



*Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 70th anniversary*

INFLUENCE OF BRIDGING GROUPS ON GAS SEPARATION PROPERTIES OF AROMATIC POLYIMIDES: A COMPARATIVE ANALYSIS

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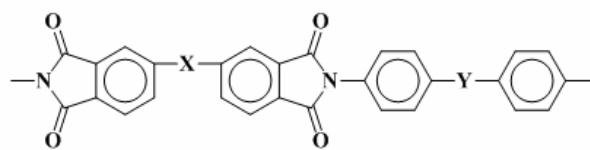
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The influence of bridging groups in the chemical structures on gas separation ability and other physical properties of a number of selected polyimides is analyzed on a system “one polymer-different gases”. The values of glass transition temperature, density, permeability and diffusion coefficients are taken from our own or from other’s published articles. All the data are comparatively analyzed in correlation with the calculated conformational parameters of the polymer chains. The study



regarding the overall selectivity of these polymers shows that the main effect is due to the bridging group located between the imide cycles.

INTRODUCTION

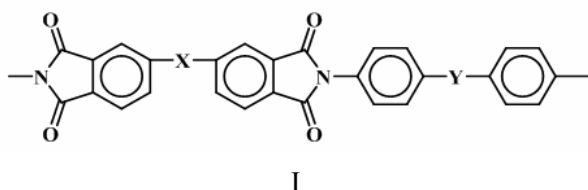
As is known, aromatic polyimides represent a class of heat-resistant and chemically stable polymers with high mechanical characteristics. This allows their use in many fields of technique, including gas separation processes through membranes which are resistant at high temperatures and pressures. To create the most efficient gas separation membranes, by a combination of selectivity and permeability, it is very important to assess the influence of individual structural groups within the polyimide repeating units on their physical and gas transport properties. Here we present a review on selected polyimide structures taken from our own or from other’s published articles and we try to correlate their physical properties, mainly their gas separation characteristics, with the presence of various bridging groups into their chains and with the values of conformational parameters of

those polymers. The conformational parameters were calculated by using a methodology developed by us previously.

CALCULATION OF CONFORMATIONAL PARAMETERS

The polyimide structures taken into consideration for the present study have the general formula I, where X and Y are various bridging groups (Table 1). For these polymers, the data on the glass transition temperature, density, and permeability and diffusion coefficients of gases were found in the published literature.¹⁻¹¹ For all of them we calculated the following parameters of conformational rigidity: Kuhn segment, characteristic ratio, Van der Waals volume, dead volume, free volume, accessible volume and occupied volume.

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The **Kuhn segment** (A_{fr}) was calculated by using the Monte Carlo method by assuming the free rotation, according to equation (1), where $\langle R^2 \rangle$ is the mean square distance between the ends of the polymer chain averaged over all possible conformations, n is the number of monomer units and l_0 is the contour length of the monomer unit being equal to the sum of segments connecting the centers of virtual bonds and it does not depend on chain conformation.¹²

$$A_{fr} = \lim_{n \rightarrow \infty} \left(\frac{\langle R^2 \rangle}{nl_0} \right) \quad (1)$$

The **characteristic ratio** C_∞ shows the number of repeating units in Kuhn segment and it was calculated with the equation (2):

$$C_\infty = \frac{A_{fr}}{l_0} \quad (2)$$

The **Van der Waals volume** (V_w) and the **dead volume** (V_{dead}) were calculated also by using the Monte Carlo method and the values of Van der Waals radii, according to published procedures.¹³⁻¹⁶ The dead volume is the volume near the monomeric unit that is not accessible to the molecule of a given gas due to its geometric dimensions. Knowing these values and polymer density, we calculated the **free volume** (V_f) with the formula (3) where N_A is the Avogadro number, M_o is the molecular weight of the repeating unit, and ρ is the density of the polymer.

$$V_f = \frac{1}{\rho} - \frac{N_A \cdot V_w}{M_o} \quad (3)$$

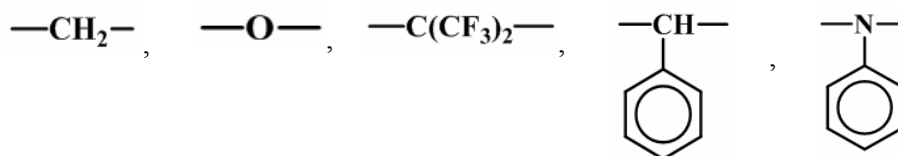


Table 1 shows the repeating units and the values of glass transition temperature,

The occupied volume (V_{occ}) is the sum of Van der Waals and dead volumes (equation 4):

$$V_{occ} = V_w + V_{dead} \quad (4)$$

The accessible volume (V_{acs}) is given by equation (5):

$$V_{acs} = \frac{1}{\rho} - \frac{N_A \cdot V_{occ}}{M_o} \quad (5)$$

To find the correlation of permeability and diffusion coefficients with accessible volume it is convenient to use the so-called **“fractional accessible volume”** (FAV), without any dimensions, which is given by equation (6).¹⁴

$$FAV = V_{acs} \cdot \rho \quad (6)$$

The permeability (P) and diffusion (D) coefficients for He, H₂, O₂, N₂, CO₂, CO and CH₄ were measured in the published works¹⁻¹¹ at different temperatures from 25°C to 50°C. We compared normalized P and D at the reference temperature 35°C using Arrhenius dependence and experimental or predicted by method¹⁷ values of activation energies.

RESULTS AND DISCUSSION

A number of 14 polyimides were analyzed, divided in four series: the first series contains –CO– bridge between imide rings (polymers **1**, **2** and **3**), the second one contains –O– bridge between imide rings (polymers **4**, **5** and **6**), the third one has –C(CF₃)₂– (polymers **7**, **8**, **9**, **10** and **11**) and the fourth one does not have any bridge between imide rings which means that the imide cycles are directly linked to each other (polymers **12**, **13** and **14**). In the diamine fragment, the phenyl rings were separated by the following bridging groups:

conformational parameters and density of the studied polymers.

Table 1

Structural units, glass transition temperature, conformational parameters, density and molecular weight of the studied polyimides
 (The numbers in square brackets show the corresponding references)

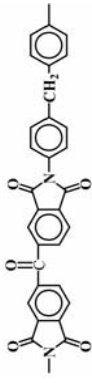
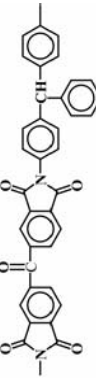
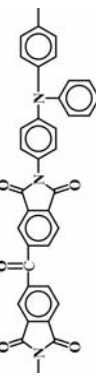
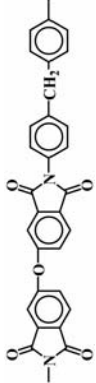
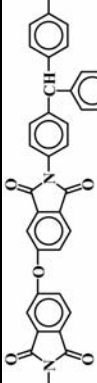
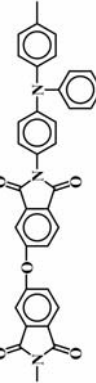
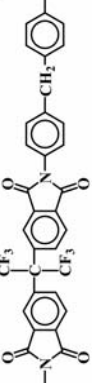
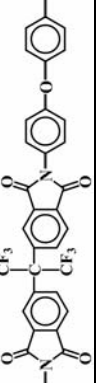
Polymer	Structural unit	T _g (°C)	l ₀ (Å)	A _{fit} (Å)	C _∞	V _w (Å ³)	V _f (cm ³ /g)	ρ (g/cm ³)	M ₀
1		276 [1]	22.37	24.23	1.08	425.956	0.2231	1.329 [1]	484.471
		280 [3]						1.346 [3]	
		280 [4]						1.346 [4]	
		282 [10]						1.33 [10]	
2		278 [1]	22.37	24.55	1.09	501.395	0.2309	1.318 [1]	560.206
3		292 [2]	22.67	33.96	1.5	497.074	0.2298	1.311 [2]	561.559
4		262 [1]	22.42	27.51	1.23	416.057	0.2166 [1]	1.339 [1]	472.460
		300 [2]						1.32 [2]	
		296 [3]						0.2205 [3]	
		264 [4]						0.2168 [5]	
		292 [5]						0.2274 [7]	
		300 [7]						1.336 [5]	
								1.32 [7]	
5		269 [1]	22.42	28.00	1.25	491.547	0.2249	1.294 [1]	548.558
6		288 [2]	22.48	28.96	1.29	487.784	0.2283	1.311 [2]	549.546
7		301 [1]	22.40	24.21	1.08	489.259	0.2260 [1]	1.405 [1]	606.484
		297 [3]						1.408 [3]	
		297 [4]						1.408 [4]	
		296 [5]						1.417 [5]	
		275 [6]						1.433 [6]	
								1.432 [2]	
8		299 [2]	22.52	31.36	1.39	481.17	0.2222	1.432 [2]	608.456
		296 [4]						1.431 [4]	

Table 1 (continued)

9		309 [8]	22.40	29.03	1.30	554.095	0.2328	1.466 [8]	742.481
10		293 [1]	22.40	25.53	1.13	500.933	0.2922	1.361 [1]	681.575
11		307 [2]	22.67	27.30	1.20	562.002	0.2423	1.365 [2]	683.572
12		300 [2] 264 [3] 296 [4]	21.16	40.60	1.92	408.64	0.2186 [2] 0.2078 [4]	1.32 [2] 1.340 [3] 1.332 [4]	456.460
13		270 [2] 290 [4]	21.29	56.03	2.63	400.11	0.2064	1.366 [2] 1.382 [4]	458.332
14		330 [2]	21.40	51.60	1.41	481.820	0.2254	1.300 [2]	533.446

T_g = glass transition temperature

l_0 = contour length of the monomer unit

A_f = Kuhn segment

C_∞ = characteristic ratio

V_w = Van der Waals volume

V_f = free volume

ρ = density

M_0 = molecular weight

Conformational rigidity of these polymers (A_{fr}) is in a rather wide range from 24 Å to 56 Å. The glass transition temperature varies between 262 and 330°C, and for the same polymer, according to different investigations, the glass transition temperature varies in the range of 262 – 300°C for polymer **4**, in the range of 275 – 301°C for polymer **7**, in the range of 264 – 300°C for polymer **12**, and in the range of 270 – 290°C for polymer **13**. This difference in the values of glass transition temperatures for the same polymer in different studies is associated with various causes, including the molecular weight of the polymer, the solvents in which the film was synthesized or cast, and the methods of removing the residual solvent.

We constructed the dependences of glass transition temperature on Kuhn segment values (Fig. 1a-d).

Earlier, it was shown that the glass transition temperatures for polymers of similar structure linearly depend on the conformational rigidity of those polymers.^{18,19} With polymer rigidity increasing, the glass transition temperature increases. On the general dependence of glass transition temperature on Kuhn segment are situated the points/values which in

Table 1 are underlined. By examining the figures 1a-d the following conclusions can be formulated:

When between imide cycles there is no bridge (directly coupled imide cycles: polymers **12**, **13** and **14**) (Fig. 1d), a sharp increase in the rigidity of the entire series of such polymers was observed; the rigidity in this series rises by 11 Å, Tg increases by 66°C, and the ratio $\Delta T_g / \Delta A_{fr}$ is 6.

When –O– bridge connects the imide cycles (polymers **1**, **2** and **3**), the conformational rigidity of such polymers increases by only 1.45 Å, the glass transition temperature rises by 16°C (Figure 1b), and the ratio $\Delta T_g / \Delta A_{fr}$ is 11.

In the series of polymers with hexafluoroisopropylidene bridge between the imide cycles (polymers **7**, **8**, **9**, **10** and **11**), the Kuhn segment increases by 3 Å, the glass transition temperature increases by 32°C (Figure 1c) and the ratio $\Delta T_g / \Delta A_{fr}$ is 10.6.

In the group of polymers having a carbonyl bridge between imide cycles (polymers **4**, **5** and **6**), the Kuhn segment increases by 5.5 Å, the glass transition temperature increases by 16°C, but the ratio $\Delta T_g / \Delta A_{fr}$ is 2.5.

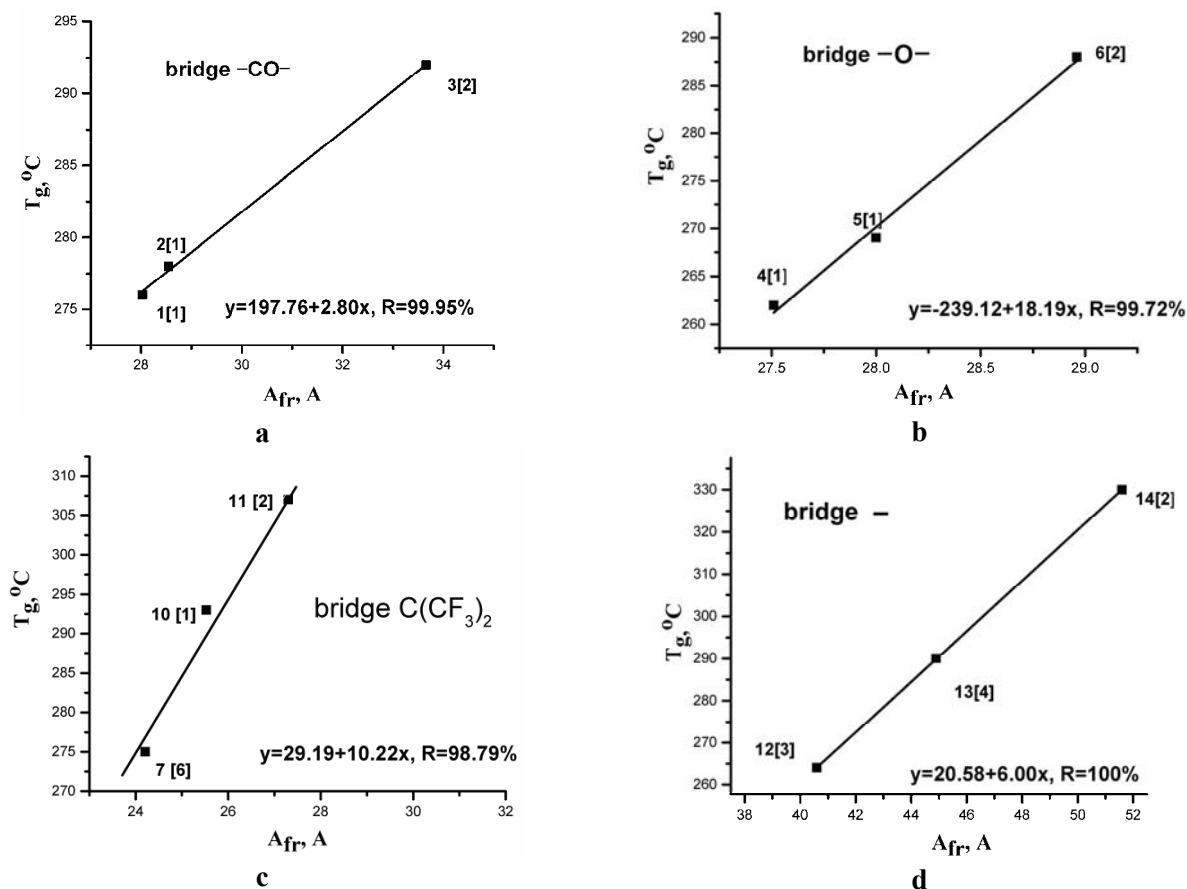


Fig. 1 – The dependence of glass transition temperature on Kuhn segment (The numbers in square brackets show the corresponding references).

Thus, it can be seen that the glass transition temperature is most sensitive to the change in polymer rigidity when the bridging group between imide rings is oxygen atom or a hexafluoroisopropylidene bridge.

Table 2 shows the coefficients of permeability and diffusion of polyimides, obtained by different researchers. The values of the permeability coefficients for the same polymer and gas in a number of cases can differ by 2 or more times.

Figures 2–5 show the dependences of the permeability coefficients on fractional accessible volume.

The dependence of the logarithm of permeability coefficients on $1/FAV$ allows us to examine systems of the type “one polymer - different gases”.¹⁴⁻²⁰ All dependencies are linear with a high correlation coefficient and they are described by the equation $y = A+Bx$. In some cases, the points corresponding to hydrogen and helium do not fall into the general dependence. For hydrogen and helium, the deviations are due to the small size of these gases and their extremely low solubility in the polymer. In addition, for helium there is no exact determination of the value of Van der Waals radius. According to various

sources, this value varies from 1.22 to 1.80 Å.²¹⁻²³ If we assume that the value of Van der Waals radius of helium atom is 1.68, the point corresponding to helium does fall on the common dependence of permeability coefficient on fractional accessible volume. Similar phenomena were observed earlier.²⁴⁻²⁵

The slope (B) of the straight line describing the dependence of permeability coefficient on fractional accessible volume represents the overall selectivity of the polymer. With its help it is possible to evaluate the influence of bridging groups on the selectivity of a polymer. The higher is the value of B, the higher is the selectivity of the polymer. Table 3 shows the values of A and B, and the correlation coefficient R for the permeability coefficients of all polymers and for the diffusion coefficients for those polymers for which the experimental data on diffusion were available. Let us compare the data given for polymer 1 in different studies^{1,3,4} (Fig. 2a and 2b): the overall selectivity found in the second study is three times higher than in the first one (Table 3), although the glass transition temperatures of these samples do not differ much. This indicates the need for correct preparation of a sample for the study of transport properties.

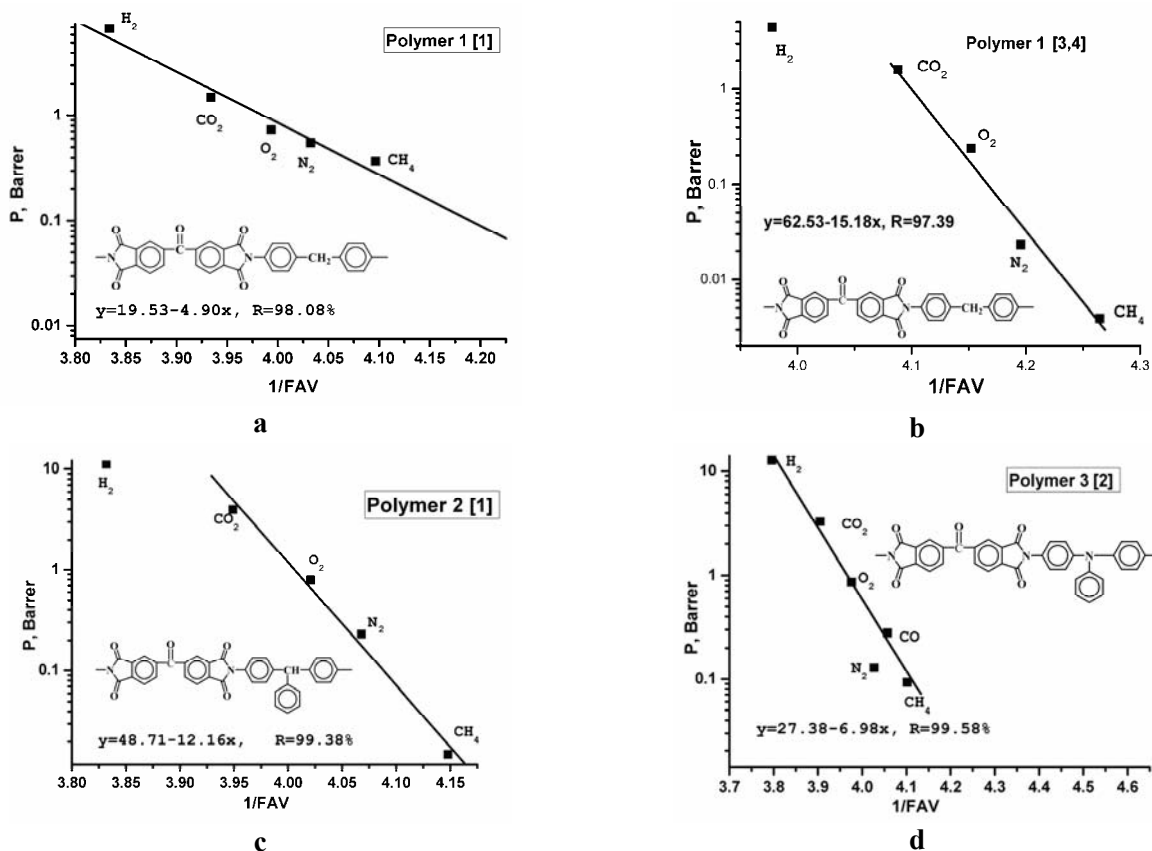


Fig. 2 – The dependence of permeability coefficient on fractional accessible volume for polymers with $-CO-$ bridge between imides cycles (The numbers in square brackets show the corresponding references).

In the case of polymer **12**, the values of overall selectivity B are equal, being 7.85 and 7.70 from data reported in reference ² (Fig. 5a) and references ^{3,4} (Fig. 5b). They differ very little, while the glass transition temperatures differ by 36°C. For polymers **7**¹ and **7**⁵, the values of B obtained from the data of different researchers are close. The glass transition temperatures obtained by these researchers are also close (Tables 1 and 3).

The highest value of B (15.32) was obtained for polymer **1**^{3,4}, which contains a carbonyl bridging group between the imide cycles and a CH_2 group in the diamine fragment. A slightly smaller value of B was obtained for polymer **7**⁵ (14.75) and **7**¹ (12.37) with a hexafluoroisopropylidene bridge in the dianhydride component and the CH_2 group in the diamine component. For polymer **1**, the overall selectivity B obtained from data of different investigators differ by more than three-fold (**1**^{3,4} and **1**¹: 15.32 and 4.90, respectively). A fairly high total selectivity, 11.02 and 12.02, respectively, was observed for polymers **2**¹ and **10**¹.

All polymers having an oxygen bridge in the dianhydride component show rather low values of overall selectivity. The lowest value of B and hence

the low value of overall selectivity for the permeability coefficients belongs to polymer **6**² containing an oxygen bridge in the dianhydride component, and the group $-\text{N}(\text{C}_6\text{H}_5)-$ in the amine component. Thus, it can be seen that the overall selectivity does not depend on the conformational rigidity.

The exception is polymer **14**² which has a low value of B and, accordingly, a low overall selectivity, a high value of Kuhn segment and a fairly high value of free volume. This behavior can be explained by the fact that the dianhydride fragment is quite rigid and while packing in glassy state the polymer forms cavities leading to an increase of the free volume. Polymer **11**² has the lowest value of total selectivity in its series ($B = 8.49$), the lowest value of the Kuhn segment, but the free volume is not the largest. In polyimides containing a hexafluoroisopropylidene fragment, the free volume increases due to repulsion between electronegative fluorine atoms.²⁶ These examples show that the packaging of aromatic polymers in the vitreous state depends on very many factors.

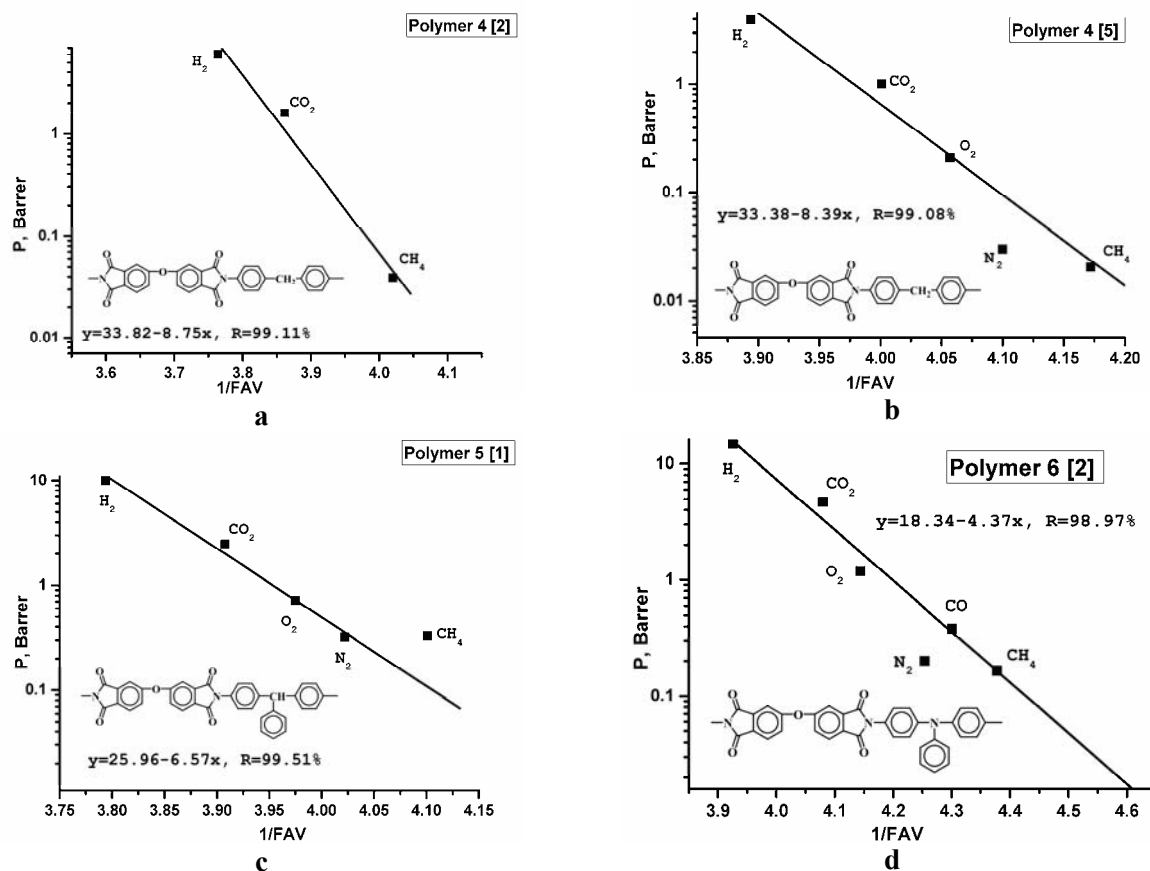


Fig. 3 – The dependence of permeability coefficient on fractional accessible volume for polymers with $-\text{O}-$ bridge between imides cycles (The numbers in square brackets show the corresponding references).

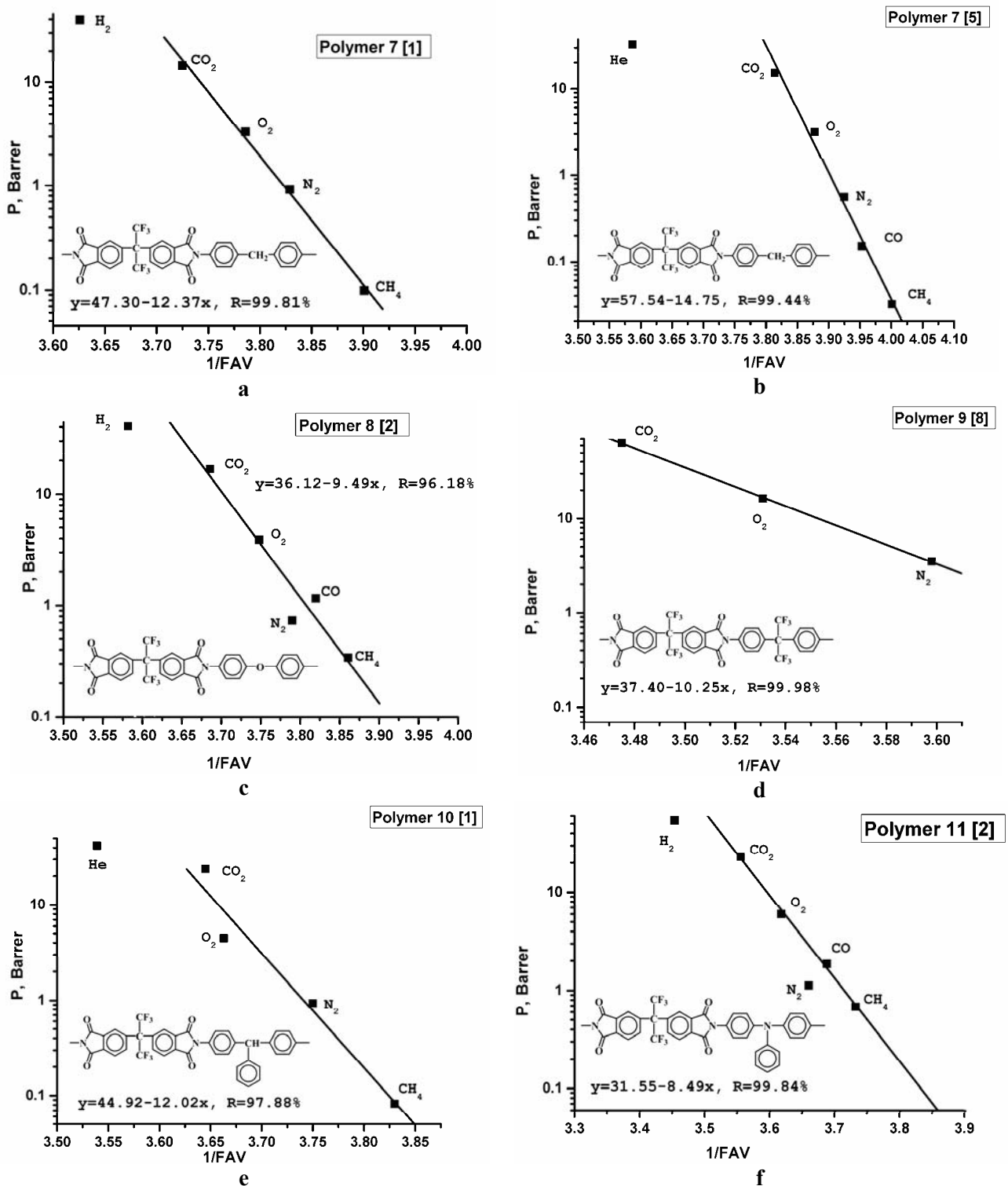


Fig. 4 – The dependence of permeability coefficient (P) on fractional accessible volume (FAV) for polymers with $-(CF_3)_2-$ bridge between imides cycles (The numbers in square brackets show the corresponding references).

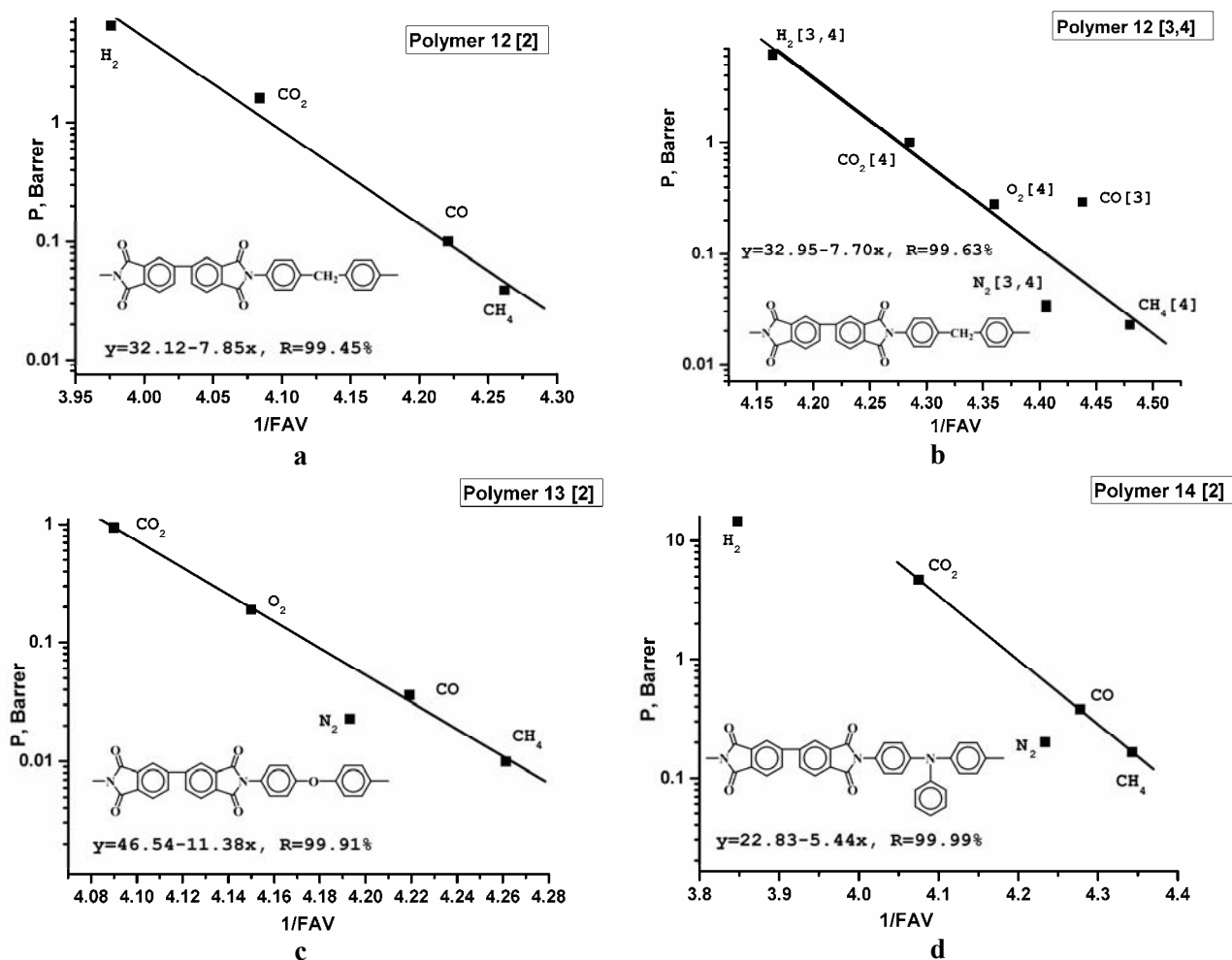


Fig. 5 – The dependence of permeability coefficient (D) on fractional accessible volume (FAV) for polymers with-bridge between imides cycles (The numbers in square brackets show the corresponding references).

Let us examine how the total selectivity (B) of a polymer is related to the free volume (V_f). Figure 6 shows the dependence of B on V_f for the four series of polymers having different bridging groups

of atoms between imide cycles. All dependencies are linear with a high correlation coefficient, although a number of points fall out of common dependencies.

Table 3

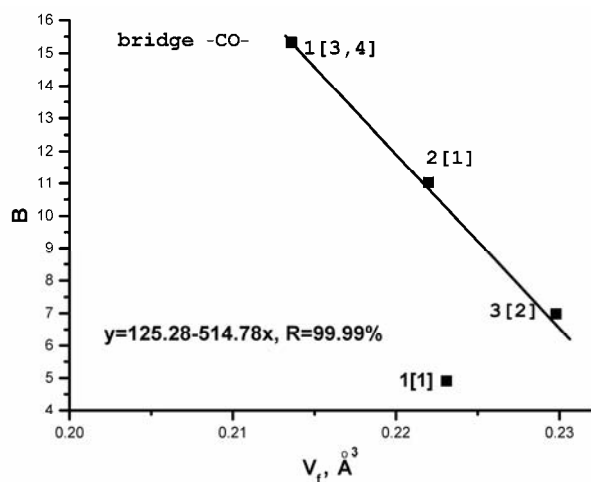
Coefficients of equation $Y=A+Bx$ for the dependence of permeability (P) and diffusion (D) coefficients on fractional accessible volume of the studied polyimides (The numbers in square brackets show the corresponding references)

Polymer	P			D			V_f	C_∞
	A	B	R	A	B	R		
1 [1]	19.53	4.90	98.08				0.2231	1.08
1 [3,4]	62.53	15.32	97.39				0.2136	1.08
1 [10]	32.76 [11]	8.29 [11]	99.17 [11]				0.2216	1.08
2 [1]	46.16	11.02	99.46				0.2220	1.09
3 [2]	27.38	6.98	99.58	16.69	4.22	86.69	0.2298	1.50
4 [2]	33.82	8.75	99.11				0.2259	1.23
4 [5]	33.38	8.39	99.08	48.38	12.03	99.66	0.2168	1.23
5 [1]	25.96	6.57	99.51				0.2249	1.25
6 [2]	16.34	4.37	98.97	19.58	4.67	94.64	0.2283	1.29
7 [1]	47.30	12.37	99.81				0.2260	1.08
7 [5]	57.54	14.75	99.44	45.67	11.63	99.29	0.2200	1.08
8 [2]	36.12	9.49	96.18	37.22	9.77	93.48	0.2222	1.39

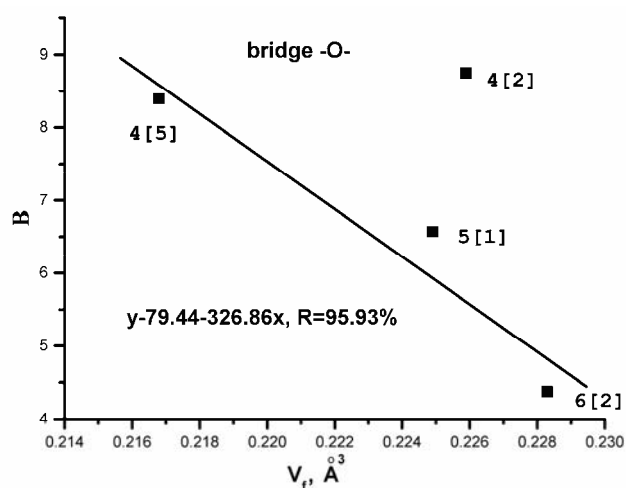
Table 3 (continued)

9 [8]	37.40	10.25	99.98	27.56	7.49	99.91	0.2328	1.30
10 [1]	44.92	12.02	97.58				0.2933	1.13
11 [2]	31.55	8.49	99.84				0.2423	1.20
12 [2]	32.17	7.85	99.45				0.2186	1.92
12 [3,4]	32.95	7.70	99.63				0.2078	1.92
13 [2]	46.54	11.38	99.91				0.2064	2.63
14 [2]	22.83	5.44	99.99				0.2254	1.41

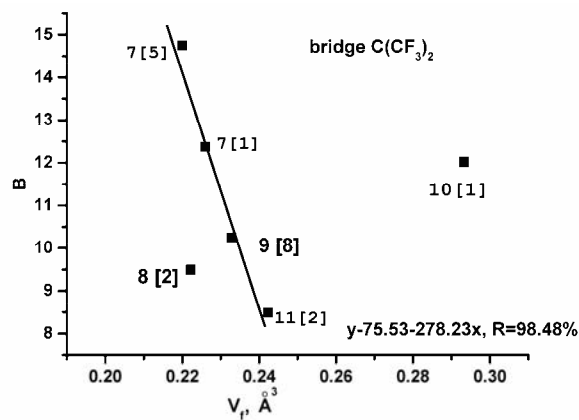
R = correlation coefficient

 V_f = free volume C_∞ = characteristic ratio

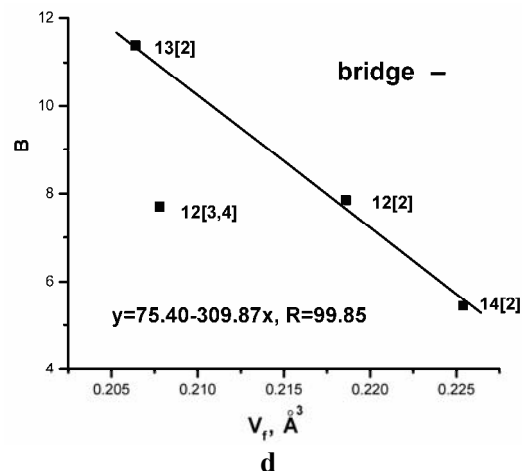
a



b



c



d

Fig. 6 – The dependence of slope B on free volume for different bridges between imides cycles
(The numbers in square brackets show the corresponding references).

These are the points corresponding to polymers: 1^1 , 4^2 , 8^2 , 10^1 , $12^{3,4}$. The slope of the straight line to the abscissa axis, B, shows how the overall selectivity of this group of polymers depends on the free volume. In all four series, when the free volume increases, the value of B decreases which means that the overall selectivity decreases. The fall in B in these groups is different. For the series of polymers having a hexafluoroisopropylidene bridge between imide heterocycles, the value of B

decreases slowly with the increase of free volume ($B = -278$). In the series having an oxygen bridge and in that having directly linked imide cycles, the value of B decreases with increasing of free volume somewhat faster. The values of B are -326 and -309, respectively. And in a group with a methylene bridge, the change in total selectivity with increasing of free volume is much faster than ($B = -514$).

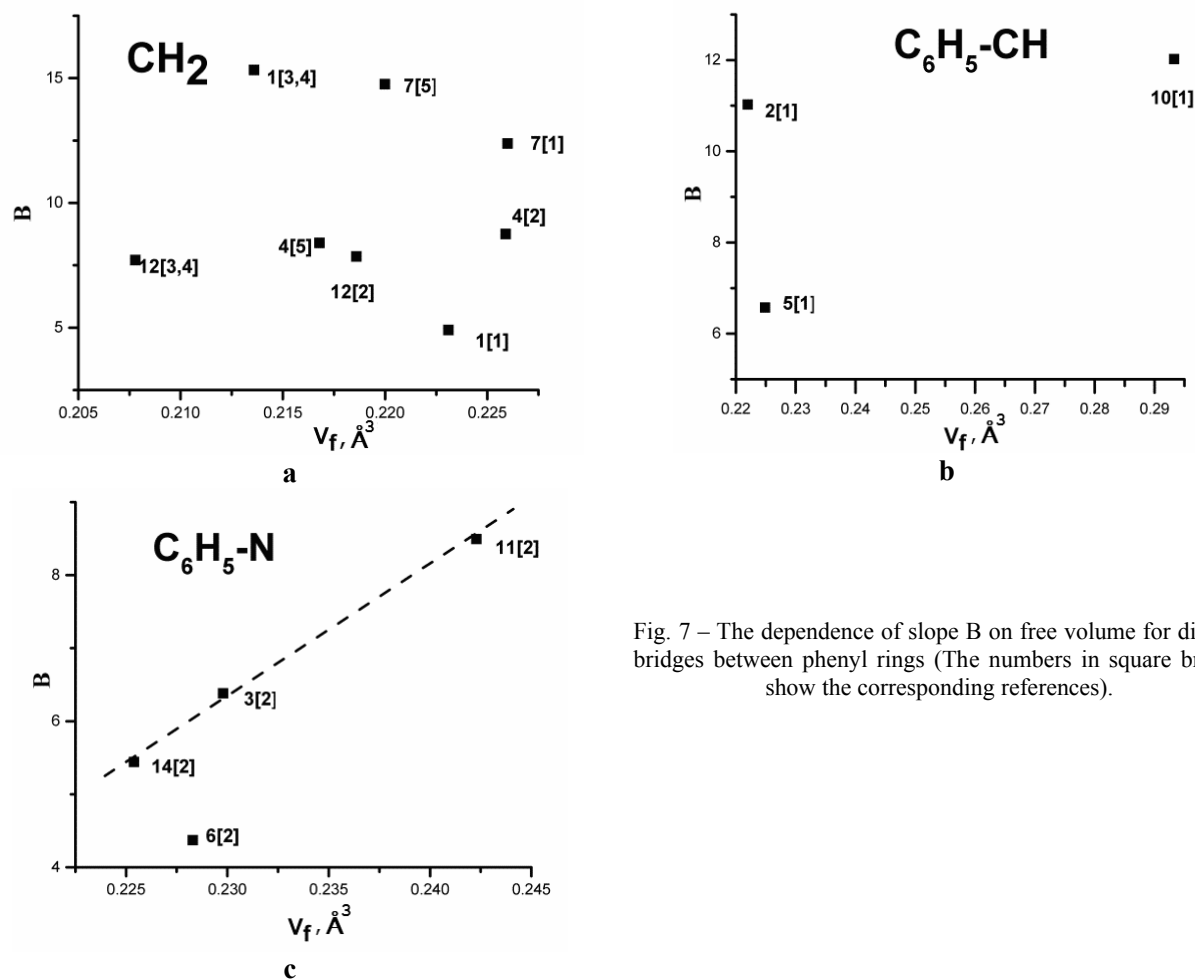


Fig. 7 – The dependence of slope B on free volume for different bridges between phenyl rings (The numbers in square brackets show the corresponding references).

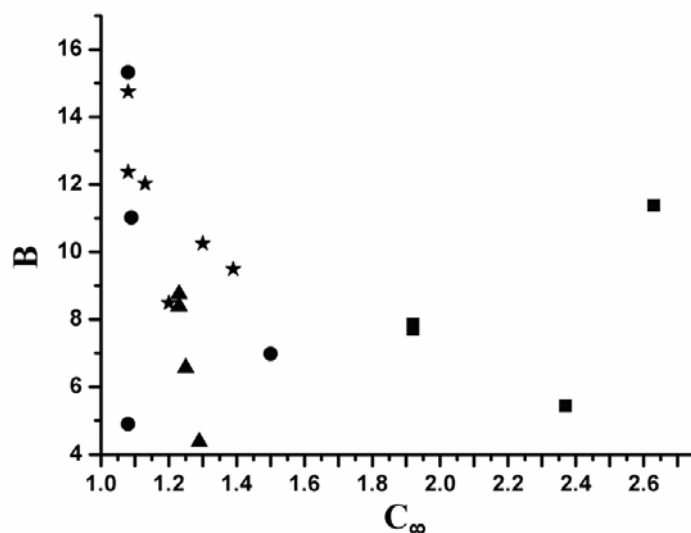


Fig. 8 – The dependence of total selectivity B on characteristic ratio C_∞ :
 \bullet bridge $-\text{CO}-$, \blacktriangle bridge $-\text{O}-$, \star bridge $-\text{C}(\text{CF}_3)_2-$, \blacksquare bridge $-$.

Thus, it can be said that for the permeability and selectivity coefficients of the polyimides, the bridging group between the imide cycles has considerable importance.

Now we examine how the bridging group between the phenyl rings in the diamine fragment of polyimide influences on the transport properties. Such examination can be performed only for

polymers containing one of the following three bridging groups between phenyl rings: $-\text{CH}_2-$, $\text{C}_6\text{H}_5-\text{CH}<$ and $\text{C}_6\text{H}_5-\text{N}<$. In Figure 7 it can be seen that there is no dependence of overall selectivity B on the free volume V_f for polymers with bridging groups $-\text{CH}_2-$ and $\text{C}_6\text{H}_5-\text{CH}<$. However, for polymers with a bridging group $\text{C}_6\text{H}_5-\text{N}<$ (Fig. 7c), an unusual dependence is observed: the overall selectivity increases with the increase of free volume. Perhaps this is due to the peculiarities of the bridging group containing nitrogen with a free electron pair.

As can be seen in Table 3, the polymers **3**² and **6**², having the bridge $\text{C}_6\text{H}_5-\text{CH}<$, exhibit the lowest selectivity of diffusion among the remaining polymers. Thus, the overall selectivity should be determined by the selectivity of solubility. Therefore, the more bridged is the nitrogen atom (more free volume), the greater is the selectivity of solubility, and, consequently, the overall selectivity.

It is interesting to construct the dependence of B on the characteristic ratio C_∞ . As can be seen in Figure 8, the dependence has a maximum around $C_\infty = 1.08$ and then it slowly decreases. At the same time, for the same polymer **1**, the scatter in the B value, obtained from data of different authors, was from 4.9 to 15, which may indicate a dependence of membrane selectivity on film formation method, for example, on complete/incomplete removal of the residual solvent.

Also, for the series of polymers containing $\text{C}(\text{CF}_3)_2$ bridging group, high overall selectivity is observed at C_∞ equal to 1.08 – 1.13. Previously, for a group of 23 polyheteroarylenes, including polyimides, a dependence of B on C_∞ with a maximum at $C_\infty = 1.5$ was observed.¹⁰ This indicates a relationship between the overall selectivity of permeability and conformational rigidity.¹¹ For polymers with C_∞ in the range 1.08 – 1.5 under different conditions of film formation, it is possible to obtain both a low selective and highly selective material, which may be due to the peculiarities of formation of the ordered supramolecular structures.¹⁰

CONCLUSIONS

A detailed study of four series of polyimides having four different bridging groups between imide rings in the dianhydride fragment and identical bridging groups between the phenyl rings

in the diamine fragment showed that the bridging group of the dianhydride fragment has a greater influence on the overall selectivity of the polyimide. In polyimides where bridging group between the phenyl rings in the diamine fragment varies, while the dianhydride fragment is identical, there is no dependence of the overall selectivity on the free volume, except for the case when the bridging group in diamine segment is $\text{C}_6\text{H}_5-\text{N}<$.

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