



GAS TRANSPORT PROPERTIES OF METATHESIS POLYNORBORNENE WITH THE SUBSTITUENTS IN THE SIDE CHAIN BASED ON β -(–)-PINENE

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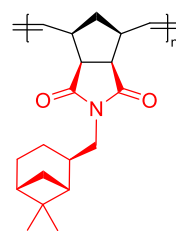
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Abstract

The gas separation properties of a high-molecular metathesis polymer based on nadimide containing β -(–)-pinene fragments, synthesized in the presence of the first-generation Grubbs catalyst, were studied. In particular, the permeability and diffusion coefficients for a wide range of gases were determined for the first time. This polymer is characterized by low values of gas permeability coefficients, corresponding to the gas permeability level of polyimides and cellulose acetate. At the same time, the selectivity of separation of gas pairs containing CO₂ and O₂/N₂ pair for the polymer explored is significantly higher than that of the related unsubstituted metathesis polynorbornene.

Key words: β -(–)-pinene, nadimide, polynorbornene, gas transport properties.



$P(\text{CO}_2) = 6.7$ Barrer
 $\alpha(\text{CO}_2/\text{N}_2) = 27.9$
 $\alpha(\text{CO}_2/\text{CH}_4) = 16.8$

Introduction

The gas transport properties of polymers play an important role in many industrial and high-tech areas [1], such as packaging industry, membrane technologies, and biomedical engineering. Nowadays, despite the development of different effective polymeric membrane materials for various gas separation processes, the most available but less effective polymers such as cellulose acetate, polysulfones, and polyimides, are used in industry. At the same time, new polymeric materials are actively developed for potential use as selective layers in membrane processes, which combine a set of the required operational characteristics (gas separation selectivity, permeability, stability of properties over time, the possibility of simple synthesis from the available raw materials, etc.) [2–4].

A key element in the development of such materials is the ability to conduct systematic studies of the polymer properties and establish relationships between the structure of the polymer and its properties. Earlier it has been shown that norbornene derivatives represent a promising platform for the synthesis of a series of polymers with different structures of both the main chain and side substituents, and a number of highly permeable membrane materials and polymers combining high selectivity relative to CO₂-containing gas vapors have been synthesized on their basis.

In turn, terpenes are available natural organic compounds that are widely used in industry for the production of polymers. The production of polymers based on terpenes has a number of advantages and is highly urgent, since it allows for reducing the environmental impact and the amount of waste.

In this work, the gas transport properties of a polymer combining in its structure the fragments and advantages of both norbornene derivatives and terpenes were studied for the first time. In particular, the main chain of the studied polymer was formed by the norbornene units, while the side substituents contain the fragments of one of the most available terpenes, namely, β -(–)-pinene.

Results and discussion

A sample of the metathesis polymer based on nadimide containing β -(–)-pinene fragments (**PNBpin**) was synthesized by the previously described method in the presence of the first-generation Grubbs catalyst (Fig. 1) [5]. The resulting polymer is high-molecular ($M_n = 9.6 \cdot 10^5$, $M_w/M_n = 3.0$), glassy, and amorphous (Table 1).

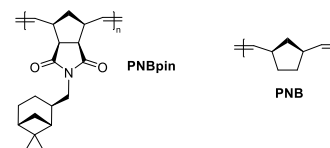


Figure 1. Structures of **PNBpin** and **PNB**.

Table 1. Selected basic properties of **PNBpin** in comparison with **PNB** and **CA**

Polymer	T_g , °C	T_d , °C	d_1 , Å	d , g/cm ³	FFV, %
PNBpin	188	405	5.4	1.179	13
PNB [6]	41	415	4.9	0.999	15
CA [7]	186	–	5.2	1.300	14.7–16.1 [8–10]

The glass transition temperature of **PNBpin** was significantly higher than that of the related unsubstituted metathesis polynorbornene (**PNB**, Fig. 1, Table 1) and was close to the glass transition temperature of cellulose acetate (**CA**), an industrial polymeric membrane material. At the same time, for all three polymers, the *d*-distances (*d*₁, Table 1), estimated from the X-ray diffraction data, and the fractions of free volume (FFV), calculated based on the polymer density and the volume occupied by the polymer molecules, were very close.

The permeability through **PNBpin** was investigated for a range of gases (He, H₂, N₂, O₂, CO₂, CH₄). The resulting values of gas permeability coefficients, selectivities, as well as diffusion and solubility coefficients are given in Tables 2 and 3. For **PNBpin**, the following series of gas permeability coefficients was observed: $P(\text{H}_2) \sim P(\text{He}) > P(\text{CO}_2) > P(\text{O}_2) > P(\text{CH}_4) > P(\text{N}_2)$, i.e., the change in the gas permeability coefficients did not fully correlate with the corresponding kinetic diameters of the gas molecules under consideration. **PNBpin** appeared to be less permeable than the unsubstituted metathesis polynorbornene (**PNB**) and was comparable in the gas permeability to **CA**. A difference in the gas permeability of **PNBpin** and **PNB** is mainly due to the difference in the diffusion coefficients (Table 2). Thus, although it is generally accepted that the introduction of bulky and rigid groups into the side chains of polymers leads to an increase in the gas permeability [4, 11], in the case of the simultaneous presence of polar groups in the side chains, the effect of introducing a bulky substituent can be leveled out, for example, as for **PNBpin**.

Table 2. Permeability, diffusivity, and solubility coefficients of various gases for **PNBpin** in comparison with **PNB** and **CA** (30 °C and 0.6 bar upstream pressure)

Polymer	Permeability coefficient, Barrer ^a					
	He	H ₂	N ₂	O ₂	CO ₂	CH ₄
PNBpin	12.7	13.0	0.24	1.50	6.7	0.40
PNB [6]	14.9	18.0	0.43	2.3	9.3	0.78
CA [7]	–	14.9	0.23	1.05	5.96	0.205
Polymer	Diffusivity coefficient (<i>D</i>), $\text{D} \cdot 10^{10}, \text{cm}^2 \cdot \text{s}^{-1}$					
	He	H ₂	N ₂	O ₂	CO ₂	CH ₄
PNBpin	–	–	170	550	140	56
PNB [6]	–	–	360	1280	550	150
Polymer	Solubility coefficient (<i>S</i>), $\text{S} \cdot 10^3, \text{cm}^3(\text{STP}) \cdot \text{cm}^{-3} \cdot \text{cm Hg}^{-1}$					
	He	H ₂	N ₂	O ₂	CO ₂	CH ₄
PNBpin	–	–	1.3	2.7	50	7.1
PNB [6]	–	–	1.2	1.8	16.8	5.3

^a 1 Barrer = $10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm} (\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg})^{-1}$.

The ideal gas separation selectivities for **PNBpin** significantly exceed the corresponding values for more permeable **PNB** and, in some cases, for **CA** (Table 3). In particular, a high value of selectivity for the CO₂/N₂ pair (more than 25) was obtained for **PNBpin**, which indicates its high potential as a promising membrane material for further detailed studies.

Experimental section

To study gas permeability, the films 80–90 μm in thickness were cast from a 5% polymer solution in chloroform. After evaporation of the solvent, the films were evacuated at room

Table 3. Ideal permeability selectivities for different pairs of gases for **PNBpin** in comparison with **PNB** and **CA**

Polymer	Ideal selectivity ($\alpha = P_i/P_j$)			
	O ₂ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂
PNBpin	6.3	27.9	16.8	54.2
PNB [6]	5.2	21.0	11.9	41.9
CA [7]	4.5	25.8	29.2	64.5

temperature for 24 h until constant weight. The coefficients of permeability and diffusion of gases through the membranes were determined by the Daines–Barrer method on a precision Helmholtz-Zentrum Geesthacht unit equipped with a Baratron pressure sensor with an accuracy of 10^{-7} atm and described in detail elsewhere [12]. The sorption coefficient was found as the ratio of the permeability coefficient to the diffusion coefficient.

Conclusions

The gas transport properties of the metathesis polynorbornene containing β-(–)-pinene fragments were studied for the first time: the permeability and diffusion coefficients were determined, and the solubility coefficients for He, H₂, O₂, N₂, CO₂, and CH₄ were calculated. It was shown that **PNBpin** is less permeable and significantly more selective than the unsubstituted metathesis polynorbornene. The gas separation selectivities of **PNBpin** for some gas pairs (O₂/N₂, CO₂/N₂) exceeded the corresponding values for cellulose acetate, an industrial polymeric membrane material.

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