Synthesis, Characterization, and Pervaporation Properties of Segmented Poly(urethane-urea)s

JACEK MUSZYŃSKI,¹ ALEKSANDRA WOLIŃSKA-GRABCZYK,¹ PIOTR PENCZEK²

¹ Institute of Coal Chemistry, Polish Academy of Sciences, Sowińskiego 5, 44-102 Gliwice, Poland

² Industrial Chemistry Research Institute (ICRI), Rydygiera 8, 01-793 Warsaw, Poland

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ABSTRACT: Poly(urethane-urea)s (PUUs) from 2.4-tolylene diisocyanate (2.4-TDI), poly(oxytetramethylene)diols (PTMO) or poly(butylene adipate)diol (PBA), and various diamines were synthesized and characterized by Fourier transform infrared spectroscopy, gel permeation chromatography, differential scanning calorimetry, and density measurements. Transport properties of the dense PUU-based membranes were investigated in the pervaporation of benzene-cyclohexane mixtures. It was shown that the pervaporation characteristics of the prepared membranes depend on the structure and length of the PUU segments. The PBA-based PUUs exhibit good pervaporation performance along with a very good durability in separation of the azeotropic benzenecyclohexane mixture. They are characterized by the flux value of 25.5 (kg $\mu m~m^{-2}~h^{-1})$ and the separation factor of 5.8 at 25°C, which is a reasonable compromise between the both transport parameters. The PTMO-based PUUs display high permeation flux and low selectivity in separation of the benzene-rich mixtures. At the feed composition of 5% benzene in cyclohexane, their selectivity and flux are in the range of 3.2 to 11.7 and 0.4 to 40.3, respectively, depending on the length of the hard and soft segments. The chemical constitution of the hard segments resulting from the chain extender used does not affect the selectivity of the PUU membranes. It enables, however, the permeability of the membranes to be tailored. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1615-1625, 1999

Key words: pervaporation; organic–organic separation; hydrophobic membranes; segmented poly(urethane-urea)s

INTRODUCTION

In recent years, membranes and membrane-related processes have gained much importance in several areas of science and technology. Among others, membrane separation processes are of growing interest in industrial applications due to their reduced energy consumption.

Pervaporation (PV) is a membrane separation process in which the separated liquid mixture is

Correspondence to: A. Wolińska-Grabczyk.

in direct contact with one side of a nonporous membrane, and the selectively permeated product is removed in the vapor state from the other side. This is achieved by applying vacuum or an inert medium to the permeate side of the membrane. The driving force for the permeation is a difference of the chemical potential between the two phases separated by the membrane, resulting in an induced concentration gradient within the membrane interphase. The transport process is generally accepted to proceed according to the solution-diffusion model¹ in the following three steps: sorption into the membrane, diffusion through the membrane, and desorption into the vapor state at the opposite side of the membrane.

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The separation is achieved because of the relative permeability of the membrane for the solution components, which depends on both thermodynamic (sorption) and kinetic (diffusion) parameters. Therefore, the membrane material is a key factor for the successful separation of a particular liquid mixture by pervaporation.

Dense polymeric films from hydrophilic polymers, such as poly(vinyl alcohol),² cellulose acetate,³ Nafion,⁴ or chitosan⁵ have been used as membranes for the dehydration of liquids, especially for the separation of the azeotropic ethanolwater mixture. On the other hand, hydrophobic membranes, which are made mainly of PDMS or PDMS-based copolymers,⁶ have been used to extract organic compounds from their aqueous mixtures. Unlike the dehydration of solvents or the removal of organic substances from water by means of pervaporation, in which a particular membrane material can be efficient in separating various mixtures, the separations of organic liquid mixtures require the membrane materials being tailored for specific separation problems. The limited number of membrane-forming materials with good transport and mechanical properties is a major obstacle of the pervaporation commercialization in this type of applications.

The membranes investigated in the separation of the mixtures of aromatic and aliphatic hydrocarbons have been made of olefinic polymers;⁷ poly(vinylidene fluoride);^{8,9} or more complex polymeric systems, like polymeric alloys of polyphosphonates,¹⁰ poly(vinyl alcohol)-poly-(allyl amine) blend in a chelate form,¹¹ and systems prepared by plasma graft-filling polymerization,¹² or by using concentrated emulsion pathway to obtain hydrophobic-hydrophilic polymer composites.¹³ Poly(ether imide) segmented copolymers,¹⁴ multiblock polymers,¹⁵ and segmented polyurethanes or poly(urethaneurea)s¹⁶⁻¹⁹ have also been studied.

Polyurethanes and poly(urethane-urea)s attract special attention as membrane materials since they can exhibit a variety of physical and chemical properties, depending on the reagents and the synthesis conditions, and can be produced easily in a commercial scale. The application of these polymers in organic liquid separations is mainly a subject of a patent literature, which demonstrates the use of polyurethanes and poly-(urethane-urea)s from polyester diols of mostly adipic acid with aliphatic glycols with more than 5 C atoms; aromatic diisocyanates, and aliphatic glycols or cycloaliphatic diamines in separating aromatic hydrocarbons from mixtures with other organic compounds;¹⁶ or the use of highly aromatic poly(urethane-urea)s from poly(ethylene adipate) diols, aromatic diisocyanates, and aromatic diamines in separating aromatics from saturates in heavy cut naphtha streams.¹⁷ On the other hand, only limited data relating the pervaporation properties of the polyurethanes and poly(urethane-urea)s with their molecular structure have been published.^{18,19}

In this article, the synthesis and characterization of novel segmented poly(urethane-urea)s (PUUs) composed of polyether- or polyester-based soft segments and various diamine-based hard segments are presented together with the study of their transport properties in pervaporation of the benzene-cyclohexane mixtures. The synthesized set of poly(urethane-urea)s, varying systematically in the structure and length of the hard as well as soft segments, was designed to study the effect of a polymer's molecular and supermolecular structure on its transport properties. Some of these materials were previously examined in our laboratory because of their thermotropic liquidcrystalline properties.²⁰ The present work is a continuation of a research focused on the investigations of the structure-transport property correlations started by us recently for liquid crystalline polyurethanes.²¹

EXPERIMENTAL

Materials

2,4-Tolylene diisocyanate (98% 2,4-TDI, Aldrich) was used as received. Poly(oxytetramethylene)diols (PTMO, $M_n = 650$, 1000, and 2000, BASF) and poly(1,4-butylene adipate) diol (PBA, $M_n = 2000$, ICRI, Warsaw) were dried before use by heating for 10 h at 90°C in vacuo. 4,4'-Diaminobiphenyl (DABP), 1,5-diaminonaphthalene (DA), *p*-phenylene diamine (PDA), and 4,4'-diaminodiphenylmethane (PP) (POCh Gliwice, Poland) were dried in the same way. Dimethylformamide (DMF, POCh Gliwice, Poland) was distilled under a nitrogen atmosphere, and the fraction 156–157°C was collected.

Synthesis of PUUs

PUUs were synthesized by a two-step polyaddition method. The composition of the starting materials and the basic characteristics of the obtained polymers are given in Table I. The synthesis of PUUs is shown in Scheme 1.

Polymer		Composition (mol)		$T_g^{\ a}$ (°C)	$T_m^{\mathrm{a,b}}$ (°C)	$M_n{}^{\mathrm{d}}$	$M_w/M_n{}^{ m d}$	% SS (Calc)	ϕ (g/cm ³)
PUU-1	TDI	PTMO-650	DABP	-30^{b}	_	26,200	1.4	55	1.391
	2	1	1			,			
PUU-2	TDI	PTMO-650	PDA	-43^{b}	196	56,900	1.6	58	1.143
	2	1	1		170 - 200	,			
					7.4 J/g				
PUU-3	TDI	PTMO-650	DA	-39^{b}	_	23,800	1.4	56	1.203
	2	1	1						
PUU-4	TDI	PTMO-650	PP	-32^{b}	180	42,600	1.7	54	1.139
	2	1	1		147 - 205				
					4.0 J/g				
PUU-5	TDI	PTMO-1000	PP	-41^{b}	185	50,600	1.7	65	1.109
	2	1	1		157 - 210				
					9.0 J/g				
PUU-6	TDI	PTMO-1000	PP	-46^{b}	_	35,300	1.6	44	1.167
	4	1	3						
PUU-7	TDI	PTMO-2000	PP	$-77^{ m b}$	—	36,500	1.6	61	1.098
	4	1	3						
PUU-8	TDI	PBA-2000	PP	-26°	160	—	—	60	1.222
	4	1	3		135 - 175				
					3.6 J/g				
PUU-9	TDI	PBA-2000	DABP	-32°	—	57,200	1.9	61	1.476
	4	1	3						
PUU-10	TDI	PBA-2000	PDA	-38°	151	49,500	2.7	66	1.235
	4	1	3		140 - 173				
					2.1 J/g				

Table I Physicochemical Characteristics of PUUs

 T_g of the macrodiols: PTMO-650 -88°C^b; PTMO-1000 -87°C^b; PTMO-2000 -83°C^b; PBA-2000 -53°C^c. Abbreviations of the names of amines: see Scheme 1.

^a DSC measurements.

 $^{\rm b}$ 10°/min.

° 40°/min.

^d GPC measurements.

The solution of PTMO (or PBA) in freshly distilled DMF was placed into a three-neck flask equipped with a reflux condenser, inert gas inlet, tap funnel, and a calcium chloride-filled drying tube and added dropwise with 2,4-TDI. The reaction mixture was stirred intensively for 1 h at 60-65°C to obtain the isocyanate-terminated prepolymer. Then, the prepolymer was cooled down to room temperature, and the solution of about 20% diamine in DMF was dropped slowly into the flask. The reaction mixture was stirred for 4 h after the temperature had reached 80°C. All polyaddition processes were carried out under dry nitrogen. The resulting polymers were precipitated in a cold methanol–water (1:1) solution and then filtered, washed, and dried under vacuum at 80°C for 24 h. All PUUs were soluble in polar aprotic solvents (DMF, DMSO) at room temperature.

Characterization of PUUs

Infrared (IR) spectra ranging from 4000 to 450 cm⁻¹ of the synthesized polymers were recorded on a Bio-Rad FTIR spectrometer using the photoacoustic method. The differential scanning calorimetry (DSC) measurements were performed with a Rheometric Scientific DSC plus apparatus under nitrogen atmosphere at the heating rate of 10°/min or at 40°/min. The glass transition temperature and melting temperature were determined from the signals of the first heating run. The gel permeation chromatography (GPC) measurements were carried out using a Knauer apparatus with DMF as a solvent at 80°C for the eluent flow rate of 1 mL per min. The MIXED-D PL gel columns and the polystyrene standards were used. The density was measured with an analytical balance by



Scheme 1 General reaction route and structures of the synthesized PUUs.

weighing the samples at room temperature in air and in distilled water.

Membrane Preparation

Dense membranes and films for the sorption experiments were prepared by pouring the required amount of the 15 wt % solutions of PUU in DMF onto a glass plate and by evaporating the solvent at 60°C for 72 h. The thickness of the resulted membranes was about 70 μ m, and the thickness of the sorption strips was about 350 μ m.

Sorption Experiments

A simple weight gain method was used to investigate the sorption kinetics. Weighed dry polymer film samples were immersed in various benzene–cyclohexane mixtures at 25°C. After a given time interval, the sample was rapidly removed from the solution, wiped with tissue paper to remove the adherent liquid, and weighed until the final equilibrium was reached. The sorption equilibrium amount of the liquid was defined as $S_{\rm eq} = 100 \cdot [(M_{\rm eq} - M_o) \cdot M_o^{-1}]$ in [g/100 g], where M_o and $M_{\rm eq}$ are the weights of the dry sample and the swollen sample at equilibrium, respectively.

Pervaporation Experiments

Pervaporation experiments were performed at 25°C for benzene-cyclohexane feed mixtures using a standard pervaporation cell. The downstream pressure was kept below 1 mm Hg, and the permeate was collected in a trap cooled by a dry-ice-acetone mixture. The pervaporation system used in this work is shown in Figure 1. The permeation rate (flux) F [kg μ m m⁻² h⁻¹] was determined from the variation in the condensate



Figure 1 Scheme of the pervaporation system.

weight with time and calculated for the standard membrane thickness. The composition of the feed and the permeate was determined by means of refractometry.

The separation factor α was defined as $\alpha = Y$ (1 - X)/X (1 - Y), where X and Y are the weight fractions of benzene in the feed and the permeate, respectively.

RESULTS AND DISCUSSION

Structure of PUUs

Segmented polyurethanes can be regarded as multiblock copolymers composed of the following two kinds of blocks: soft segments derived from a macrodiol and hard ones, which are a reaction product of a diisocyanate and a chain extender. The length of the hard segment depends on the kind and molar ratio of the compounds used in the reaction, whereas the soft segment length results from the molecular weight of the macrodiol. Because of the thermodynamic incompatibility of the two segments, a microphase separation occurs, resulting in a domain morphology of the segmented polyurethanes. The hard segments form a pseudocrosslinked physical network, which is responsible for the mechanical properties of the material. The soft segments create soft domains, which impart elastic properties to the material. The factors that are known to affect the degree of phase separation in polyurethanes include the segment polarity, length, and crystallizability; the tendency for the hard segment-soft segment interaction (e.g., via hydrogen bonding); the overall sample constitution; and the molecular weight.²² As a result, polyurethanes can be obtained with the soft domain composed of soft segments only or of a mixture of soft and hard segments.

Transport of small molecules through segmented polyurethanes has been shown to proceed in the soft domains.²³ Therefore, their structure and the dynamics of the soft segments should determine the transport properties of the polyurethane-based membrane material. It is also expected that hard domains can influence the overall transport process due to their ability to suppress membrane swelling.

In this work, a set of (PUU)s varying in the chemical constitution of both segments and in their length is presented. The applied modifications regarding hard segments are due to the different chain extenders used in the PUU synthesis and the different initial composition of the reagents, whereas the variations in the kind and molecular weight of the soft segments come from the macrodiol chosen. A schematic representation of the structure of the PUUs is shown in Scheme 1. The basic physicochemical characteristic of the synthesized PUUs is given in Table I.

Differential Scanning Calorimetry

The synthesized polymers exhibit the second-order transition in the low temperature region, being characteristic for T_{σ} of the PUU soft segments and the first-order transition of a low enthalpy in the high temperature region for the PUUs formed from the PP or PDA diamines. This high temperature transition can be attributed to the melting of the hard segments from the regions of a paracrystalline order. Second-order transition with regard to the hard segments was not detected in the DSC thermograms as reported by other authors.²⁴ Comparing the T_g value of the polyure than esoft segment with the T_g value of the respective macrodiol, the extent of the phase separation may be estimated according to the rule that the higher the difference between the both values, the lower the degree of phase separation. The glass transition temperature values for the series of PUU-4 to PUU-7 listed in Table I show that the deviation from the $T_{\ensuremath{g}}$ value of the respectively $T_{\ensuremath{g}}$ tive macrodiol increases with the decrease in the soft segment length. Thus, the higher phase mixing occurs for the PUU with shorter soft segments. It can also be seen from Table I that the hard segment length slightly influences the phase separation degree for these polymers.

Comparing the T_g values of PUU-7 and PUU-10, which are composed of the soft segment originating from the different macrodiols of the same length ($M_n \cong 2000$), with the T_g values of the respective macrodiols, it can be noticed that the polymer based on PTMO exhibits a higher degree of phase separation. Since the deviation from the T_g value of PTMO (2000) is small for PUU-7, the assumption can be made that this polymer is composed of almost pure soft domains.

The data given in Table I also show some differences in the T_g values for the series of PUU-1 to PUU-4 and PUU-8 to PUU-9 differing in the structure of the hard segments. For the both series of polymers, the lowest T_g value was found for the PUUs obtained using the PDA diamine chain extender. The highest phase separation degree observed for the both polymers can be attributed to the chemical structure of PDA (only one aromatic ring between the amine groups) and the high symmetry of the resulting rigid segment.



Figure 2 Exemplary FTIR spectrum of PUU-4.

FTIR Spectroscopy

A representative FTIR spectrum of the synthesized PUUs is shown in Figure 2. There are two regions in the IR spectrum that can be useful for the determination of the phase separation degree as follows: $3600-3100 \text{ cm}^{-1}$, which includes the hydrogen-bonded N-H stretching vibration and the free N—H stretch, and 1750-1670 cm⁻¹, which includes carbonyl symmetric stretching vibrations. As can be seen from the example given in Figure 2, the latter one is well resolved and composed of several peaks. Following the interpretation given by other authors,²⁵ the peak at 1740 cm^{-1} is attributed to the carbonyl groups not involved in hydrogen bonding. The peak at 1730 cm^{-1} is characteristic for urethane groups that are hydrogen-bonded to the oxygen bridge of peaks at 1702 and 1713 cm⁻¹ are assigned to the urethane groups involved in the ordered and lessordered hydrogen-bonded structures, respectively. The peak at 1725 cm^{-1} is attributed to the urethane groups in the association with other urethane groups. The intensity of the peak at 1730 cm^{-1} in comparison to other ones within the carbonyl band suggests the extent of the microphase separation.

Figure 3 illustrates the effect of the hard and soft segment length of the PUUs synthesized from PTMO, TDI, and PP diamine on the characteristic peaks in the carbonyl region. Considering the position of the peaks and their relative intensities, it can be noticed that PUU-6, which is composed of the longest segments, exhibits the highest phase separation degree. In the case of PUU-6, the highfrequency component is seen at 1724 cm⁻¹, suggesting that a strong physical network is formed from the urethane groups. For PUU-5 with shorter hard segments, the maximum of this component is moved toward higher frequency and is found at 1729 cm⁻¹, indicating the presence of the urethane groups mixed into the soft domains. PUU-4 seems to be the less-separated system due to the position of the high-frequency peak, which is placed at 1733 cm⁻¹, and its slightly higher intensity when compared with other peaks from this region. The similar effect of phase mixing can be observed for other polymers from the series of PUU-1 to PUU-4 (Fig. 4), though the ordered structures of a different order degree are also observed within this group of polymers, as is suggested by three or four (PUU-4) peaks at the low-frequency position.

Based on both the IR and DSC data obtained so far, it has be found out that the correlations between the structure of the investigated PUUs and their phase separation degrees fit the general rule saying that the longer the segments are or the less the polar nature of the soft segment is, the higher the phase separation degree is. The effect



Figure 3 FTIR spectra of PUUs in the carbonyl band region: (1) PUU-4; (2) PUU-6; (3) PUU-5.



Figure 4 FTIR spectra of PUUs in the carbonyl band region: (1) PUU-3; (2) PUU-1; (3) PUU-2; (4) PUU-4.

of the hard segment structure on the phase separation degree is hardly detectable due to some discrepancies between the IR and DSC data.

Pervaporation Characteristics of PUUs

Effect of the Chemical Constitution of the Hard Segments on the Pervaporation Properties of PUUs

The pervaporation characteristics, that is, the total and specific permeation flux and separation factor of benzene over cyclohexane, and the sorption equilibrium amount of the liquid mixture in the PUUs are listed in Tables II and III. Two series of the PUUs varying in the hard segment structure were studied: the PUUs composed of the PTMO(650)-based soft segments and short hard segments (x = 1) and the PUUs constructed from the PBA(2000)-based soft segments and longer hard segments (x = 3). The variations introduced into the hard segments were the same for the both series and came from the type of a diamine chain extender applied in the PUU synthesis.

For the membranes prepared from the PTMObased PUUs (PUU-1, 2, 3, and 4), the very similar separation factors were observed in the pervaporation of the benzene-cyclohexane mixtures (Table II). The same result was obtained for the PBA-based PUUs (PUU 8, 9, and 10; Table III), indicating that the differences in the chemical constitution of the hard segments do not affect the separation ability of the PUUs. However, the presented data show that the structure of the hard segments affects, to some extent, the permeability of the membranes studied. The higher flux values are noticed for PUU-2 and PUU-10, the hard segments of which are formed from the PDA diamine. Since the soft segment weight fraction within the series is similar (Table I), this result may be explained by the shorter length of the PDA diamine-based hard segments when compared with other diamines that, in turn, account for a smaller size of the hard domains and the

Table IIPervaporation Properties and Sorption Equilibrium Values of thePTMO-650-Based PUUs for a Benzene-Cyclohexane Mixture at 25°C

		5 Wt % Benzene						
	(kg μm	Flux $h^{-2} h^{-1}$)	Separation Factor	S				
Membrane	Total	Benzene	(α)	(g/100 g)				
PUU-1	1.2	0.3	7.1	14.58				
PUU-2	2.1	0.5	6.4	17.64				
PUU-3	1.4	0.4	6.7	14.04				
PUU-4	1.3	0.3	6.4	15.17				

		40 Wt % Ben	zene	56 Wt % Benzene				
	[kg μn	Flux n m $^{-2}$ h $^{-1}$		(kg μm	Flux 1 m ⁻² h ⁻¹)		S _{eq} (g/100 g)	
Membrane	Total	Benzene	Separation Factor (α)	Total	Benzene	Separation Factor (α)		
PUU-8 PUU-9 PUU-10	6.9 5.7 9.8	$5.7 \\ 4.7 \\ 8.0$	6.9 6.9 6.6	$25.5 \\ 20 \\ 25$	$22.9 \\ 17.4 \\ 21.7$	5.8 5.3 5.3	$36.70 \\ 33.04 \\ 41.64$	

Table III Pervaporation Properties and Sorption Equilibrium Values of the PBA-Based PUUs for Benzene-Cyclohexane Mixtures at 25°C

increased area available for transport. The highest values of the sorption equilibrium amounts observed for PUU-2 and PUU-10 compared with other PUUs within the series can support the explanation given above. On the other hand, a higher diffusion rate through the both polymers might be expected since each of them exhibits the lowest T_g value within the series (Table I).

Effect of the Soft Segment and Hard Segment Length on the Pervaporation Properties of PUUs

Pervaporation performance of the PUUs synthesized from PTMO, TDI, and PP diamine, varying in the length of the segments, is presented in Table IV. Considering the transport data for PUU-6 and PUU-5 of different hard segment length (x = 3 and x = 1, respectively), one can notice the significant differences in the flux and selectivity values. Much higher separation ability along with the extremely reduced permeability is observed for the PUU-6 with longer hard segments. The decrease in permeability of PUU-6 may be explained by the significantly lower weight fraction of the permeable soft domains as well as by the better capability of the hard domains built from longer hard segments to suppress the swelling of the soft domains. The limited membrane swelling could also be responsible for the higher separation factor observed for this polymer. However, the sorption equilibrium values for the both polymers do not vary much from each other. On the other hand, the differences in the chemical nature of the soft domains as well as in the soft segment dynamics of PUU-5 and PUU-6 seem not to be significant enough due to a small difference in their T_g values to account for the observed differences in the pervaporation properties. As can be seen from the data presented in Table IV, the resistance of the investigated membranes to the 56% benzene-cyclohexane mixture is higher for the PUUs with a higher hard segments content (PUU-6 versus PUU-5). It can indicate, therefore, that the role of hard domains in restricting the membrane swelling becomes important in the separation of the benzenerich mixtures.

The comparison of the pervaporation performance of PUU-6 and PUU-7 varying in the soft

		5 Wt	% Benzene		56 Wt % Benzene			
	Flux (kg μ m m ⁻² h ⁻¹)				Flux (kg $\mu m m^{-2} h^{-1}$)		~	G
Membrane	Total	Benzene	Separation Factor (α)	S _{eq} (g/100 g)	Total	Benzene	Separation Factor (α)	S _{eq} (g/100 g)
PUU-4	1.3	0.3	6.4	15.17	61.3	46.6	2.5	43.56
PUU-5	10.2	2.1	5.0	29.66	nonre	sistant	—	57.10
PUU-6	0.4	0.2	11.7	24.02	58.70	43.2	2.2	49.55
PUU-7	40.3	5.8	3.2	53.95	nonre	sistant		75.02

Table IV Pervaporation Properties and Sorption Equilibrium Values of the PTMO-Based PUUs for Benzene-Cyclohexane Mixtures at 25°C

		12 Wt % Benz	ene	24 Wt % Benzene			
	kg μm	Flux $h m^{-2} h^{-1}$)	a	kg μm	a		
Membrane	Total	Benzene	Separation Factor (α)	Total	Benzene	$\frac{\text{Separation}}{\text{Factor}} (\alpha)$	
PUU-7 PUU-8	$70.4 \\ 0.2$	19.3 0.12	2.8 13.2	$\begin{array}{c} 152.0\\ 1.28\end{array}$	$\begin{array}{c} 65.5\\ 0.71 \end{array}$	2.4 9.7	

Table V Pervaporation Properties of PUUs for Benzene-Cyclohexane Mixtures at 25°C

segment length ($M \cong 1000$ and 2000, respectively) shows that the increase in the soft segment length raises the permeability of the membrane to a higher degree than the decrease in the hard segment length (PUU-6 and PUU-5) discussed above. The similar result has also been observed for the PUU-4 and PUU-5 pair; the effect of the increased length of the soft segment (the change in the molecular weight from 650 to 1000) on the membrane permeability is, however, less pronounced than in the previous case. Moreover, unlike the former pair of polymers (PUU-6 and PUU-7), for which the increase in permeability was accompanied by a drastic decrease in selectivity, the selectivity of the PUU-4 and PUU-5 pair is almost not affected by the changes in the soft segment length.

Analysis of the influence of the soft and hard segment length on the pervaporation properties of PUUs with regard to the variations in the weight fraction of the soft segments shows that there is no simple relation between both factors. Thus, the more complex morphological approach should have to be applied to explain the variations observed.

Effect of the Chemical Constitution of the Soft Segments on the Pervaporation Properties of PUUs

The pervaporation properties of the PUUs differing in the kind of soft segments can be compared following the example of PUU-7 and PUU-8 used in the pervaporation experiments of the benzenecyclohexane mixtures containing 12 or 24% benzene by weight (Table V). Both polymers are composed of the same PP diamine-based hard segments of x = 3 and soft segments of the same length ($M \cong 2000$), which are based either on PTMO (PUU-7) or PBA (PUU-8) macrodiols. As can be seen from Table V, the investigated polymers exhibit extremely different pervaporation properties, ranging from very good separation ability accompanied, however, by a low permeability of PUU-8 to a very good permeability but low selectivity of PUU-7. The lower selectivity of PUU-7 when compared with PUU-8 results from a less polar nature of its soft domains that is due to the less polar character of the PTMO-based soft segments and to the complete phase-separated morphology. The observed effect is also intensified by a huge swelling of PUU-7, even in mixtures with low benzene content that increases the permeability but reduces the selectivity.

Effect of the Feed Composition on the Pervaporation Parameters for PUU-Benzene–Cyclohexane Systems

The effect of the feed composition on the separation factor and the permeation flux of the PUU-based membranes is shown in Figures 6 and 5, respectively. Although the decrease in selectivity and the increase in permeability with the increase of the benzene concentration in feed can be observed for all the investigated polymers, the character of these variations is slightly different and depends on the PUU structure. For the PTMO-based PUUs, the increase in benzene content up to about 15%, particularly critical for PUU-6, induces the drop in selectivity, followed by only small changes in the separation factor values up to 60% benzene in feed. The initially significant differences in the selectivities of these polymers, coming from the different length of the soft or hard segments, also become smaller as the benzene content in the separated mixture increases. Effect of the feed composition on the pervaporation performance of the PBA-based PUU is slightly different since the systematic decrease in the selectivity over the whole range of the benzene feed concentrations has been found



Figure 5 Effect of the feed composition on the total flux for pervaporation of benzenecyclohexane mixtures through PUU membranes: (\blacklozenge) PUU-4; (\blacklozenge) PUU-6; (\bigcirc) PUU-7; (\blacktriangle) PUU-8.

(Fig. 6). The membrane swelling, which is responsible for the observed lost of the selectivity, results, on the other hand, in the huge increase in the membrane permeability, particularly when the less permeable (and the most selective at the same time) PUU-6 and PUU-8 are taken into account.

CONCLUSIONS

The synthesized segmented PUUs exhibit the domain morphology of a different extent of microphase separation, as was shown by the results of the IR and DSC measurements. The correlations between the structure and the phase separation degree fit the general rule saying that the longer the segments are or the less polar the soft segments are, the higher the phase separation degree is. The pervaporation performance of PUUs in the separation of benzene–cyclohexane mixtures is closely related to the molecular and supermolecular structure of these polymers. The PBA-based PUUs exhibit good pervaporation properties along with a very good durability in separation of the azeotropic benzene-cyclohexane mixture. The PTMO-based PUUs display high permeation flux and low selectivity in the separation of the benzene-rich mixtures, which is mainly due to the huge swelling of the membranes. At the feed composition of 5% benzene in cyclohexane, where the membrane swelling is strongly reduced, the intrinsic properties of the PUUs become decisive.

The hard segment structure coming from the diamine chain extender used in the PUU synthesis does not affect the transport properties of the investigated membranes; however, the differences in the length of the hard and/or soft segments result in the membrane materials of diverse pervaporation properties. Although the background for the observed relationships is not quite understood yet, the effect of the segment length on the pervaporation performance of the membrane creates a new way of tailoring the transport properties of membrane materials.



Figure 6 Effect of the feed composition on the separation factor for pervaporation of benzene-cyclohexane mixtures through PUU membranes: (\blacklozenge) PUU-4; (\blacklozenge) PUU-6; (\bigcirc) PUU-7; (\blacktriangle) PUU-8.

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