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Optimisation of Transport Properties of Polyurethane-Based Pervaporation Membranes by a Polymer Molecular Structure Design

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Summary: This article discusses the relationship between a molecular structure of segmented polyurethanes and their permselectivity and permeability in the pervaporation separations of organic/organic mixtures and in the removal of VOC from water. The structural variations within this group of polymers were designed based on general physicochemical considerations and were achieved at the synthesis stage by using reagents of various chemical structures and molecular weights and in different initial molar ratios. Therefore, the homologous series of polyurethanes, having well defined and widely modified molecular structures, could be investigated.

The pervaporation performances of the obtained polymers are described with respect to the various model binary mixtures simulating the feeds of commercial interest, like: benzene/cyclohexane mixtures with a low (5 wt. %) and a high (56 wt. %) benzene content, or benzene/water, ethanol/water, and acetone/water mixtures.

The concept of a membrane material tailoring for a particular separation problem is also demonstrated.

Keywords: polyurethanes, membranes, pervaporation, transport properties

Introduction

Pervaporation is a membrane separation process, which combines the evaporation of volatile components with their permeation through a selective membrane. The separation of components of a liquid mixture is therefore determined by the differences in their vapour pressures and in the rates they permeate through the membrane. The solution-diffusion mechanism developed by Lonsdale[1] has been widely accepted for describing the transport of molecules in the membrane.

This process involves the sorption of components from a liquid phase into a membrane at the feed side, their diffusion through the membrane, and finally desorption of the components at the permeate side of a membrane. The efficiency of the pervaporation process is controlled mainly by the intrinsic properties of the polymers used for membranes preparation. The

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chemical composition, structure, and morphology of the polymer govern the nature and magnitude of possible interactions between polymer segments and penetrant molecules, the accessibility of sorption sites within the polymeric matrix, and the mobilities of penetrant molecules related to component interactions, polymer chain segmental mobility, and the associated free volume content and its distribution. The variations of these factors enable the membrane materials with diverse transport property to be prepared. On the other hand, the selection and evaluation of membrane materials most suitable for achieving a desired separation requires the correlations between the membrane permeability and permselectivity, and the polymer composition, structure or morphology to be well established. The investigation of pervaporation structure - property relationships was performed by Tanihara et al[2,3]. The objective of their work was to study the effect of the free volume of polyimides containing methyl-substituted phenylenediamines moieties on the transport and sorption of benzene and cyclohexane[2]. They also studied the influence of the kind, length and content of the polyether-based segments in poly(ether imide) segmented copolymers on their pervaporation performance in the separation of benzene-cyclohexane, benzene-n-hexane, and acetone-cyclohexane mixtures[3]. Jonquieres et al[4,5] carried out the investigations of polyurethaneimide and polyureaimide block copolymers with polyether or polyester-based soft segments, applied in the separation of EtOH/ETBE mixtures. These studies were focused on the effect of the soft segment nature and size on the pervaporation properties of the block copolymers. The results obtained by them showed correlations between flux and soft segment molecular weight, and between selectivity and segment polarity, as well as between flux and soft segment weight fraction.

There have also been reports about the relationships between transport properties and structure of segmented polyurethanes[6÷8]. Ohst et al[6] investigated influence of chemical nature of the soft segments, as well as other structural parameters, like: hard segment weight fraction or chemical crosslinking, on the pervaporation performance of polyurethanes in the separation of toluene/cyclohexane mixtures. Cao et al[8] studied the pervaporation properties of the polyester-based polyurethanes in the separation of styrene/ethylbenzene mixtures and also found some relations between the transport data and the polyurethane composition. Sensitivity of solution and transport processes to the variations in polymer composition and structure, processing conditions and other variables, as well as to the nature of the penetrant requires, however, much more data to be available to establish mechanism and expressions relating solubility and transport with the molecular properties and characteristics of the components.

Therefore, the objective of our research is to study the solution, diffusion, and permeation of liquids in polymeric materials with well-defined overall structure and morphology easily modified in a controlled way. Segmented polyurethanes seem to be the most versatile membrane materials for these purposes. They exhibit good film-forming properties, mechanical stability of the membranes, very easy processability, and the possibility of utilising of a wide spectrum of the reagents with broad variabilities in molecular weights and molar compositions for their synthesis.

The goal of the studies presented here has been on the effect of variation in the soft and hard segment chemical constitution and length on permselectivity and permeability of the segmented polyurethanes (PU) in the separation of organic/organic mixtures and in the removal of VOC from water. The pervaporation performances of the investigated PUs have been described with respect to the various model binary mixtures simulating the feeds of commercial interest, like: benzene/cyclohexane mixtures with a low (5 wt.%) and a high (56 wt.%) benzene content, or benzene/water, ethanol/water, and acetone/water mixtures.

Experimental Part

Materials and membrane preparation

Poly(oxytetramethylene) diols (PTMO, M_w = 650, 1000, 2000, BASF), poly(oxyethylene) diol (PEO, M_w = 1000, Aldrich), poly(1,4-butylene adipate) diol (PBA, M_w = 2000, ICRI, Warsaw) and polybutadiene diol (PBUT, M_w = 1200, Aldrich) were used as precursors of the polyurethanes (PU) soft segments.

4,4'-bis(2-hydroxyethoxy) biphenyl (BHBP, synthesised in our laboratory), hydroquinone bis(2-hydroxyethyl) ether (HQE, Aldrich), and 4,4'-diaminodiphenyl methane (PP, POCh, Poland) were used as chain extenders (Et). 2,4- Tolylene diisocyanate (TDI, 98 wt. % 2,4-TDI, Aldrich) was used as a diisocyanate component (DI).

PUs were synthesised in DMF solution either by a two-step polyaddition method or in the reaction of equimolar amounts of a diisocyanate and a macrodiol. The two-step procedure comprises the formation of a prepolymer by end-capping of a selected macrodiol with a diisocyanate being in excess in the reaction mixture, and then the chain extension by adding suitable amount of a low-molecular weight diol or diamine. The details of the polyurethane synthesis have been described elsewhere [9].

PU membranes of thickness of about 70-140 μm were prepared by casting the 15 wt. % solution of PU in DMF onto a glass plate and by evaporating the solvent at 60°C for 72 h.

Structures of the PUs studied are shown in Fig. 1.

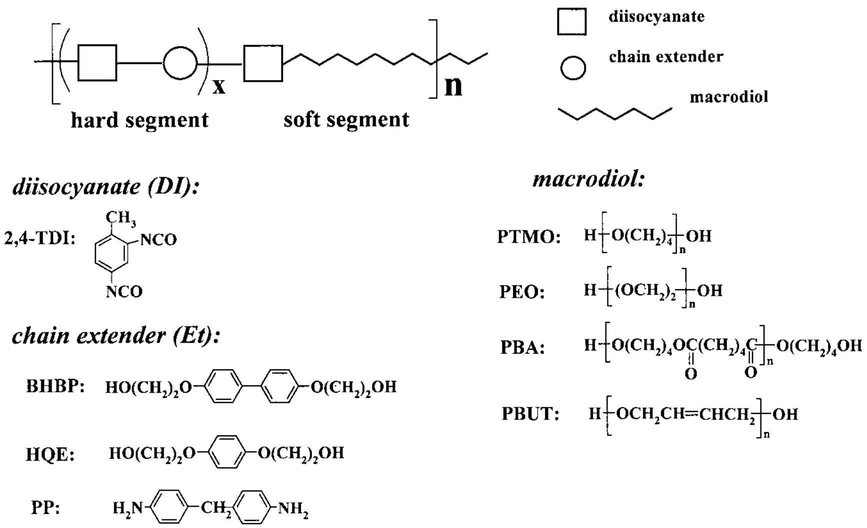

Figure 1. Structures of PUs of a general formula $(DI\text{-}Et)_x\text{-}DI\text{-}macrodiol\text{-}M_w$

The composition and physical properties of the synthesised PUs are listed in Table 1.

The glass transition temperatures T_g were determined from the differential scanning calorimetry (DSC) measurements performed with a Rheometric Scientific DSC Plus apparatus under nitrogen atmosphere at the heating rate of 10°/min.

The molecular weights of PUs were determined by gel permeation chromatography (GPC) with a Knauer apparatus in DMF solvent, calibrated by polystyrenes.

The density was measured with an analytical balance by weighing the samples at room temperature in air and in distilled water.

Pervaporation experiments

Pervaporation experiments were performed at 25°C using a standard pervaporation cell in a batch system. The downstream pressure was kept below 1 mm Hg, and the permeate was collected in a trap cooled by liquid nitrogen. The permeation rate, described as normalised flux F [kg $\mu m/m^2h$], was determined from the variation in the condensate weight with time calculated for a standard membrane thickness of 1 μm.

The compositions of the feed and permeate were determined using refractometry or gas chromatography. The selectivity α was defined as:

$$\alpha = \frac{Y(1-X)}{X(1-Y)} \quad (1)$$

where X and Y are the weight fraction either of organic component for organic/water mixtures, or of the component which permeates preferentially through the membrane, in the feed and permeate, respectively.

The following binary feed mixtures were separated: 5 wt. % benzene/cyclohexane, 56 wt. % benzene/ cyclohexane, 0.065 wt. % benzene/water, 5 wt. % acetone/water and 8 wt. % ethanol/water.

Table 1. Composition and physical properties of PUs

Polymer	Composition [mol]	Soft segments fraction $_{(calc.)}$ [wt. %]	Density [g/cm^3]	M_n	M_w/M_n	T_g [°C]
TDI-PTMO-650	TDI PTMO-650 1 1	79	1.112	-	-	-34
TDI-PTMO-1000	TDI PTMO-1000 1 1	85	1.093	-	-	-52
TDI-PTMO-2000	TDI PTMO-2000 1 1	92	1.072	-	-	-77
TDI-PEO-1000	TDI PEO-1000 1 1	85	1.242	-	-	-42
TDI-PBUT-1200	TDI PBUT-1000 1 1	87	1.029	-	-	-63
(TDI-BHBP)$_1$-TDI-PTMO-650	TDI BHBP PTMO-650 2 1 1	51	1.161	38 900	2.7	-31
(TDI-HQE)$_1$-TDI-PTMO-650	TDI HQE PTMO-650 2 1 1	54	1.122	58 800	2.0	-32
(TDI-PP)$_1$-TDI-PTMO-650	TDI PP PTMO-650 2 1 1	54	1.151	42 600	1.7	-32
(TDI-PP)$_1$-TDI-PTMO-1000	TDI PP PTMO-1000 2 1 1	65	1.109	50 600	1.7	-52
(TDI-PP)$_1$-TDI-PTMO-2000	TDI PP PTMO-2000 2 1 1	78	1.083	44 000	1.7	-83
(TDI-PP)$_3$-TDI-PTMO-1000	TDI PP PTMO-1000 4 3 1	44	1.167	35 300	1.6	-46
(TDI-BHBP)$_3$-TDI-PBA-2000	TDI BHBP PBA-2000 4 3 1	57	1.232	58 000	2.2	-30
(TDI-PP)$_3$-TDI-PBA-2000	TDI PP PBA-2000 4 3 1	61	1.222	68 000	2.5	-26

Results and Discussion

Structure and characterisation of segmented polyurethanes

Polyurethane elastomers (PU) studied in this work as membrane materials are linear block copolymers of $(AB)_n$ type, composed of alternating soft and hard blocks. The schematic representation of the PU structure is given in Fig. 1. The highly polar and rigid hard segments of these copolymers are formed by the reaction of a diisocyanate with a low molecular weight diol or diamine in the extension step of the PU synthesis, or in case no chain extender is used, with a macrodiol component of the reaction mixture. The soft segments, the glass transition temperature (T_g) of which is below the room temperature, come from a macrodiol component. Incompatibility between both segments leads to their separation and to the formation of hard and soft-segment domains. The extent of microphase separation, associated with such factors as segment polarity, length and symmetry, tendency for hard and soft-segment interaction, or overall sample composition and crystallinity, strongly affects the two-phase domain structure of PUs. Some morphological models illustrating the domains' structure in highly phase-separated PUs (A and C) and in the systems where the phase separation is incomplete (B and C) are given in Fig. 2.

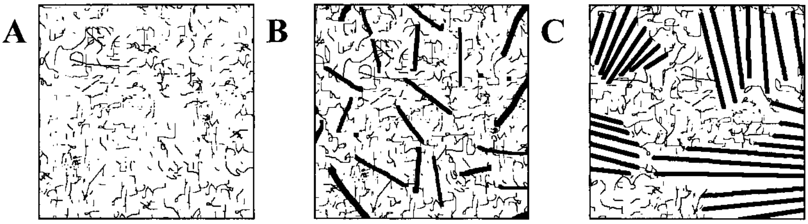

Figure 2. Schematic representation of some of the domains' structure in the PUs studied: A – amorphous soft segment regions, B – amorphous solution of hard and soft segments, C – lesser ordered, non-crystalline hard-segment domains

It has been postulated that only soft domains are permeable to gases and liquids[10]. The hard-segment domains, with a very strong dipole-dipole interactions and hydrogen bonding, and with some degree of order depending on the structure of the hard segment, act as fillers or physical crosslinks for the rubbery soft segment matrix. Hence, their volume fraction, size and distribution is expected to affect the transport of small molecules by suppressing membrane swelling, as well as by influencing the path of the permeating molecules. On the other hand, some of the urethane segments dispersed in the rubbery matrix of PUs showing a low degree of phase separation may have an impact on the nature of the soft segment-domains.

In this work, transport properties of the series of PUs varying in the chemical constitution and length of both segments are presented and discussed. The applied structural modification regarding hard segments were due to the different chain extenders used in the PU synthesis and to the different initial composition of the diisocyanate and diol reagents ($x=0\div3$ in Fig. 1). The aromatic diols or diamine along with the aromatic diisocyanate were used to assure a sufficient mechanical strength of the resulting polymers which enable them to withstand the harmful conditions of some pervaporation experiments. The soft segments modifications consisted in application of macrodiols of different chemical constitution ranging from a non-polar and without any potential for hydrogen bonding polybutadiene (PBUT:$\delta=17.1$ $(MPa)^{1/2}$), through polar polyethers (PTMO: $\delta=17.6$ $(MPa)^{1/2}$, PEO: $\delta=20.2$ $(MPa)^{1/2}$), to polyester (PBA: $\delta=19.5$ $(MPa)^{1/2}$) which can form strong hydrogen bonds with hard segments. The length of the soft segments resulting from the macrodiol molecular weight was another structural parameter examined with regard to the PU transport properties. The various molecular structures of the synthesised PUs are shown in Fig.1, whereas their compositions and physical properties in Table 1. The abbreviations used in Table 1 are based on a general formula $(DI\text{-}Et)_x$-DI-macrodiol-M_w, where DI, Et and macrodiol refer to diisocyanate, chain extender and macrodiol, respectively, x refers to the number of the repeat units within the hard segment resulting from the initial molar ratio of DI/Et, and M_w refers to the molecular weight of a macrodiol.

All polymers, the molecular structure of which have been programmed according to the concept shown, exhibit good film forming properties due to the sufficient high value of their molecular weights. Most of the materials with a high soft segment weight fraction can be regarded as soft elastomers, when compare to the more rigid ones obtained from the PUs with a lower soft segment content. The PUs synthesised from the more polar macrodiols are more rigid then their less polar analogue of the same composition.

As shown in Table 1, density of the investigated PUs ranges from 1.029 g/cm^3 for TDI-PBUT-1200 to the values above 1.2 g/cm^3 for polar PEO and PBA- based PUs. PTMO-based polyurethanes show a linearly decreasing density on increasing molecular weight of the soft segment and on decreasing length of the hard segments. Accordingly, T_g corresponding to the PU soft segments decreases from -30°C to -80°C on increasing the soft segment length that can be correlated to the increase in free volume. The highest T_g values of the PBA-based soft segments as well as higher T_g value for TDI-PEO-1000 comparing with TDI-PTMO-1000 coincide with higher densities of the respective polymers and are due to greater attractive forces between macromolecules and to a larger chain stiffness.

Performance of segmented polyurethanes in the separation of organic compounds from water

Permeation of volatile organic compounds (VOC) through pervaporation membrane is dominated by concentration polarisation effects. These effects become especially important as selectivity and flux through the membrane increase, that is the case of the removal of benzene from water using PU-based membranes. To reduce effect of concentration polarisation, a high stirrer speed of ~1000 rpm, as well as membranes above 100 μm in thickness were used in all VOC/water pervaporation experiments. Based on the literature data [11,12], it was assumed that for these conditions boundary layer resistance can be negligible. Moreover, each experiment was conducted in exactly the same way to make a comparison between the performance of the different polyurethane-based membranes valid.

Three solutes of a high vapour pressure have been studied which vary from each other substantially as for their polarity and molecular size: a non-polar aromatic hydrocarbon (benzene: δ=18.8 $(MPa)^{1/2}$, V=89.4 cm^3/mol), a moderately polar ketone (acetone: δ=20.3 $(MPa)^{1/2}$, V=74.0 cm^3/mol), and a hydrogen-bonded solvent (ethanol: δ=26.6 $(MPa)^{1/2}$, V=58.5 cm^3/mol). The pervaporation conditions, like feed temperature and downstream pressure were the same in all pervaporation experiments (25°C, < 1 mm Hg), whereas the feed compositions were associated with a particular mixture. The pervaporation performance of the all PU membranes tested is shown in Table 2. Each set of results is the average of several experiments performed with various membranes prepared from a given polymer. The polymers of the same molecular structure obtained in the separate synthesis were also tested to reduce the influence of the incidental factors concerning the synthesis conditions.

The measure of the separation achieved by various PU membranes in benzene/water pervaporations, given in Table 2, is the weight fraction of benzene in permeate solution. The values of the flux and benzene content, used to illustrate the differences in performance between PU membranes of different molecular structure, were determined disregarding the effect of the feed side boundary layer resistance and the feed concentration changes. The detailed analysis of the both effects with respect to the membrane transport properties justifying such a procedure will be presented in a separate paper.

The influence of the soft segment chemical constitution and length on the pervaporation performance of the PU membranes have been investigated using PUs with the highest weight fraction of the soft segments resulting from their molecular structure characterised by x=0 (Fig. 1)

Table 2. Pervaporation properties of PUs in VOC/water separations at 25°C

PU	Benzene/Water (0.065 wt. %)		Acetone/Water (5 wt. %)		Ethanol/Water (8 wt. %)	
	Flux $[\mathrm{kg\ \mu m\ m^{-2}h^{-1}}]$	Benzene in permeate [wt.%]	Flux $[\mathrm{kg\ \mu m\ m^{-2}h^{-1}}]$	α	Flux $[\mathrm{kg\ \mu m\ m^{-2}h^{-1}}]$	α
TDI-PTMO-650	3.8	60	0.9	0.8	0.9	0.6
TDI-PTMO-1000	5.0	49	2.6	2.4	2.6	1.6
TDI-PTMO-2000	5.8	50	2.4	4.0	2.3	2.7
TDI-PEO-1000	22.5	0	25.7	0.1	25.9	0.1
TDI-PBUT-1000	3.1	79	0.5	4.4	0.5	0.9
(TDI-BHBP)$_1$-TDI-PTMO-650	1.6	44	0.6	0.6	0.9	0.2
(TDI-HQE)$_1$-TDI-PTMO-650	1.4	45	0.5	0.2	0.7	0.1
(TDI-PP)$_1$-TDI-PTMO-650	2.2	51	0.7	0.2	0.6	0.1
(TDI-PP)$_1$-TDI-PTMO-1000	3.3	44	1.7	1.7	1.6	0.8
(TDI-PP)$_3$-TDI-PTMO-1000	2.1	28	0.7	0.1		

For benzene separation, it can be seen from Table 2, that PTMO and PBUT-based PUs all display both high permeability and permselectivity. The best separation, enabling benzene to be concentrated 1200 fold, has been achieved by hydrophobic PBUT-based membrane. These membranes are also more selective to a moderately polar acetone than to a strong hydrogen-bonded ethanol. However, the separation obtained are relatively modest ($\alpha<4.4$) or even inverted in some cases ($\alpha<1$), indicating that water ($\delta=47.9\ (\mathrm{MPa})^{1/2}$, $V=18.0\ \mathrm{cm^3/mol}$) is transferred in preference to organic solvent. The PEO-based membrane, much more polar that PTMO-based one, appeared to be exclusively water permselective independent of the separated mixture.

Comparing the results obtained for PTMO-based membranes with various soft segment length, the sequence of decreasing length describes the decrease in permeability, and for hydrophilic solvents, also the decrease in selectivity to the values below 1.

This is believed to be due to a reduction in free volume for PUs with a decrease of the soft segment length, which is illustrated by the increasing T_g and density values induced by the growing ratio of the hydrogen-bonding urethane groups to the tetrahydrofurane sequences. The reduced selectivity in the separation of polar solvents can be attributed either to a reduced mobility of the soft segments that promote transport of smaller water molecules, or to an enhanced affinity of water molecules towards a polymer chain due to the increased concentration of the urethane groups.

The influence of the hard segment chemical constitution and length on the membrane performance has been investigated using PUs synthesised from various chain extenders and different TDI/Et initial molar ratios. As shown in Table 2, various hard segments of general formula $(\text{TDI-Et})_1$-TDI have similar effects upon the separation from water of benzene, acetone and ethanol. Significant differences in performance can be observed for all these separations, however, when the length of the hard segment, expressed by x, is considered. Comparing the results of membranes described by the formula $(\text{TDI-PP})_x$-TDI-PTMO-1000 or TDI-PTMO-650 with any of $(\text{TDI-Et})_1$-TDI-PTMO-650, it can be noticed that the longer hard segment the lower both permeability and selectivity. This is probably due to the transport restrictions imposed by the hard segment domains, like the reduced membrane area available for transport, or more tortuous path the permeating molecules have to travel. It seems likely that the mobility limitations will inhibit the diffusion of the larger organic molecules to a greater extent than of the small water molecules, leading also to a decreased selectivity.

Performance of segmented polyurethanes in the separation of benzene/cyclohexane mixtures

In contrary to the removal of organic compounds from their dilute water solutions, the process of organic/organic separation is stronger influenced by a feed composition. The high affinity of organic liquid to polymeric material increases its solubility with increasing concentration, and exerts a plasticizing effect on segmental motions in the polymer chain. This effect extends the temperature range for segmental rotation to lower temperatures, depressing the T_g values, and brings about an increase in size of the transport corridor. As a result permeation rate is enhanced and selectivity lowered. Thus, the composition of a separated organic mixture has to be taken into account in membrane material development.

In this work transport phenomenon of organic/organic pervaporation through PU membranes has been studied for benzene/cyclohexane mixtures of a low (5 wt.%) and a high (56 wt.%)

benzene content. The pervaporation characteristics of the investigated membranes are given in Table 3.

Table 3. Pervaporation properties of PUs for benzene/cyclohexane mixtures at 25°C

PU	5 wt. % Benzene		56 wt. % Benzene	
	Flux [kg μm m^{-2}h^{-1}]	α	Flux [kg μm m^{-2}h^{-1}]	α
TDI-PTMO-1000	14.2	4.6	non-resistant	
TDI-PEO-1000	< 0.01	not measured	< 0.01	not measured
TDI-PBUT-1000	49	2.2	non-resistant	
(TDI-BHBP)$_1$-TDI-PTMO-650	0.22	15.6	31.3	2.4
(TDI-HQE)$_1$-TDI-PTMO-650	0.8	9.8	non-resistant	
(TDI-PP)$_1$-TDI-PTMO-650	1.3	6.4	61.3	2.5
(TDI-PP)$_1$-TDI-PTMO-1000	10.2	5.0	non-resistant	
(TDI-PP)$_1$-TDI-PTMO-2000	46.6	3.2	non-resistant	
(TDI-PP)$_3$-TDI-PTMO-1000	0.5	7.1	58.7	2.2
(TDI-BHBP)$_3$-TDI-PBA-2000	< 0.01	not measured	5.0	21
(TDI-PP)$_3$-TDI-PBA-2000	< 0.01	not measured	26.0	5.8

All PU membranes were preferentially permeable to benzene over cyclohexane for the both feed mixtures, including TDI-PEO-1000 one, the permeability of which was below the measurement limit in given pervaporation conditions (F<0.01 kg μm m^{-2}h^{-1}). It can be seen from the data presented in Table 3 that the decreasing resistance of the membranes to the 56 wt.% benzene mixture generally follows the set of the decreasing solubility parameter values of the PU soft segments. This is to be expected since mechanical strength or cohesive energy increases as the polarity and frequency of the functional groups increases. The performance of the PTMO-based PUs for the separation of azeotropic benzene/cyclohexane mixture is disappointing. Although the mechanical strength of those membranes can be enhanced by controlling the hard segment length or/and structure, the membrane swelling is not diminished enough to increase their permselectivity much above 2.

When the benzene content in the separated mixture decreases, it is shown, that the phenomena of swelling get diminished enabling the correlations between the structure variables and the transport properties to be better observed.

A comparison of the performance of $(TDI\text{-}PP)_1$-TDI-PTMO-M_n membranes varying in the soft segment length indicates that the longer soft segments the higher permeability accompanied by the lower selectivity. These correlations complement the data presented earlier[9], and are similar to that found by other authors for polyurethanes[6,8] or other block copolymers[3,5].

It seems likely that the observed differences in permeability can be attributed to the intrinsic differences in the soft segment mobility, illustrated by the T_g values related to the soft segment length (Table 1), which are much more pronounced by the plasticizing effect of the separated mixture. Following the same trend, that the longer soft segment the greater mobility and free volume, and the higher swellability, PU membranes with longer soft segments become much more permeable and less selective.

Comparing the transport data for PUs of general formula $(TDI\text{-}PP)_x$-TDI-PTMO-1000 varying in the hard segment length, one can notice the significant differences in the flux, and to a lesser extent, in the selectivity values. The sequence of increasing hard segment length describes the decrease in membrane permeability along with some enhancement in its separation ability. The observed decrease in permeability may be explained by the reduced membrane area available for permeating molecules, due to the lower fraction of the permeable soft domains, as well as by the tortuosity factor imposed by the hard domains. Since for organic/organic separations the role of hard domains in suppressing membrane swelling is thought to be crucial, the better capability of the hard domains made from longer hard segments in restraining membrane swelling provides another account for its higher selectivity and diminished permeability. The higher concentration of polar sites which could interact with benzene molecules, and could be expected in the permeable regions of PUs with longer hard segments, may also play a role in membrane selectivity enhancement.

It is interesting to compare the pervaporation results for $(TDI\text{-}Et)_1$-TDI-PTMO-650 membranes varying in the hard segment structure, as a consequence of various chain extenders used for PU synthesis. The significant improvement in membrane selectivity, however at the expense of permeability, has been achieved by replacing the diamine-based chain extender, PP, by the diol-based one, HQE, or more successfully BHBP. In our earlier studies[9] concerning the transport properties of PUs synthesised using different chain extenders from the family of aromatic diamines, it was found out that the chemical constitution of the hard segment studied did not affect the separation ability of PUs. Results showing the lack of any effect of the hard segment nature on pervaporation performance of the block copolymers[3,6] along with evidences that such correlations exist[5], have also been presented in literature. It appears likely that the origin of those sometimes confusing conclusions comes from the chemical constitution of the hard segments which differ one another substantially.

It is difficult to describe a mechanism by which the pervaporation performance of PU membranes can be influenced by the hard segment structure. Taking into account the smaller molecular size of benzene molecules (benzene: V=89.4 cm^3/mol, cyclohexane: V=108.7 cm^3/mol) the preferential diffusion of benzene through the membrane is awaited. Furthermore, since benzene molecule has π-electrons, it may stronger interact with polar groups from a polymer chain than cyclohexane (benzene: $\delta=18.6$ $(MPa)^{1/2}$, cyclohexane: $\delta=16.8$ $(MPa)^{1/2}$) leading to the enhanced benzene permselectivity. Therefore, it can be assumed that the better pervaporation performance of the BHBP-based membrane, when compare with HQE- or PP-based ones, is a consequence of its specific morphology which facilitates transport of benzene molecules according to the principles discussed above and/or more effectively suppresses membrane swelling. However, more structural studies are needed in order to explain the transport behaviour observed.

Conclusions

Polyurethane-based membranes showing diverse pervaporation characteristics in the separation of benzene/cyclohexane mixtures and in the removal of VOC from water have been produced. It was demonstrated that the source of a variation in transport properties is the molecular structure of the polyurethanes which can easily be programmed by using reagents of various chemical structures and molecular weights, and in different initial molar ratios for the PU synthesis. The general approach has been presented that may facilitate the evaluation of a polyurethane molecular structure for achieving a desire separation. For hydrocarbons separation from water, a high both selectivity and permeability membrane can be produced from polyurethanes composed of long non-polar (PBUT) or moderately polar (PTMO) soft segments and very short hard segments (x=0), since these polymers provide adequate solubility selectivity of the organic versus water. Selectivity to other organic compounds, acetone and ethanol, is substantially lowered. It is due to much weaker interactions between polymer segments and organic molecules, and stronger components interactions that gives rise to the competition between the solubility selectivity and mobility selectivity favouring water. For benzene/cyclohexane separations, like for other organic/organic separations, the plasticizing effect of the feed solution components reducing membrane selectivity while enhancing its permeability has to be taken into account. Using membranes produced from polyurethanes composed of the more polar soft segments (PBA vs. PTMO), this effect is demonstrated to be diminished. The significant separation enhancement may be achieved by the use of polyurethanes with shorter soft segments and/or, to a lesser extent, with longer hard segments. Although the increase in the hard segment length mainly leads to the decline of permeability while only moderately enhancing selectivity, the modification of the hard segment chemical constitution can yield the much improved separation performance of the membrane. Based on the discussion of this paper, it can be concluded that the membrane materials with tailor-made transport properties can be obtained as a result of the structural modifications demonstrated, however, more general structure-property relationships are to be found.

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