Pervaporation and Gas Separation Membranes Made from Polyimide/Polydimethylsiloxane Block Copolymer

JAN SCHAUER,[1,*] PETR SYSEL,[2] VLADIMÍR MAROUŠEK,[2] ZBYNĚK PIENTKA,[1] JIŘÍ POKORNÝ,[2] and MIROSLAV BLEHA[1]

[1]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, and [2]Department of Polymers, Institute of Chemical Technology, 166 28 Prague 6, Czech Republic

SYNOPSIS

Polyimide/polydimethylsiloxane block copolymers were prepared from oligoimides based on 2-aminopyridine-terminated 3,3'-oxybis(phthalic anhydride) and 1,4-bis(4-amino-α,α-dimethylbenzyl)benzene, and 3-aminopropyl-terminated oligo(dimethylsiloxane)s. Selectivity of homogeneous membranes prepared from the copolymers depends on the polydimethylsiloxane (PDMS) content: Selectivity of copolymers with up to approximately 20 wt % of PDMS is similar to that of polyimide homopolymer, whereas selectivity of copolymers containing more than 20 wt % of PDMS resembles that of pure PDMS. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The industrial and economic importance of pervaporation and gas separation has considerably increased in recent years. In both membrane operations, however, new polymeric membranes with good stability and improved fluxes and selectivities are needed. Much attention has been devoted to polyimides with their excellent thermal, chemical, and mechanical stability. Polyimide membranes for gas separations have generally high separation factors but their permeabilities are very low compared with those of polydimethylsiloxane (PDMS) membranes.[1] In pervaporation, polyimide membranes, when used to separate industrially important ethanol–water mixtures, preferentially transport water with a high degree of selectivity,[2] but exhibit relatively poor total permeability and cannot, therefore, compete with commercial membranes based on poly(vinyl alcohol). On the other hand, efficient ethanol permselective membranes are required for concentrating ethanol from its aqueous solutions, e.g., from the fermentation broth. PDMS is a typical example of an ethanol permselective material. As it has poor

film-forming properties, ultrathin PDMS membranes cannot be prepared. This disadvantage may be overcome by using copolymers of PDMS[3-7] which combine specific properties of PDMS and polyimide. The aim of this research was the synthesis and characterization of a block copolymer system composed of polyimide and PDMS segments, preparation of membranes, and their use in pervaporation and in separation of gases.

EXPERIMENTAL

Chemicals

5,5'-Oxybis-1,3-isobenzofuranedione (3,3'-oxydiphthalic anhydride, ODPA; Chriskev), was dried overnight at 180°C in vacuum before using. 1,4-Bis(4-amino-α,α-dimethylbenzyl)benzene (Bisaniline P, BIS P; Mitsui Petrochemical Industries, Ltd.) was used as received. 2-Aminopyridine (2-AP; Aldrich) was recrystallized from a mixture of chloroform/petroleum ether. Octamethylcyclotetrasiloxane (D4; Fluka) was distilled under vacuum over calcium hydride before using. 1,3-Bis(3-aminopropyl)tetramethyldisiloxane (DSX; ABCR) was used as received. N-Methyl-2-pyrrolidone (NMP), 1,2-dichlorobenzene (DCB), and chlorobenzene (CB)

were distilled under vacuum over phosphorus pentoxide and stored under an inert atmosphere.

## Synthesis of the 2-Aminopyridine-terminated ODPA-BIS P Oligoimides

To an ODPA solution in NMP 2-AP, and after 1 h, BIS P was added and the reaction was allowed to proceed 24 h.[8] Before imidization, a reverse Dean–Stark trap with DCB and a condenser was fitted to the reaction flask, and by adding DCB, the reaction mixture was brought to the composition NMP/DCB 9 : 1 by volume and the solid content 15 wt %. After 24 h at 170°C, the solution was cooled to room temperature and then precipitated into a water/methanol mixture. The collected polymers were dried to a constant weight in a vacuum. Molecular weights, M_n, of the polyimide oligomers were in the range 6000–18,500.

Synthesis of the 3-Aminopropyl-terminated Dimethylsiloxane Oligomers

The amino-terminated oligomers were prepared by an anionic ring-opening equilibration polymerization of D_4 initiated with potassium siloxanolate in the presence of 1,3-bis(3-aminopropyl)tetramethyldisiloxane.[9] A stirred mixture of D_4, DSX, and the catalyst (1 mol %) was heated at 150°C for 5 h. After cooling (50–70°C), low molecular weight compounds were stripped under vacuum. Molecular weights, M_n, of siloxane oligomers were in the range 950–4700 (by potentiometric titration with HCl).

Synthesis of the Polysiloxane/Polyimide Block Copolymers

The copolymers were prepared with the theoretical molecular weight, M_n, 40,000 g/mol by transimidization using an excess of the oligoimide. A solution of an oligoimide and oligosiloxane in CB (solid content 10 wt %) was heated to 125°C for 2 h. After cooling to room temperature, the polymer was precipitated into methanol. The collected product was dried to a constant weight in a vacuum. Copolymers were analyzed by ^{1}H-NMR spectroscopy. Synthesized polysiloxane/polyimide block copolymers have the following structure:
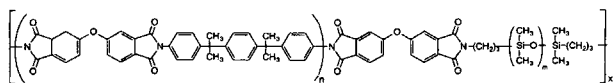
Membrane Preparation

A 5% polymer solution in chloroform was cast onto a glass plate and spread out with a casting knife. The solvent was evaporated slowly at room temperature over a few days. The membranes tested were homogeneous films with a thickness of 20 ± 2 μm.
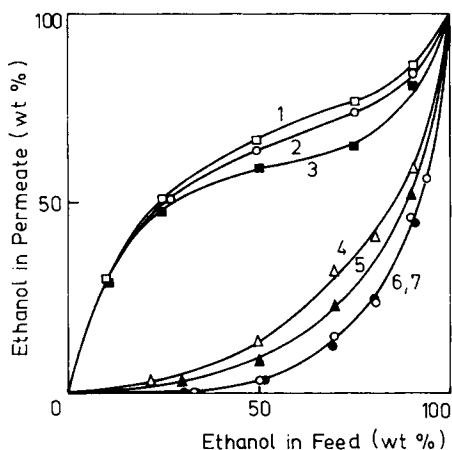
Pervaporation

The pervaporation apparatus used consisted of a pervaporation cell with a membrane area of 43 cm² and a glass apparatus equipped with traps cooled by liquid nitrogen to condense the permeate. The feed mixture was circulated between the thermostatted bath (25°C) and the upstream side of the membrane in the cell. The downstream pressure was kept at 400 Pa. The composition of the feed and of the permeate was determined by gas chromatography and, in the case of water–alcohol mixtures, by refractive index measurements using calibration curves. The total flux J at a steady state (measured approximately 4 h after the start) was obtained from $J = Q/At$, where Q is the total amount of liquids permeated during experimental time interval t and A is the effective surface area.

Gas Separation

Gas-transport properties of the membranes were studied using a laboratory-made high-vacuum apparatus with a static permeation cell. Permeabilities were determined from a pressure increase in the calibrated product side of the cell. Pressure was measured with a precision capacitance manometer CCM-10; the membrane area was 1.24 cm². The accuracy of measurement was about 2%. Selectivities were expressed by the ratio of pure gas permeabilities.

RESULTS AND DISCUSSION

As pervaporation is a process that combines evaporation of volatile components of a liquid mixture with their permeation through a membrane by a solution–diffusion mechanism, its selectivity depends on the following three properties of the organic liquid: affinity to the membrane, size of the molecule, and vapor pressure. In particular cases, different properties may take the predominant role. It was observed[10,11] that for glassy polymers the permeability is determined mainly by the diffusivity (depending on the size of the permeating molecules),

Figure 1 Dependence of ethanol contents in permeate and in the feed in the pervaporation of the ethanol–water mixture: (1) PDMS membrane; (2–6) membranes from block copolymer containing 30, 20, 17, 15, and 10 wt % of PDMS units, respectively; (7) polyimide membrane.

while for elastomeric polymers, the solubility contribution is decisive. The polyimide here prepared is a distinctly glassy polymer whose T_g depends somewhat on molecular weight ($T_g = 252°C$ for $M_n = 40,000$, $247°C$ for $M_n = 18,500$, and $228°C$ for $M_w = 6000$), while PDMS is a typical rubbery material at room temperature.

Figure 1 shows the dependence of ethanol contents in the permeate and feed in the pervaporation of the ethanol–water mixture for membranes with various PDMS contents. As expected, while the pure PDMS membrane preferentially transported ethanol over nearly all the range of feed composition (curve 1), the polyimide homopolymer membrane preferentially transported water (curve 7). The selectivity of block copolymers depended, however, on the PDMS content in the block copolymer: Copolymers with up to approximately 20 wt % of PDMS preferentially transported water and behaved, hence, similarly to the polyimide homopolymer, whereas copolymers with 20 wt % and more of PDMS preferentially transported ethanol and, hence, their selectivity resembled that of pure PDMS. It may be concluded that in the former copolymers glassy polyimide forms a continuous phase within the dispersed PDMS rubbery phase and that there is a percolation point at 20 wt % of PDMS, where PDMS begins to form continuous channels within the copolymer matrix.

Membranes made from copolymers with PDMS contents below and above the percolation point behave in an opposite way with respect to permeands with different molecular weights and different in-

teractions with polymers. While the permeability of copolymers with PDMS content below the percolation point depends in the first place on the bulkiness of the permeand (Fig. 2, curves 5a–c), the permeability of copolymers with PDMS content above the percolation point depends to a considerable extent on the affinity of the permeand to the membrane material, which is related, e.g., to solubility parameters. The value of the solubility parameter of *tert*-butyl alcohol ($\delta = 21.7$ MPa$^{1/2}$) is closest to that of PDMS[12] ($\delta = 14.9$ MPa$^{1/2}$), followed by the solubility parameters of 1-propanol and ethanol ($\delta = 24.3$ MPa$^{1/2}$ and $\delta = 26.0$ MPa$^{1/2}$, respectively). The order of permeabilities of membranes with high PDMS contents is the same as the order of these solubility parameters (Fig. 2, curves 2a–c). As to rubbery polymers, the solubility contribution is decisive[10,11]: Membranes made from copolymers with selectivities influenced by the order of solubility parameters should contain a rubbery continuous phase.

The prepared membranes were used to separate a fully organic mixture: ethanol–toluene. While ethanol has a low affinity for the tested materials (degree of swelling is smaller than 0.6 wt % for all the used membranes), pure toluene has a high affinity (degree of swelling is greater than 100 wt %). Figure 3(a) shows the dependencies of toluene permeation for a membrane from a block copolymer containing 15 wt % of PDMS units (whose selectivities in the separation of the ethanol–water mixture were virtually identical with those of polyimide homopolymer), for a membrane from a block copolymer containing 30 wt % of PDMS (whose se-
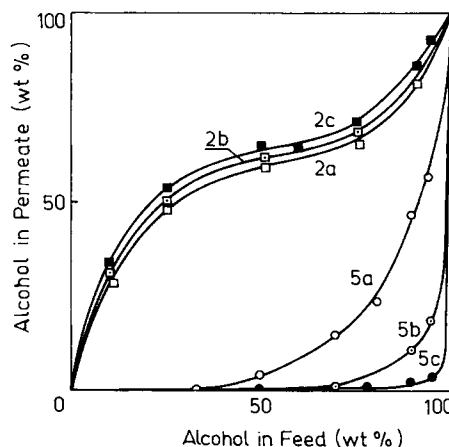
Figure 2 Dependence of alcohol contents in permeate and in the feed in pervaporation of an alcohol–water mixture. For designation of curves, see Figure 1: (a) ethanol; (b) 1-propanol; (c) *tert*-butyl alcohol.
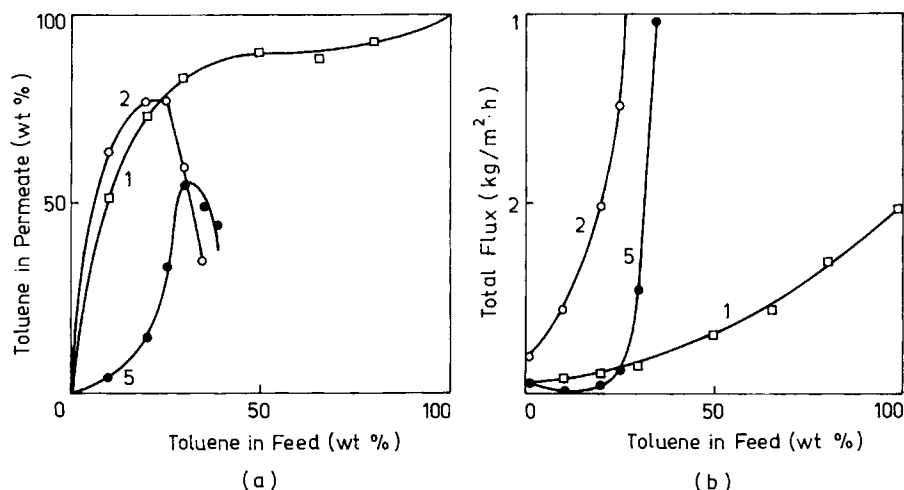
Figure 3   Dependence of toluene content (a) in permeate and (b) of total flux on toluene content in the feed in pervaporation of the ethanol–toluene mixture. For designation of curves, see Figure 1.

lectivities in the separation of the ethanol–water mixture were virtually identical with those of pure PDMS), and for a membrane from crosslinked PDMS. Figure 3(b) shows the dependencies of total fluxes through the membranes on the composition of the feed mixture. When the concentration of toluene in the feed mixture is low, membranes are only swollen a little (degree of swelling in 1% toluene is less than 15 wt % for all membranes tested), and in the case of the block copolymer with 15 wt % of PDMS units (curve 5), smaller molecules of ethanol permeate the membrane preferentially. If the concentration of toluene in the feed is increased (up to approximately 30 wt %), the total flux through the membrane increases and the membrane is preferentially permeated by a good solvent like toluene. When the concentration of toluene in the feed is further increased, the flux through the highly swollen membrane is dramatically increased but the

membrane loses its selectivity. The behavior of the membrane with a continuous rubbery phase (curve 2) differs by the preferential permeation of toluene (good solvent) even in the range of low toluene concentrations in the feed and is similar to that of pure PDMS (curve 1). However, as the PDMS membrane is chemically crosslinked, it keeps its selectivity over all the range of toluene concentrations in the feed.

The results of measurements of gas permeabilities are presented in Table I. As none of the studied gases specifically react with the membrane material, the permeabilities are determined by the size of diffusing molecules and by the higher solubility of carbon dioxide: $P(N_2) < P(O_2) < P(CO_2)$. It is further shown in the table that with decreasing content of PDMS all permeabilities decrease. In the range between 15 and 18% PDMS, a substantial change in the structure of the membrane occurs. As in pervaporation, copolymers with PDMS content above

Table I   Gas Transport Properties

Sample No.	Contents PDMS (wt %)	Permeability (Barrer)			Selectivity	
		$P(N_2)$	$P(O_2)$	$P(CO_2)$	O_2/N_2	CO_2/N_2
1	100	440	933	4550	2.1	10.6
2	30	29	64	330	2.2	11.4
3	20	3.3	8.3	48	2.5	14.6
4	17	1.4	3.2	16	2.3	11.0
5	15	0.26	1.5	12.8	5.5	47
6	10	0.23	1.5	9.6	6.3	42
7	0	0.12	0.79	5.7	6.8	54

1 Barrer = $1 \cdot 10^{-10}$ cm^3 (STP) cm/(cm^2 s cmHg).

that at the percolation point separate gases like PDMS. Copolymers with smaller PDMS content have selectivities like polyimide, i.e., more than twice higher than the former ones. The presence of a small amount of PDMS increases the permeability and the performance of membranes and simultaneously maintains the high selectivity of polyimide.

Permeation behavior of polymers depends on their primary structure (chemical composition) and their secondary structure (polymer chain arrangement). A good example of the influence of the secondary structure is the selectivity of polybutadiene membranes in the pervaporation of alcohol–water mixtures[13]: The uncrosslinked membrane transports water preferentially, whereas the crosslinked membrane is permselective toward alcohol. In the system studied by us, the selectivities of the block copolymers were essentially the same as those of the dominant copolymer component. This means that, on the block length level, the secondary structure of the components was not influenced by their copolymerization. In this way, permeation behavior gave information about the morphology of the copolymers. On the other hand, as our aim was to prepare membranes with improved permeation properties, we must explore more intimate means of combining polyimide and siloxane qualities.

CONCLUSIONS

In pervaporation and in separation of gases, selectivity of block copolymers polyimide/PDMS depends on the PDMS content in the block copolymer: The selectivity of the copolymers with up to approximately 20 wt % of PDMS is similar to that of the polyimide homopolymer (this means that polyimide forms a continuous phase within the dispersed PDMS rubbery phase), whereas the selectivity of the copolymers containing more than 20 wt % of PDMS resembles that of pure PDMS (PDMS forms continuous channels within the copolymer matrix).

REFERENCES

1. R. T. Chern, W. J. Koros, H. B. Hopfenberg, and V. T. Stannet, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 753 (1983).
2. K. Okamoto, N. Tanihara, H. Watanabe, K. Tanaka, H. Kita, A. Nakamura, Y. Kusuki, and K. Nakagawa, *J. Membr. Sci.*, **68**, 53 (1992).
3. S. Takegami, H. Yamada, and S. Tsuji, *J. Membr. Sci.*, **75**, 93 (1992).
4. E. Akiyama, Y. Takamura, and Y. Nagase, *Makromol. Chem.*, **193**, 1509 (1992).
5. J. Y. Lai, S.-H. Li, and K.-R. Lee, *J. Membr. Sci.*, **93**, 273 (1994).
6. J. A. Kerres and H. Strathmann, *J. Appl. Polym. Sci.*, **50**, 1405 (1993).
7. S. J. Mecham, V. N. Sekharipuram, M. E. Rogers, G. W. Meyer, Y. J. Kim, and J. E. McGrath, *Polym. Prepr.*, **35**(2), 803 (1994).
8. P. Sysel, J. R. Babu, M. Konáš, J. S. Riffle, and J. E. McGrath, *Polym. Prepr.*, **33**(2), 218 (1992).
9. J. E. McGrath, P. M. Sormani, C. S. Elsbernd, and S. Kilic, *Makromol. Chem. Macromol. Symp.*, **6**, 67 (1986).
10. J. Schauer and M. Bleha, *J. Appl. Polym. Sci.*, **46**, 1807 (1992).
11. H. Strathmann, C.-M. Bell, and J. Kerres, *Desalination*, **77**, 259 (1990).
12. A. F. Barton, Ed., *Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, CRC Press, Boca Raton, FL, 1990.
13. M. Yoshikawa, T. Wano, and T. Kitao, *J. Membr. Sci.*, **89**, 23 (1994).