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Comparison of transport properties of hyperbranched and linear polyimides

Karel Friess[a*], Petr Sysel[b], Evgenia Minko[b], Michal Hauf[b], Ondřej Vopička[a], Vladimír Hynek[a], Kryštof Pilnáček[a], Milan Šípek[a]

[a]*Department of Physical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic*
[b]*Department of Polymers, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic*
Tel: +420 22044 4029; Fax: +420 22044 3175; email: Karel.Friess@vscht.cz

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ABSTRACT

The non-porous, flat membranes were prepared from the novel hyperbranched polyimide based on 4,4′,4″-triaminotriphenylmethane (MTA) and 4,4′-oxydiphthalic anhydride (ODPA) and also from the linear polyimide (LPI) based on 4,4′-methylenedianiline (MDA) and ODPA. The permeability coefficients of hydrogen, carbon dioxide, oxygen, nitrogen and methane in the membrane prepared from hyperbranched polyimide were 2–3.7 times higher than those in the membrane from LPI at comparable selectivities.

Keywords: Gas permeation; Non-porous flat membrane; Hyperbranched polyimide

1. Introduction

Polyimides exhibit very good overall stability at temperatures from −150 to 250°C. These rigid polymers with a high glass transition temperature are mostly used in (micro)electronics, aircraft industry and as separation membranes [1].

Non-porous, flat polyimide membranes show high separation factors (selectivities) in separation of selected gas mixtures but low permeability both of gases with larger molecules and organic vapors [2,3]. The permeability in a polymer depends on the solubility and the diffusivity of the permeating species in that polymer. When the difference in the solubilities is low mostly glassy polymers are used and the separation is more based on the difference in diffusivity which is also governed by the free volume of polymer [4].

From the point of view of a controllable free volume, hyperbranched polymers are a very attractive candidate to the membranes with convenient transport properties. It is reported that according to the results of computer simulation there are many accessible cavities of atomic and slightly larger size in the rigid hyperbranched polymers, i.e. also polyimides [5,6], contributing to the free volume.

In this paper we present the transport properties of membranes made of the novel hyperbranched polyimide based on the commercially available 4,4′,4″-triaminotriphenylmethane (MTA) and 4,4′-oxydiphthalic anhydride (ODPA) for hydrogen, nitrogen, oxygen, carbon dioxide and methane. The comparison with transport properties of the linear polyimide (LPI) based on 4,4′-methylenedianiline (MDA) and ODPA have been made.

2. Materials and method

2.1. Chemicals

4,4′-Oxydiphthalic anhydride (ODPA) was heated to 170°C for 5 h in a vacuum before use. MDA (both Aldrich, Czech Republic) and MTA (Dayang

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[*] Corresponding author

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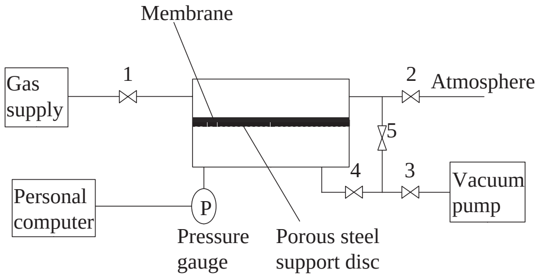

Fig. 1. Scheme of the manometric integral permeameter

Chemicals, China) were used as received. 1-Methyl-2-pyrrolidone (NMP; Merck, Czech Republic) was distilled under vacuum over phosphorous pentoxide, and stored in an inert atmosphere.

Gases in the gas cylinders (Siad, Czech Republic) were used as received (nitrogen 99.99 vol%, oxygen 99.5 vol%, methane 99.0 vol%, carbon dioxide 99.0 vol%, hydrogen 99.90 vol%).

2.2. Preparation

The hyperbranched polyamic acid (HBPAA) and linear polyamic acid (LPAA) were prepared in a two necked flask equipped with a magnetic stirrer and a nitrogen inlet/outlet. At room temperature, a 4 wt% ODPA solution in NMP was added dropwise to a 4 wt% solution of MTA or MDA in NMP (ODPA/MTA and ODPA/MDA molar ratios were 1:1). This reaction mixture was then stirred at room temperature for 24 h.

A solution of either HBPAA or LPAA in NMP was spread onto a glass substrate. The resulting thin layer was kept at gradually increased temperatures, finally at 230°C for 1 h. The thickness of the transparent self-standing films obtained was about 50 μm.

2.3. Characterization

IR spectra were recorded on a Nicolet 740 spectrometer using either liquid samples (solutions of polyamic acids) or KBr pellets (solid polyimides). Dynamic thermogravimetric measurements (TGA) were performed in air using a TG-750 Stanton-Redcroft (heating rate 10°C min^{-1}). Dynamic mechanical analysis (DMA) was performed using a DMA DX 04T (RMI, Bohdanec, Czech Republic) at 1 Hz and in the temperature range 25–400°C with the temperature gradient 3°C min^{-1}. The intrinsic viscosities of the HBPAA and LPAA were measured using a capillary viscometer in NMP at 25°C.

2.3.1. Permeation measurements

The self-developed manometric integral apparatus, the scheme of which is shown in Fig. 1, was used. The membrane is placed in the stainless steel cell (Mikropur, Czech Republic), the feed side of the cell is connected to the pressure reducing valve fitted to the gas cylinder, and to the gas burette opened to the atmosphere. The permeate side of the cell, equipped with the pressure gauge (Ceravac, Oerlikon Leybold Vacuum, Germany), can be isolated by the valve 4 as well as connected to the atmosphere or to the vacuum pump (Trivac, Oerlikon Leybold Vacuum, Germany). The diameter of the circle membrane is 50 mm and it is sealed in the cell with the Viton o-ring; the diameter of the active area is 41 mm. The certain leakage of the evacuated system is smaller than or equal to 2 Pa per hour in the permeate side of the permeameter (50 mL), the measuring pressure interval is 133 Pa and the minimum pressure is approximately 0.45 Pa.

The Integral Measurement and the Initial Flow Measurement [7] are used in this work to determine the permeability of the pure gases in the investigated membranes. Before the integral experiment, both sides of the cell are evacuated by opening the valves 3, 4, 5 and then isolated by closing all the valves. The measurement starts when the measured gas is introduced to the feed side of the cell by opening the valves 1 and 2. The continuous flux of the measured gas through the feed side of the cell to the atmosphere ensures purity of the gas and its pressure equal to the atmospheric pressure (Greisinger electronic, Germany); the increase of the pressure in the permeate side is monitored.

The Initial Flow Measurement begins from the steady-state permeation, when the measured gas is continuously introduced to the feed side of the cell and then vented to the atmosphere. At the same time, permeate is pumped away through the opened valves 4 and 5. The measurement starts when the valve 4 is closed; the pressure increase in the permeate side is monitored and afterwards corrected to the spontaneous pressure increase due to the certain leakage.

The gas permeability is calculated from the slope of the linear part of the pressure increase at the steady state as follows

$$P = \frac{V_\mathrm{d}}{\mathrm{R}TA} \cdot \frac{l}{p_1} \cdot \frac{\mathrm{d}p_2(\tau)}{\mathrm{d}\tau},$$

where V_d is the volume of the permeate side of the cell, l is the thickness of the membrane, $p_2(\tau)$ signs the linear part of the permeate-side pressure dependence, R is the universal gas constant, T is the temperature, A is the

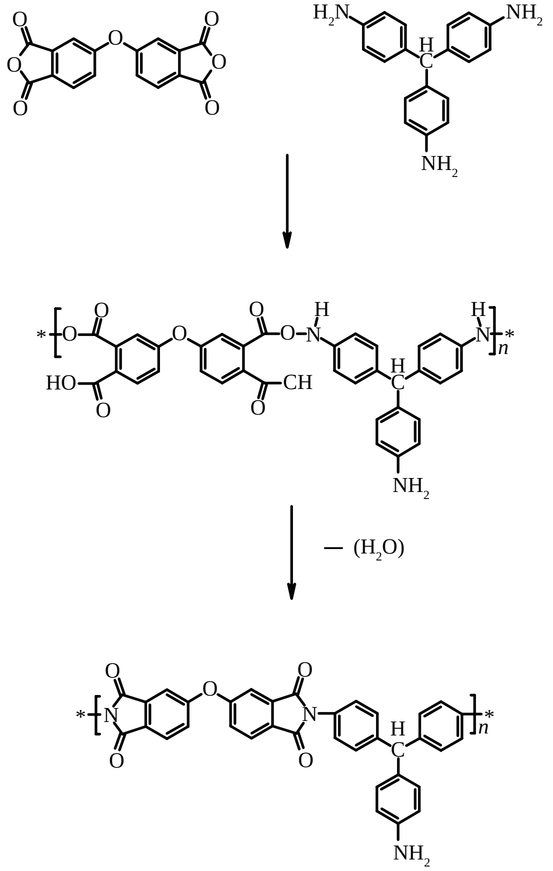

Fig. 2. Preparation of the hyperbranched polyimide HBPI (ODPA-MTA)

active area of the membrane and p_1 is the atmospheric pressure.

The values of permeation coefficients varied within the accuracy of measurement up to 20% especially in the case of methane and nitrogen due to their extremely low permeation.

3. Results and discussion

The main aim of this work was the comparison of the properties, especially transport characteristics of gases, of the hyperbranched and LPI based on the similar monomer base. The hyperbranched polyimide (HPBI) was prepared from commercially available MTA and ODPA (Fig. 2). Due to the fact that a molar ratio of the three MTA and bifunctional monomers was 1:1 the amine end-capped HBPI(ODPA-MTA) was formed.

The LPI was synthesized from the bifunctional monomers MDA and ODPA in a molar ratio 1:1 [LPI(ODPA-MDA)] (Fig. 3).

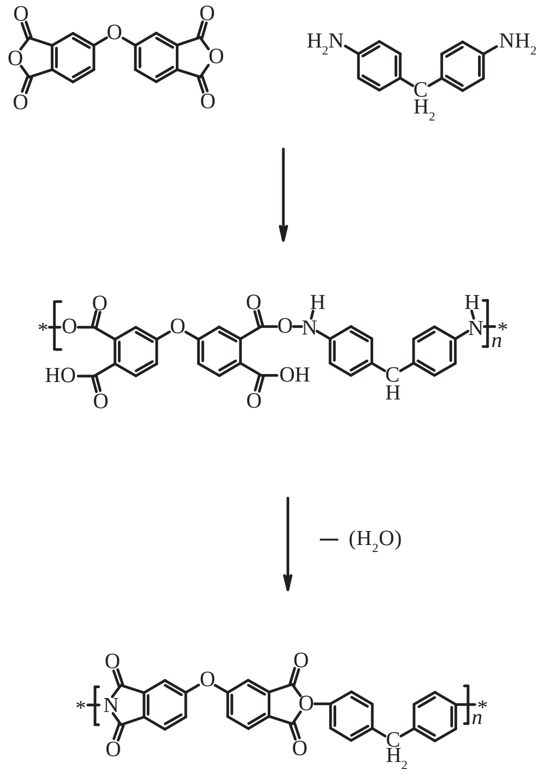

Fig. 3. Preparation of the linear polyimide LPI (ODPA-MDA)

The intrinsic viscosities reflecting the molar masses of the polymers were 16 mL g^{-1} for HBPI(ODPA-MTA) and 36 mL g^{-1} LPI(ODPA-MDA).

Polyimide precursors (HPAA and LPAA) were transformed into HBPI and PI, respectively, using thermal exposition. The obtained materials were analyzed by IR spectroscopy (Figs. 4, 5). The absence of the band at 1,683–1,685 cm^{-1} [amide group of polyamic acid—see the spectra of HBPAA(ODPA-MTA) and HLPAA(ODPA-MDA)] confirms the practically total transformation of the precursor into polyimide.

The absorption bands at 1,777 and 1,723–1,726 cm^{-1} (symmetric and asymmetric stretching of the ring carbonyl groups) and 1,366–1,378 cm^{-1} (stretching of the ring C-N bond), are distinct in the spectrum of HBPI(ODPA-MTA) and LPI(ODPA-MDA) and characterize the formation of imide structures.

The properties of above specified polymers were discussed in our previous paper in detail [8]. The glass transition temperature (T_g) of the HBPI(ODPA-MTA) was slightly higher than that of the LPI(ODPA-MDA) (287 vs. 276°C). Interactions between the terminal amino groups may be one reason for the higher T_g of the amine-terminated hyperbranched structure.

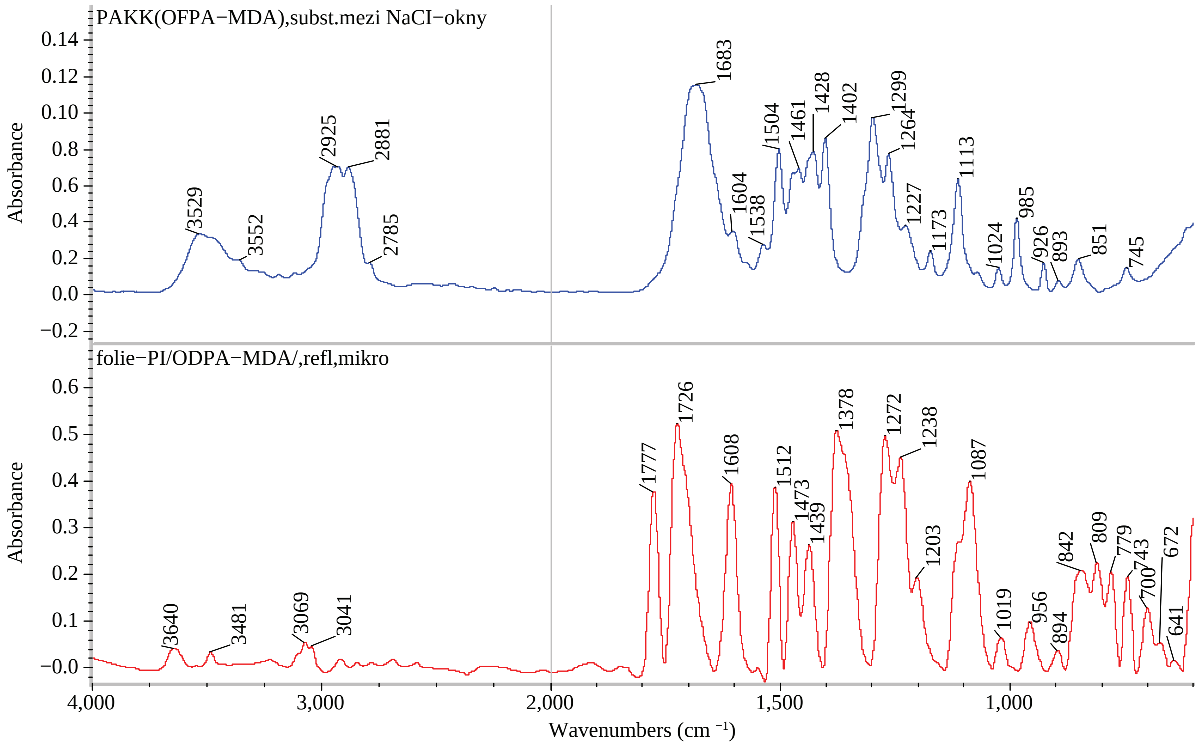

Fig. 4. IR spectra of LPAA(ODPA-MDA) (top) and LPI(ODPA-MDA) (bottom).

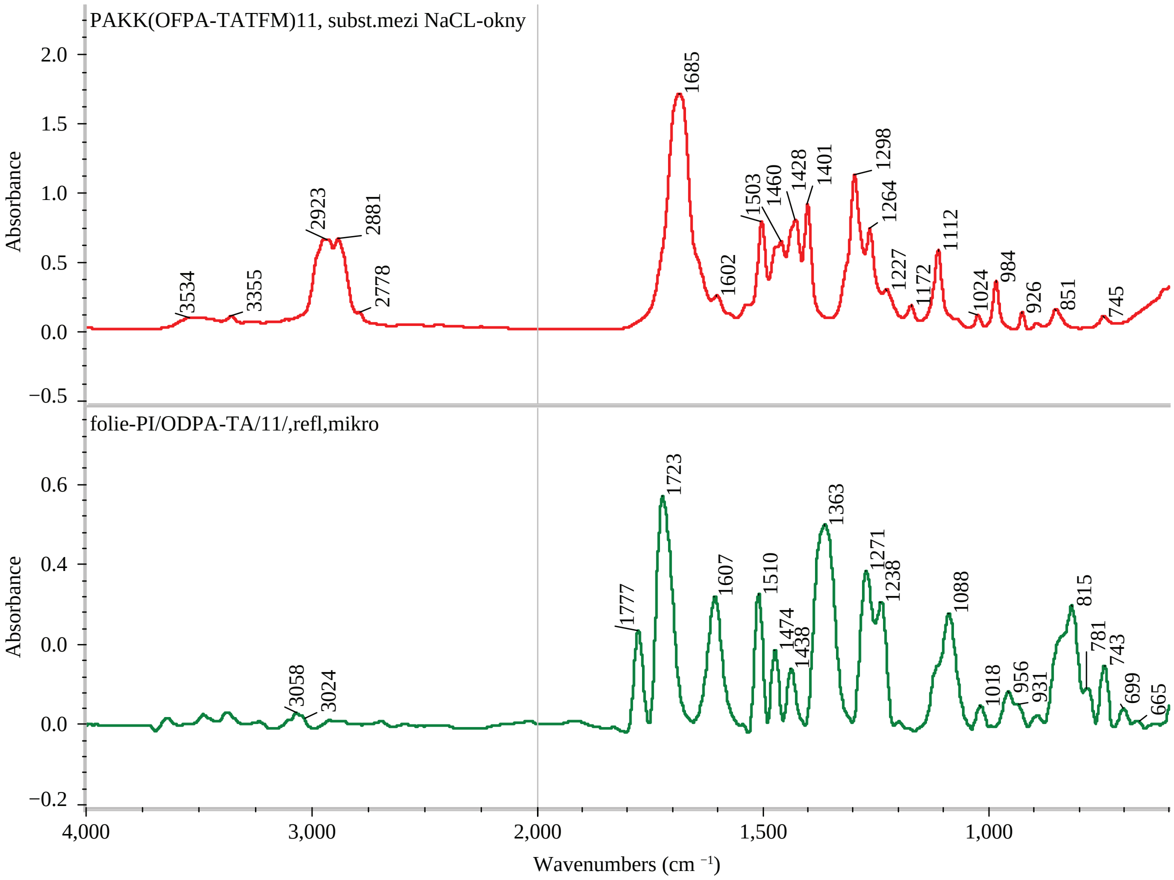

Fig. 5. IR spectra of HPAA(ODPA-MTA) (top) and HBPI(ODPA-MTA) (bottom).

Table 1
Permeability coefficients for HBPI(ODPA-MTA) and LPI(ODPA-MDA) membranes

Material	HBPI(ODPA-MTA)	LPI(ODPA-MDA)
Gas	Permeability coefficient (10^{18} mol m^{-1} s^{-1} Pa^{-1})	
Hydrogen	2,700	1,350
Carbon dioxide	714	1,92
Oxygen	149	66
Nitrogen	24	11
Methane	5.2	1.6

On the other hand, the thermooxidative stabilities (evaluated as the temperatures corresponding to 10 wt% loss during thermogravimetric analysis with a temperature gradient of 10°C min^{-1}) of the LPI (566°C) was higher than that of the corresponding HBPI (509°C). The lower thermal stability of the HBPI might be due to deficiencies in their chain entanglements resulting from a lower number of physical crosslinks.

The permeability coefficients of the selected gases are summarized in Table 1 and separation factors (selectivities) of the selected gas pairs shows Table 2. It is very favorable from the point of the potential applications that the permeability coefficients in the HBPI(ODPA-MTA) membrane are higher than those in LPI(ODPA-MDA) one. The increase is the highest for carbon dioxide (3.7 times), the lowest for hydrogen (2 times). To make deeper conclusions concerning this phenomenon it is necessary to determine the diffusion and solubility coefficients for each gas in our future work.

The selectivities given in Table 2 are ideal ones. Nevertheless, we showed in [2,3] that transport properties of gases can be monitored separately (the presence of a gas does not influence the permeability neither another gas nor a organic vapor). The essential finding is that the selectivities of hyperbranched polyimide are comparable with those of linear one for oxygen/nitrogen and carbon dioxide/methane. The drop was only found for the case hydrogen/methane, but the absolute value (more than 500) is comparable with very valuable data in the literature.

Table 2
Ideal selectivity values for HBPI(ODPA-MTA) and LPI(ODPA-MDA) membranes

Material	HBPI(ODPA-MTA)	LPI(ODPA-MDA)
Gas/gas	Ideal selectivity	
Oxygen/nitrogen	6.2	6.1
Carbon dioxide/methane	137	110
Hydrogen/methane	519	785

4. Conclusions

Comparison of experimental permeation data of linear and hyperbranched polyimides revealed nearly 4 times higher values of gas permeability coefficients of HBPI. Despite this fact, determined selectivities of hyperbranched polyimides did not make worse.

Acknowledgements

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