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Pervaporation properties of ethynyl-containing copolyimide membranes to aromatic/non-aromatic hydrocarbon mixtures

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Abstract

2,2′-diethynylbenzidine and a series of copolyimides containing such a diamine moiety were synthesized. The crosslinking behaviors of these copolyimides were studied by differential scanning calorimetry and infrared measurements. Pervaporation (PV) properties of these copolyimide membranes to aromatic/non-aromatic hydrocarbon mixtures were investigated. The crosslinked membranes exhibited higher separation factors of benzene over cyclohexane than the corresponding uncrosslinked ones. The sorption results revealed that the increase in diffusivity selectivity was mainly responsible for the improvement in separation factor of PV. However, this improvement seemed still limited. In addition, tetracyanoethylene, an electron acceptor having high affinity for ethynyl-containing materials and aromatics, was homogeneously dispersed in one of these copolyimide matrices and such a membrane displayed high PV performance toward benzene/cyclohexane and toluene/i-octane mixtures. For example, it had a specific permeation flux Ql of 0.44 kg μm m^{-2} h^{-1} and a separation factor α of 48 at the feed composition of 50% benzene in cyclohexane, and $Ql = 1.1$ kg μm m^{-2} h^{-1} and $\alpha = 330$ at the feed composition of 45% toluene in i-octane at 70°C. Unlike the case of crosslinking, both the increases in solubility selectivity and diffusivity selectivity contributed to the improvement in separation factor of PV. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 2,2′-Diethynylbenzidine; Copolyimide; Pervaporation

1. Introduction

Separation of aromatic/non-aromatic hydrocarbon mixtures and aromatic isomers such as benzene/cyclohexane (Bz/Cx), toluene/i-octane (Tol/i-Ot), and xylene isomers through membranes using the pervaporation (PV) technique has attracted increasing attention in recent years because of its advantages of energy and cost savings over conventional fractional distillation processes. Research work in this field has mainly concentrated on the development of membranes with high separation performance and good stability. It is generally thought that, for PV, the permselectivity of a polymeric membrane is mainly due to the solubility selectivity, because the diffusivity selectivity is considered to be low or negative, judging from the molecular size of the penetrants. To achieve high solubility selectivity, the membrane is required to have high affinity for one component and little affinity for the other component(s). However, excessive affinity causes significant swelling of the membrane and results in loss of selectivity and mechanical strength. Therefore, to increase solubility selectivity and to suppress membrane swelling become two crucial factors for the development of high separation performance membranes. For the latter, although some methods have been proposed such as polymer alloy [1,2], plasma-grafted filling membrane [3–5], micro-phase separated structure [6,7], incorporation of flexible units to highly rigid polymer chains [8], and crosslinking [8], the related literature seems still limited. Furthermore, it is necessary to make more efforts to elucidate the relationship between the chemical structure of membrane materials and their PV properties.

Polyimides, known for their excellent thermal, mechanical, and physical properties, have been extensively studied for gas separation processes. We previously investigated that polyimide membranes having methyl-substituted phenylenediamine moieties [8], micro-phase separated structure [7] or functional groups [9] displayed fairly high PV performance to Bz/Cx and/or benzene/n-hexane (Bz/n-Hx) mixtures. Although polyimides generally have good chemical resistance, most of the polyimide membranes previously we reported still significantly swelled during the PV process, especially when the feed mixtures are of rich aromatics. Crosslinking is an ordinary method for the improvement of mechanical properties and resistance to chemical

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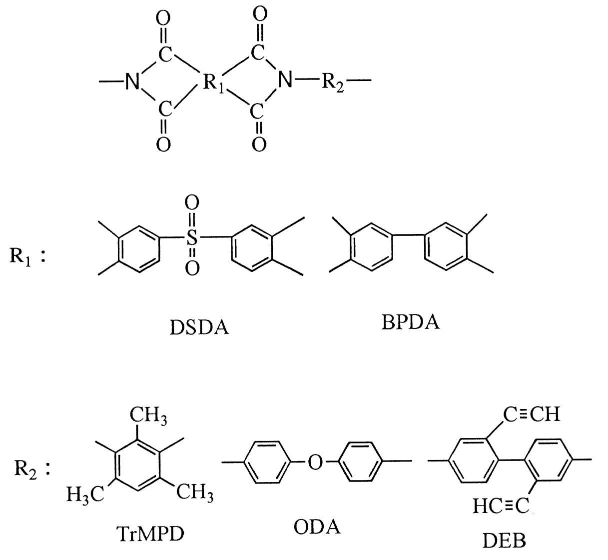


Fig. 1. Chemical structures of copolyimides.

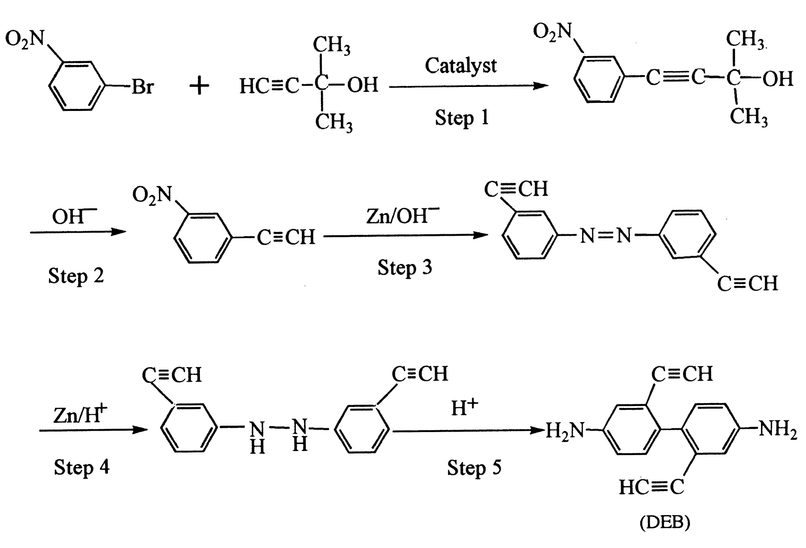
solvents of polymers. For PV, mild crosslinking is also considered to be a way to ensure the durability of polymeric membrane at extreme conditions, such as those situations when the fraction of the permeate in the feed mixture leads to excessive swelling of the membrane [1]. Recently, some literature reported that the incorporation of acetylene units to polyimides could significantly improve the thermal and mechanical properties and chemical resistance to organic solvents after they were crosslinked at high temperature [10–12]. In this paper, a series of ethynyl-containing copolyimides which could be thermally crosslinked were prepared and their PV properties to Bz/Cx mixture were investigated to study the effects of crosslinking. Moreover, by use of the strong electron donor feature of ethynyl, a novel method to suppress membrane swelling as well as to increase the solubility selectivity of membranes was proposed, in which tetracyanoethylene (TCNE), a strong electron acceptor having very high affinity for electron donors such as ethynyl-containing materials and aromatic compounds (formation of charge transfer (CT) complex), was homogeneously dispersed in one of these ethynyl-containing copolyimide matrices. The PV properties of this kind of membrane were also studied in detail.

2. Experimental

2.1. Materials and membrane preparation

The chemical structures of various copolyimides prepared in this study are shown in Fig. 1. The dianhydride moieties, 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA), were purified by sublimation before use. The diamine moieties, 2,4,6-trimethyl-1,3-phenylenediamine (TrMPD) and 4,4′-diaminodiphenyl ether (ODA), were also purified by sublimation before use. *N*-methyl-2-pyrollidone (NMP) and *N*,*N*-dimethylacetamide (DMAc) were distilled and dried over 4 Å molecular sieves. The acetylene-containing diamine moiety 2,2′-diethynylbenzidine (DEB) was synthesized according to the reported method [13]. The synthetic route for this compound is briefly shown in Scheme 1. The chemical structure of the prepared product was confirmed by infrared (IR) and ^{1}H NMR spectra. Its melting point was determined to be 173°C from its differential scanning calorimetry (DSC) curve (Fig. 2).

All the polyimides were prepared according to an ordinary two-step method. In general, to a thoroughly dried four-neck flask equipped with a mechanical stirring device, were added diamine comonomers and NMP solvent. After the diamines were completely dissolved, stoichiometric amount of dianhydride was added in several portions. The total solid



Scheme 1.

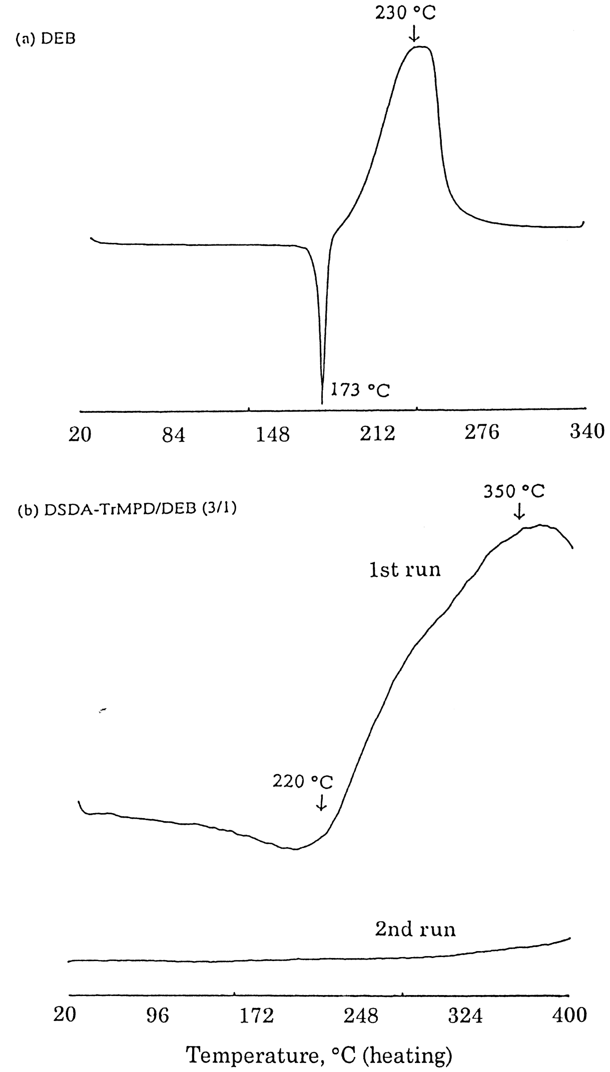


Fig. 2. DSC curves of DEB and DSDA-TrMPD/DEB (3/1) copolyimide.

content was kept about 18 wt%. The polymerization reaction was carried out at room temperature for 8–12 h to give a viscous polyamic acid precursor. Then the reaction solution was diluted to about 5 wt% with additional NMP solvent followed by chemical imidization with excess amount of the mixture of acetic anhydride and triethylamine. The reaction solution was further stirred for 16 h at room temperature and then poured into excessive methanol. The precipitate was collected by filtration and dried at 80°C in vacuo.

The BPDA and DSDA-based polyimide membranes were prepared by casting their solutions in CH_2Cl_2 and DMAc onto glass plates and then dried at room temperature and 80°C in an air oven, respectively. The as-cast membranes were further dried at 100°C for 20 h in vacuo to remove residual solvent followed by thermal treatment at 350°C for 0.5 h in vacuo when crosslinking of membranes was required.

The TCNE-containing membranes were prepared by casting the solutions of DSDA-TrMPD/DEB (3/1, in molar ratio throughout this paper) copolyimide and TCNE in DMAc onto glass plates and then dried at 80°C in an air oven. The obtained membranes were further dried at 100°C for 20 h in vacuo to remove residual solvent.

2.2. Measurements

DSC was measured with Seiko DSC-5200 at a heating and cooling rate of 10 K min^{-1}. Thermogravimetric analysis (TGA) was measured with JEOL MS-TG/DTA220 at a heating rate of 5 K min^{-1}. IR spectra were determined with Horiba FT-200 instrument.

PV experiments were carried out according to a literature method [8]. The effective membrane area was 22 cm^2. The downstream pressure was maintained below 130 Pa. In the case of BPDA-based copolyimide membranes, steady state permeation was attained in 5–8 h after the membranes were contacted with the feed solutions. In the case of DSDA-based copolyimides, the membranes were primarily allowed to permeate pure benzene at 70°C for 1 day before actual PV measurement. We called this process the benzene-conditioning of the membrane. Composition analysis was performed on a gas chromatograph equipped with 3-m columns packed with DOP 30% Uniport R 60/80. The PV separation factor of aromatics over aliphatics α is defined as

$$\alpha = Y(1-X)/X(1-Y) \qquad (1)$$

where X and Y are weight fractions (%) of aromatic components in the feed and permeate, respectively.

In the case of sorption in pure hydrocarbon solvents (benzene (Bz), cyclohexane (Cx) and n-hexane (n-Hx)), precisely weighed dry membrane sheets (about 0.2 g per sheet) were immersed into the solvent and kept at 70°C (Bz or Cx) or 60°C (n-Hx) for 24 h, then taken out, wiped with tissue paper and quickly weighed on a microbalance. The sorption amount S is defined as

$$S = (W_s - W_d)/W_d \times 100(\%) \qquad (2)$$

where W_d and W_s are the weight of dry and corresponding solvent-swollen membrane sheets, respectively.

The sorption in mixed hydrocarbons (Bz/Cx or Bz/n-Hx) was performed in a similar way. Membrane sheets of about 0.02 g were immersed into the solvent and kept at 70°C for 24 h, then taken out, wiped with tissue paper, quickly transferred to sample bottles where about 0.05 g NMP had been added separately. The bottles were covered and then heated at 100°C for 25 min with the Headspace Sampler instrument (HS 40, Perkin Elmer) to release the solvents absorbed in membrane sheets, which were then automatically collected and analyzed with a gas chromatography device (GC-17A, Shimadazu). The sorption separation factor α_S was calculated from Eq. (1) as in the PV by redefining X and Y as weight fractions of aromatic components in the solvent mixture and membrane, respectively.

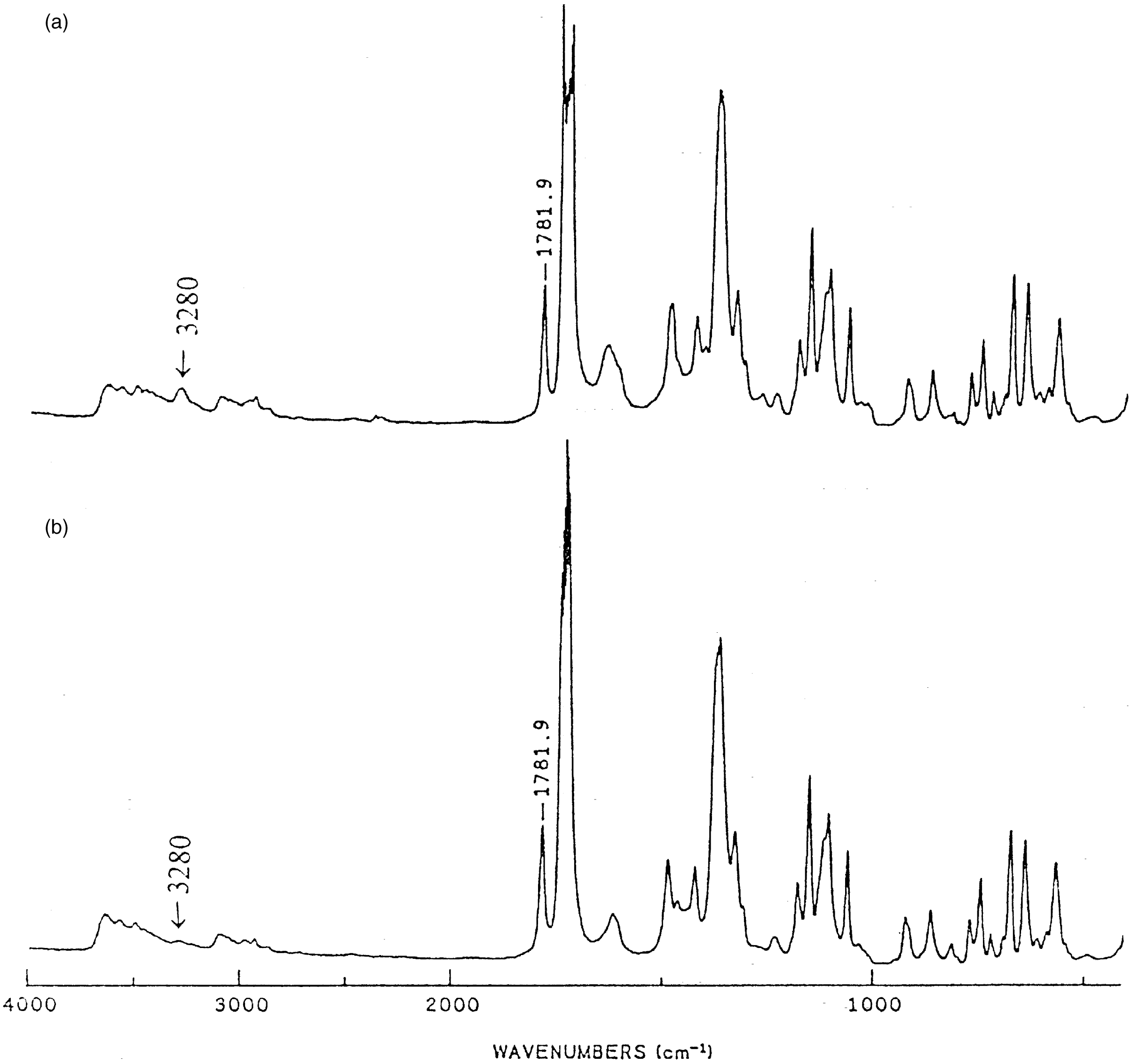


Fig. 3. IR spectra of DSDA-TrMPD/DEB (3/1) copolyimide membrane with different heat treatment: (a) as-cast; (b) 350°C, 0.5 h.

3. Results and discussion

3.1. Crosslinking of membranes

It is well known that ethynyl-containing polymers can be thermally crosslinked without releasing any small molecules. In this study, the crosslinking reaction between ethynyl groups of DEB units in copolyimides were examined by DSC and IR measurements. Since one DEB molecule contains two ethynyl groups and the steric hindrance effect is not so significant as that of the diamines having acetylene units in the backbone as reported in the literature [10–12], DEB and DEB-containing copolyimides can easily undergo crosslinking reaction by thermal treatment. Fig. 2 shows the DSC curves of DEB and its copolyimide DSDA-TrMPD/DEB (3/1). In the case of DEB, the exotherm appeared soon after it was melted and reached a maximum at 230°C indicating that the monomer itself was very easily thermally crosslinked. In the case of the copolyimide DSDA-TrMPD/DEB (3/1), the starting exotherm temperature shifted to 220°C and reached a maximum at 350°C on the first run but no such an exothermic peak was observed on the second run, indicating that crosslinking of the copolyimide was also readily carried out by the thermal treatment. The exotherm was due to the crosslinking reaction of ethynyl groups rather than decomposition of the polymer judging from the fact that in the temperature range of 220–400°C no appreciable weight loss was observed from its TGA curve. Similar DSC curves were observed for other DEB-containing copolyimides.

Fig. 3 shows the IR spectra of the as-cast and the corresponding thermally treated (350°C, 0.5 h) DSDA-TrMPD/DEB (3/1) copolyimide membranes, respectively. The intensity of the absorption band at 3280 cm^{-1} which was attributed to the stretch vibration of H–C(≡) bond greatly decreased after the thermal treatment, whereas the intensity

Table 1
Density of copolyimide membranes

Sample	Density ($\mathrm{g\ cm^{-3}}$)
DSDA-TrMPD/DEB (9/1), uncrosslinked	1.272
DSDA-TrMPD/DEB (9/1), crosslinked	1.307
DSDA-TrMPD/DEB (3/1), no TCNE	1.281
DSDA-TrMPD/DEB (3/1), 10 wt% TCNE	1.330

of the characteristic absorption band of imide ring at 1781.9 $\mathrm{cm^{-1}}$ (C=O asymmetrical stretching) remained unchanged. The reaction degree of ethynyl groups was estimated to be 82% according to the intensity ratio of these two absorption bands at 3280 $\mathrm{cm^{-1}}$ in Fig. 3(a) and 3(b).

The physical properties of these DEB-containing copolyimides changed greatly after the heat treatment. Table 1 shows the change of density of DSDA-TrMPD/DEB (9/1) copolyimide. The crosslinked membrane displayed larger density than the uncrosslinked one. In addition, these copolyimides exhibited quite different solubility behaviors after being thermally treated at high temperature as shown in Table 2. All the thermally treated copolyimides were insoluble but could swell in all solvents tested. The colors of the copolyimide membranes also changed from almost colorless to yellow after thermal crosslinking.

3.2. Effects of crosslinking on PV properties

BPDA- and DSDA-based copolyimides were employed to study the crosslinking effects on PV properties to Bz/Cx mixture. The specific permeation fluxes, Ql, and the separation factors of benzene over cyclohexane, $\alpha_{\mathrm{Bz/Cx}}$, at feed composition, X_{Bz} (wt% of benzene), of 50–60% and 50–70°C are listed in Table 3. All the DEB-containing copolyimide membranes which were thermally crosslinked at the high temperature displayed relatively better PV performance than the corresponding uncrosslinked copolyimide and homopolyimide (TrMPD-based) membranes. The DSDA-TrMPD/DEB (9/1) membrane, for example, had Ql of 4.1 kg μm $\mathrm{m^{-2}\ h^{-1}}$ and $\alpha_{\mathrm{Bz/Cx}}$ of 14 after thermal crosslinking, whereas it had $Ql = 7.6$ kg μm $\mathrm{h^{-1}}$ and $\alpha_{\mathrm{Bz/Cx}} = 7.0$ before crosslinking at $X_{\mathrm{Bz}} = 60\%$ and 70°C. On the contrary, polyimide membranes containing no DEB unit did not show such a kind of thermal treatment effect. For example, DSDA-TrMPD membranes which were treated under different conditions (100°C, 20 h; 200°C, 20 h; 350°C, 0.5 h) displayed similar Ql and $\alpha_{\mathrm{Bz/Cx}}$ values as shown in Table 3. This clearly indicates that the improvement in the separation factor of DEB-containing copolyimide membranes was really due to the crosslinking. Furthermore, we can find that a membrane containing a larger molar fraction of DEB tended to have a higher separation factor due to higher crosslinking density. However, if the crosslinking density is too large, the membrane becomes brittle. DSDA-TrMPD/DEB (3/1) membrane, for example, became somewhat brittle after thermal crosslinking at 350°C for 0.5 h and could not be used for PV measurement. Therefore, relatively flexible units such as an ether bond were incorporated into the polymer structure to improve the mechanical strength. Crosslinked DSDA-TrMPD/DEB/ODA (2/1/1) membrane was found tough enough for PV measurement and displayed the highest separation factor among the membranes listed in Table 3. In addition, the DSDA-based membranes generally displayed lower specific permeation fluxes but higher separation factors than BPDA-based ones, probably because the former had relatively more dense packing structures.

Table 4 lists the sorption results of uncrosslinked and crosslinked DSDA-TrMPD/DEB (9/1) copolyimide membranes. The total sorption amount hardly depended on crosslinking treatment indicating that the decrease in Ql in the PV of the crosslinked membrane was mainly due to the decrease in diffusion coefficient rather than the decrease in sorption. For the sorption in a Bz/Cx mixture of $X_{\mathrm{Bz}} = 60$ wt%, the benzene content, Y_{Bz}, in the crosslinked membrane was a little larger than that in the uncrosslinked membrane indicating a slight increase in sorption separation factor. Since

Table 2
Solubility behaviors of the studied copolyimides

(Co)polyimide	Heat treatment [a]	Solubility [b]		
		NMP	DMAc	CH_2Cl_2
BPDA-TrMPD	No	−	−	+
DSDA-TrMPD/DEB (9/1)	No	−	−	+
	Yes	−	−	−
DSDA-TrMPD	No	+	+	−
DSDA-TrMPD/DEB (9/1)	No	+	+	−
	Yes	−	−	−
DSDA-TrMPD/ODA/DEB (6/1/1)	No	+	+	−
	Yes	−	−	−
DSDA-TrMPD/ODA/DEB (2/1/1)	No	+	+	−
	Yes	−	−	−

[a] 350°C, 0.5 h.

[b] +, soluble; −, insoluble.

Table 3
Crosslinking effects on PV properties of DEB-containing copolyimide membranes to Bz/Cx mixtures at 70°C

Membrane	Heat treatment	l (μm)	X_{Bz} (wt%)	Ql (kg μm m^{-2} h^{-1})	$\alpha_{\mathrm{Bz/Cx}}$	Reference
BPDA-TrMPD [a]	200°C, 20 h	44	55	9.1	7.1	[8]
BPDA-TrMPD/DEB (9/1) [a]	350°C, 0.5 h	21	55	7.4	10.4	[b]
DSDA-TrMPD	100°C, 20 h	43	50	10.2	7.7	[b]
	200°C, 20 h	30	50	11.0	6.8	[b]
	350°C, 0.5 h	39	50	10.6	7.3	[b]
DSDA-TrMPD/DEB (9/1)	100°C, 20 h	22	60	7.6	7.0	[b]
	350°C, 0.5 h	18	60	4.1	14.0	[b]
DSDA-TrMPD/ODA/DEB (6/1/1)	350°C, 0.5 h	14	60	3.4	13.3	[b]
DSDA-TrMPD/ODA/DEB (2/1/1)	100°C, 20 h	20	55	2.1	13.1	[b]
	350°C, 0.5 h	28	50	1.5	21	[b]
BTDA-TrMPD [a]	–	10	50	1.8	9.4	[8]
BTDA-TrMPD (UV) [a]	–	10	50	0.056	24	[8]
BTDA-6FDA (1/1)-TrMPDs[a]	–	15	50	9.5	5.0	[8]
BTDA-6FDA (1/1)-TrMPD (UV) [a]	–	15	50	1.3	7.9	[8]

[a] at 50°C; BTDA and 6FDA denote 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, respectively.

[b] This study.

PV separation factor α is the product of sorption separation factor α_S and diffusion separation factor α_D, i.e. $\alpha = \alpha_S \cdot \alpha_D$, the increase in PV separation factor of the crosslinked membrane was mainly due to the increase in diffusion separation factor. This was probably because this kind of crosslinking hardly changed the solubility parameter of the copolyimide, while membrane swelling was effectively suppressed and the decrease in the diffusion coefficient of cyclohexane was larger than that of benzene.

We have previously reported that the photocrosslinking of polyimide membranes was not effective in PV, because the reduction in the permeation flux was too large comparing with the increase in the selectivity [8]. However, the present crosslinking displayed quite different effects. *Ql* did not decrease so much, whereas $\alpha_{\mathrm{Bz/Cx}}$ increased by a factor comparable with the case of photocrosslinking. This is probably because the present crosslinking did not cause polymeric chain packing as tight as in the case of photocrosslinking, whereas in both cases membrane swelling was effectively suppressed. Furthermore, we can conclude that crosslinking effects on PV performance are complex; different crosslinking processes may cause different effects on PV properties.

3.3. Effects of the incorporation of TCNE on PV properties

Since the essential distinction between aromatics and aliphatics is that aromatics have highly conjugated π electrons while aliphatics do not, it can be deduced that the introduction of an electron acceptor should be helpful for the improvement of solubility selectivity of a membrane. TCNE can form CT complexes with aromatic hydrocarbons (electron donors). Sukwattanasinitt et al. reported that arylamine polymers containing ethynyl units can form a CT complex with some electron acceptors and the ethynyl units can even react with TCNE at room temperature [14]. So, the introduction of TCNE to polymeric membranes may be an effective method to suppress membrane swelling as well as to improve the solubility selectivity of membranes resulting in a significant increase in separation factor of aromatics over non-aromatics. A DSDA-TrMPD/DEB (3/1) copolyimide membrane with added TCNE (10% by weight) was used as an example to examine this assumption. Table 5 shows the PV properties of this kind of membrane to four binary aromatic/aliphatic systems. For comparison, the PV properties of the corresponding TCNE-free membrane was also listed in this table. It is obvious that the TCNE-containing

Table 4
Sorption results of crosslinked and uncrosslinked DSDA-TrMPD/DEB (9/1) copolyimide membranes toward Bz/Cx system

Sample	X_{Bz} (wt%)	S [a] (wt%)	Y_{Bz}	α_S	α_D
DSDA-TrMPD/DEB (9/1)	100	35	100	–	–
uncrosslinked	60	25	78.4	2.4	2.9
	0	0.8	0	–	–
DSDA-TrMPD/DEB (9/1)	100	35	100	–	–
crosslinked	60	22	80.2	2.7	5.2
	0	0.6	0	–	–

[a] g/100 g dry polymer.

Table 5
PV properties of DSDA-TrMPD/DEB (3/1) membrane ($l = 21\ \mu$m) containing 10 wt% TCNE to aromatic/non-aromatic hydrocarbon mixtures

Feed mixture	X_{aro} (wt%)	Ql (kg μm m^{-2} h $-$ 1)	$\alpha_{aro/ali}$
Bz/Cx [a]	50	4.2	11.0
Bz/Cx	50	0.44	48
		1.1 [b]	30 [b]
Bz/n-Hx [c]	50	2.8	9.1
Tol/i-Ot [c]	45	1.1	330
Tol/n-Ot [c]	40	2.1	13.0

[a] No TCNE and $l = 25\ \mu$m.
[b] After 3 experimental weeks.
[c] After Bz/Cx system measurement was finished.

membrane displayed a much higher separation factor of benzene over cyclohexane and lower specific permeation flux than the corresponding TCNE-free one. The decrease in Ql was mainly due to the strong interaction between ethynyl units in polymer chains and TCNE molecules resulting in significant suppression of membrane swelling, whereas the improvement in PV separation factor was due to the increases in both sorption separation factor and diffusion separation factor as shown in Table 6. The diffusion coefficients of Bz, Cx and n-Hx were calculated from

$$D_i = q_i 1/(C_{i1} - C_{i2}) \qquad (3)$$

where D_i is the concentration-averaged diffusion coefficient, $q_i 1$ is the specific permeation flux, and C_{i1} and C_{i2} are the concentration of component i in the membrane at the feed side and permeate side, respectively. In a Bz/Cx mixture of $X_{Bz} = 50$ wt%, the sorption separation factor and diffusion separation factor increased about 50% and 90%, respectively.

As shown in Table 5, the separation factors of aromatics (toluene (Tol) and Bz) over branched (i-octane (i-Ot)) or cyclic (Cx) aliphatics were much larger than those of aromatics over linear aliphatics (n-Hx and n-octane (n-Ot)). This is because the linear aliphatics had much larger diffusivity coefficients than cyclic or branched ones. The largest separation factor (over 300) was obtained for the Tol/i-Ot system. This phenomenon has been observed with other polyimide membranes [9].

The feed composition dependence and temperature dependences on PV properties of the membrane toward Bz/Cx mixtures are shown in Figs 4 and 5, respectively. The feed composition dependence was determined by two experimental runs; after that, the temperature dependence was determined. It displayed an ordinary PV behavior as observed with most polymeric membranes, i.e. the specific permeation flux increased and the separation factor decreased with an increase in benzene content of feed and temperature. For separating Tol/i-Ot mixture, this membrane displayed a similar behavior to the case of the Bz/Cx system. Furthermore, as can be seen from Fig. 4, the durability of this membrane was not so good. The specific permeation flux increased and the separation factor decreased with experimental runs. This is probably because a small amount of TCNE gradually diffused into the feed solution from the membrane although the strong interaction between TCNE and ethynyl groups significantly suppressed this process. Nevertheless, the membrane maintained high separation factor even after one and a half months.

Comparing the PV results listed in Tables 3, and 5, we can find that the TCNE-addition method is even more effective than the thermal crosslinking method. As discussed above, the thermal crosslinking treatment only resulted in suppression of membrane swelling and therefore the enhancement of diffusivity selectivity, whereas the solubility selectivity and diffusivity selectivity significantly increased due to the high affinity of TCNE for aromatics and the strong interaction between TCNE molecules and ethynyl groups in the copolyimide structure. Therefore, the TCNE-addition method made the membrane display even higher separation factors than the crosslinking method.

The most serious disadvantage of the TCNE-addition method is the loss of TCNE from the membrane leading to relatively poor durability of the membrane. This disadvantage can be overcome by chemically bonding electron acceptor molecules to polymer chains.

Table 6
Sorption results of TCNE-containing and TCNE-free DSDA-TrMPD/DEB (3/1) copolyimide membranes

Sample	X_{Bz} (wt%)	S [a]		Y_{Bz} (wt%)	α_S	D [b]		α_D
		Bz	Cx			Bz	Cx	
DSDA-TrMPD/DEB (3/1),	100	30	–	100	–	–	–	–
no TCNE	50	15.6	5.4	74.3	3	5.3	1.6	3.7
	0	–	0.5	0	–	–	–	–
	0 [c]	–	7.1	0	–	–	–	–
DSDA-TrMPD/DEB (3/1),	100	20	–	100	–	5.4	–	–
10 wt% TCNE	50	9.2	2.2	80.9	4.4	2.4	0.38	6.9
	0	–	0	0	–	–	–	–
	0 [c]	–	0.6	0	–	–	–	–
	50 [d]	9.5	1.5	86.4	6.5	5.5	4.1	1.3

[a] g/100 g dry polymer.
[b] 10^{-8} cm^2 s^{-1}.
[c] n-Hx at 60°C.
[d] Bz/n-Hx.

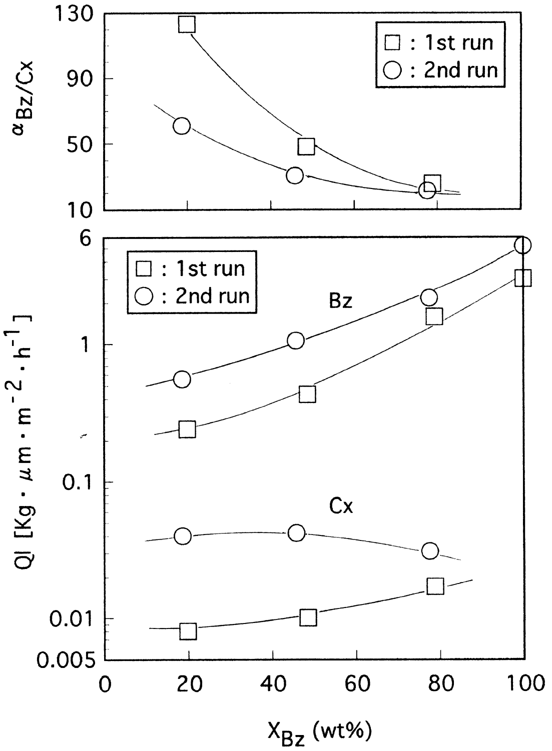


Fig. 4. Feed composition dependence on PV properties of TCNE-containing DSDA-TrMPD/DEB (3/1) copolyimide membrane toward Bz/Cx mixtures at 70°C.

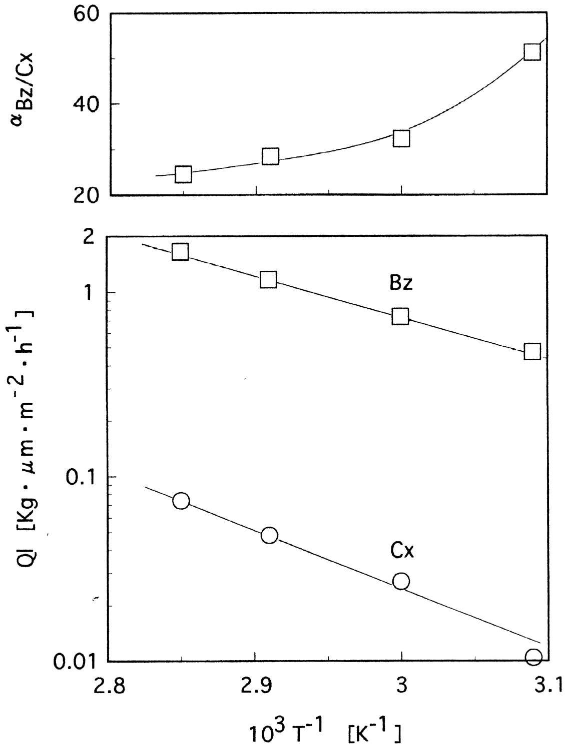


Fig. 5. Temperature dependence on PV properties of TCNE-containing DSDA-TrMPD/DEB (3/1) copolyimide membrane at the feed composition of $X_{Bz} = 50$ wt%.

4. Conclusions

1. The thermal crosslinking reaction of DEB-containing copolyimides was confirmed by DSC and IR measurement. These copolyimides were readily crosslinked at 350°C for 0.5 h.
2. Crosslinking of DEB-containing copolyimide membranes was somewhat effective for the improvement of separation factors of aromatics over aliphatics. The crosslinked membranes displayed higher PV separation factors and lower specific permeation fluxes than the corresponding uncrosslinked ones.
3. The introduction of TCNE to DSDA-TrMPD/DEB (3/1) copolyimide membrane greatly increased the separation factors of aromatic over cyclic and branched aliphatic hydrocarbons, although the specific permeation fluxes decreased.
4. The improvement in separation factor of thermally crosslinked membranes was mainly due to the increase in diffusivity selectivity rather than solubility selectivity, whereas for the TCNE-addition method both the increases in solubility selectivity and diffusivity selectivity contributed to the increase in PV separation factor.
5. The introduction of TCNE to DEB-containing copolyimides was more effective on the improvement of PV separation factor of aromatics over aliphatics than the crosslinking method of this study.

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