Divinyl Benzene Cross-Linked HTPB-Based Polyurethaneurea Membranes for Separation of *p-/o*-Xylene Mixtures by Pervaporation

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ABSTRACT: Cross-linked hydroxy terminated polybutadiene (HTPB)-based polyurethaneurea (PU), HTPB-divinyl benzene (DVB)-PU, was synthesized by a three-step polymerization process. It was first used as membrane material to separate *p-/o*-xylene mixtures by pervaporation (PV). The effects of the content of cross-linker DVB, feed concentration, and operating temperature on the PV performance of HTPB-DVB-PU membranes were investigated. The membranes demonstrated *p*-xylene permselectivity as well as high total flux. The introduction of DVB significantly enhanced the temperature resistance ability of the HTPB-DVB-PU membranes. With increasing DVB content, the separation factor increased while the total flux decreased a little. The highest separation factor reaches 2.01 and the total flux is 33 g/m^{2}h with feed concentration of 10 wt % *p*-xylene at 30°C. These PV performances with increasing DVB content were explained in terms of the view point of chemical compositions and physical structures of the HTPB-DVB-PU membranes. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1968–1976, 2012

Key words: polyurethaneurea; cross-linker DVB; membranes; pervaporation; *p-/o*-xylene mixture

INTRODUCTION

Separation of xylene isomer mixtures is an important process in the production of pure xylenes because of the wide application of xylenes in chemical industry, e.g., they are used for the production of polyesters, motor fuels, and other chemicals such as terephthalic acid, phthalic anhydride, isophthalic acid etc.[1] However, xylenes are always produced as an isomer mixture and conventional separation techniques, such as adsorption process using molecular sieves and low temperature fractional crystallization, are energy intensive due to the similar structures and physical–chemical properties of xylene isomers. Pervaporation (PV) has been considered as a promising technique for separation of azeotropic mixtures, isomeric components, and close-boiling point systems. So PV is potentially an alternative process for the separation of isomeric xylenes.[2]

Nowadays, a major hurdle limits the practical use for pervaporative separation xylene isomers is a lack of proper membrane materials with high flux and separation factor. Since early 1980s, a great deal of research has focused on selecting PV membranes in separation of xylene isomers. In general, there are three main types of membranes that have been attempted in separating xylene isomers, i.e., inorganic membranes,[3–9] polymer membranes,[1,10–14] and organic–inorganic hybrid membranes.[15,16] Inorganic membranes always have high selectivity, but it is still necessary to reduce the preparation costs and improve permeation rate. For polymer membranes, the separation factor of *p-/o*-xylene mixtures was still unsatisfied. Schleiffelder and Staudt-Bickel[12] used cross-linked polyimide for *p-/o*-xylene separation, resulting in a selectivity of 1.15–1.47. Kusumocahyo prepared DNB-cellulose acetate membrane for *p-/o*-xylene separation, the best separation factor for *p-/o*-xylene is 1.70. Organic–inorganic hybrid membranes are becoming prevalent in PV researching. But in the separation of xylene mixtures, the main matrix is composed of polymer materials and the over-swelling of the hybrid membranes in xylene mixtures inhibits the increasing of the separation factor. So it is still a need for improving the PV performance of polymer membranes.

In general, rubbery polymer membranes incline to have high permeation rate in PV process because of their flexible polymer chains.[17] It may achieve higher separation factor when appropriate cross-linkage is introduced. Polyurethaneurea (PU) is a kind of rubbery membrane materials, which can be prepared by the reaction of flexible soft segment (polyol) with rigid hard segment (diisocyanate and chain extender, viz. diol, diamine). Different kinds of PU membranes have been used for removal of organic compounds from aqueous solutions,[18–22] dehydration of ethanol,[23] and separation of benzene/cyclohexane mixture by PV.[24] The chemical structure and composition of soft segment and hard segment would greatly impact the affinity of PU membrane to the permeant. Therefore, a well-tuned PU membrane can be a candidate for separating xylene isomers, e.g., a polyetherurethane membrane prepared by Lue exhibiting *o*-xylene permselectivity and the soft segment of polyether was considered having strong affinity to *o*-xylene.[16] HTPB-based PU, HTPB-PU, membranes have soft segment of polybutadiene (PB) and rigid segment of urea, which have been used earlier for separation of organic-water mixtures[23,25] and gas mixtures.[26] But none report for the *p-/o*-xylene mixtures can be found.

In this study, Cross-linked hydroxy terminated polybutadiene (HTPB)-based PU, HTPB-divinyl benzene (DVB)-PU, was synthesized by a three-step polymerization process for separating *p-/o*-xylene mixtures. The membranes were characterized by Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analyzer (TGA), respectively. The effects of the content of cross-linker DVB, feed concentration, and operating temperature on the PV performance of HTPB-DVB-PU membranes were investigated.

EXPERIMENTAL

Materials

HTPB (hydroxyl value = 0.8 mmol KOH g^{-1}) with average molecular weight of 2500 (M_n, in g/mol) was bought from Qilushihua Co. (Shandong, China). Dibutyltindilaurate (DBTDL, catalyst) and toluene 2,4-diisocyanate (TDI, L.R) from Hangzhou Electronical Group Auxiliary Chemical Co. (Hangzhou, China) were used without further purification. Divinyl benzene (DVB) from Aldrich was used as cross-linker, and 2,2-azobis(2-methylpropionnitrile) (AIBN) recrystallized from ethanol was used as the initiator. Solvent tetrahydrofuran (THF) was dried by molecular sieves. Chain extender, 3,3′-dichloro-4,4′-diaminodiphenymethane (MOCA), was obtained from Hangzhou Congsun Chemical Co. (Hangzhou, China). *O*-xylene and *p*-xylene were obtained from Shanghai Chemical Reagent Factory, China.
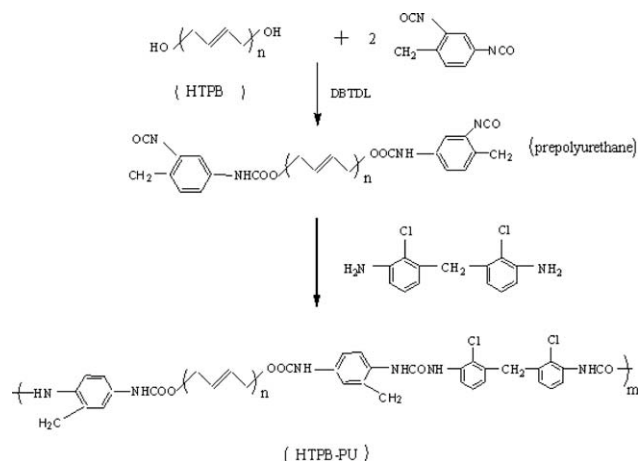
Scheme 1 Synthesis of HTPB-PU.

### Preparation of HTPB-DVB-PU membrane

Prepolyurethane was prepared by the reaction of HTPB and TDI in THF at 30°C for 1 h in the presence of 0.05 wt % DBTDL as catalyst maintaining NCO : OH mole ratio of 2 : 1. Polyurethaneurea of HTPB-PU was prepared by adding the chain-extender MOCA (OH : NH_2 = 1 : 1) to the prepolyurethane under mechanical stirring for 15 min. Polyurethaneurea of HTPB-DVB-PU was prepared through a 6 h cross-linking reaction at 60°C after the prescribed amounts of cross-linker DVB and initiator AIBN were added into the solution. The entrapped bubbles were then removed from the viscous solution by vacuum evacuation. After that, the HTPB-DVB-PU solution with DVB content of 0–9 wt % (the ratio of DVB weight to weight of HTPB) and polymer concentration of 30 wt % was cast on a clean glass plate and left overnight at room temperature followed by thermal curing at 80°C for 3 h. The structures of prepolyurethane and HTPB-DVB-PU are shown in Schemes 1and 2. The thickness of the obtained HTPB-DVB-PU membranes was kept about 100 μm for PV measurement and 300 μm for degree of swelling (DS) measurement.

FTIR measurement

The chemical structures of HTPB, prepolyurethane, and HTPB-DVB-PU samples were confirmed by FTIR using a Bruker Vector22 type spectrometer. The samples for FTIR measurements were obtained by spreading a thin film of their solutions in THF on a potassium bromide flake and evaporated the solvent under vacuum at room temperature.

TGA measurement

Thermal stability of the HTPB-DVB-PU was examined with a Perkin–Elmer Pyris 1 TGA. The temperature profile was from 60 to 600°C at a heating rate of 20°C/min.
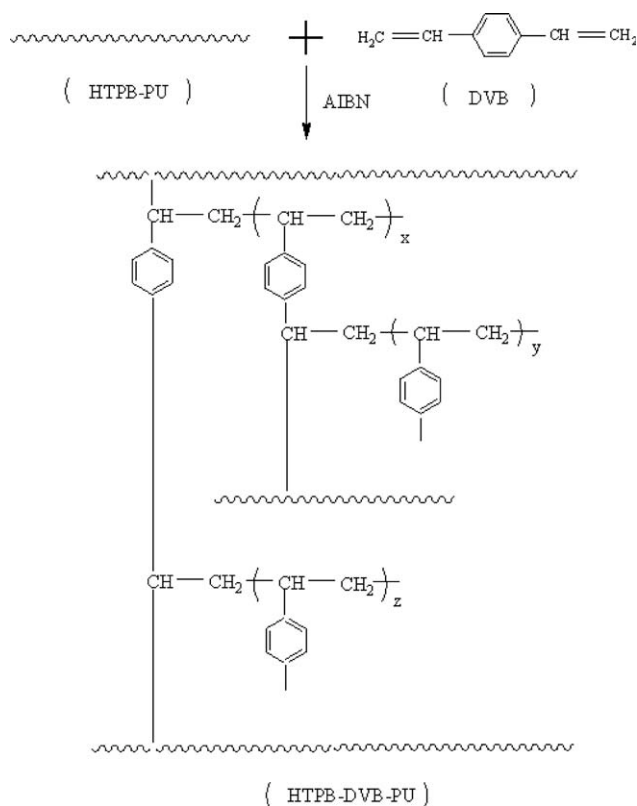
Scheme 2 Synthesis of HTPB-DVB-PU.

DSC measurement

The DSC curves of HTPB-DVB-PU were obtained through a Perkin–Elmer Pyris 1 DSC under nitrogen (N_2) atmosphere at a heating rate of 20°C/min from −150 to 200°C. The DSC curves were obtained from a second heating cycle to remove heat history.

Density measurement

The density of the HTPB-DVB-PU membranes was determined by specific pycnometer at 30°C and three parallel measurements were carried out for each sample. Before density measurement, the membrane samples were dried in vacuum oven at 30°C for 3 days.

DS measurement

The dried PU membranes without substrate were weighed and immersed into a p-/o-xylene mixture and pure p-xylene in a sealed vessel at 30°C until equilibrium was reached. The membranes were then taken out of the vessel, wiped quickly with a filter paper, and weighed. The DS of a membrane was then determined from eq. (1).

$$DS = \frac{m_S - m_0}{m_0} \times 100\%, \tag{1}$$

where m_0 and m_S are the weights of dry and swollen membrane, respectively.

Determination of sorption selectivity and diffusion selectivity

A dried HTPB-DVB-PU membrane with determined weight was immersed in p-/o-xylene mixture with 10 wt % p-xylene in a sealed vessel at 30°C until equilibrium was reached. The swollen HTPB-DVB-PU membrane was wiped with a tissue paper quickly and placed into a container. The solution absorbed in the swollen membrane was desorbed under reduced pressure and collected in a cold trap. The composition of the solution in the swollen membrane was obtained by measuring the xylene concentration by gas chromatography in the collected solution. The xylene composition in the membrane and in the feed solution determines the sorption selectivity, $\alpha_{sorp,p\text{-}/o\text{-xylene}}$, as expressed in eq. (2).

$$\alpha_{sorp,p\text{-}/o\text{-xylene}} = (M_{p\text{-xylene}}/M_{o\text{-xylene}})/(F_{p\text{-xylene}}/F_{o\text{-xylene}}), \tag{2}$$

where $F_{p\text{-xylene}}$ and $F_{o\text{-xylene}}$ are the weight fractions of p-xylene and o-xylene in the feed, and $M_{p\text{-xylene}}$ and $M_{o\text{-xylene}}$ are the weight fractions of p-xylene and o-xylene in the swollen membrane, respectively. According to the solution-diffusion mechanism, separation and permeation characteristics for organic liquid mixtures through polymeric dense membranes by PV are based on the solubility of the permeants into the polymer membrane (sorption process), and the diffusivity of the permeants in the polymer membrane (diffusion process). In general, the relation between them for p-/o-xylene mixture can be written by eq. (3):

$$\alpha_{diff,p\text{-}/o\text{-xylene}} = \alpha_{sep,p\text{-xylene}}/\alpha_{sorp,o\text{-xylene}}. \tag{3}$$

Pervaporation measurement

The PV experiments were carried out by the set-up as previously reported.[22] The vacuum system of the downstream side was maintained at about 350 Pa. The experiments were carried out in a continuous steady state at a constant temperature. The permeation solution was collected in cold traps by condensation with liquid nitrogen. The compositions of the permeate and the feed solution were determined by gas chromatography. The permeation flux (J) and separation factor ($\alpha_{sep,p\text{-}/o\text{-xylene}}$) for all membranes were calculated according to the following equations,

$$J = \frac{\Delta g}{S \times \Delta t}, \tag{4}$$

$$\alpha_{sep,p\text{-}/o\text{-xylene}} = (P_{p\text{-xylene}}/P_{o\text{-xylene}})/(F_{p\text{-xylene}}/F_{o\text{-xylene}}), \tag{5}$$

where Δg is the permeation weight collected in cold traps during the operating time Δt; S is the
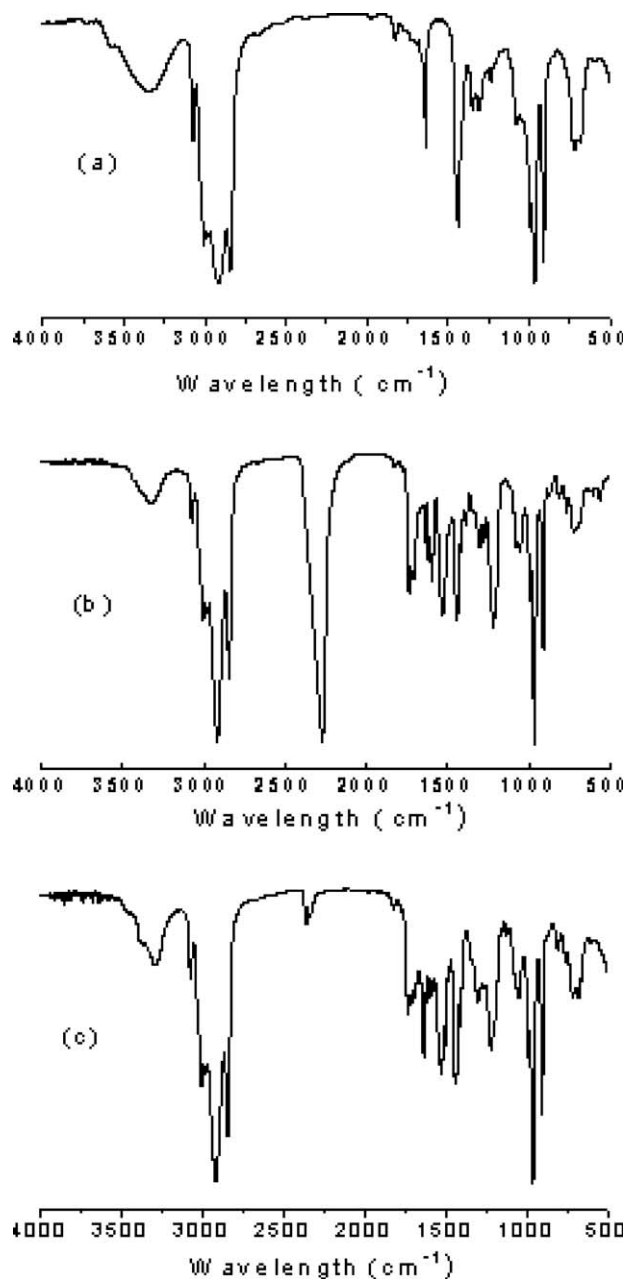
Figure 1 FTIR spectra of (a) HTPB; (b) prepolyurethane; and (c) HTPB-DVB-PU.

membrane area (18.1 cm^2); $P_{p\text{-xylene}}$ and $P_{o\text{-xylene}}$ are the weight fractions of *p*-xylene and *o*-xylene in permeate, respectively.

RESULTS AND DISCUSSION

Characterization of HTPB-DVB-PU

Figure 1 shows the FTIR spectra of HTPB, prepolyurethane, and HTPB-DVB-PU. Compared with the FTIR spectrum of HTPB, the strong absorption near 2270 cm^{-1} for asymmetric —NCO stretch appeared in prepolyurethane, and disappeared in the FTIR spectrum of HTPB-DVB-PU. This indicates completion of the

reaction of chain extending. Appearance of other new peaks at 1738 cm^{-1} (C=O) and 1531 cm^{-1} (N—C) in the spectrum of prepolyurethane confirmed formation of urethane group (—NHCOO—).

Figure 2 shows the DSC thermogram of two samples of HTPB-DVB-PU with 5 and 9 wt % DVB content, respectively. Only one glass transition temperature (T_g), −75°C, for both samples was observed. In our previous work,[21] two T_gs of HTPB based PU without cross-linking, HTPB-PU, were observed. One is −75°C which could be ascribed to the hydrophobic domains of soft segments (polybutadine) and the other is 65°C which could be ascribed to hydrophilic domains of hard segments (urethane). That is to say in HTPB-PU membranes microphase separation occurred owing to the poor compatibility between polybutadine segments and urethane segments. While in the HTPB-DVB-PU membranes, the introduction of cross-linkage made the hard segments of urethane well dispersed in the hydrophobic domains formed by polybutadine segments. Because, on the one hand, the cross-linking made the polymer chains less mobile, and on the other hand, the hard segments were compellingly separated. That means the microphase separation will be weakened and the phase size will become smaller.

Figure 3 shows the TGA curve of two samples of HTPB-DVB-PU with 5 and 9 wt % DVB content, respectively. The weight loss of HTPB-DVB-PU starts at about 250°C. It means HTPB-DVB-PU membranes meet the thermal stability requirement for PV.

PV performance of HTPB-DVB-PU membranes

Effect of DVB content in HTPB-DVB-PU

Figure 4 shows the effect of DVB content on the PV performance for separation of *p-/o*-xylene mixture
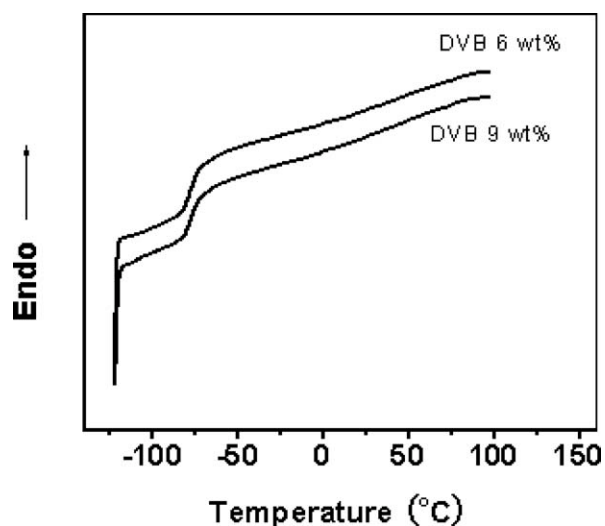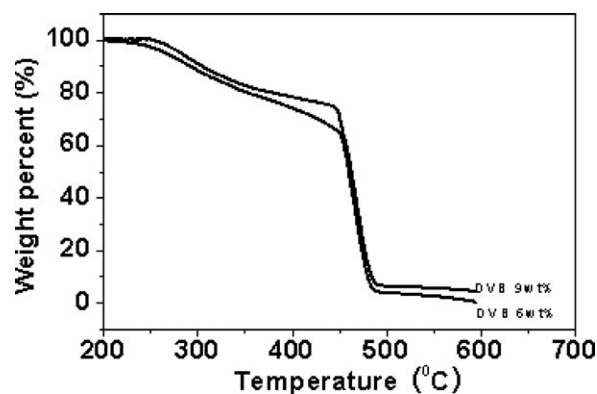

Figure 2 DSC thermogram of HTPB-DVB-PU membranes.

Figure 3 TGA curve of HTPB-DVB-PU.

through HTPB-DVB-PU membranes at 30°C. From Figure 4(a), the *p*-xylene in permeate through HTPB-DVB-PU membranes with different DVB content was much higher than that in the feed. These results suggest that HTPB-DVB-PU membranes have high *p*-xylene permselectivity for a 10 wt % *p*-xylene *p*-/*o*-xylene mixture. Meanwhile, both the separation factor and *p*-xylene in permeate increased with increasing DVB content. From Figure 4(b), the *p*-xylene and *o*-xylene permeability through HTPB-DVB-PU mem-
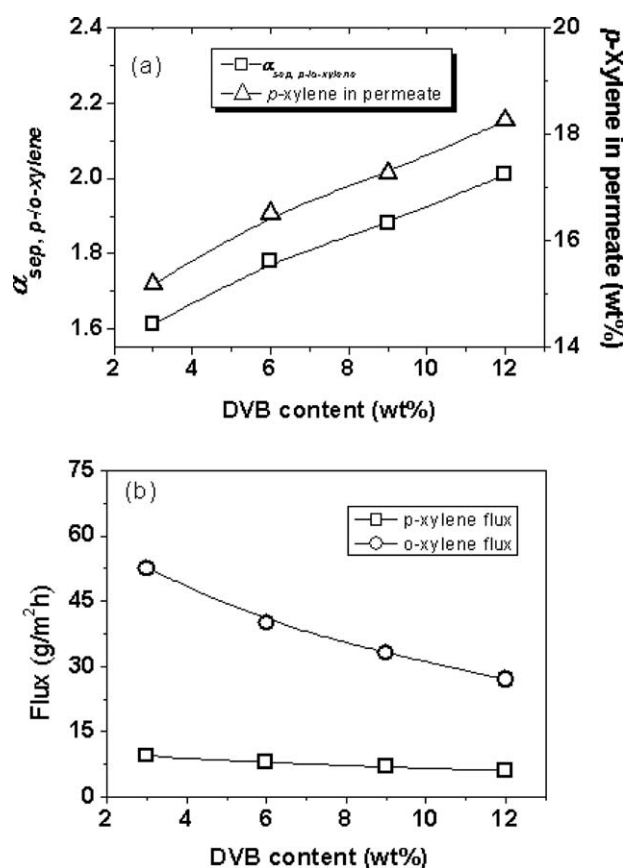

Figure 4 Effect of DVB content on (a) $\alpha_{sep,p\text{-}/o\text{-xylene}}$ and *p*-xylene in permeate; (b) permeation flux for separating *p*-/*o*-xylene mixture through HTPB-DVB-PU membranes during PV(*p*-xylene in feed: 10 wt %, feed temperature 30°C).
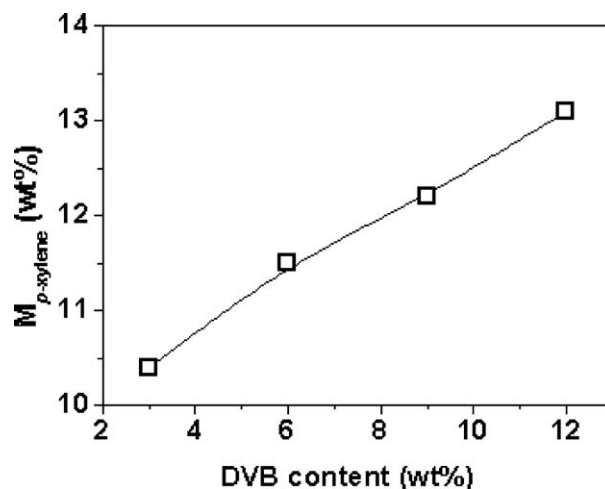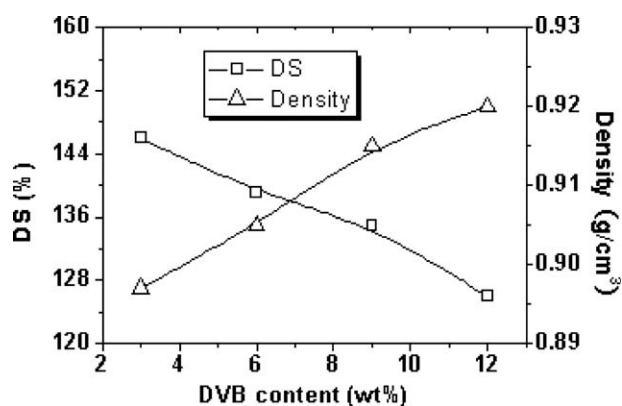
Figure 5 Effect of DVB content on *p*-xylene concentration of *p*-/*o*-xylene mixtures in HTPB-DVB-PU membranes, $M_{p\text{-xylene}}$, immersed in a 10 wt % *p*-xylene *p*-/*o*-xylene mixture at 30°C.

branes decreased with increasing DVB content. In general, the PV performance for separation of organic mixtures is based on the solubility of permeants into the polymer membrane (sorption process) and the diffusivity of the permeants in the polymer membrane (diffusion process). The solubility and diffusivity of the permeants are significantly influenced by the chemical and physical structures of the polymer membranes. First, to discuss the effect of the introduction of DVB into the HTPB-DVB-PU membranes for sorption process, *p*-xylene absorption into the membrane was measured.
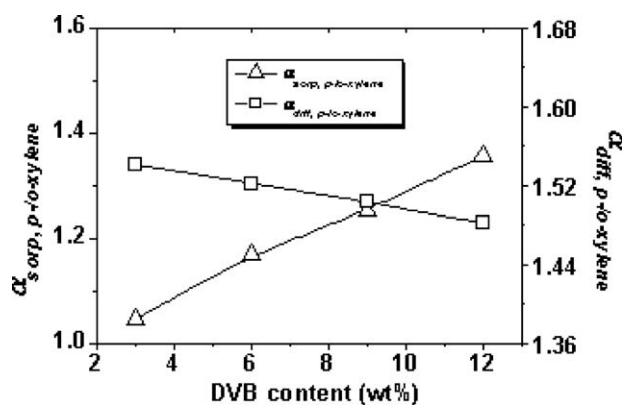
Figure 5 shows effect of DVB content on *p*-xylene concentration of *p*-/*o*-xylene mixtures in HTPB-DVB-PU membranes, $M_{p\text{-xylene}}$, after swollen in *p*-/*o*-xylene mixture with 10 wt % of *p*-xylene at 30°C. As can be seen Figure 5, $M_{p\text{-xylene}}$ increased with increasing DVB content. This result suggests that DVB could enhance the affinity of HTPB-DVB-PU membranes to *p*-xylene. This can be attributed to the increase of DVB content in HTPB-DVB-PU membranes, which has more strong affinity to *p*-xylene than to *o*-xylene. The solubility parameter of DVB network (calculated according to group contribution method) is 16.6 $J^{1/2}/cm^{3/2}$, which is close to that of *p*-xylene, 18.0 $J^{1/2}/cm^{3/2}$, than to that of *o*-xylene, 18.2 $J^{1/2}/cm^{3/2}$.[14] The increasing of *p*-xylene concentration of *p*-/*o*-xylene mixtures in the HTPB-DVB-PU membranes increased with increasing DVB content supports the enhancement of *p*-xylene permselectivity showed in Figure 4(a).

Figure 6 shows effect of DVB content on DS of HTPB-DVB-PU membranes immersed in a 10 wt % *p*-xylene *p*-/*o*-xylene mixture at 30°C and the density dry HTPB-DVB-PU membranes. As can be seen from Figure 6, the density of dry HTPB-DVB-PU
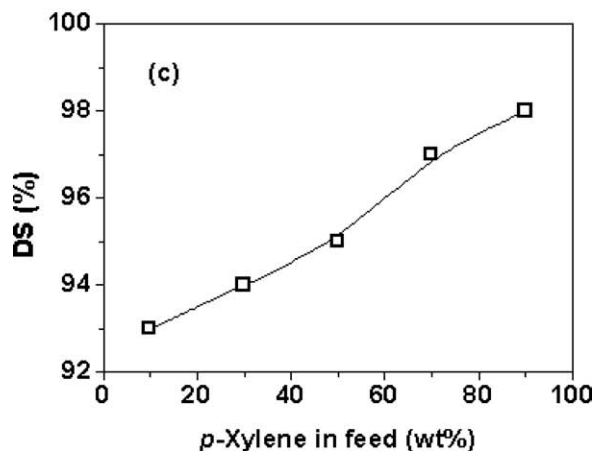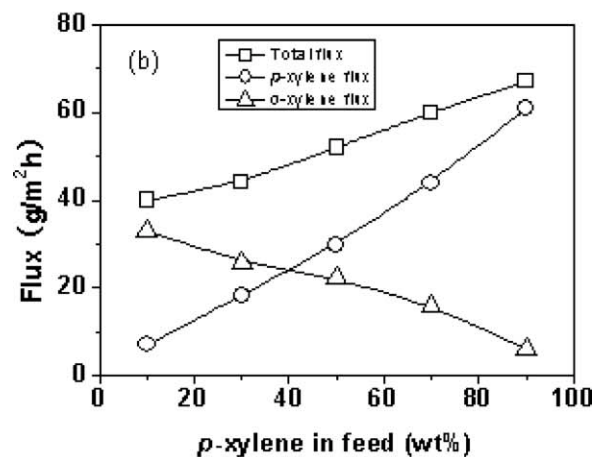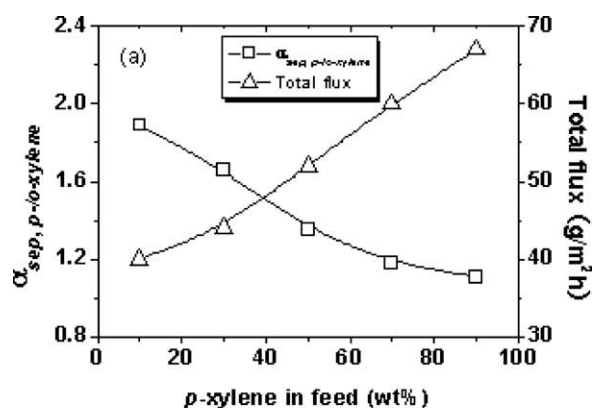
Figure 6 Effect of DVB content on DS of HTPB-DVB-PU membranes immersed in a 10 wt % *p*-xylene *p*-/*o*-xylene mixture at 30°C and the density dry HTPB-DVB-PU membranes.

membranes increased and the DS of HTPB-DVB-PU membranes decreased with increasing DVB content. This is owing to two effects: one is that more cross-linking restrained the mobility of chains of HTPB-DVB-PU membranes, and the other is that the micro-phase separation is weakened and the defect between hydrophobic and hydrophilic phase reduced. As a result, the permeation flux of both *p*-xylene and *o*-xylene through HTPB-DVB-PU membranes declined with the increase of DVB content. Compared with HTPB-PU membrane (without cross-linking),[21] all of the HTPB-DVB-PU membranes have lower densities (HTPB-DVB-PU, from 0.89 to 0.92, HTPB-PU, 0.95 g/cm^3). The smaller density of HTPB-DVB-PU membranes can be explained that the introduction of cross-linkage made urethane (urea) segments congregate more difficult and dispersed evenly in the matrix formed by PB segments. That is to say, the micro phase separation was weakened as confirmed by the single T_g of HTPB-DVB-PU. So, HTPB-DVB-PU has more homogeneous but loser chain structure because the incompatibility between polar urethane (urea)

Figure 7 Effect of DVB content on the sorption selectivity $\alpha_{sorp,p\text{-}/o\text{-xylene}}$, and the diffusion selectivity, $\alpha_{diff,p\text{-}/o\text{-xylene}}$, for a 10 wt % *p*-xylene *p*-/*o*-xylene through HTPB-DVB-PU membranes during PV.

Figure 8 Effect of *p*-xylene in feed on the PV performances of HTPB-DVB-PU membrane, (a): $\alpha_{sep,p\text{-}/o\text{-xylene}}$ and total flux; (b): xylene flux; (c) the equilibrium degree of swelling of HTPB-DVB-PU (DVB content: 9 wt %, feed temperature: 30°C).

segments and PB segments which leads to formation of a membrane with lower density.

Figure 7 shows effect of DVB content on the sorption selectivity, $\alpha_{sorp,p\text{-}/o\text{-xylene}}$, and the diffusion selectivity, $\alpha_{diff,p\text{-}/o\text{-xylene}}$, for *p*-/*o*-xylene mixture with 10 wt % of *p*-xylene through the HTPB-DVB-PU membranes. As can be seen from Figure 7, the sorption

TABLE I
Comparison of PV Results of HTPB-DVB-PU Membrane for *p-/o*-Xylene Mixtures (50 wt% *p*-xylene in Feed) with Literatures

| Membrane (thickness μm)	Temperature (°C)	Normalized *p*-xylene flux (kgμm/m²h)	Separation factor (*p*-/*o*-xylene)	Reference
Cellulose tripropionate[a]	25	0.264[b]	0.85	[14]
Cellulose acetate butyrate[a]	25	0.13[b]	0.79	[14]
MFI zeolite (1.5)	26	0.11	0.94	[8]
PU (55)	25	12.05	0.73	[16]
PU–zeolite (55)	25	8.83	0.53	[16]
Polyacrylic acid/γ-cyclodextrins (30)	25	0.077	1.16	[2]
Polyethylene (30)	31	2.25	1.37	[1]
Polypropylene (20)	26	1.70	1.30	[1]
Poly(vinyl fluoride) (25)	43	0.14	1.39	[1]
Cellulose acetate (25)	81	0.15	1.56	[1]
Nylon (25)	128	0.15	1.42	[1]
DNB-cellulose acetate (40)	25	0.032	1.70	[10]
Copolyimide[a]	65	0.89	1.47	[12]
HTPB-DVB-PU (200)	30	5.97	1.35	This work

[a] Not specified.
[b] Unit in kg/m²h.

selectivity increased while the diffusion selectivity of HTPB-DVB-PU membranes decreased with increasing DVB content. In general, the separation factor, $\alpha_{sep,p-/o-xylene}$, for *p-/o*-xylene mixtures in PV can be defined by the sorption selectivity, $\alpha_{sorp,p-/o-xylene}$, and the diffusion selectivity, $\alpha_{diff,p-/o-xylene}$, from eq. (3). So it is clear that the increase in the separation factor of HTPB-DVB-PU membranes depended significantly on the increase in the sorption selectivity. The drop in diffusion selectivity suggests that the permeation of the *p*-xylene molecules is more disadvantageous than that of *o*-xylene with increasing DVB content. From the above results, we can see that *p*-xylene permselectivity of the cross-linked HTPB-DVB-PU membranes with increasing DVB content were mainly governed by the sorption process.

Effect of feed concentration

Figure 8 shows effect of *p*-xylene concentration in feed on: (a) the separation factor, $\alpha_{sep,p-/o-xylene}$, and total flux, (b) *p*-xylene flux and *o*-xylene flux, (c) DS of HTPB-DVB-PU membrane with DVB content of 9 wt % for separating *p-/o*-xylene mixtures at 30°C. From Figure 8, it can be seen that with the increase of *p*-xylene concentration in feed, $\alpha_{sep,p-/o-xylene}$ and *p*-xylene flux also increased, while total flux and *o*-xylene flux decreased. This is because the driving force of *p*-xylene was enhanced and that of *o*-xylene was depressed with increasing *p*-xylene concentration. But the separation factor decreased with the increase of *p*-xylene concentration in feed, which can be explained that HTPB-DVB-PU membrane was much swollen in the PV process with higher *p*-xylene concentration in feed as can be confirmed by Figure 8(c).
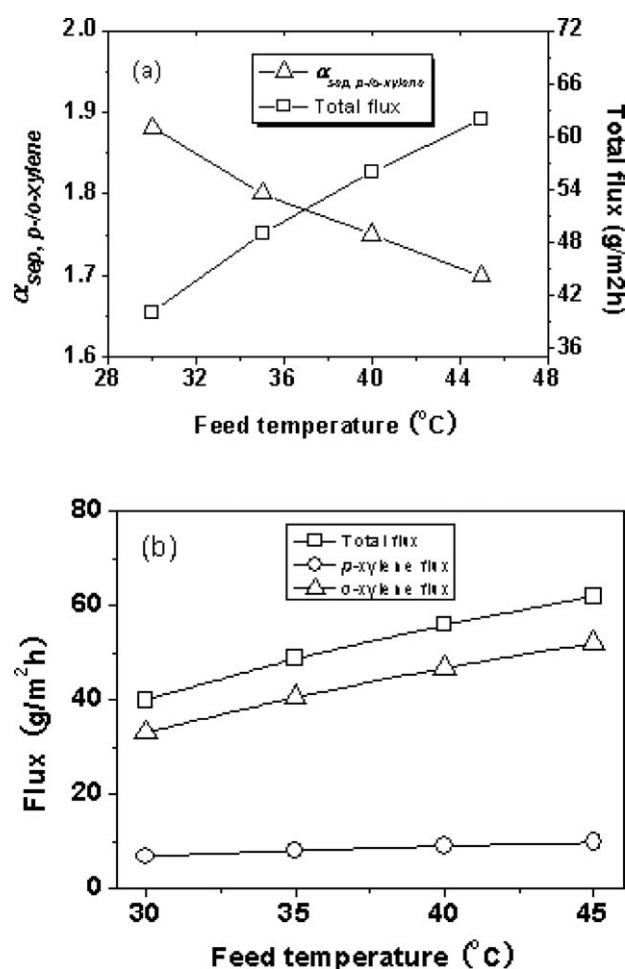
Figure 9 Effect of feed temperature on the PV performance of HTPB-DVB-PU membrane, (a): $\alpha_{sep,p-/o-xylene}$ and total flux; (b): xylene flux (*p*-xylene in feed, 10 wt %, DVB content 9 wt %).
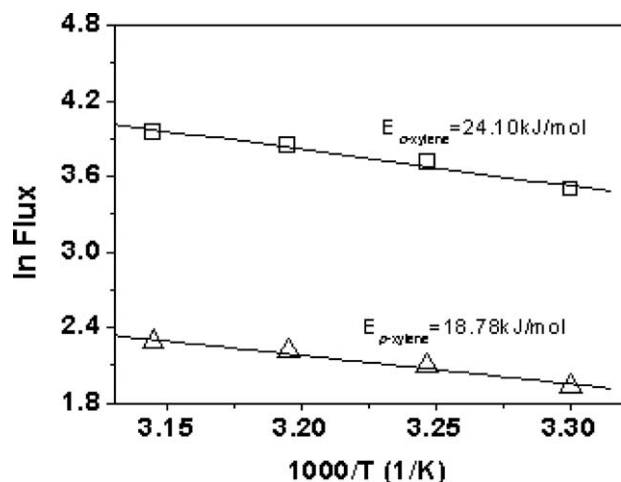
Figure 10 Arrhenius plots of the HTPB-DVB-PU membrane (*p*-xylene in feed, 10 wt %, DVB content 9 wt %).

Table I compare the PV performance for separating *p*-/*o*-xylene mixtures (50 wt % *o*-xylene in feed) using various membranes from 25 to 128°C. The highest normalized *p*-xylene permeation flux (defined as the *p*-xylene flux multiplied by the membrane thickness) and separation factor are below 3 kgμm/m²h and 2. The HTPB-DVB-PU membrane in this study exhibited comparatively higher normalized flux and separation factor compared with other membrane materials.

Effect of feed temperature

Figure 9 shows temperature effect on the PV performance of HTPB-DVB-PU membranes. The separation factor decreased while the total flux increased with increasing temperature from 30 to 45°C. This can be attributed to the enhanced movement of polymer segments and the driving force between two sides of the membranes with increasing of temperature. Obviously, it favors the permeation of *o*-xylene to that of *p*-xylene in this study. It is interesting that a high separation factor of more than 1.7 is retained even at 45°C. The temperature dependence of experimental data of both total and partial fluxes generally follows Arrhenius equation below:

$$J_i = J_{i,0} \exp(-E/RT), \qquad (6)$$

where E has been considered to be the activation energy. Figure 10 shows a plot of ln$J$ versus $1000/T$ for the HTPB-DVB-PU membrane with DVB content of 9 wt %. Two linear lines for *p*-xylene and *o*-xylene were obtained at the range of the temperature studied. The permeation activation energies of *p*-xylene and *o*-xylene through the HTPB-DVB-PU membrane are 18.78 KJ/mol and 24.10 KJ/mol, respectively. The larger activation energy of *o*-xylene is due to its bigger molecular volume (0.680 nm) than that of *p*-

xylene (0.585 nm).[8] The larger permeation activation energy of *o*-xylene implies that *o*-xylene permeation flux is more sensitive to increased temperature compared with that of *p*-xylene permeation flux.

CONCLUSIONS

Cross-linked HTPB-based PU (HTPB-DVB-PU) was synthesized by a three-step polymerization process. HTPB-DVB-PU shows one T_g, excellent thermal stability, and good film-forming property. The PV performance for separation of *p*-/*o*-xylene mixtures have been evaluated with respect to DVB content, *p*-xylene in feed and operating temperature. All HTPB-DVB-PU membranes demonstrate higher *p*-xylene selectivity as well as high flux. With the increasing of DVB content in membrane, the separation factor increased while the permeation flux decreased. The highest separation factor reaches 2.01 and the total flux is 33 g/m²h with feed concentration of 10 wt % *p*-xylene at 30°C, when the DVB content in HTPB-DVB-PU membrane was 12 wt % in membrane. This can be attributed to the introduction of the cross-linkage by DVB, which enhanced the affinity to *p*-xylene and the density of the membranes and thus improved the sorption selectivity of *p*-xylene. The increase of the density of HTPB-DVB-PU membranes weakened the DS, so as to restrain the permeation of both *p*-xylene and *o*-xylene through HTPB-DVB-PU membranes.

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