

Properties of heteroaromatic polymers for gas separation

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Summary

The gas separation properties of new aromatic polyoxadiazole (POD) and polytriazole (PT) membranes have been investigated. A wide range of permeability and selectivity was found for polymers with 4,4'-diphenyl-ether unit (POD-DPE and PT-DPE), 4,4'(2,2'-diphenyl)hexafluoropropane (POD-HF), 1,1',3-trimethyl-3-phenylindane (POD-PIDA) and 5-tert-butylisophthalic (POD-TBI) units incorporated into the backbone. The differences found in permeability and selectivity, as well as the dual sorption parameters of POD-PIDA and POD-DPE polyoxadiazoles are discussed in terms of their free volume determined by group contribution.

Introduction

The advances and growth in the field of gas separation membranes have encouraged the research for even better polymers and membranes. An important element contributing to the success of gas separation technology is the development of new membrane materials with high permeabilities and selectivities.

Polyoxadiazoles (POD) are heteroaromatic polymers with excellent properties. The synthesis of these heteroaromatic polymers has deserved much attention (1), due to their industrial application as thermally stable and chemically resistant materials. Recently, these polymers have been used in the preparation of dense membranes for petrochemical applications in CO₂ separation from natural gas and in enhanced oil recovery processes involving CO₂ injection (2-4).

The gas permeability (P) through a polymer is controlled by the product of two different parameters, solubility and diffusivity, as shown in Equation 1. The solubility coefficient (S) is related to physico-chemical interactions, while the diffusivity coefficient (D) takes into account the mobility of the gas-polymer system (4).

$$P = S \times D \quad \text{Equation 1}$$

The selectivity (α) quantifies the ability of a membrane to separate a gas mixture. It is often defined as the ratio of permeabilities of gases as shown in Equation 2. This parameter can be affected by the type of polymer (chemical structure, polarity, packing density) or the type of the gas (condensability, molecular size, polarity or feed composition).

$$\alpha_A = P_A / P_B = (S_A / S_B) \times (D_A / D_B) \quad \text{Equation 2}$$

The dual mode theory of gas sorption (5) has been used to describe the solubility of gases in glassy polymers. This theory is the combination of Henry's and Langmuir's laws. In terms of the gas pressure, the total solubility coefficient (S) is written as:

$$S = K_D \times p + (C'_H \times b \times p / 1 + b \times p) \quad \text{Equation 3}$$

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where K_D , C'_H and b are the corresponding values for the pure components of the Henry's coefficient, Langmuir's coefficient and Langmuir's affinity parameter, respectively, and p is the pressure of the pure gas sorption measurements.

The fundamental assumption of dual mode sorption theory is the existence of two distinct populations of gas molecules in a polymer matrix. One population is sorbed into the polymer matrix according to Henry's law and the second population is sorbed in the excess of free volume of the glassy polymer, described by the Langmuir's law (5).

In this work, the PODs have shown to be a class of polymers with different properties as a function of the chemical structure of the repeat units. The results of the CO_2 permeability, the CO_2/CH_4 selectivity and the CO_2 sorption isotherms observed for the polyoxadiazole with the 4,4'-diphenyl-ether unit (POD-DPE), the derived polytriazole with the same functional group (PT-DPE), and also the polyoxadiazoles with the 4,4'(2,2'-diphenyl)hexafluoropropane (POD-HF), the 1,1',3-trimethyl-3-phenylindane (POD-PIDA) and the 5-tert-butylisophthalic (POD-TBI) units incorporated into the backbone are presented.

Experimental

Polymerization Procedure: In a 250 ml three-necked, round-bottom flask, equipped with a mechanical stirrer and a nitrogen inlet tube, 237 g poly(phosphoric acid) (PPA, Fluka A.G., FRG) were added. After heating the PPA, 5.04 g (38.7 mmol) hydrazine sulphate (HS, Janssen Chimica, Holland) was mixed to PPA and the temperature was raised to 150°C. Then, 10.0 g (38.7 mmol) aromatic dicarboxylic acid was added and the resulting mixture was kept at 150°C under constant stirring for 4h. The reaction mixture was poured into tepid water, treated with 0.5 M NaOH, and kept overnight under stirring in water at 50°C. The product was recovered by filtration and dried under vacuum at 80°C. The purification was carried out by dissolving the product in a good solvent, most frequently formic acid, and reprecipitating in water. The polymerization reaction with other diacids was carried out using the proportions of diacid/HS and PPA/HS equal to 1 and 15, respectively, as well as the same time and temperature conditions. The POD-DPE was the precursor polymer to obtain the PT-DPE. The preparation used was essentially the same as the method described elsewhere(1).

Membrane preparation: The films of POD-DPE, PT-DPE, POD-PIDA, POD-HF and POD-TBI were cast at room temperature onto glass plates from formic acid, trifluoro acetic acid, chloroform, trifluoro acetic acid and m-cresol solutions, respectively, containing 10% (w/w) polymer. After evaporation of the solvent, the glass plates were submersed into a water bath and the transparent films were dried in a vacuum oven during at least 24 h at 80°C.

Gas permeation set-up: Gas transport properties of polyoxadiazoles membranes were evaluated in a set-up constructed at the Department of Chemical Technology of Twente University (Enschede, Holland), according to ASTM-D1434-80, and using a mixture of 75% CH_4 and 25% CO_2 at 23°C. The downstream side was vacuum and in all cases a pressure difference of 6 bar over the membrane was applied.

Gas sorption set-up: The equilibrium sorption of CO_2 by polyoxadiazoles was measured by the pressure decay method. The polymer sample under the form of a film was placed in the cell and an adequate copper seal was used to avoid leakage.

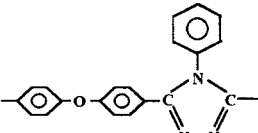
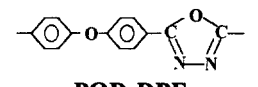
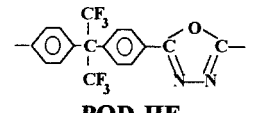
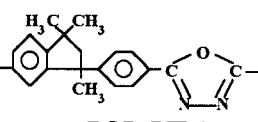
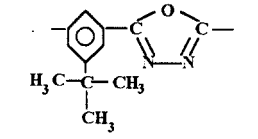
Other methods of characterization: The density measurements were performed according to ASTM-D792-66. Thermogravimetric Analysis (TGA) experiments were carried out in a Perkin-Elmer TGA-7 associated with a system-4 microprocessor controller and a Thermal Analysis Data Station (TADS) model 3700. About 5 mg of dry polymer sample

were treated under nitrogen stream from 100 to 150°C at 10°/min, cooled and then heated from 100 to 700°C, at the same conditions. Differential Scanning Calorimetry (DSC) were carried out in a Perkin-Elmer DSC-7, using the polymer sample as a film, under a heating rate of 20°/min under nitrogen stream from 100 to 450°C. Wide Angle X-ray Diffraction (WAXD) experiments were carried out in a Philips diffractometer, model PW1710, with copper irradiation ($\text{CuK}\alpha = 1.5418 \text{ \AA}$).

Results and Discussion

Table 1 shows the results obtained for polytriazole and polyoxadiazoles from several characterization techniques. The WAXD experiments led to low interchain distance (or d_{spacing}) for the POD-DPE sample. This polymer, which is characterized by the presence of the ether flexible linkage, showed to have the lowest free volume (V_{free}), when compared with other polymers. The low permeability and extremely high selectivity of POD-DPE could be explained as due to the efficient packing density.

Table 1: Effect of the functional group on the physical properties and the gas permeabilities of POD

Mero	Tg (°C)	d_{spacing} (Å)	V_{free} (cm^3/g)	P_{CO_2} (Barrer) ^a	Selectivity (CO_2/CH_4)
 PT-DPE	290.0	4.28	0.032	3-4	46-51
 POD-DPE	341.0	3.89	0.026	0.3 - 1.4	100 -200
 POD-HF	282.5	5.87	0.124	70 - 130	26 - 36
 POD-PIDA	320.0	5.30	0.214	66 - 140	15 -25
 POD-TBI	319.0	3.64	0.144	50 - 80	12

a - 1 Barrer = $1 \times 10^{-10} \text{ cm}^3 \times \text{cm} / \text{cm}^2 \times \text{s} \times \text{cmHg}$

The PT-DPE, obtained from POD-DPE sample, showed a high permeability value, three order of magnitude higher than its precursor. However, its selectivity has decreased a factor of two. The increase in permeability has been ascribed to the disordered state, print to the polymer matrix, by the introduction of the phenyl group.

The highest permeability values were found for POD-PIDA, POD-HF and POD-TBI polymers, which contain bulky groups in the backbone. As expected, the POD-PIDA sample showed the highest free volume and CO₂ permeability values.

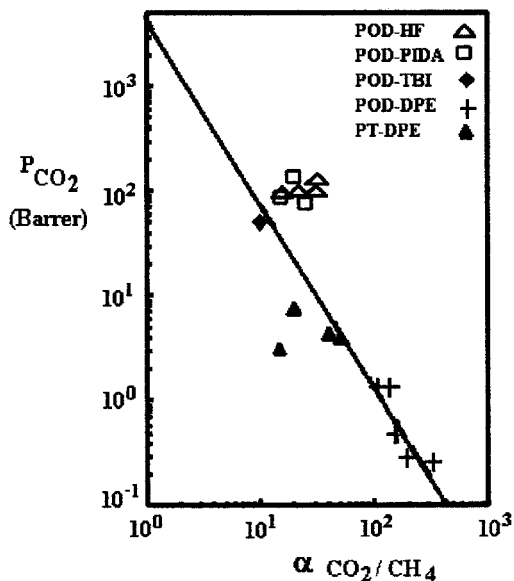


Figure 1: CO₂ Permeability versus CO₂/CH₄ selectivity for POD samples and for PT-DPE, after heat treatment at 150°C/ 24h.

Polyoxadiazoles membranes, as well as most of the customary membrane materials, have a very broad range of gas separation properties as a function of the chemical structure, as shown in Figure 1.

The performance of polyoxadiazoles with high CO₂ permeability and high CO₂ selectivity was investigated by equilibrium sorption, using the pressure decay method. Figure 2 shows the CO₂ sorption isotherms for POD-PIDA and POD-DPE at 23°C. The sorption isotherm for POD-PIDA shows higher solubility coefficients than the POD-DPE. This result could be due to the stiffer chemical structure of POD-PIDA and probably to its lower gas-polymer matrix interaction.

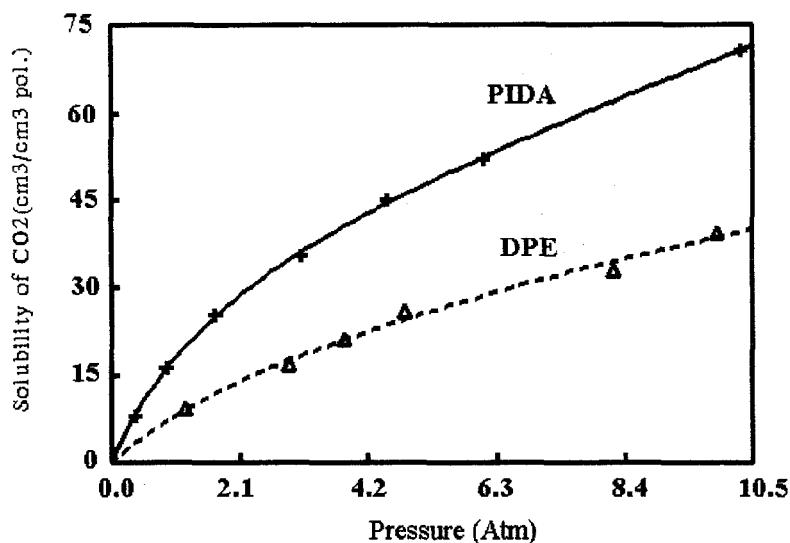
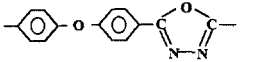
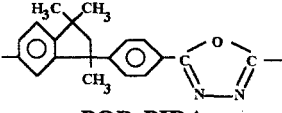


Figure 2: Carbon dioxide sorption isotherm for POD-PIDA and POD-DPE samples.

From a theoretical point of view, it is difficult to correlate the dual mode sorption model parameters with any bulk physical property of the polymer (see Table 2), but based on the rigorous analysis of different polymers (5) and from the present results, it is possible to consider that when the Henry's coefficient (K_D) decreases, the chain flexibility increases. The free volume and the T_g are physico-chemical properties capable of giving information about the polymer matrix. The results show that the polymer with the highest free volume has stiff chains creating higher overall free volume. Hence, the solubility coefficient will be enhanced. As shown in Table 2, the values of b do not change significantly from those observed for other glassy polymers (5).

Table 2 : Dual mode sorption model constants for POD.

Polymer	CO ₂ isotherms			S _{CO2}	T _g	V _{free}
	K _D	C _H	b	(P=5,0 atm)	(°C)	(cm ³ /g)
 <p>POD-DPE</p>	1.88	27.72	0.27	26.03	341	0.026
 <p>POD-PIDA</p>	3.48	41.32	0.51	45.16	320	0.214

K_D has units of cm³(STP)/ cm³(polymer-atm), C_H has units of cm³(STP)/cm³(polymer), b has units of atm⁻¹.

Conclusions

The carbon dioxide/methane separation observed for the polymers under study are significantly enhanced when bulk groups are incorporated into the main chain. However, incorporating a diphenyl-ether (DPE) moiety into the polymer backbone yields a polymer with a remarkable high selectivity.

The carbon dioxide sorption isotherms for the POD-DPE and POD-PIDA membranes show that a bulk group in the membrane matrix enhances the carbon dioxide sorption capacity. The lower CO₂ sorption capacity of POD-DPE may be due to a higher affinity with the gas molecules.

References

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