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Sorbate-induced structural rearrangements and permeation of gases in the polyphenylene oxide copolymer

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Abstract

Rearrangements of the porous structure of the glassy polyphenylene oxide copolymer occurring in the course of its swelling in the atmosphere of several gases and the subsequent relaxations were investigated using the low temperature nitrogen adsorption technique. The values of porosity (ε) and BET surface area (S_{BET}) were used to quantify the copolymer's free volume accessible to N_2 molecules at 77 K. The magnitude and the rate of changes of the copolymer's free volume invoked by its conditioning in vacuum, N_2, O_2, CH_4, CO_2 and C_3H_6, were analysed in terms of ε and S_{BET}. These characteristics of the polymer structure were found to depend upon the sorbate nature, its pressure, exposure time and temperature. Swelling of the copolymer that occurs in certain atmospheres results in the expansion of the free volume, which is reflected in the increased values of ε and S_{BET}. In accordance with the magnitude of the copolymer swelling under experimental conditions employed in this study, the gases can be qualitatively ranked as follows: $C_3H_6 > CO_2 > CH_4 > O_2 \approx N_2$. The swollen polymer, being placed in the environment of a lower swelling ability, experiences structural relaxations. The relaxations result in a decrease of the free volume, which is reflected by a decrease in the values of ε and S_{BET}. Gas permeability of glassy polymer membranes is directly related to the conditioning history of a polymer: the state of the glassy polymer characterised by the increased values of porosity and BET surface area corresponds to the more permeable state of a membrane. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Glassy polymer membranes; Gas transport; Swelling

1. Introduction

Polymers exposed to certain gases and vapours often experience swelling, which can dramatically alter sorption and diffusion characteristics of polymers as shown, e.g. in Refs. [1–4]. In relation to the glassy polymer membranes, the phenomenon of swelling, first reported by Barrer et al. [5], is known since 1950s. Pronounced swelling with an increase in membrane permeability and a decrease in separation selectivity has been reported for a number of glassy polymer membranes, carbon dioxide being the most commonly used conditioning agent [3,4]. Meanwhile, membrane separation is potentially applicable to a large variety of gaseous mixtures. With a 15% annual rate of growth in the membrane market [6], the range of polymeric membranes and gas separation processes used on an industrial scale is likely to expand in a near future. However, the prospects of membrane gas separation technologies strongly depend inter alia on the problem of polymers' swelling. Investigations of various aspects of swelling for an increasing variety of gases and polymers therefore constitute an essential element of research efforts in the field of membrane gas separation.

The present paper is not considering the macroscopic aspect of swelling, which is defined as "an increase in the volume of the polymer sample resulting from sorption of a low molecular weight liquid or its vapour" [11]. Its subject is the sorbate-induced changes in the structure of the intrinsic intermolecular microvoids that apparently constitute the free volume of glassy polymers and are responsible for the gaseous transport through the polymeric membranes.

The existence of such microvoids, their characterisation and role in the gaseous transport were examined in our earlier studies. A series of glassy polymers of the polyphenylene oxide family (PPOs) was investigated using the low temperature nitrogen adsorption and ^{129}Xe NMR spectroscopy techniques [7,8,10]. The experimental data obtained were indicative of a developed system of interconnected microcavities existing in the polymers. A

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continuous three-dimensional network of molecular-sized interstices between the rigid-chain macromolecules most likely constitutes this intrinsic microporosity of PPOs that belongs to the free volume of the polymers. The micropores are probably of the 'throat and cavity' type, where a cavity may possess several throats. Effective diameters of the pore throats are in the range of ca. 0.4 nm at 77 K, increasing up to ca. 0.5 nm as the temperature rises to ambient. At these temperatures, the intrinsic micropores are accessible for the molecules of simple gases. Apparently, it is through these micropores that the gas transport in the dense polyphenylene oxides membranes occurs, with pore throats playing a role of a size calibre for the molecular sieve effect that manifests itself in membrane separations of certain gaseous mixtures.

It was also demonstrated in the above-cited studies that nitrogen adsorption in PPOs at 77 K does not induce any changes in the structure of the polymers. This proves that the nitrogen adsorption measurements reveal true sorption behaviour of the polymers. Besides, this technique has been found to be very sensitive to the changes in the sorption characteristics of polyphenylene oxides. This allows one to monitor the changes of the microstructure of the polymers, and of the free volume in particular, by evaluating their adsorption parameters in the standardised conditions.

The present paper extends our previous investigations of the intrinsic microporosity of glassy polymers to monitoring the rearrangements of the polymer structure, induced by conditioning in different environments. The choice of a particular copolymer as an object of this study was motivated by the relatively high permeabilities and selectivities of the copolymer membranes in separation of various gaseous mixtures, as well as its good mechanical properties, chemical stability and easy processability in the membrane fabrication [8–10].

2. Experimental

2.1. Polymer

The copolymer of polyphenylene oxide series containing 2.5 mol% of 2,6-diphenyl-1,4-phenylphenol and 97.5 mol% of 2,6-dimethyl-1,4-phenylphenol moieties, hereinafter referred to as Copolymer 1, was kindly supplied by the Institute of Chemical Technology (Novosibirsk, Russia). The copolymer with the glass transition temperature above 200 °C [12,13] was found to be random and amorphous [14]. According to the manufacturer, the viscosity average molecular mass of the copolymer M_v is ca. 100 000.

2.2. Membranes

The polyphenylene oxide copolymer membranes were prepared by casting the carefully filtered chloroform solution of the polymer onto a polished glass plate, followed by drying in air and annealing in vacuum at temperature gradually increasing from ambient to 373 K. At this temperature, the films were kept in vacuum overnight prior to gas permeability measurements.

In the propene permeation experiments, the membrane of the aromatic poly(amide imide) copolymer was also used. The membrane was kindly provided by Dr Yu.P. Kuznetsov (Institute of Macromolecular Compounds, St Petersburg, Russia).

2.3. Gases

Compressed gases produced in Russia were used without additional purification. According to the manufacturers, purity of the gases were as follows: N_2, 99.9%; O_2, 99.9%; CH_4, 99.995%; CO_2, 99.7%; C_3H_6, 99.99%.

2.4. Techniques

Adsorption–desorption isotherms of nitrogen were measured at 77 K using an ASAP 2400 instrument (Micromeritics). Slow diffusion of nitrogen in polymers at this temperature does not allow sorption equilibrium for the typical dense membrane films of 50–70 μm thickness to be achieved at reasonable exposure times. Therefore, adsorption isotherms were measured with powder samples of the polymer.

For the discussion that follows it is appropriate to note that the sorption isotherms of various gases (e.g. oxygen, nitrogen, C_1–C_3 hydrocarbons) at room temperature in both membrane and powder samples of polyphenylene oxides are identical [10]. Besides, the identical NMR spectra of sorbed ^{129}Xe (which are known to be highly sensitive to the immediate environment of the sorbed probe molecule [15,16]) were registered for the membrane and the powder sample of Copolymer 1. It was concluded on this basis that the membrane preparation procedure does not influence the intrinsic microporosity of the polymers, i.e. their free volume accessible to the gas molecules. At the given conditions (pressure, temperature and composition of the gas phase), the intrinsic microporosity is fully determined by the polymer composition. Consequently, the information provided by low temperature nitrogen adsorption in the powder sample is believed to adequately reflect the structure of the polymer's free volume accessible to N_2 molecules at 77 K. In this (microscopic) aspect, the powder and membrane samples are identical.

The membrane permeability measurements were performed in the laboratory set-up with on-line GC analysis as described in Ref. [9]. In the present paper, the membrane gas permeabilities are characterised in terms of their permeability coefficients expressed in Barrers [17]: $1\ \text{Barrer} = 1 \times 10^{-10}\ \text{cm}^3(\text{STP})\ \text{cm}\ \text{cm}^{-2}\ \text{s}^{-1}\ (\text{cmHg})^{-1}$. The conversion coefficient to SI units is $1\ \text{Barrer} = 3.35 \times 10^{-16}\ \text{mol m m}^{-2}\ \text{s}^{-1}\ \text{Pa}$.

3. Results and discussion

3.1. Swelling and structural characteristics of the polymer

We have earlier suggested that with respect to gas sorption and diffusion glassy polyphenylene oxides at temperatures from cryogenic up to ambient can be considered as analogues to microporous solids. The method of low temperature nitrogen adsorption has been shown to be a sensitive tool, adequately reflecting the intrinsic microporosity of the polymers. The latter is believed to be formed by a continuous three-dimensional network of intermolecular microvoids of the throat and cavity type. These molecular-sized micropores with an effective diameter of the pore throats ca. 0.4 nm constitute a part of the total free volume of a polymer. Similar conclusions addressed to other highly permeable glassy polymers but based on different experimental techniques have been made by other researchers [18,19].

Typical nitrogen adsorption–desorption isotherms recorded for the Copolymer 1 conditioned in various atmospheres (vacuum, air, CO_2, C_3H_6) are shown in Fig. 1(a)–(d). The values of BET surface area (S_{BET}) calculated by the standard procedure utilised by an ASAP-2400 instrument, and those of intrinsic microporosity of the polymer were employed as quantitative characteristics of the isotherms. The microporosity (ε) was estimated as suggested in Ref. [8] using the equation

$$\varepsilon = V_{void}/(V_{void} + V_{substance}) = V_{void}/(V_{void} + 1/\rho)$$

where V_{void} is the volume of sorbed nitrogen, cm^3 (liquid)/g; $V_{substance}$ is the volume occupied by 1 g of the non-porous polymer body, cm^3/g. $V_{substance}$ is a reciprocal of the polymer true density ρ, i.e. $V_{substance} = 1/\rho$.

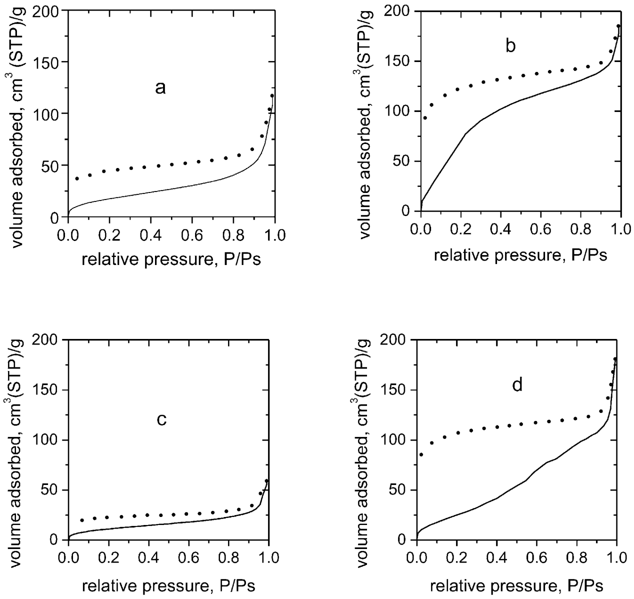

Fig. 1. Low temperature nitrogen adsorption–desorption isotherms for Copolymer 1 conditioned in air at 298 K and atmospheric pressure (a), propene at 298 K and 0.8 MPa (b), vacuum at 373 K (c), carbon dioxide at 298 K and 5.6 MPa (d). Adsorption branches are shown as solid lines, desorption branches as dotted lines.

Analogous to the procedure suggested for the microporous solids in Ref. [20], the values of sorbed volume V_{void} were determined from the desorption branches of isotherms at $P/P_S = 0.9$. The ratio of densities for gaseous and liquid nitrogen used in the calculations was taken as $1\ cm^3$ gas (STP) $= 1.548 \times 10^{-3}\ cm^3$ (liquid), and the value of true density for the copolymer $\rho = 1.13\ g/cm^3$ [7].

3.2. Structural characteristics of the polyphenylene oxide copolymer in different conditioning environments

Variables in the conditioning experiments with the polyphenylene oxide Copolymer 1 were (a) atmosphere (vacuum, air, nitrogen, oxygen, methane, carbon dioxide and propene); (b) gas pressure; (c) exposure time. Conditioning in the presence of permanent gases (N_2, O_2 and CH_4) was studied at the absolute pressures up to 10 MPa. The condensable gases were employed at equal relative pressures of $P/P_S \approx 0.9$ (the corresponding absolute pressures were ca. 5.6 MPa for CO_2 and ca. 0.8 MPa for C_3H_6).

Prior to the nitrogen adsorption measurements, the conditioned sample was removed from the conditioning environment and evacuated in the adsorber of the ASAP instrument for 1 h at room temperature. This treatment removes a conditioning gas without any detectable relaxations of the polymer structure. This was repeatedly confirmed in our studies by the adsorption–desorption scanning of low temperature nitrogen adsorption isotherms of polyphenylene oxides, which revealed their excellent reproducibility.

In each conditioning experiment, the exposure times were kept long enough to ensure that the quasi-equilibrium state of the polymer has been achieved. The latter means that no appreciable changes in S_{BET} and ε were registered for the same sample at longer exposure times under the same experimental conditions. The experimental results on porosity of Copolymer 1 conditioned in C_3H_6 and CO_2 at various exposure times are presented in Fig. 2. As can be seen, with allowance made for a possibly imperfect interpolation at short exposures, the structural transformations of

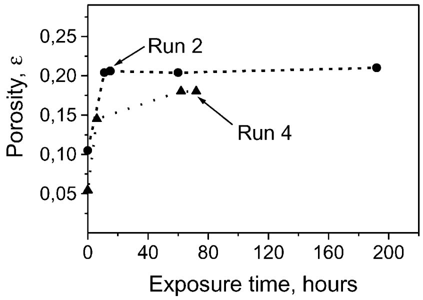

Fig. 2. Porosity of Copolymer 1 upon conditioning in C_3H_6 (circles) and CO_2 (triangles) at various exposure times. Experimental conditions: room temperature, $P/P_S \approx 0.9$. The arrows indicate data points presented in Table 1.

Table 1
Surface area S_{BET} and porosity ε of polyphenylene oxide Copolymer 1 conditioned in different environments

Run	Atmosphere	Temperature (K)	Pressure		Exposure time	S_{BET} (m^2/g)	Porosity ε
			Absolute (MPa)	Relative (P/P_S)			
1	Air	290–300	0.1	–	3 years	67.0	0.105
2	C_3H_6	298	0.8	0.9	15 h	407.2	0.206
3	Vacuum	373	< 0.001	–	48 h	42.2	0.054
4	CO_2	298	5.6	0.9	72 h	102.7	0.18
5	Vacuum	350	< 0.001	–	30 h	44.1	0.058
6	N_2	295	10	–	25 h	44.3	0.059
7	CH_4	295	10	–	24 h	60.9	0.085
8	Vacuum	380	< 0.001	–	24 h	32.1	0.042
9	CH_4	298	1.0	–	31 days	35.7	0.047
10	O_2	298	8	–	120 h	37.1	0.049

the polymer triggered by its conditioning are essentially completed in the first 10–20 h of exposure. Duration of the copolymer conditioning experiments summarised in Table 1 was therefore chosen to be at least 24 h (with the exception of C_3H_6 where the structural parameters clearly stabilised at their highest level after ca. 10 h of exposure, as seen from Fig. 2). Note that the initial state of the polymer, in the CO_2 conditioning experiments summarised in Fig. 2, was that specified in Table 1 under Run 3. The initial state in the C_3H_6 conditioning experiments was that specified in Table 1 under Run 1, except for the point at 60 h exposure time (this point was measured with the sample annealed in vacuum at 350 K for 137 h and characterised by the value of $\varepsilon = 0.053$). As one can see, conditioning of the polymer in this strongly swelling environment brings its structural characteristics to the identical final value, independent of the initial state of the sample.

Our results show that the values of the structural parameters of the copolymer are very sensitive to the sample's history, namely the pressure of a conditioning gas, temperature and exposure time. This important feature was taken into account by choosing a procedure for bringing the copolymer sample to the same initial state prior to each conditioning experiment. The procedure included vacuum annealing of the sample at elevated temperature (typically ca. 370 K). This treatment produced the sample with the lowest S_{BET} and ε values.

As can be seen from the experimental data summarised in Table 1, the polymer conditioned in propene at ca. 300 K and high relative pressure ($P/P_S \approx 0.9$) is characterised by the highest S_{BET} and ε (compare Runs 1 and 2). Swelling in carbon dioxide at the same temperature and relative pressure is less pronounced (Runs 3 and 4). Exposure to nitrogen at 295 K and 10 MPa did not induce any changes in S_{BET} and ε compared to the sample annealed in vacuum (Runs 5 and 6). Certain increase in the structural characteristics was noted upon conditioning of this sample in methane at ca. 300 K and 10 MPa (Runs 6 and 7), while only minor changes were observed at 1 MPa even at exposures as long as 1 month (Runs 8 and 9). Upon conditioning in oxygen at 295 K and 8 MPa which was performed immediately after exposure to methane at 1 MPa, increases in S_{BET} and ε were minimal (Runs 9 and 10).

In accordance with the magnitude of the polymer swelling achieved under the experimental conditions employed in this study, the gases can be qualitatively ranked as follows: $C_3H_6 > CO_2 > CH_4 > O_2 \approx N_2$. This sequence illustrates that propene induces the most significant swelling, while oxygen and nitrogen at moderate pressures (up to ca. 5–10 MPa) and ambient temperatures are essentially non-swelling gases for the polyphenylene oxide copolymer.

The magnitude of changes of the structural characteristics is lower at low pressures of the swelling gases. Methane, the gas showing a moderate swelling ability at high pressure, induces only an insignificant increase in the structural characteristics of the polymer at 1 MPa (compare Runs 6–7 and 8–9). Increase in ε and S_{BET} provoked by the conditioning in CO_2 and propene at equal relative pressures $P/P_S \approx 0.15$ (absolute pressures 0.85 and 0.13 MPa, respectively) was also significantly smaller than that registered at higher pressures of these gases [8,10]. The sequence of gases corresponding to their swelling action at lower pressures though remains the same, i.e. $C_3H_6 > CO_2 > CH_4$.

Temporal variations of porosity ε and surface area S_{BET} were monitored to characterise the dynamics of the polymer swelling. The dependencies of ε and S_{BET} vs. time for the sample conditioned in CH_4 at 1 MPa (Fig. 3(a)) indicate that the rate of structural rearrangement is the highest during the first few hours. A similar swelling dynamics was observed for the polymer conditioned in CO_2 at 5.6 MPa (Fig. 3(b)). In the latter case, the polymer porosity increases from $\varepsilon = 0.062$ (the sample annealed in vacuum) to $\varepsilon = 0.146$ during the first 6 h of conditioning, reaching the value $\varepsilon = 0.180$ in 72 h.

The swollen sample left in air at room temperature following its conditioning in CO_2 slowly relaxes to the state of a 'less open' microporosity. This was demonstrated by the repetitive measurements of nitrogen adsorption over a period of 6 months that revealed a continuous decrease in the values of ε and S_{BET} (Fig. 4). Similar to swelling, the rate

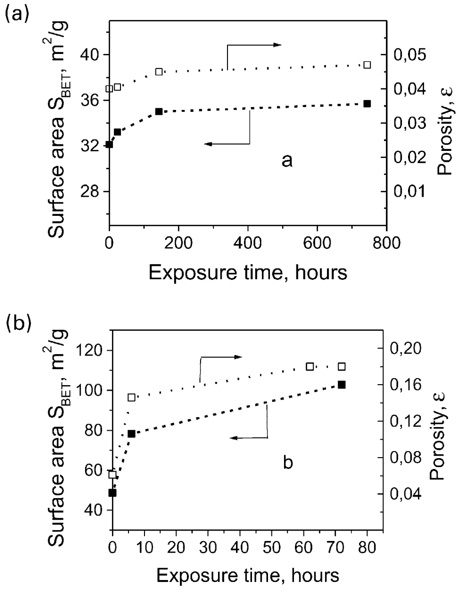

Fig. 3. Dynamics of Copolymer 1 swelling in methane at 298 K and 1.0 MPa (a), and carbon dioxide at 298 K and 5.6 MPa (b).

of structural rearrangements involved in the relaxations is highest in the initial period.

Summarising the earlier results, we can now conclude that the effect induced by the conditioning of the polyphenylene oxide copolymer on the characteristics of its intrinsic microporosity is determined by the nature and the partial pressure of a conditioning gas as well as the exposure time. In good agreement with the practice of membrane gas separation technologies, the results of low temperature nitrogen adsorption show in particular that propene and carbon dioxide are much stronger swelling agents than the permanent gases—methane, oxygen and nitrogen. Furthermore in the present study, it is shown that propene is a stronger swelling agent than carbon dioxide with respect to the polyphenylene oxide.

Upon swelling, the intrinsic microporosity of the polyphenylene oxide apparently retains its open structure of the ‘pore-and-throat’ type, but accessibility of the polymer free volume to nitrogen molecules increases significantly. This conclusion is based on the following experimental results: (i) the nitrogen adsorption–desorption isotherm is of the same type (typical of the pre-existing pore-and-throat type micropores), regardless of the conditioning environment (Fig. 1); (ii) the values of S_{BET} and ε significantly increase upon exposure to the swelling gas (CO_2 or C_3H_6). In turn, an increase in S_{BET} and ε due to the polymer swelling can result from two factors: (1) an increase in the effective diameter of those intrinsic micropores, which are accessible to nitrogen in the non-swollen polymer, and/or (2) an increase in the numbers of accessible micropores. As estimated in our previous studies using ^{129}Xe NMR spectroscopy technique, an increase in the effective pore diameter due to the polymer swelling is relatively insignificant even at high degrees of swelling (ca. 0.01 nm vs. an average pore diameter ca. 0.5 nm). Such change per se cannot account for the observed increase in the polymer’ porosity caused by swelling (Table 1). More important in this respect seems to be the opening of new pathways for the transport of nitrogen molecules through the polymer matrix. Higher adsorption capacities of polyphenylene oxides towards oxygen relative to nitrogen at 77 K [7] indicate that a significant portion of the intrinsic micropores in the non-swollen state of the polymer has throats of the effective diameter smaller than that needed for the nitrogen molecule to enter the pore, but large enough for the smaller oxygen molecule (kinetic diameters of nitrogen and oxygen molecules are 0.364 and 0.346 nm, respectively [21]).

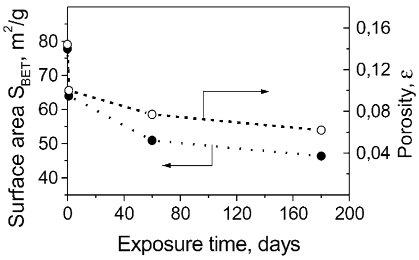

Fig. 4. Dynamics of Copolymer 1 relaxation in air at room temperature and atmospheric pressure after swelling in carbon dioxide at 298 K and 5.6 MPa.

It is, therefore, suggested that an increase in the portion of the polymer free volume accessible to N_2 molecules is mainly due to the expansion of the throats of the intrinsic micropores, which opens pathways previously inaccessible to the transport of gas in the polymer. If a considerable portion of the intrinsic micropores in the non-swollen state of the polymer has the throats with an effective diameter just below that of nitrogen molecule (which seem to be the case for the polyphenylene oxide), then even an insignificant increase in the pore diameter caused by swelling can make the polymer’s free volume much more accessible to the sorbate.

3.3. Structural rearrangements and permeation of a swelling gas in the glassy polymer membranes

The sorbate-induced changes in the intrinsic microporosity of a glassy polymer are closely related to the transport characteristics of the polymeric membrane, i.e. the larger the values of ε and S_{BET} is, the higher is the membrane permeability. This conclusion is supported by the results of propene permeation through the Copolymer 1 membrane coupled with the analysis of structural characteristics of the polymer. The S-shaped permeability vs. pressure dependence with an abrupt increase of permeability registered for the membrane was shown to be in a good correlation with the values of porosity (ε) for the copolymer, conditioned under the corresponding pressures of propene [8].

Permeability vs. pressure dependencies characterised by the drastic increase of permeability at certain gas pressures

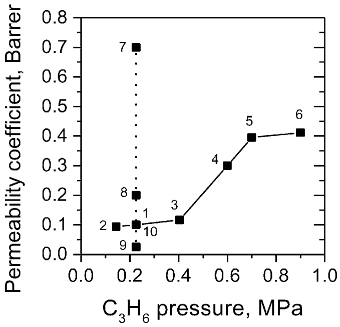

Fig. 5. Permeability coefficients vs. propene pressure for the aromatic poly(amide imide) membrane at 298 K.

seem to be rather typical for permeation of propene (and perhaps of other strongly swelling gases) through the glassy polymer membranes. In our studies such dependencies were also registered for permeation of propene through the membranes made of highly permeable poly(vinyltrimethyl silane) and poorly permeable aromatic poly(amide imide) copolymer, or PAI. The experimental data on propene permeation through the PAI membrane are presented in Fig. 5. Numbers at the points designate the sequence of experiments. In the series of Runs 1–6, the membrane was conditioned overnight at the corresponding propene pressure prior to each run. As one can see, in the pressure range 0.15–0.4 MPa the permeability coefficient increases only slightly with the propene pressure. The curve rises much more sharply above 0.4 MPa, and the permeability vs. pressure dependence reaches a plateau above 0.7 MPa.

After Run 6, the membrane was evacuated for 14 h at room temperature (ca. 293 K) to a residual pressure ca. 1 Pa. The value of permeability coefficient measured in the next run (7) was found to be nearly seven times higher than that determined in the Run 1. Subsequent evacuation of the membrane for 14 h at 323 K resulted in the permeability coefficient equal to 0.20 Barrer (8), which is still significantly higher than the value registered in Run 1. Additional vacuum annealing for 120 h at 323 K resulted in a permeability coefficient of 0.025 Barrer (Run 9)—well below the value registered in Run 1. Finally, the membrane was kept at room temperature for 48 h in propene at 0.23 MPa. Subsequent measurements of the permeability coefficient (Run 10) produced a value 0.10 Barrer, i.e. the initial level of the membrane permeability observed in Run 1 was restored.

Thus, almost a 30-fold range of permeability coefficients (0.025–0.7 Barrer) was registered for the poly(amide imide) membrane at the same propene pressure. These very large variations in the membrane permeability were completely reversible. Note that the permeability coefficients of the PAI membrane were constant throughout each run of ca. 6–7 h duration. Following the analogy of the polyphenylene oxides membranes, the above-described differences in permeabilities of the glassy PAI membrane can be assigned to the differences in the intrinsic microporosity of the polymer (i.e. sizes and/or numbers of the gas transport pathways) resulting from the conditioning procedures.

4. Conclusions

Sorbate-induced structural rearrangements of the glassy polyphenylene oxide copolymer in their relation to the molecular transport through the gas separation membrane were investigated using the low temperature nitrogen adsorption technique. The values of porosity (ε) and BET surface area (S_{BET}) were used as quantitative characteristics of the intrinsic microporous structure of the copolymer. The two parameters (ε and S_{BET}) provide similar structural information.

Conditioning of the copolymer in vacuum, N_2, O_2, CH_4, CO_2 and C_3H_6 was monitored. The intrinsic microporosity of the copolymer, apparently formed by a continuous network of intermolecular microvoids, was found to change reversibly depending upon the chemical nature of a sorbate, gas pressure and exposure time. Swelling of the copolymer that occurs in certain atmospheres results in the expansion of the free volume accessible to N_2, which is reflected in the increased values of ε and S_{BET}. In accordance with the magnitude of the polymer swelling achieved under the experimental conditions employed in this study, the gases can be qualitatively ranked as follows: $C_3H_6 > CO_2 > CH_4 > O_2 \approx N_2$. The most significant swelling was induced by propene, while oxygen and nitrogen at moderate pressures (up to ca. 5–10 MPa) and ambient temperatures are essentially non-swelling gases for the polyphenylene oxide copolymer.

The swollen polymer, being placed in the environment of a lower swelling ability, experiences structural relaxations. The relaxations include a decrease in the free volume, which is reflected by the decrease in the values of ε and S_{BET}.

Dynamics of swelling and that of the structural relaxation of the swollen polymer were monitored. As the conditioning environment changes, the highest rate of structural rearrangements in the course of transition to the new state of the polymer is achieved at the initial period.

Gas permeability of glassy polymer membranes is closely related to the conditioning history of a polymer: the state of the glassy polymer characterised by the higher values of porosity and BET surface area corresponds to the more permeable state of the membrane.

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