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Gas transport properties of polybenzoxazinoneimides and their prepolymers

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Abstract

Three types of imide-containing polyamic acids (polybenzoxazinoneimide prepolymers), namely, a homopolymer, a copolymer, and a polymer–metal complex were synthesized and used for homogeneous membranes preparation. These membranes exhibited good physico-mechanical properties and also chemical and hydrolytical stability. Their gas separation properties were measured and analyzed by correlation with macromolecular packing density. Polybenzoxazinoneimide membranes were prepared by heating prepolymer membranes to 220 °C. Difference between gas separation properties of membranes based on polybenzoxazinoneimides and those of their prepolymers was estimated. Gas transport properties of all novel membranes were compared with those of known membranes by using Robeson's diagram. It was established that a polybenzoxazinoneimide membrane including a polymer–metal complex is the most effective among membranes studied here.

Keywords: Polybenzoxazinoneimide; Membranes; Gas separation

1. Introduction

Polymer for gas separation membranes must exhibit a specific physical parameters in order to endow membranes with high transport properties [1,2]. Chemical and thermal resistance of polymers is also required for their use in membrane technologies. It has been established that polyheteroarylenes possessing the above properties are among the most promising membrane materials [3–6]. In the present work, transport properties of novel polyheteroarylenes: polybenzoxazinoneimides, which combine valuable properties of two polymer classes—polyimides and polybenzoxazinones, were studied.

Aromatic polyimides have been extensively studied in the processes of gas and vapour separation [7–12]. Structural order of polyimides, their high packing density, enhanced glass transition temperature, thermodynamic properties, etc. determine their high permselectivity in gas separation [13]. Although polyimides exhibit great advantages there are some problems complicating their practical application. Polyimide prepolymers, polyamic acids used in membrane formation are hydrolytically unstable. Therefore, their molecular weight rapidly drops during storage [14].

Poly(benz-3,1-oxazinone-4)s are characterized by lower thermal resistance than polyimides and inferior physico-mechanical properties, but their prepolymers exhibit a markedly higher hydrolytic stability [15]. The difference in the isomeric structure of amic acid groups, which are transformed into imide or benzoxazinone rings, is responsible for the drastic difference in tendency to degradation with time.

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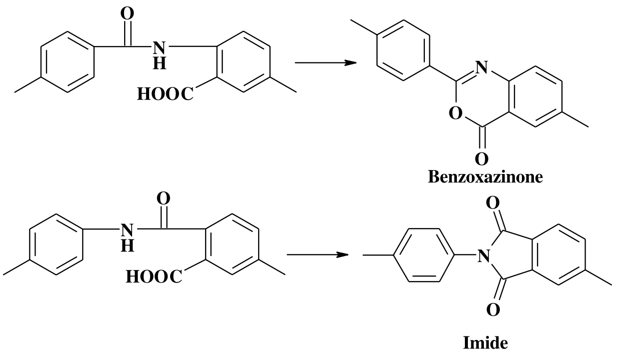
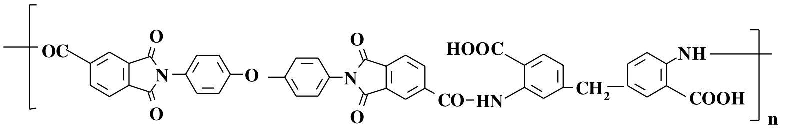
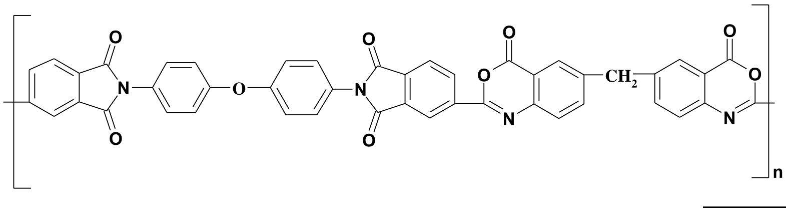


Polybenzoxazinoneimide (PBOI) contains polyimide and polybenzoxazinone fragments in the backbone chain [16]. PBOI exhibits high mechanical properties, thermal stability about 400 °C and insoluble in known solvents. The PBOI prepolymer is an imide-containing polyamic acid (PI-PAA) of the following structure.



PI-PAAs exhibit good physico-mechanical properties, chemical resistance to all solvents except for amide solvents (*N*-methylpyrrolidone, dimethylformamide, dimethylacetamide) and are hydrolitically stable. According to data in Ref. [11], the reduced viscosity of a PI-PAA solution did not change at room temperature for 4 months. These PI-PAAs containing many functional groups in each elementary unit can be of interest as membrane materials, especially in pervaporation. In our previous work [17], pervaporation properties of PI-PAA as a top layer of composite membranes have been studied in the separation of aqueous/organic mixtures.

PI-PAA is transformed into PBOI after dehydration and cyclization. So far PBOI has not been studied as a membrane material.



The aim of the present work is to study transport properties of both PI-PAA and PBOI in gas separation. The effect of polymer structure changes on gas separation properties will also be estimated. For this purpose, the PI-PAA homopolymer, its copolymer, and polymer–metal complex (Scheme 1) were synthesized and used for membrane preparation.

2. Experimental

2.1. Materials

Monomers and solvents purification and syntheses of PI-PAAs (Scheme 1) were carried out by techniques described in Refs. [16,17]. Methylenebis(anthranilic acid) was used without additional purification. Thionyl chloride was distilled, and the fraction at 75.5 °C was taken off. *N*-Methylpyrrolidone was dried over calcium hydride and distilled; bp = 78 °C at 10 mm Hg.

The synthesis of 2,2′-biquinoline-4,4′-dicarboxylic acid was achieved by the Pfitzinger reaction using isatin and acetoine [18].

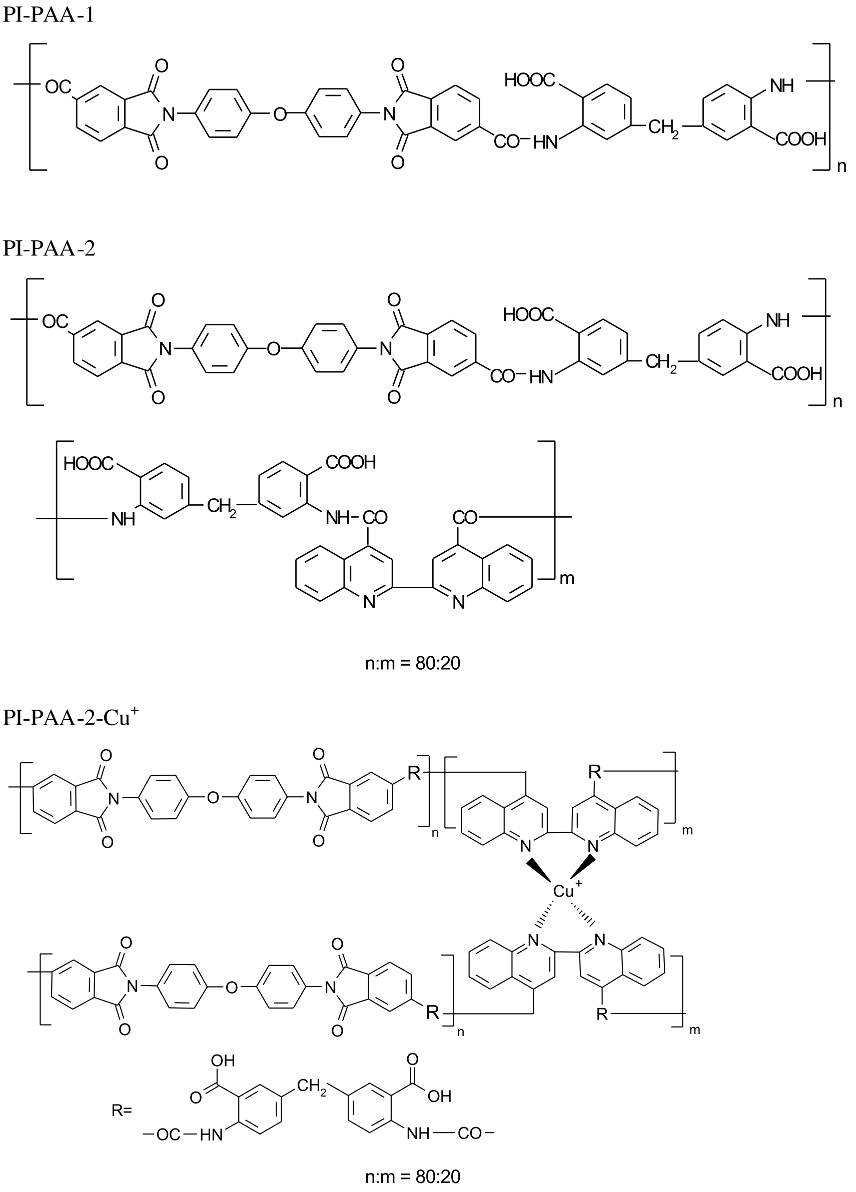
2.1.1. Synthesis of dichloroanhydride of 2,2′-biquinoline-4,4′-dicarboxylic acid

A single-neck round-bottom flask equipped with a reflux condenser was charged with 2,2′-biquinoline-4,4′-dicarboxylic acid (0.016 mol) and thionyl chloride (250 ml). After boiling for 4.5 h, the mixture was cooled. The resulting crystals were filtered, washed with toluene, and dried. The yield was 93%. The synthesized dichloroanhydride melts at 251–252 °C.

The syntheses of *N*,*N*′-diphenyl oxide-bis(trimellitimido) acid and its dichloroanhydride have been described in Ref. [16].

2.1.2. Synthesis of imide—containing polyamic acid (PI-PAA-1)

A two-neck flask equipped with a stirrer was charged with methylenebis(anthranilic acid) (0.002 mol) and *N*-methylpyrrolidone (6.5 ml), and the mixture was stirred until the acid was completely dissolved. The solution was cooled to −15 °C. The dichloroanhydride of *N*,*N*′-diphenyl oxide-bis-(trimellitimido) acid (0.002 mol) were added to the solution. After stirring the suspension at −15 °C for 50 m, the cooling was stopped, and propylene oxide (0.05 ml) was added. The mixture was stirred at room temperature for 4–5 h.



Scheme 1. Chemical structure of imide-containing polyamic acids.

2.1.3. Synthesis of imide-biquinoline-containing polyamic acid (PI-PAA-2)

A PI-PAA-2 copolymer was synthesized using the above described technique with one exception at the stage of dichloroanhydride addition. The dichloroanhydride of 2,2′-biquinoline-4,4′-dicarboxylic acid (0.0004 mol) and the dichloroanhydride of *N*,*N*′-diphenyl oxide-bis(trimellitimido) acid (0.0016 mol) were added to the reaction flask for PI-PAA-2 copolymer preparation.

2.1.4. Synthesis of polymer–metal complex (PI-PAA-2-Cu$^+$)

A PI-PAA-2-Cu$^+$ complex was obtained by adding PI-PAA-2 dissolved in *N*-methylpyrrolidone to an equimolar amount of cuprous chloride dissolved in *N*-methylpyrrolidone. The complex formation was carried out in a flask with a stirrer for a few minutes at room temperature. The solution of PI-PAA-2-Cu$^+$ had an intense violet color. It should be emphasized that metal-polymer complex formation is accompanied by a marked increase in viscosity of polymer solution. The reason is intermolecular cross-linking of PI-PAA-2 chains. To avoid a decrease in polymer solubility, a 1:4 molar ratio of two anhydrides was chosen for synthesis PI-PAA-2 copolymer.

2.2. Membranes preparation

Homogeneous PI-PAA membranes (~20–30 μm thick) were obtained by casting a 10 wt% PI-PAA solution in *N*-methylpyrrolidone on a glass plate. The solvent was evaporated at 80 °C in air. Membranes were dried at 80 °C in vacuum to the constant weight.

Homogeneous PBOI membranes (∼20 μm thick) were obtained by heating PI-PAA membranes at 220 °C for 2 h. According to IR spectroscopy, a degree of cyclization (dehydration with benzoxazinone rings formation) was 97–99%.

2.3. Methods of investigation

2.3.1. Density determination

The density ρ (g/cm^3) was determined by the flotation method in a mixture of carbon tetrachloride and toluene at 20 °C. The specific volume v_{sp} (cm^3/g) was calculated from the equation $v_{sp}=1/\rho$.

2.3.2. Permeation measurement

Gas permeability through membranes was determined by using a laboratory high vacuum apparatus with a static permeation cell with an effective membrane area of 5.25 cm^2 at 30 °C. Gas under constant pressure higher than the atmospheric pressure was brought into the feed part of the previously evacuated apparatus. Permeability was determined from the increase of pressure in calibrated volume of the product part. Gases under study were N_2, O_2, CO_2, and H_2.

3. Results and discussion

3.1. Gas separation membranes

To estimate gas transport properties of new polymers which combine units of polyimide and polybenzoxazinone in the backbone, three types of prepolymers or imide-containing polyamic acids were synthesized. They are a PI-PAA-1 homopolymer, a PI-PAA-2 copolymer, and a PI-PAA-2-Cu$^+$ polymer–metal complex (Scheme 1). It has been established that these PI-PAAs are hydrolytically stable for several months [17]. These polymers were used for the preparation of two groups of homogeneous membranes. The first group of membranes was used as prepared and had the same abbreviation as polymers: PI-PAA-1, PI-PAA-2, and PI-PAA-2-Cu$^+$. The second group of membranes was heated to 220 °C. Thermal treatment led to dehydration with benzoxazinone rings formation in polymer backbone chains. Thus, PBOI-1, PBOI-2, and PBOI-2-Cu$^+$ membranes were prepared.

Thermally initiated physical transformation of PI-PAA films have been studied in Ref. [16]. According to IR spectroscopy, conversion of amic acid groups to oxazinone rings begins at 190–195 °C and stops at 280 °C. Cyclization begins when the temperature markedly exceeds T_g of PI-PAA. Cyclization ceases when the temperature is approximately equal to T_g of PBOI. Table 1 lists T_g of PI-PAA and PBOI that have been determined in Refs. [16,18].

The first group of membranes (PI-PAA) exhibited chemical resistance to all solvent except of NMP,

Table 1
Transport and physical properties of polybenzoxazinoneimides and their prepolymers

Membrane	T_g,[a] (°C)	ρ (g/c m^3)	V_{sp} (cm^3 /g)	Permeability, barrers[b]				Selectivity		
				N_2	O_2	CO_2	H_2	O_2/N_2	H_2/N_2	CO_2/N_2
PI–PAA–1	185	1.375	0.727	0.018	0.138	0.69	3.32	7.7	184	38.3
PBOI-1	271	1.421	0.703	0.0053	0.082	0.26	2.56	15	483	49.1
PI-PAA-2	145	1.364	0.733	0.025	0.160	0.80	3.00	6.4	120	32.0
PBOI-2	245	1.378	0.725	0.012	0.097	0.37	2.85	8.0	238	30.8
PI-PAA-2-Cu$^+$	150	1.391	0.719	0.011	0.099	0.36	2.34	8.9	210	32.7
PBOI-2-Cu$^+$	–	1.465	0.682	0.0039	0.060	0.27	3.70	14.8	960	67.5

[a] Data from Refs. [16,18].

[b] 1 Barrer = 10^{-10} cm^3 cm/cm^2 s cm Hg.

dimethylacetamide, and dimethylformamide. The second group of membranes (PBOI) was practically insoluble in any solvents. Both groups of homogeneous membranes (dense films ∼20 μm thick) were hydrolytically stable and exhibited high mechanical properties (elongation at break up to 100%, tensile strength up to 160 MPa).

3.2. Transport properties

The transport of N_2, O_2, CO_2, and H_2 was measured for six homogeneous membranes. It was found that the membranes studied in this work exhibit relatively low permeability and high selectivity in separation of all the above gases.

Gas separation properties are listed in the Table 1. The order of membranes arrangement in the Table 1 is convenient for comparing properties of prepolymers and the corresponding PBOI and for considering changes in properties from homopolymers to copolymers and to polymer–metal complexes in each membrane group. The data on density and specific volume are also listed in the Table 1. Specific volume ($1/\rho$) was used as a measure of macromolecular packing density because free volume calculation by Bondy's method was a difficult problem for complicated structures of copolymers and polymer–metal complexes.

For a more detailed analysis of the results, the properties of individual membrane groups should be considered.

3.2.1. Properties in the following groups: homopolymers, copolymers, and polymer–metal complexes

The analysis of changing gas transport properties in group: homopolymer, copolymer, and polymer–metal complex was made for the PI-PAA membranes.

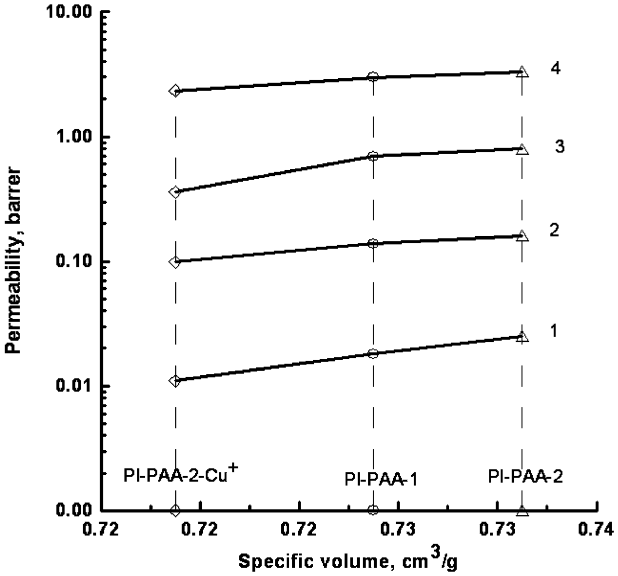


Fig. 1. Dependence of gas permeability on specific volume for PI-PAA membranes. (1) N_2, (2) O_2, (3) CO_2, and (4) H_2.

The effect of polymer structure modification was estimated by correlation between macromolecular packing density and transport properties of homogeneous membranes. Fig. 1 shows the dependence of gas permeability for PI-PAA membranes on their specific volume.

It can be seen from Fig. 1 the increase of specific volume in the following order: PI-PAA-2-Cu^+ < PI-PAA-1 < PI-PAA-2, which leads to some increase of gas permeability. It is noteworthy that the specific volume of the PI-PAA-2 copolymer is higher than that of the PI-PAA homopolymer. The reason may be structure disordering during copolymer synthesis when two different diamines are used simultaneously. The increase in PI-PAA-2 specific volume is responsible for increasing in membrane permeability. The PI-PAA-2-Cu^+ polymer–metal complex is characterized by lower specific volume than that of homopolymer. Denser packed cross-linking structure of the PI-PAA-2-Cu^+ membrane exhibits stronger resistance to gas transport. This is expressed in decreasing gas permeability.

Fig. 2 shows in detail ideal selectivities for several gas pairs. Variation in selectivity of PI-PAA membranes depends on macromolecular packing density. PI-PAA-1 homopolymer exhibits high selectivity for all gas pairs, for example O_2/N_2 selectivity is equal to 7.7. The selectivity value is higher for PI-PAA-2-Cu^+ and lower for PI-PAA-2 than that for PI-PAA-1. In general, selectivity of gas separation increases in the following order: PI-PAA-2 < PI-PAA-1 < PI-PAA-2-Cu^+.

A similar change of gas transport properties occurs in another group of homogeneous membranes based on PBOI.

3.2.2. Change of properties after the PI-PAA → PBOI transition

PI-PAA dehydration with oxazinone ring formation in the PBOI final structure is a complex process that leads to considerable change in polymer physical properties [16,18]. The polymer transformation leads inevitably to a change in gas separation properties.

Table 1 lists permeability coefficients for N_2, O_2, CO_2, and H_2, and also ideal selectivity of these gases separation for six homogeneous membranes. It can be seen that the transformation of PI-PAA in PBOI changes significantly the selectivity and the permeability of homopolymer membranes. In all cases, gas permeability decreases with an increase in gas molecule size. These data are presented in Fig. 3 as the correlation dependence of gas permeability on the kinetic diameter of gas molecules, $\log P = \phi(d^2)$. The plot is not quite linear for PI-PAA-1 and PBOI-1 homopolymers. The similar character of curves can be obtained for the other four polymers. The reason may lie in rigid-chain structure of our polymers. It is known [2] that the dependence of $\log P = \phi(d^2)$ may be linear only for simple flexible chain polymers. In rigid-chain polymers, packing disruptions and very small scale motions are more responsible for the transient 'gaps' that allow diffusion as opposed to the case of flexible chain polymers.

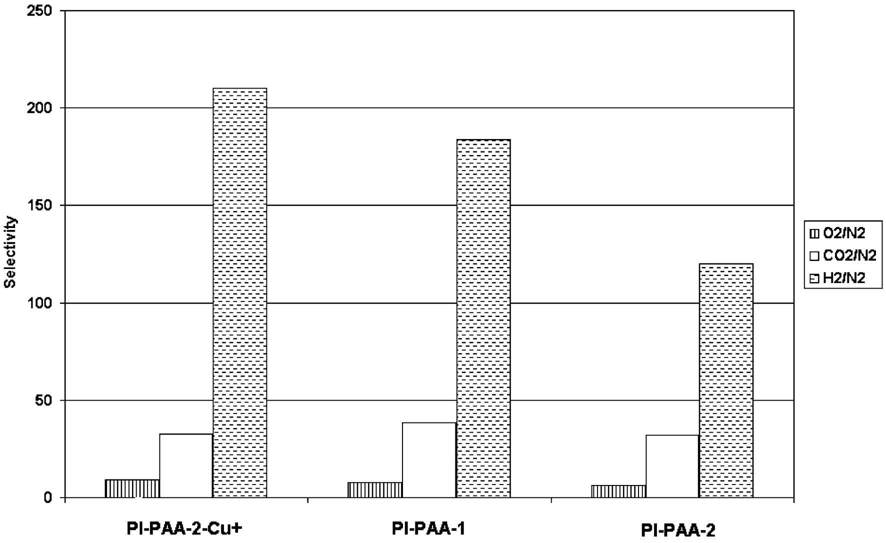


Fig. 2. Gas selectivities of O_2/N_2, CO_2/N_2, and H_2/N_2 for PI-PAA membranes.

According to data in the Table 1 for copolymer, the difference between the properties of PI-PAA-2 and PBOI-2 is much less than in the case of homopolymers, especially in selectivity. Repeated measurements of PI-PAA-2 and PBOI-2 permeability gave the same results. Gas separation properties of PBOI-2 were lower than expected. This suggested that cyclization of disordered PI-PAA-2 structure gives a wider distribution of free volume in PBOI-2 membrane than in the case of homopolymers.

The most essential change of properties occurs in membranes based on polymer–metal complex. PI-PAA-2-Cu^+ dehydration gives a PBOI-2-Cu^+ membrane with elongation at break 16% and tensile strength 110 MPa. High density of PBOI-2-Cu^+ leads to decreasing gas permeability. In the case of the large N_2 molecule, permeability decreases to the greatest extent. This is accompanied by a significant increase in H_2/N_2 selectivity.

3.2.3. Comparison with known membranes

To determine the position of our membranes among the known gas separation membranes, their transport properties were plotted on the Robeson's diagram [19]. Some years ago Robeson analyzed data on permeability and selectivity for a large number of polymers and established the position of the upper bound line for several gas pairs. Fig. 4 shows the upper bound line for membrane separation of the O_2/N_2 mixture and the data on O_2/N_2 permselectivity for the six membranes under study. It is evident that two of our membranes, PBOI-1 and PBOI-2-Cu^+, are located higher than the Robeson's upper bound line. These membranes

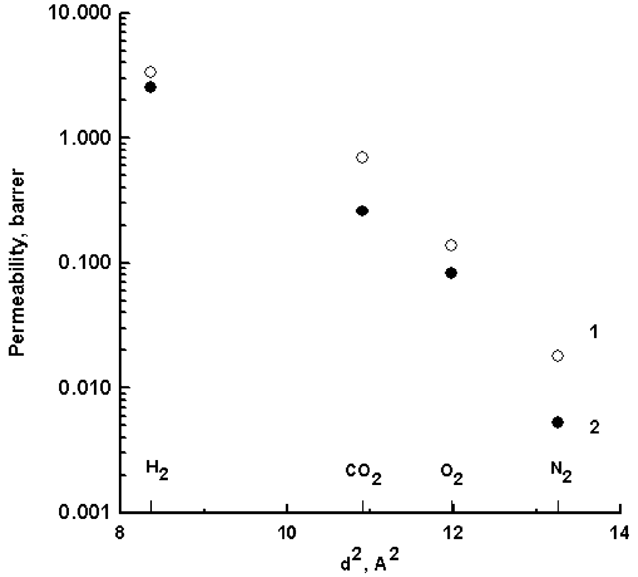


Fig. 3. Dependence of gas permeability vs. kinetic diameter of gas molecules for (1) PI-PAA-1 and (2) PBOI-1 homopolymers.

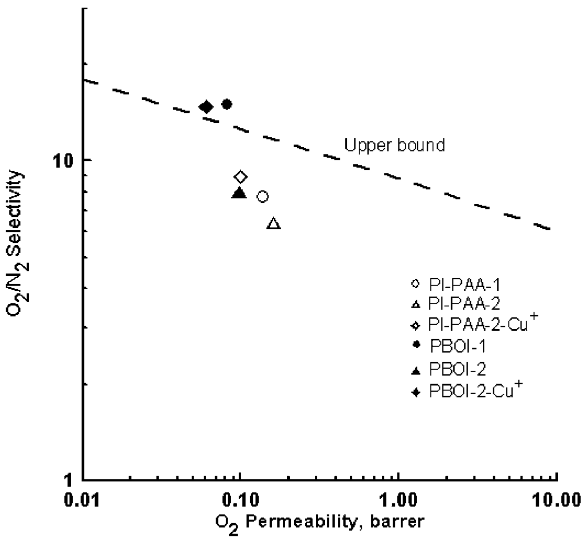


Fig. 4. Permeability/permselectivity diagram for O_2/N_2 gas pair. Upper bound line was taken from Robeson's diagram [19].

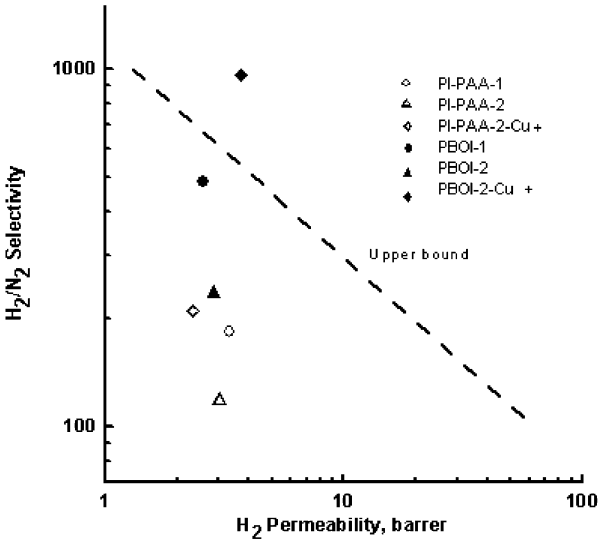


Fig. 5. Permeability/permselectivity diagram for H_2/N_2 gas pair. Upper bound line was taken from Robeson's diagram [19].

make it possible to separate the O_2/N_2 mixture more effectively than the known membranes.

Fig. 5 demonstrates the upper bound line for separating the H_2/N_2 mixture and data on H_2/N_2 permselectivity of the six membranes under study. In this case the PBOI-2-Cu^+ membrane exhibits higher gas separation properties than known membranes.

4. Conclusions

Gas transport properties of new polymers combining polyimide and polybenzoxazinone units were studied for two groups of homogeneous membranes. The first group was based on prepolymers (PI-PAA). The second group was based on PBOI membranes. It was established that in each membrane group specific volume increases in the following order: polymer–metal complex < homopolymer < copolymer. Gas permeability increases in the same order. Note that the density of the PI-PAA-2 copolymer is lower than that of the PI-PAA homopolymer. The reason may be structure disordering during copolymer synthesis when two different diamines are used simultaneously. The PI-PAA-2-Cu^+ polymer–metal complex is characterized by enhanced density of cross-linked structure, the lowest permeability, and high selectivity.

The transformation of the first group PI-PAA membranes in PBOI by heating to 220 °C leads to decreasing gas permeability and a significant increase in selectivity. The greatest changes in properties occur in membranes based on polymer–metal complex.

Gas transport properties of novel membranes were compared with those of known membranes by using Robeson's diagram. Two of our membranes, PBOI-1 and PBOI-2-Cu^+, make it possible to separate the O_2/N_2 mixture more effectively than known membranes. The PBOI-2-Cu^+ membrane is located higher than Robeson's upper bound line for separating the H_2/N_2 mixture.

Acknowledgements

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