groups (4.1 + 2), and this decreases permeability. The effects of BS strongly depend on the rigidity of main chain, so we always deal with the case 1 + 4.1. At last in the pro-

cess of search for and creation of novel materials of gas separation membranes one must always pay attention on difficulties (or easiness) of synthesis, observed yields and cost of preparation of the polymer.

There is huge literature on introduction of BS (mainly $SiMe_3$ groups) into carbochain, predominantly vinylic and polyene chains [4, 5]. On the other hand, there are reasons to consider the efficacy of introduction of other BS and into the chains of other nature, into the products of polycondensation (polyimides, polyamides, etc.). According to this, we plan in this brief review to compare these two directions of the works. Usually, in the literature they are considered independently.

TYPES OF SUBSTITUENTS

Let us consider the main types of BS introduced into various polymer chains. It should be noted that the definition of BS is not well defined. Thus, replacement of H by Me the latter can be considered as bulky, but we shall not consider such trivial cases. However, in some cases for example the group CF_3 can be considered as BS. It is convenient to consider separately BS introduced into carbochain polymers or polycondensation materials (Table 1).

It is seen that substituents introduced into the first group of polymers are distinguished by lower structural variation: they differ mainly by the central atom in symmetrically substituted nonpolar group. The

¹ The article was translated by the authors.

Table 1. Structure of some studied BS

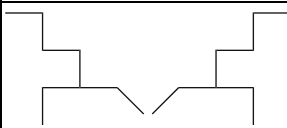
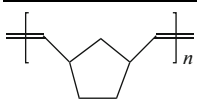
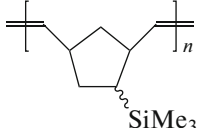
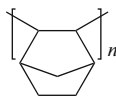
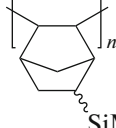
Type	Substituent					
Carbochain polymers	SiMe ₃	SiEt ₃	GeMe ₃	Tert-Bu	SiPh ₃	CHMe ₂
Polycondensation materials	Ph(Ph) ₃	NPh ₂	Tert-Bu		Adamantyls	

Table 2. The influence of introduced SiMe₃ groups on the permeability of polymers of different classes

Polymer	<i>P</i> , Barrer				Ref.
	O ₂	N ₂	CO ₂	CH ₄	
 $T_g = 43^\circ\text{C}$	2.8	1.5	15.4	2.5	[6]
 $T_g = 113^\circ\text{C}$ SiMe ₃	30	7.2	89	17	[6]
 $T_g > 350^\circ\text{C}$	10.8	2.7	49.1	—	[7]
 $T_g > 340^\circ\text{C}$ SiMe ₃	780	297	4350	—	[8]
—[CH ₂ —CH(Ph)]— $T_g = 108^\circ\text{C}$	2.9	0.53	12.4	0.79	[9]
—[CH ₂ —CH(PhSiMe ₃)]— $T_g = 135^\circ\text{C}$	56	16.0	227	34	[10]

substituents introduced into polycondensation materials are more versatile.

SUBSTITUENTS OF GROUP I

There are numerous and compelling proofs of increases of gas permeability due to introduction of substituents I from Table 1. (first and foremost SiMe₃). Though quantitative comparison of substituted and non-substituted polymers is possible not in all the cases. Thus, non-substituted analog of PVTMS, the first studied polymer of this group, is PE, whose transport parameters are determined not only by its chemical structure, but also by its crystallinity. The same is true for polyacetylene. Table 2 is an illustration of this effect. It shows how introduction of SiMe₃ groups into amorphous polymer chains with different chemical structure increases the permeability of the modified polymer. Meanwhile, even from this table it is obvious that in the case of more rigid main

chains (e.g. addition polynorbornene) more drastic effects are observed.

Starting from the earliest studies of the materials of this group [4] it was assumed that the reasons for increases of permeability is a displacement of chains after the introduction of SiMe₃ and related groups (symmetrical and non-polar substituents). Bearing this in mind it could be possible to expect maximum effects for larger substituents. However, analysis of numerous experimental data indicates that this is not so. Table 3 shows the data on gas permeability of disubstituted polyacetylenes containing BS of different nature and size.

It is obvious that there exists an optimal size of a substituent (SiMe₃) that provides maximum permeability. An estimate shows that van der Waals volume of SiMe₃ groups is 92 Å³, while for SiEt₃ group this value is much greater (131 Å³). It is amazing that such simple observation confirmed also in other cases have not

obtained so far serious explanation in the frameworks of computer atomistic modeling.

Meanwhile, other obvious and plausible effects of the structure on the transport properties are fulfilled well. Thus, all the polymers considered in Table 2 have rather short repeat units, so the "concentration" of SiMe₃ groups in them is high, and the observed effects are great. If BS is introduced into polymer with longer repeat unit the increases in permeability are more modest. This is the case for example of substituted polysulfone [11]. Introduction of several SiMe₃ groups into repeat units results in additional increases in gas permeability [12].

Since permeability coefficient P includes kinetic (diffusion coefficient D) and thermodynamic (solubility coefficient S) contributions, i.e. $P = DS$, it is of interest to consider how the introduction of BS affects the parameters D and S . The changes of the values D and S can be depending on the structure of main chains as is seen for metathesis and addition polynorbornenes. Thus, introduction of SiMe₃ groups into the structure of metathesis polynorbornene increases the diffusion and solubility coefficients of gases by a factor 3–4 [13]. More drastic increase of these parameters is observed for similar chemical modification of addition polynorbornene [13].

The effects of SiMe₃ groups on the solubility and diffusion coefficients in polymers can be illustrated by Figs. 1 and 2. Figure 1 indicates that a conventional glassy polymer (in this case polycarbonate) has solubility coefficients S much smaller than S values of polymers containing SiMe₃ substituents.

Introduction of this substituent leads also to increase in the diffusion coefficients, however, simultaneously a reductions of diffusion selectivity (the

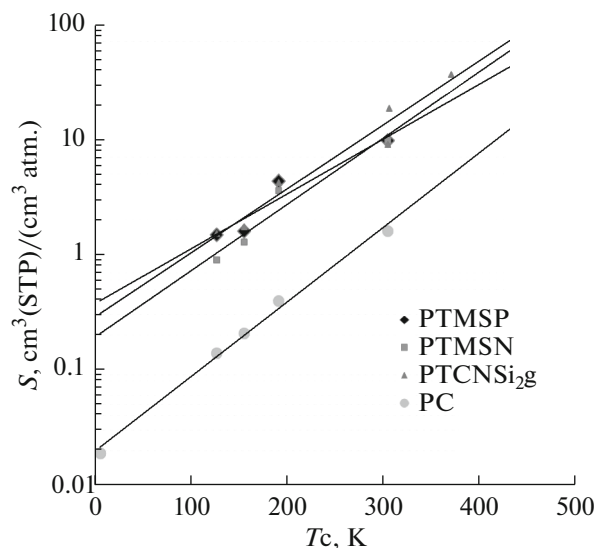


Fig. 1. Correlation of the solubility coefficients with critical temperature of gases in polymers with SiMe₃ groups and polycarbonate [14–16].

Table 3. Gas permeability of polyacetylenes –C(R₁)=C(R₂)– [5]

R ₁	R ₂	$P(O_2)$, Barrer	$P(N_2)$, Barrer
Me	SiMe ₃	6100	3400
Me	SiEt ₃	860	430
Me	GeMe ₃	1800	1200
H	Tert-Bu	130	43

slopes of dependence of D versus squared kinetic diameters of gases d) is observed (Fig. 2).

Interpretation of the data shown in these figures and given in Tables 1–3 obviously indicates the role of free volume V_f . Several methods are known for estimation of free volume in polymers [17]. The simplest though rather approximate Bondi's method [18] is based on measured polymer density ρ (or reciprocal parameter, specific volume $V_{sp} = 1/\rho$) and use of tabulated van der Waals radii of the atoms. According to this method V_f can be presented as

$$V_f = V_{sp} - 1.3V_w, \quad (1)$$

where V_w van der Waals volume of the repeat unit of the polymer. Often another, dimensionless parameter is used, fractional free volume FFV:

$$FFV = V_f/V_{sp}. \quad (2)$$

The literature gives numerous examples of satisfactory correlations D and P with the values V_f or FFV:

$$\ln P = \ln P_o - A/V_f, \quad (3)$$

$$\ln P = \ln P'_o - A'/FFV, \quad (4)$$

$$\ln D = \ln D_o - B/V_f, \quad (5)$$

$$\ln D = \ln D'_o - B'/FFV. \quad (6)$$

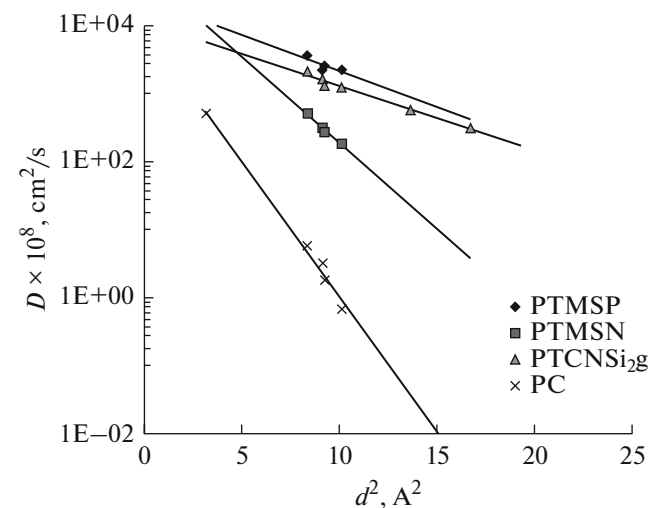
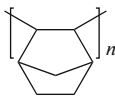
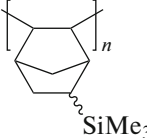
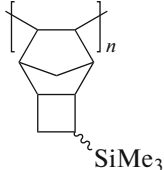
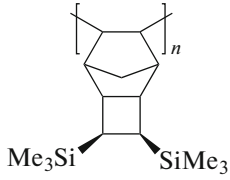
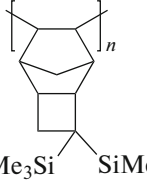


Fig. 2. Correlation of D with d^2 for the polymers containing SiMe₃ group and polycarbonate [14–16].

Table 4. Parameters of free volume in glassy polymers: FFV and the volume of FVE V_f (\AA^3) according to PALS [8, 12, 15, 19]

Polymer	FFV	V_f (\AA^3)
Polystyrene	0.135	102
Poly(trimethylsilyl styrene)	0.19	219
Poly(vinyltrimethyl silane)	0.195	345
Poly(trimethylsilyl propyne)	0.35	1320
	0.15	289
	0.275	776
	—	642
	—	1317
	—	1630

The FFV values for different polymers are given in Table 4. In addition it presents the values of free volume elements (FVE) (in \AA^3) in the same polymers based on positron annihilation lifetimes spectroscopy (PALS), the most reliable method for investigation of free volume in polymers [17, 19]. This table shows that introduction of SiMe_3 group into main chains of polymers having different structure results in increases in free volume. The same conclusion can be made according to the computer modeling of the structure of glassy polymers [20].

An extremely important characteristics of a membrane material is the combination of gas permeability and selectivity. They are envisaged on so-called Robeson diagrams [21]. An example of such diagram for the polymers with bulky substituents of the group I is given in Fig. 3.

The polymers containing SiMe_3 group prevail in this diagram. Depending of the structure of the main chain the permeability coefficients vary in the range of four orders. However, the “compensation effect” or “trade-off behavior” holds: more permeable polymers are less selective, so the cloud of the data points are located parallel to the Upper Bound line. It can be also noted that for the considered polymers not a single point is situated above Upper Bound [21].

Robeson diagram for another gas pair is shown in Fig. 4.

This figure indicates that the permeability coefficients of carbon dioxide change in very wide ranges (4 orders) and reach for some polymers the values of 40000 Barrer, so we observe a very strong influence of the polymer structure on its permeability. Meanwhile, the cloud of the data points again like in the case of O_2/N_2 pair is located below Upper Bound.

SUBSTITUENTS OF GROUP II

The transport parameters of polycondensation materials containing BS were reported for a big group of polymers. A detailed review of these results can be found in recent monograph [23]. Structure of some materials of this group are given in Table 5, their properties are discussed below.

The most popular BS of the second group of polymers is tert-Bu. Examples of the effects of introduction of this group into various polycondensation materials are given in Table 6. As it was seen that the variation of permeability of the polymers of the first group was achieved by variation of the rigidity of the main chain (Table 2), here variation of permeability is attained via changes of the structure of the main chain and especially appearance of other BS. Thus, for polymers PCP1 and PCP2 [24] the values of T_g are 303 and 330°C, respectively. Meanwhile, much stronger are the effects of free volume: FFV is 0.143 and 0.062 for the same pair of polymers. It is also important that for the most of studied structures several BS are present in the repeat unit. Thus, for example in [24] greater permeability of the polyamide was induced by the presence of tert-Bu and oxy-adamanyl-containing groups. In the polymers described in [25] such effect was caused by the presence of phenyl group symmetrically substituted by three tert-Bu radicals. It can be noted that the presence of the fourth tert-Bu group results in further increases in gas permeability.

As the works [27] and [28] indicate if only one tert-Bu group is present the observed permeability is much lower (no wonder because the repeat unit is very large).

As has been mentioned the structure of BS introduced into polycondensation materials varies in much greater extent than in the case of the substituents of group I. This is illustrated by Table 7. For example, the polymers studied in the works [29] and [30] contain

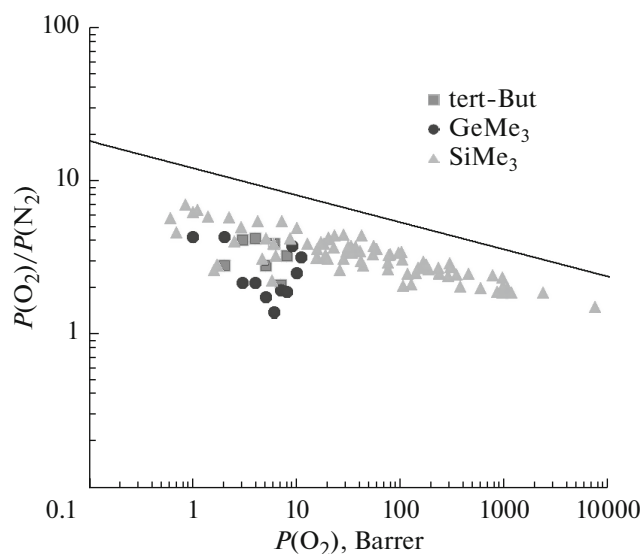


Fig. 3. Robeson diagram [21] for the pair O_2/N_2 in glassy polymers with BS. The source of the data is Database of TIPS [22]. The line is Upper bound of 2008 [21].

very large aliphatic substituents. The polyamide studied in [31] contains CPh_3 side groups. These examples can be continued.

The reasons for variation of gas permeability are the changes of the diffusion coefficients as Tables 8 and 9 show, while the solubility coefficients much weaker depend on polymer structure. For explanation of such trend studies of free volume in these materials (estimation of FFV and computer modeling) were very helpful. In particular, FFV values presented in these tables show that the diffusion coefficients correlate with the fraction of free volume, whereas for the solubility coefficients such correlation is absent. It can be also noted that the values of FFV in these polymers are as a rule smaller than for the polymers of the first group, though some exceptions are sometimes observed [31].

For some polyamides modeling using molecular dynamics (MD) was performed. This method provides detailed information on free volume and its size distribution. It also allows one to make independent assessment of the values D and S , so independent possibility appears to compare experimental and calculated values for D , S and FFV of a specific polymer, as well as for other polymers studied by the same method. Investigation of polyamides [25] via MD showed that integral free volume in the polymer increases when the size of the probe used in the calculations increases in the range from 0 to 20 \AA^3 . At the zero size of the probe fractional free volume reached the value 40%. It means that small microcavities prevail in the polymer.

The shape of size distribution of free volume elements can be different depending on the nature of the main chain and substituents. In some cases several

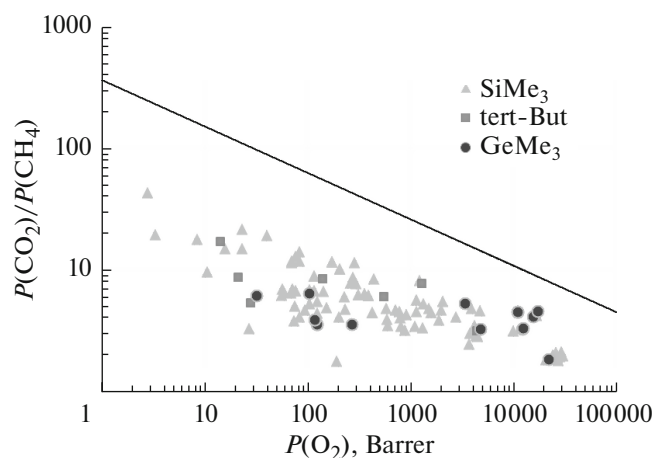


Fig. 4. Robeson diagram [21] for the pair CO_2/CH_4 in glassy polymers with BS. The source of the data is Database of TIPS [22]. The line is Upper bound of 2008 [21].

maxima are present [24], sometimes such distribution can have a form of distorted Gauss function [25, 31]. An example of such size distribution is given on Fig. 5 for polyamide PCP15 studied in [31].

Common feature, however, for all the studied materials is that the observed size distribution is located within the range $20\text{--}80 \text{ \AA}^3$ whereas for the polymers with substituents of the first group the size of microcavity can reach the value of 1300 \AA^3 (Table 4).

Robeson diagrams can be plotted also for polycondensation materials with different BS. They are shown in Figs. 6 and 7 for the pairs O_2/N_2 and CO_2/CH_4 .

It is of interest to make a comparison with the Robeson diagrams for carbochain polymers with substituents of the first group (Figs. 3 and 4). It can be noted that for polycondensation materials the values $P(O_2)$ are in the range 1–50 Barrer and $P(CO_2)$ in the range 10–200 Barrer. So these are much less permeable polymers than those considered in Figs. 3 and 4. Meanwhile, on Robeson diagram for O_2/N_2 pair (Fig. 5) many data points (first and foremost of polyamides and polyimides) are located above the Upper Bound. On the other hand, on the diagram for another gas pair the cloud of data points are located below and parallel Upper Bound as is the case for the first group of polymers. Therefore, each group of polymers has its own advantages and shortcomings, and this should be taken into account while selecting membrane materials for separation certain gas mixtures.

CONCLUSIONS

We have considered membrane gas separation properties of the two groups of glassy polymers: highly permeable polymers distinguished by enlarged free volume and containing BS of the type MR_3 , where $M = Si, Ge, C$, and $R = Me, Et, Ph$ (the first group)

Table 5. Structure of polycondensation materials

Polymer	Structure of the repeat unit
PCP1	
PCP2	
PCP3	
PCP4	

Table 5. (Contd.)

Polymer	Structure of the repeat unit
PCP5	
PCP6	
PCP7	
PCP8	
PCP9	
PCP10	
PCP11	

Table 5. (Contd.)

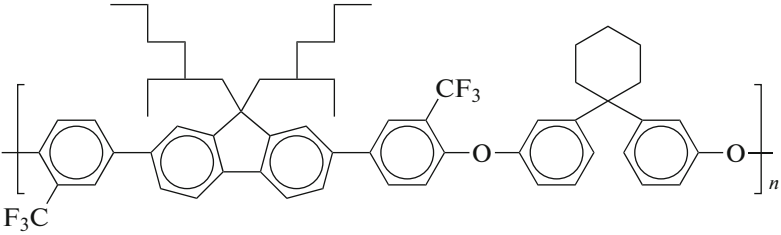
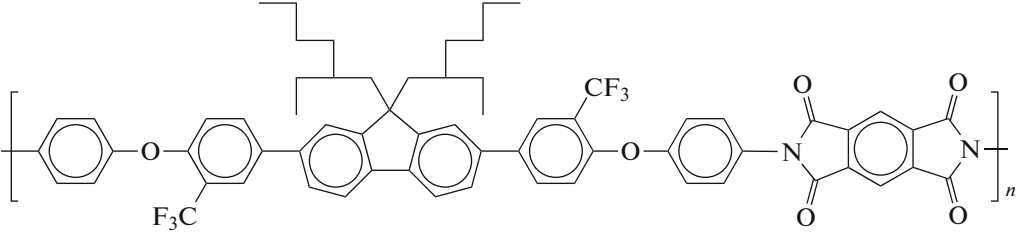
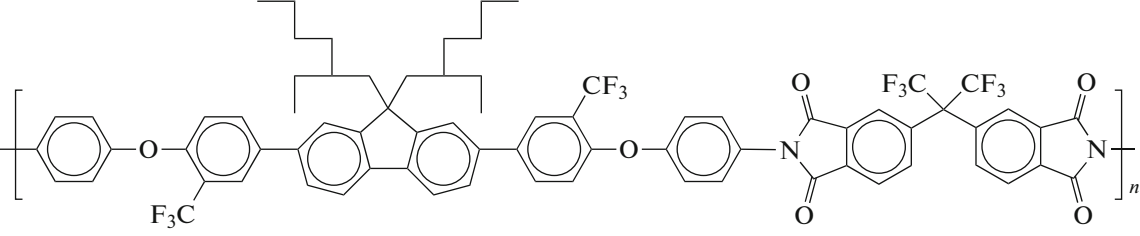
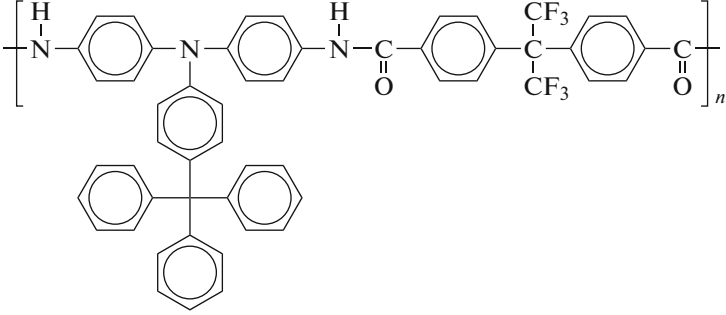
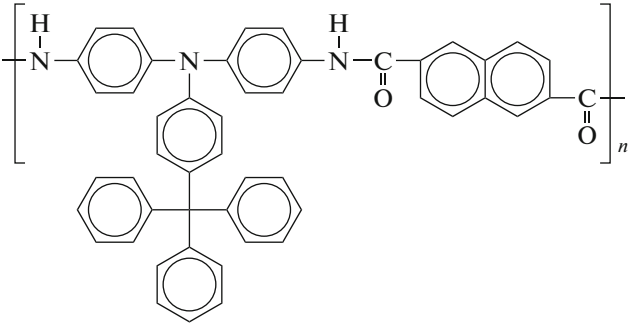
Polymer	Structure of the repeat unit
PCP12	 <p>The structure of the repeat unit for PCP12 consists of a central fluorene core. The 2-position of the fluorene is substituted with a propyl group. The 9-position is substituted with a 4-(trifluoromethyl)phenoxy group. The 7-position is substituted with a 4-(cyclohexylidene)phenoxy group. The entire structure is enclosed in brackets with a subscript 'n'.</p>
PCP13	 <p>The structure of the repeat unit for PCP13 features a central fluorene core with a propyl group at the 2-position and a 4-(trifluoromethyl)phenoxy group at the 9-position. The 7-position is substituted with a 4-(phthalimido)phenoxy group. The structure is shown in brackets with a subscript 'n'.</p>
PCP14	 <p>The structure of the repeat unit for PCP14 has a central fluorene core with a propyl group at the 2-position and a 4-(trifluoromethyl)phenoxy group at the 9-position. The 7-position is substituted with a 4-(bis(trifluoromethyl)phthalimido)phenoxy group. The structure is shown in brackets with a subscript 'n'.</p>
PCP15	 <p>The structure of the repeat unit for PCP15 is a polyamide. It consists of a central nitrogen atom bonded to a 4-phenylphenyl group and a 4-(trifluoromethyl)phenyl group. The nitrogen is also bonded to a hydrogen atom. The 4-(trifluoromethyl)phenyl group is further substituted with a trifluoromethyl group and a carbonyl group. The carbonyl group is bonded to a 4-phenylphenyl group. The structure is shown in brackets with a subscript 'n'.</p>
PCP16	 <p>The structure of the repeat unit for PCP16 is a polyamide. It consists of a central nitrogen atom bonded to a 4-phenylphenyl group and a 4-(trifluoromethyl)phenyl group. The nitrogen is also bonded to a hydrogen atom. The 4-(trifluoromethyl)phenyl group is further substituted with a carbonyl group. The carbonyl group is bonded to a 4-phenylphenyl group. The structure is shown in brackets with a subscript 'n'.</p>

Table 6. Effect of *tert*-Bu groups on gas permeability

Polymer	<i>P</i> , Barrer				Ref.
	O ₂	N ₂	CO ₂	CH ₄	
PCP1	13	1.3	53.5	1.1	[24]
PCP2	3.5	0.3	12.6	0.2	
PCP3	20.2	2.5	86.0	2.9	[25]
PCP4	10.8	1.4	41.5	1.7	
PCP5	44	6	173	7.2	[26]
PCP6	17.8	2.6	70	2.7	
PCP7	0.89	0.15	4.12	0.17	[27]
PCP8	0.19	0.030	0.73	0.033	

Table 7. Permeability coefficients of polycondensation materials with different BS

Polymer	<i>P</i> , Barrer				Ref.
	O ₂	N ₂	CO ₂	CH ₄	
PCP11	10.5	1.3	40.8	0.79	[29]
PCP12	15.5	1.75	62.8	1.1	
PCP13	8.5	0.42	35.2	0.45	[30]
PCP14	17.1	1.0	73.9	1.1	
PCP15	33.4	3.9	141	3.2	[31]
PCP16	18.1	2.2	78	1.8	

and polycondensation materials (polyamides, polyimides, etc..) with various BS (the second group). It was noted that the introduction of such BS into different main chains results in increases in gas permeability, diffusivity and free volume. The most efficient substituent of the first group is SiMe₃. Introduction of BS leads to greater increases in permeability in the cases of more rigid main chains. For the first group of substituents when the nature of main chains is varied one observes very wide changes in the permeability coefficients (within 4 orders). On the Robeson diagrams the

cloud of the data points for these polymers is located parallel to the Upper Bound and does not pass above it. Much greater diversity of BS has been considered for the second group. Their introduction results in less drastic changes of permeability. The best results were obtained when two different BS are present in polymer molecules, for example *tert*-Butyl and adamantyl groups. On the Robeson diagram for the pair O₂/N₂ for this group of materials the data points are located above Upper Bound in many cases, i.e., they demon-

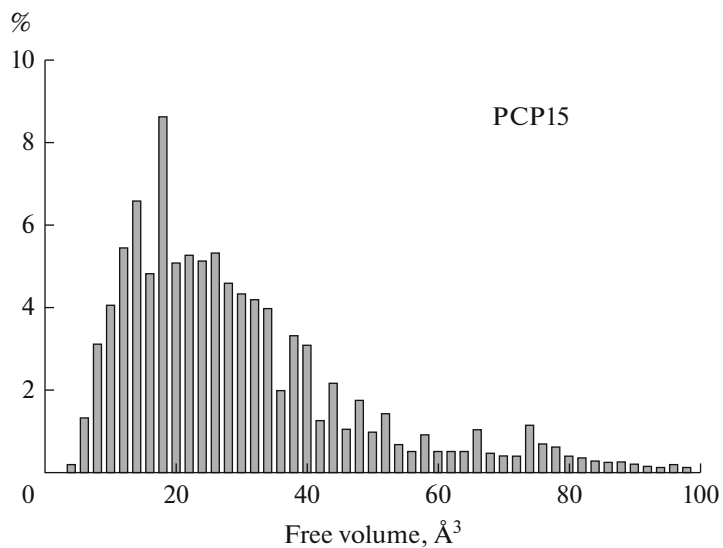
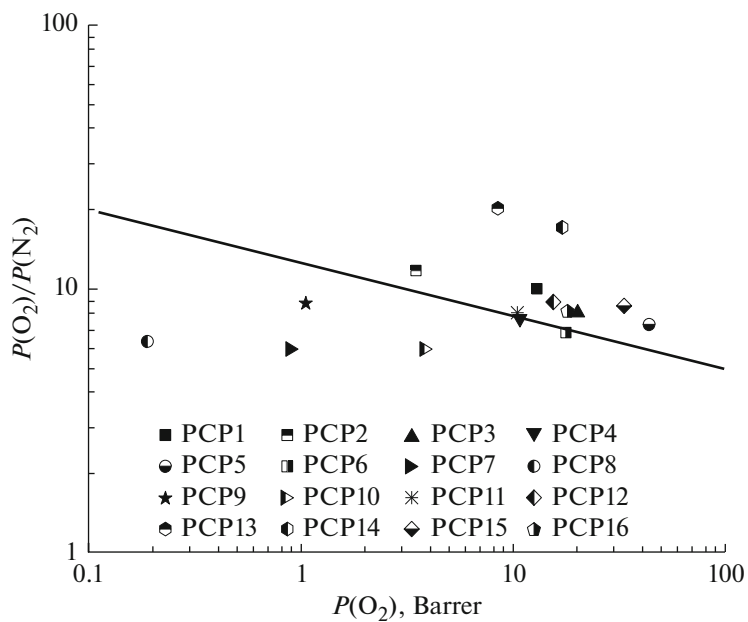
Table 8. Effects of *tert*-Bu group on FFV and diffusion and solubility coefficients in some polycondensation materials [24]*

Polymer	FFV ^{exp}	FFV ^{mod}	<i>D</i> (O ₂), 10 ⁷ cm ² s ⁻¹	<i>S</i> (O ₂), cm ³ (STP) cm ⁻³ atm ⁻¹
PCP1	0.143	0.139	0.85	1.2
PCP2	0.062	0.063	0.12	2.2

* The values FFV^{exp} are obtained via Bondi's method using experimental density, while FFV^{mod} are the results of calculation by means of molecular dynamics method.

Table 9. Diffusion and solubility coefficients in some polycondensation materials

Polymer	FFV ^{exp}	FFV ^{mod}	$D(O_2), 10^7 \text{ cm}^2 \text{ s}^{-1}$	$S(O_2), \text{cm}^3(\text{STP}) \text{ cm}^{-3} \text{ atm}^{-1}$
PCP15	0.315	0.340	0.98	1.6
PCP16	0.229	0.210	0.40	2.0

**Fig. 5.** Size distribution of free volume in polyamide PCP15 [31].**Fig. 6.** Robeson diagrams for the pair O_2/N_2 . The line is Upper bound according to Robeson [21].

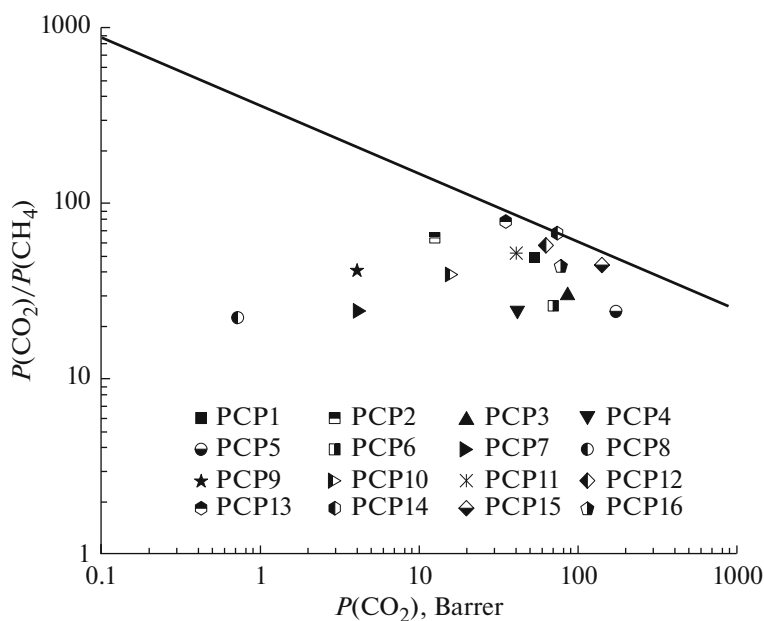


Fig. 7. Robeson diagrams for the pair CO_2/CH_4 . The line is Upper bound according to Robeson [21].

strate excellent gas separation properties (selectivity) of these polymers.

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