Desalination and Water Treatment
www.deswater.com

34 (2011) 211–215
October

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2859

Mixed matrix membranes based on hyperbranched polyimide and mesoporous silica for gas separation

Petr Sysel[a],*, Evgenia Minko[a], Michal Hauf[a], Karel Friess[b], Vladimir Hynek[b], Ondrej Vopicka[b], Krystof Pilnacek[b], Milan Sipek[b]

[a]*Department of Polymers, Institute of Chemical Technology, Technicka 5, 166 28 Prague 6, Czech Republic*
Tel. +420 22044 3196; Fax: +420 22044 3175; email: Petr.Sysel@vscht.cz
[b]*Department of Physical Chemistry, Institute of Chemical Technology, Technicka 5, 166 28 Prague 6, Czech Republic*

Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

The novel mixed matrix membranes were prepared from the hyperbranched polyimide based on 4,4´,4´´-triaminotriphenylmethane and mesoporous silica MCM-41 (up to 16 wt.%). The permeability coefficients of hydrogen, carbon dioxide, oxygen, nitrogen and methane in the membranes increased and oxygen/nitrogen or carbon dioxide/methane selectivities decreased slightly with the silica content. The absolute values of permeability coefficients were fairly influenced by the method of additive incorporation to the polymeric matrix.

Keywords: Gas permeation; Mixed matrix membrane; Hyperbranched polyimide; Mesoporous silica; 4,4′,4′′-triaminotriphenylmethane; Oxygen/nitrogen selectivity

1. Introduction

Aromatic polyimides are an important class of high performance polymers. Linear and crosslinked aromatic polyimides exhibit excellent chemical and mechanical stability even at elevated temperatures up to 250°C. They are mostly used in (micro)electronics and aircraft industry, as well as in space exploration and as membranes in separation technologies [1]. Non-porous, flat polyimide membranes show high separation factors (selectivities) in separation of selected gas mixtures but a low permeability of these gases [2].

Hyperbranched polymers, having highly branched structure and a large number of terminal groups, introduce a new class of macromolecular architecture. From the point of view of a controllable free volume, hyperbranched polymers are a very attractive candidate to the membranes with convenient transport properties [3]. The permeability coefficients of hydrogen, carbon dioxide, oxygen, nitrogen and methane in the membrane made of hyperbranched polyimide (HBPI) based on 4,4´,4´´-triaminotriphenylmethane (MTA) were 2–3.7 times higher than those in the membrane from the linear polyimide based on 4,4´-diaminodiphenylmethane (MDA) at comparable selectivities [2]. Nevertheless, searching for a more significant permeability increase is desirable from the point of view of potential applications of these polyimide membranes in a larger scale.

As one of the possibilities how to influence the gas transport characteristics of polymeric membranes, the mixed matrix mebranes consisting of a polymer matrix and porous materials (e.g., zeolites, porous silica) have been investigated [4]. The polysulfone membranes containing mesoporous silica MCM-41 showed higher gas permeabilities in comparison with that prepared from the net polymer only without a significant decrease in their selectivities [5]. The materials based on a hyperbranched polyimide and mesoporous silica have not been described yet.

---

*Corresponding author.

Presented at the AMS6/IMSTEC10, The 6th conference of the Aseanian Membrane Society in conjunction with the 7th International Membrane Science and Technology Conference, Sydney Australia, November 22–26, 2010

From this point of view the preparation and characterization of membranes combining these components appear as highly topical. Therefore, the new mixed matrix membranes prepared from HBPI based on the commercially available MTA and mesoporous silica MCM-41 were made and their transport characteristics were studied in this work.

2. Materials and methods

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 Chemicals, China) were used as received. Mesoporous silica MCM-41 (Aldrich) having a pore size 2.5–3 nm and surface area 1000 $m^2 g^{-1}$ (Aldrich catalogue) was heated to 120°C for 3 h in an oven before use. 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

Synthesis of hyperbranched (HBPAA) and linear (LPAA) polyamic acids

HBPAA and 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 or ODPA/MDA molar ratios were 1:1). This reaction mixture was then stirred at room temperature for 24 h.

Preparation of mixtures of HBPAA with MCM-41

Procedure A:
The calculated amount of MCM-41 particles was added to the 4 wt.% solution of polyimide precursor (HBPAA) in NMP under stirring with a magnetically driven stirrer. The preparation of mixture (suspension) under stirring proceeded for 12 h.

Procedure B:
The calculated amount of MCM-41 was added to the 4 wt.% solution of MTA in NMP. After 12 h stirring a 4 wt.% ODPA solution in NMP was added dropwise to this reaction mixture and it was allowed to react for 24 h at room temperature under nitrogen atmosphere.

Preparation of membranes based on HBPI or linear polyimide (LPI) or HBPI and MCM-41

A solution of either HBPAA or LPAA or a suspension of MCM-41 in HBPAA solution were spread onto a glass substrate (treated with chlorotrimethylsilane). The resulting thin layer was kept at 60°C for 12 h, 100°C for 1 h, 150°C for 1 h, 200°C for 2 h and 250°C for 1 h. The thickness of the self-standing films obtained was about 50–100 μm.

2.3. Characterization

IR spectra were recorded on a Nicolet 740 spectrometer using a reflective mode. Dynamic thermogravimetric measurements (TGA) were performed in air using a TG-750 Stanton-Redcroft (heating rate 10°C min^{-1}). The glass transition temperatures were found by using a dynamic mechanical analysis (an instrument DMA DX04T (RMI, Bohdanec, Czech Republic) operating at 1 Hz and in the temperature range 25–400°C with a temperature gradient 3°C min^{-1}). The mechanical properties were determined with an Instron-3365 testing instrument. Scanning electron microscopy was made by using a microscope Jeol JSM-5500 LV. The material cross section areas were covered by a deposited platinum layer prior to measurement. The permeation measurements were conducted using the self-developed manometric integral apparatus, the detailed description of which is given in [2]. The values of permeation coefficients vary within the accuracy of measurement up to 20% if experiments are repeated (especially in the case of methane due to its extremely low permeation).

3. Results and discussion

HBPI containing up to 16 wt.% of MCM-41 were prepared. The products with the silica content about 20 wt.% and higher showed a poor mechanical stability. The starting materials for the HBPI preparation were commercially available ODPA and MTA (Fig. 1) [2]. The molar ratio of MTA and ODPA was 1:1 and under this condition the amine end-capped HBPI was formed. HBPAA was transformed (imidized) to HBPI using thermal exposition up to 250°C. The materials (HBPAA and HBPI) were analyzed by IR spectroscopy. The absence of the band at about 1680 cm^{-1} (amide group of HBPAA) in the HBPI spectrum confirms the practically total transformation of the precursor to HBPI (Fig. 2). The similar observation was made for the imidization of LPAA to LPI [2].

MCM-41 (Mobil Composition of Matter-41) was used as the mesoporous silica. Our microscopic (SEM) observations have showed that the size of MCM-41 particles does not exceed 1 μm. Due to the pore size of MCM-41

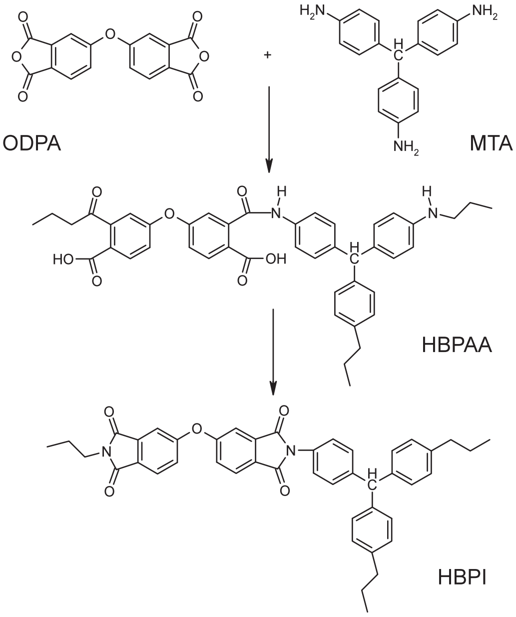

Fig. 1. Preparation of HBPI based on ODPA and MTA.

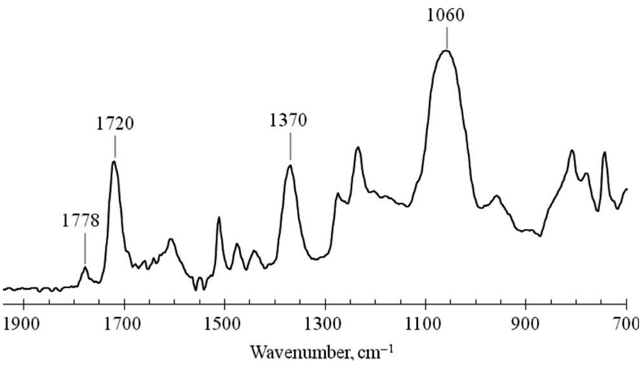

Fig. 2. IR spectrum of the A-5 material.

about 2.5–3 nm (kinetic diameters of hydrogen, carbon dioxide, oxygen, nitrogen and methane are 0.289, 0.33, 0.346, 0.364 and 0.38 nm, respectively) the increase in gas permeability in the mixed matrix membranes has been ascribed to a reduced resistance to gas flow inside the pores (channels) of MCM-41 and a stronger contribution of sieving effect and/or gas – additivum interactions has not been expected [5]. From this point of view, a possible level of the polymer penetration into silica pores could play an important role in transport characteristics. It has led us to compare the final materials prepared using two different procedures. The first approach involves mixing HBPAA with silica particles (procedure A in 2.2.) followed by imidization; the second one is based on the mixing of momomers with the additive (in the presence of NMP) followed by polymerization (procedure B) and imidization. It is thought that the pores should be more accessible for the polymer matrix by using Procedure B.

So, two series (designated as A and B) of polymer matrix membranes were prepared. Each of them includes the samples with the theoretical content 5 wt.% (A-5 or B-5), 10 wt.% (A-10 or B-10) and 16 wt.% (A-16 or B-16) of MCM-41. They were (as in the case of pure HBPI and LPI [2]) characterized by using IR spectroscopy. The absorption bands at about 1780 and 1720 cm^{-1} (symmetric and asymmetric stretching of the ring C-N bond), together with the band at 1370 cm^{-1} (stretching of the ring C-N bond) characterizing the formation of imide strucures [2] are distinct in all spectra. The broad absorption band having the maximum at about 1060 cm^{-1} appears in the spectra of mixed matrix materials. It belongs to the Si-O-Si bond and confirms the MCM-41 incorporation in the products (Fig. 2).

The thermal and mechanical properties of these materials are summarized in Table 1.

The effect of MCM-41 on the thermooxidative degradation of these materials was studied using a dynamical thermogravimetric analysis in the temperature range

Table 1
Thermal and mechanical properties of HBPI and HBPI containing MCM-41

Material	T_g[a] (°C)	T[b] (°C)	Ash[c](%)	Tensile strength (MPa)	Tensile modulus (GPa)
HBPI	377	509	0	46	1.17
A-5	372	522	5	35	0.80
A-10	368	513	9	12	0.36
A-16	365	502	11	–	–
B-5	383	522	5	12	0.67
B-10	375	514	8	12	0.40
B-16	380	505	12	6	0.20

[a] glass transition temperature (using dynamic mechanical analysis).

[b] temperature corresponding to 10 wt.% weight loss (using dynamic thermogravimetric analysis, interval RT – 800°C, gradient 10°C min^{-1}, air atmosphere).

[c] residue after heat treatment (specified in the footnote[b]).

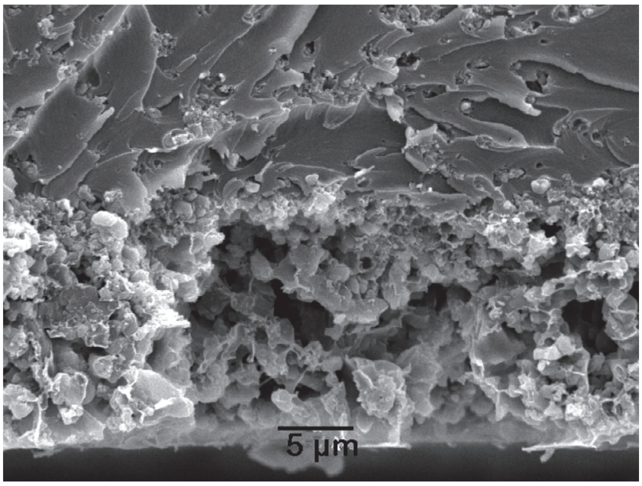

Fig. 3. SEM photograph of the B-16 material.

from room temperature (RT) to 800°C in an air atmosphere. The temperatures corresponding to 10 wt.% weight loss decrease very slightly with MCM-41 content in both series A and B and they are close to the value for pure HBPI (a maximum difference 13°C). An increase in ash (residue) content from A-5/B-5 to A-16/B-16 supports a successful MCM-41 incorporation into polymer matrix. The glass transition temperatures (based on the maximum of the mechanical loss peak in the dynamic mechanical spectra) slightly decrease in the series A and do not almost show any dependence in the series B with MCM-41 content. The tensile strength and modulus of HBPI containing MCM-41 are lower (more in the series B) in comparison with those for pure HBPI and they decrease with the additive content. These results suggest that MCM-41 at these low concentrations contributes to a loosening of the molecular packaging of HBPI chains more than to an HBPI reinforcement. Our microscopic analyses of the mixed matrix materials (using a scanning electron microscopy) also show certain problems with a MCM-41 dispersation in the HBPI matrix (Fig. 3). The layer richer in MCM-41 is formed at the bottom of the materials (independently of the sample history) due to its tendency to agglomerate. The image also shows that the polyimide adheres well to the silica particles.

The gas permeability coefficients are collected in Table 2 and Table 3 shows separation factors (selectivities) of the selected gas pairs. The selectivities given in Table 3 are ideal ones. Nevertheless, we showed in [6] that transport properties of gases can be monitored separately (the presence of a gas does not influence the permeability another gas). For all tested gases, the permeability coefficients almost increase in proportion to the MCM-41 amount present in the mixed matrix membrane. But only the permeability coefficients of B-10, B-16 and A-16 (hydrogen, oxygen) exceed those for pure

Table 3
Ideal selectivity values for LPI, HBPI, HBPI containing MCM-41

Material	Gas/gas	
	Oxygen/nitrogen	Carbon dioxide/methane
	Ideal selectivity	
LPI	6.1	120
HBPI	6.2	137
A-5	10.7	–
A-10	9.3	160
A-16	8.7	112
B-5	8.6	84
B-10	6.3	67
B-16	5.3	180

Table 2
Permeability coefficients for LPI, HBPI, HBPI containing MCM-41

Material	Gas				
	Hydrogen	Carbon dioxide	Oxygen	Nitrogen	Methane
			Permeability coefficient (10^{18} mol m^{-1} s^{-1} Pa^{-1})		
LPI	1,350	192	66	11	1.6
HBPI	2,700	714	149	24	5.2
A-5	909	214	44	4.1	–
A-10	1,920	431	93	10	2.7
A-16	2,970	514	157	18	4.6
B-5	2,122	545	103	12	6.5
B-10	4,217	1,010	232	37	15
B-16	5,132	1,064	221	42	5.9

HBPI. For example, the addition of 10 wt.% MCM-41 to HBPI resulted in respective 38 and 58% (series A) and 36 and 35% (series B) decrease in the permeability coefficients of oxygen and nitrogen. Consequently, the oxygen/nitrogen selectivity increased from 6.2 for the pure hyperbranched polyimide to 9.3 (series A) but only to 6.3 in the series B for the HBPI containing 10 wt.% MCM-41. The accuracy of the methane permeability measurement (see 2.3.) can influence to a certain degree the very high (and hopeful) carbon dioxide/methane selectivities (in comparison with e.g., [7]). On the contrary, it is not probably influenced by the material structural changes in consequence of the repeated experiments (differences about 5–10% were found for more permeable gases).

The permeability coefficients (Table 2) and selectivities (Table 3) for the linear analogue (LPI) to the hyperbranched product (HBPI) were also determined. During its preparation, the bifunctional 4,4´-diaminodiphenylmethane was substituted for the trifunctional 4,4´,4´´-triaminotriphenylmethane. The lower values of gas permeability coefficients for LPI suggest that HBPI based on the commercially available trifunctional amine MTA is a hopeful choice for testing the mixed matrix membranes based on it in a larger scale.

4. Conclusions

The mixed matrix membranes based on HBPI and MCM-41 (up to 16 wt.%) were prepared by two different procedures. The membranes prepared by the procedure A (MCM-41 added to the HBPI precursor) show lower permeabilities but higher selectivities in comparison with the membranes prepared by the procedure B (MCM-41 added to the monomers). Membranes prepared by the procedure B containing 10 and 16 wt.% MCM-41 show the higher gas permeability coefficient in comparison with those for pure HBPI. Therefore, it is probable – in contradiction with our assumption – that the preparation by employing the procedure B provides the mixed matrix membranes with more accessible pores (channels) for gases. Due to the very high and hopeful selectivities (oxygen/nitrogen 5.3–10.7 and carbon dioxide/methane 67–180) it seems that the contribution of an incidental poor polymer-additive interface is not decisive. A loosening of the molecular packaging of HBPI chains influences thermal and mechanical properties of mixed matrix membranes. This disorder probably contributes to the gas permeability increase with the silica content more than a creation of continuous pathways through silica pores. But it is necessary to examine these contributions to the permeation characteristics in detail in our future work.

Acknowledgements

This work was supported by the grants GA CR 104/09/1357 and MSM 6046137302. The financial support from specific university research (MSMT No. 21/2010–013 and 21/2010–011) is also acknowledged.

References

[1] P.M. Hergenrother, The use, design, synthesis, and properties of high performance/high temperature polymers: an overview, High Perform. Polym., 15 (2003) 3–45.

[2] K. Friess, P. Sysel, E. Minko, M. Hauf, O. Vopička, V. Hynek, K. Pilnacek and M. Sipek, Comparison of transport properties of hyperbranched and linear polyimides, Desalin. Water Treat., 14 (2010) 165–169.

[3] J. Fang, K. Hidetoshi and K. Okamoto, Gas separation properties of hyperbranched polyimide membranes, J. Membr. Sci., 182 (2001) 245–256.

[4] T.-S. Chung, L.Y. Juany, Y. Li and S. Kulprathipanja, Mixed matrix membranes comprising organic polymers with disperse inorganic fillers for gas separation, Prog. Polym. Sci., 32 (2007) 483–507.

[5] B.D. Reid, F.A. Ruiz-Trevino, I.H. Musselman, K.J. Balkus, Jr. and P. Ferrari, Gas permeability properties of polysulfone membranes containing the mesoporous molecular sieve MCM-41, Chem. Mater., 13 (2001) 2366–2373.

[6] P. Sysel, V. Sindelar, M. Kubonova, K. Friess, V. Hynek and M. Sipek, Membranes based on modified polyimides for gas and organic vapours separations, Desalination, 236 (2009) 46–50.

[7] L.M. Robeson, The upper bound revisited, J. Membr. Sci., 320 (2008) 390–400.