Pervaporation Separation of Styrene–Ethylbenzene Mixture Using Poly(hexamethylene sebacate)-Based Polyurethane Membranes

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ABSTRACT: A series of poly(hexamethylene sebacate) (PHS), with molecular weight in a range of 890–2200, based polyurethanes (PU), were synthesized by solution polymerization with different kinds of isocyanate and chain extender and two kinds of polymerization methods. All the PHS-based PU membranes exhibited selectivity towards styrene during the pervaporation of styrene–ethylbenzene mixtures, and the properties of sorption and pervaporation were related to the composition of the PU membranes. Membranes with a low hard-segment content and by two-stage polymerization method exhibited high permselectivity. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 753–761, 1999

Key words: polyurethane membrane; styrene–ethylbenzene mixtures; polyisocyanate; permselectivity; pervaporation

INTRODUCTION

Separation of the styrene–ethylbenzene mixture is industrially significant. Styrene is produced by dehydrogenation of ethylbenzene, which is obtained from petroleum refining. Through the reaction process, removal of the product, styrene, is very important. However, the separation of the styrene–ethylbenzene mixture by distillation is a very energy-intensive process. Pervaporation (PV) is expected to be a very useful technique for the separation of such liquid mixtures.

In the separation of the organic solvent mixtures by PV, many polymer membranes have been studied. In separation of the benzene–cyclohexane mixtures, Shinohara et al. has reported that 2-hydroxyethyl methacrylate–methyl acrylate graft copolymer membranes[1] and 2-hydroxy-3-(diehtylamino)propyl methacrylate–styrene copolymer membranes with cyanuric choloride[2] exhibited excellent benzene permselectivity. In order to depress the swelling of polymer membranes caused by organic solvent, the hydrophilic polymers are used. Lee et al. used poly(vinyl alcohol)–poly(allyl amine) blend membrane,[3] and Cabasso used alloy membranes of cellulose acetate and various polyphosphonates.[4] Yamaguchi et al. have prepared filling-polymerized membranes, which are modified by graft copolymerization of methyl acrylate in a porous, high-density polyethylene membrane as membranes for the separation of hydrocarbons.[5] Isomeric xylenes have been separated by the PV method through a number commercially available polymeric membrane.[6,7] In the above studies, separation was achieved by differences in solubility and/or diffusivity of the penetrant molecules to the polymer. Mulder et al.[8] investigated the permeation and separation

characteristics of isomeric xylenes through cellulose ester membranes from polymer–penetrant interaction. Wytcherley and McCandless[9] separated *m*- and *p*-xylene mixtures by the PV technique in the presence of CBr_4 as a selective feed complexing agent. Separation of olefins from paraffins has been achieved by inserting selective carriers into membranes, such as compounds of silver and mercury, which are capable of forming molecular complexes with olefins.[10–13]

In this study, in order to separate styrene from the styrene–ethylbenzene mixture by pervaporation, poly(hexamethylene sebecate) (PHS)-based polyurethane (PU) membrane was synthesized. The effect of the composition of the PU membranes on pervaporation properties was investigated.

EXPERIMENTAL

Materials

As the soft-segment component, PHS with different molecular weight was synthesized by two kinds of ways and refined by precipitation from the benzene solution with methanol. The average molecular weight of the four kinds of synthesized PHS is 2200, 1600, 1270, and 890, respectively. Isocyanates used in this study are diphenylmethane-4,4′-diisocyanate (MDI)-, 2,6-tolylene diisocyanate (TDI)-, and hexamethylene diisocyanate (HDI)-based multifunctional polyisocyanate and 1,4-butanediol (1,4-BD) and 3,3′-dichloro-4,4′-diaminodiphenyl methane (MOCA), which were purchased from WAKO Pure Chemical Industries, Ltd., and are used as chain extender. The main formulae of the materials are shown in Table I. Dibutyltin dilaurate (DBTDL) and tetrahydrofuran (THF) were also from the same maker and used as catalyst and solvent, respectively.

Preparation of Polyurethane Membranes

One-Stage Polymerization Conditions

Proper weights of PHS, chain extender, and solvents with suitable ratios of THF were added to the reaction vessel under a nitrogen atmosphere. After adding a suitable amount of isocyanate to the vessel and mixing evenly, the mixture was heated to 60°C slowly. The reaction proceeded in presence of the catalyst DBTDL and was stopped as the —NCO groups were completely consumed, which was confirmed by the disappearance of the infrared (IR) absorption at 2280 cm^{-1}.

Two-Stage Polymerization Conditions

First, a prepolymer was prepared from PHS and isocyanate. The PHS and DBTDL were solved in THF with nitrogen inlet, and then the isocyanate was added. This solution was heated to 60°C slowly with stirring. After a period of time, the prepolymer was obtained from the reaction. Then the chain extender, 1,4-BD, or MOCA was added to the prepolymer, and the mixture was stirred continuously for several minutes to ensure uniform mixing of all ingredients.

Membranes for testing were prepared by casting the solution mixture onto a filter paper with a doctor knife. The solvent in the casting membrane was evaporated at 40°C for 10 h. In order to promote the crosslink reaction, the membrane was postcured in 140°C for 20 h.

The compositions of PU membranes obtained by above polymerization methods with different *MW*. PHS, isocyanates, are chain extender are shown as abbreviations like PHS1600–MR–1,4-BD and 1/2/1. PHS1600 refers to the molecular weight of PHS, MR isocynate, and 1,4-BD extender; and 1/2/1 refers to the molar ratio of each component, respectively.

Sorption Experiment

The dried PU membranes were immersed into the styrene–ethylbenzene mixtures at 20°C. After a period of time, the membrane samples were removed from the test bottles, and surface-adhered liquid drops were removed by carefully pressing between smooth filter paper wraps and weighed immediately on a digital balance to the nearest accuracy of ±0.0001 g. The uptake due to solvent absorption at time t, Mt, and equilibrium uptake M_e could be determined.

PV Apparatus and Measurements

Figure 1 shows the experimental scheme used for the pervaporation measurements. Membrane with an effective area of 44 cm^2 was installed in a two-compartment stainless-steel cell. About 300 mL of styrene–ethylbenzene mixture, which is feed solution, was put into the upside of the cell. The pressure at the downstream side and temperature were maintained at 0.3 torr and 25°C. The permeate vapor was collected in cold traps, which were cooled by liquid nitrogen. Two traps can be used alternatively, allowing to get the permeate stream sampling continuously without interrupting the operation of the unit. The concentrations in the feed solution and permeate were deter-

Table I   Materials for PU Membranes

Abbreviation	Main Formula	Description
PHS	$-[-O-(-CH_2)_6-O-CO-(-CH_2)_8-CO-]_n-$	Poly(hexamethylene sebacate)

Isocyanates:

MR	(structure: polyisocyanate with three NCO groups and CH₂ bridges, $n = 2 \sim 4$)	Polyisocyanate based on MDI
PHDI	(isocyanurate ring structure with $(CH_2)_6NCO$ groups)	Polyisocyanate based on HDI
PTDI	(branched structure with $CH_2\,NCO$ and $OCONH$ groups)	Polyisocyanate based on TDI

Extenders:

1,4-BD	$HO-(-CH_2-)_4-OH$	1,4-butanediol
MOCA	H_2N-(aromatic ring, Cl)$-CH_2-$(aromatic ring, Cl)$-NH_2$	3,3′-dichloro-4,4′-diminodiphenyl methane

mined by gas chromatography. The permselectivity factor α was defined as follows:

$$\alpha = (P_S/P_E)/(F_S/F_E)$$

where F_S and F_E are the weight fractions of styrene and ethylbenzene in the feed solution, and P_S and P_E are those of the permeate, respectively.

RESULTS AND DISCUSSION

Absorption Properties of PU Membranes

Sorption results of styrene and ethylbenzene mixtures in different concentration to a PHS-based PU membrane are shown in Figure 2 as a relation of uptake (g/g membrane) and time. Because PHS can dissolve in styrene but cannot dissolve in ethylbenzene, it shows that the amount of sorption increased with the increase of styrene in feed and over a period of time to the final equilibrium value. In Figure 3, M_t/M_e are plotted as a function of $t^{1/2}$. It indicates that the sorption rate depends on the concentration of mixture absorbed in membrane, and this effect increases with the increase of styrene concentration in the feed. In order to investigate the relation of the structure of a membrane and its sorption property, sorption

1. Thermostated bath   2. Pervaporation cell
3. Cold traps 4. Pressure meter 5. Vacuum pump

Figure 1 Schematic diagram of the pervaporation apparatus.

tests of membranes from different PHS molecular weights, hard segment contents, and NCO–OH rates were carried out in a feed mixture with styrene concentration of 0.25 mole fraction, and their results are shown in Figures 4–10.

Figure 4 shows that the uptake in membrane increased with the increase of the molecular weight of PHS. From the relation of M_t/M_e and $t^{1/2}$ (Fig. 5), it is found that the sorption rates of membranes from higher molecular weight of PHS depended more strongly on the mixture in the membranes than that of membranes from the lower molecular weight of PHS did. In a PU polymer membrane, increase of the PHS molecular

Figure 3 M_t/M_e versus $t^{1/2}$ for the membrane of PHS 1270 with a different feed concentration.

weight would induce in higher swelling of soft segments and, therefore, an easier absorption of mixture. The concentrations of mixture absorbed in membranes above were investigated by a desorption test. By gas chromatography (GC), the vapor gathered from desorption was analyzed, and the result is shown in Figure 6. It reveals that

Figure 2 Weight absorbed of the membrane as a function of time (membrane: PHS1270–MR–1,4-BD, 1/3/1).

Figure 4 Weight absorbed of the membrane with different MW of PHS as a function of time (membranes: PHS–MR–1,4-BD, 1/3/1).

Figure 5 M_t/M_e versus $t^{1/2}$ for membranes with different PHS MW.

the PHS-based PU membranes indeed showed a highly preferential absorption of styrene to the mixture of styrene and ethylbenzene. And the concentration of styrene absorbed decreased with the increase of PHS molecular weight, which indicates that after styrene absorption, the swelling of membrane occurred; as a result, ethylbenzene sorption happened easily at the same time, and

Figure 6 Concentration of styrene in the membrane as a function of the MW of PHS with 0.25 (mole fraction) styrene in feed.

Figure 7 Weight absorbed of the membrane with a different hard segment content as a function of time (membranes: PHS1270–PHDI–1,4-BD).

this phenomena became more significant with the increase of PHS molecular weight.

The content of hard segment and the rate of NCO and OH (or NH_2) of a PU also have an effect on its property of sorption, whose results of uptake in membranes from PHS molecular weight of 1270 and 890 as a function of time are shown in Figures 7 and 8. It is known that the sorption of mixture decreased with the increase of the content of hard segment and the rate of NCO and OH. In Table II, the styrene concentrations that are absorbed in membranes are shown. It shows that NCO–OH rate has a significant effect on this concentration, as following: the concentration increased with the increase of NCO–OH rate, and the hard segment content didn't show great influence on the styrene concentration in membrane.

Pervaporation Properties of PU Membranes

The characteristics of the pervaporation experiment are represented by the permselectivity α and the permeate flux J, as listed in Table III. All the membranes show permselectivity of styrene in the styrene–ethylbenzene mixture. However, various factors, such as the composition of the membrane and the polymerization method, have an effect on the transport phenomenon of pervaporation.

Figure 8 Weight absorbed of the membrane with a different NCO–OH rate as a function of time (membrane: PHS890–MR–1,4-BD).

Effect of the MW of PHS

The transport phenomenon of pervaporation separation through a nonporous polymer membrane is generally described by a solution-diffusion mechanism containing the following three steps: sorption, diffusion, and desorption. The desorption step of the vapor at the permeant side is very rapid and nonselective due to the low pressure, which is much lower than the vapor pressure of the vapor at operating temperature, at the downstream side. Only the equilibrium sorption and transverse diffusion through the membrane determine the pervaporation performance. Gener-

ally, the membrane must have sufficient mechanical strength to withstand the pervaporation experiments. At the beginning of this study, a PU membrane prepared from PHS with molecular weight 5400 was tested in absorption experiment. After 24 h, the volume of the membrane increased with a great deal, and the membrane showed a soft gel. These phenomena indicate that when styrene was absorbed in the membrane the swelling of the polymer gave significant damage to the membrane (data was not shown here). When the molecular weight of PHS used for preparing membrane decreased, it was shown that the phenomena of swelling got increasingly improved. In order to investigate the effect of the molecular weight of PHS on pervaporation properties of the membrane, four kinds of PHS were synthesized with molecular weight from 890–2200. The permselectivity factor α and permeant flux J of the membranes are listed in Table II and shown in Figure 2, respectively. Comparing with α and J of membranes, which have same composition, it is clear that the flux increases with the increase of molecular weight of PHS, while the permselectivity decreases in contrast. When the molecular weight of the PHS reaches 2200, obviously, the flux of the PU membrane shows a great increase, but the permselectivity decreases close to 1.0 (Fig. 9). Although styrene and ethylbenzene have almost the same molecular size, the difference in selectivity occurred by different solubility in styrene and ethylbenzene to the membrane. These phenomena suggest that swelling of the PHS-based PU membrane has a significant influence on the permeability of the PU membrane. Increase of the length of the soft segments of PU membrane might increase the swellability of the soft segments. As a result, the PU membrane

Table II Sorption of Styrene by PHS-based PU Membranes Exposed to Styrene–Ethylbenzene Mixture of 0.25–0.75 Mol Fraction at 20°C

Membranes	Hard Content and NCO–OH	Styrene Absorbed
PHS1270–PHDI–1,4-BD:	Hard segment content:	
1/2/1	0.40	0.33
1/3/2	0.51	0.35
1/4/3	0.59	0.34
1/6/5	0.68	0.34
PHS890–MR–1,4-BD:	NCO–OH:	
1/1.5/1	0.75	0.43
1/2/1	1.0	0.48
1/2.5/1	1.25	0.55
1/3/1	1.5	0.61

Table III Composition and Some Properties of PU Membranes

Composition	NCO–OH	J (g m^{-2} h^{-1})	α	Composition	NCO–OH	J (g^{-1} m^{-2} h^{-1})	α
PHS2200–MR–1,4-BD				PHS890–MR–1,4-BD			
1/2/1	1.0	1843.2	1.02	1/1.5/1	0.75	352.6	2.06
1/3/1ᵃ	1.5	1678.4	1.04	1/2/1	1.0	298.5	2.76
1/3/1	1.5	1603.4	1.08	1/2.5/1	1.25	263.6	3.82
PHS1600–MR–1,4-BD				1/3/1ᵃ	1.5	235.6	4.21
1/2/1	1.0	602.1	1.45	1/3/1	1.5	227.1	4.89
1/2.5/1	1.25	587.1	1.51	PHS890–MR–MOCA			
1/3/1ᵃ	1.5	576.5	1.54	1/3/1	1.5	245.1	4.18
1/3/1	1.5	553.5	1.59	PHS890–PHDI–MOCA			
PHS1270–PHDI–1,4-BD				1/3/1	1.5	251.1	4.23
1/2/1	1.0	644.4	1.54	PHS890–PHDI–1,4-BD			
1/3/2	1.0	573.9	1.58	1/3/1	1.5	275.6	3.82
1/4/3	1.0	483.7	1.55	PHS890–PTDI–MOCA			
1/6/5	1.0	397.5	1.56	1/3/1	1.5	242.5	4.42
PHS1270–MR–1,4-BD				PHS890–PTDI–1,4-BD			
1/2/1	1.0	434.4	1.78	1/3/1	1.5	255.2	4.36
1/3/1	1.5	349.2	2.14				
1/3/1ᵃ	1.5	367.3	1.90				

ᵃ Polymerized by the one-stage method, and the others by the two-stage method.

with a high molecular weight of the PHS becomes more permeable and shows a lower permselectivity. This result is similar to that of Jonquieres et al.[14]

Effect of Isocyanates and Extenders

The permselectivity and the flux of the PU membranes based on PHS at molecular weight 890 with different isocyanates and extenders by a two-stage polymerization method shown in the data in Table III. The level of permselectivity of the PU membrane with 1.4-BD as the extender increases, and permeability decreases in the following sequence: MR > PTDI > PHDI. The extender also has the following effect on permselectivity and permeability: higher permselectivity and lower permeability is obtained from the PHDI-based PU membrane with MOCA as extender rather than that of the MR- or PTDI-based PU membranes. It suggests that increasing aromatic content have effect on the permeability and permselectivity of the PU membranes. This result is similar to that of McBride et al.[15] The increase of the aromatic content causes to further restrict the motion of the soft segments and improves the resistibility of the PU membranes to swelling. In the case of MR-based PU membrane with MOCA as extender, lower permselectivity and higher permeability are shown. This result can be explained as follows. The intermolecular reaction of isocyanate and extender, which contributes to form network, decreases presumably due to the steric effects. By comparing of the effect of isocyanates and extenders, it is shown that an increase of the aromatic content in isocyanates has more of an effect on the pervaporation property of the PU membrane than that in the extender.

Figure 9 Effect of the *MW* of PHS on pervaporation PHS–MR–1,4-BD: 1/3/1 (two-stage polymerization).

NCO Content Effect

The NCO/OH ratio is defined as the number ratio between the material containing NCO groups in isocyanate and those containing OH groups in

Figure 10   Effect of the NCO–OH value on the pervaporation PHS890–MR–1,4-BD (two-stage polymerization).

Figure 11   Effect of the hard segment content on pervaporation PHS1270–PHDI–1,4-BD (two-stage polymerization).

polyester and extender. The NCO contents may make a contribution to the different crosslinking density. As the NCO/OH ratio becomes larger than one, the three-dimensional structures or polar urea structures can be formed, and the numbers of urethane groups are increased. The existence of the three-dimensional structure and chemical crosslink will restrict the mobility of the PHS chains, and the increase of those polar groups (urea and urethane) enhances the intermolecular attraction of hard segments. These tend to decrease the permeability and give a higher permselectivity, as shown in Figure 10.

Effect of Hard Segment Content

Figure 11 shows that when the hard segment contents get higher, the vapor permeability becomes lower, and the permselectivity keeps almost the same value. Generally, the hard segments are acting as filler particles and a kind of crosslinks to restrain the motion of soft segments. The great number of hard segments (assumed to be essentially impermeable) may serve to produce a more tortuous route for the diffusing molecules. This results in a low value for the diffusivity and, therefore, a low permeability. On the other hand, when increasing the hard segment contents, the swelling of the PHS should be restrained to give a higher permselectivity. But the results in this study showed that the permselectivity kept almost the same value in spite of the increase of the hard segment contents. This result indicates that

the restriction of the motion of soft segment by hard segment is a kind of physical restriction (a kind of packing or stacking) rather than by being chemically crosslinked. The capability of the hard segment to diminish soft segment mobility shows no significant effect on the swelling of the PHS soft segments, and this causes the low permselectivity of the PHS-based PU membrane.

One- and Two-Stage Polymerization Method Effects

Table IV shows the permselectivity factor and the flux of the PU membranes based on PHS at various molecular weights and with different polymerization methods. Regardless of the molecular weight of the PHS, permselectivities of the two-stage process are all higher, and permeabilities

Table IV   Effect of Polymerization Method on Pervaporation

MW	One-Stage		Two-Stage	
	Flux	α	Flux	α
2200	1678.4	1.04	1603.4	1.08
1600	576.5	1.54	553.4	1.59
1270	367.3	1.90	349.2	2.14
890	235.6	4.21	227.1	4.89

Results are for the PHS–MR–1,4-BD-based PU membrane (flux: $g^{-1}\,m^{-2}\,h^{-1}$).

are lower than that of the corresponding one-stage process.

Abouzahr et al.[14] reported that one-stage polyurethanes result in a broader distribution of hard segment than the two-stage of the same stoichiometry, and the materials with the narrow distribution give polymers of significantly higher modulus than one having a broader distribution. When either or both of the segments have narrow molecular weight distributions, a more perfected physical network is formed, and this gives the polymers with greater tensile strength and elongation at break.

In the case of the PHS-based PU membranes, the results of pervaporation suggest that this kind of network had been built in the membranes formed by the PHS obtained from two-stage process and improved the resistibility of the membrane to swelling.

CONCLUSIONS

PU membranes based on PHS as soft segment and a series of isocyanates and chain extenders were synthesized by solution polymerization in different polymerization method to separate styrene–ethylbenzene mixture by pervaporation. Four kinds of PHS with different molecular weights from 890 to 2200, and isocyanates and chain extenders with different contents of aromatic component, were used. The entire PHS-based PU membranes exhibited selectivity towards styrene during the pervaporation of styrene–ethylbenzene mixtures, and the pervaporation fluxes and permselectivity factors were related to the polymer structure. The experimental results revealed that decreasing the soft segment length (decrease the PHS molecular weight) caused an increase in the permselectivity and brought about a decrease in the permeability. In contrast, increasing the hard segment content gave a decrease in the permeability and not an increase in the permselectivity. Studying the PU membranes with different isocyanates showed that increasing the aromatic content resulted in an increase in the permselectivity with a decrease in the permeability. Increasing NCO content produced a decrease in the permeability and an increase in the permselectivity, and the two-stage polymerization method showed an increase in the permselectivity.

It may be concluded that decreasing the molecular weight of the PHS, increasing the length of the hard segment content, and increasing the NCO content serve to restrict the mobility of the soft chain segments physically or chemically. This mobility restriction is at a level such that the permselectivity and the permeability of the PU membranes are affected.

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