

Synthesis and Characterization of Polyimides with Pendant Phosphonate Ester Groups

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ABSTRACT: A polyimide from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 2,4,6-trimethyl-1,3-phenylenediamine (TrMPD), which has less efficient packing of polymer chains and displays very high gas permeability, was methyl-brominated and then phosphorylated by the reaction of $-\text{CH}_2\text{Br}$ with triethyl phosphite. The degree of phosphorylation upto 200% (two phosphonate ester groups per repeating unit) was achieved. Phosphorylation increased the sorption amount of benzene but decreased that of cyclohexane. Phosphorylated polyimide membranes were crosslinked thermally and/or with diamine. The amine-crosslinked membranes with P content of 5.9–8.3 wt% have high performance of pervaporation of benzene–cyclohexane mixtures; for example, specific permeation flux of $10 \text{ kg } \mu\text{m m}^{-2} \text{ h}^{-1}$ and separation factor of 15 at 343 K and benzene composition in feed of 50 wt%.

KEY WORDS Polyimide / Chemical Modification / Pervaporation / Phosphorylation / Membrane / Benzene/Cyclohexane Separation /

Separation of aromatics from hydrocarbons is one of the separation processes in petroleum refining where membranes may offer significant impact. For application of membranes to this separation process, it is necessary to develop aromatic-permselective membranes with high performance.

In the last decades, many materials have been studied to aim at pervaporation (PV) of aromatic/non-aromatic hydrocarbon mixtures such as benzene/cyclohexane.^{1–10} The selectivity in the PV of these mixtures 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. For the high solubility selectivity, membranes should have high affinity for aromatic components and little affinity for the other components. However, excessive affinity for aromatics causes the significant swelling of the membranes and results in loss of the selectivity and mechanical strength. In the design of aromatic-permselective membranes, it is important to suppress the swelling in addition to enhancing the solubility to aromatics. Among the materials investigated by now, the highest performance has been reported for the membranes of polymer alloys of poly(styrene diethylphosphonate) (PS-P) and cellulose acetate (CA), that is, specific permeation flux, Ql , of $\sim 20 \text{ kg } \mu\text{m m}^{-2} \text{ h}^{-1}$ and separation factor of benzene over cyclohexane, $\alpha_{\text{Bz/CH}_6}$, of 12–40, depending on the phosphorylation degree, at 351 K and benzene composition in feed, x_{Bz} , of 50%.¹ This high performance was attributed to both diethylphosphonate groups with affinity to benzene and CA reducing the membrane swelling.

Polyimides with excellent thermal, chemical and mechanical stability have attracted much attention due to their practical use in gas separation and dehydration of alcohol liquid and vapor.^{11,12} However, most of the polyimides having good durability to organic liquids

are not permeable to them. Polyimide from 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA) and 2,4,6-trimethyl-1,3-phenylene diamine (TrMPD) has less efficient packing of polymer chains, and as a result displayed high permeability with low selectivity, that is, $Ql = 9 \text{ kg } \mu\text{m m}^{-2} \text{ h}^{-1}$ and $\alpha = 7$ at 323 K and $x_{\text{Bz}} = 50$ wt%. It is interesting to introduce functional groups with affinity to aromatics into this polyimide and to investigate the PV performance.

This paper deals with synthesis and characterization of BPDA–TrMPD polyimides having pendant phosphonate ester groups. Their PV properties to benzene/cyclohexane mixtures are also briefly described, and will be reported in detail elsewhere.

EXPERIMENTAL

Preparation of Polyimide

BPDA was used as acid dianhydride and TrMPD was used as diamine. They were purified by vacuum sublimation before use. The precursor polyamic acid was prepared at a concentration of 15 wt% solids by slow addition of a stoichiometric amount of BPDA to a mechanically stirred solution of TrMPD in *N,N*-dimethylacetamide (DMAc) under nitrogen at room temperature. The solution was stirred for about 6 h. The polyamic acid solution thus obtained was diluted with DMAc to 5 wt% and chemically imidized by addition of a mixture of acetic anhydride and triethylamine (4-fold molar quantity to base units of the polyamic acid). After stirring at room temperature for 1 h and then at 323 K for additional 2 h, the reaction solution was poured into methanol. The polyimide precipitated was washed several times with methanol and then purified by repeated reprecipitation from dichloromethane (DCM) solution into methanol. After dried *in vacuo*, the polyimide was kept in a desiccator.

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Bromination of Polyimide

Bromination of BPDA-TrMPD polyimide was carried out by the following four procedures, using bromine, *N*-bromosuccinimide (NBS), and 1,3-dibromo-5,5-dimethyl hydantoin (DBMH) as brominating reagents.

Procedure I. A 0.3 wt% solution of the polyimide in DCM was poured into a reaction flask with a condenser, which was set at a point 20 cm away from a 150 W W-halogen lamp. A 1 wt% solution of DBMH in DCM was added dropwise to the magnetically stirred and refluxing polyimide solution under illumination. The dropping speed was very slow in order to avoid formation of insoluble solid. With adding the DBMH solution, the reaction was continued until a trace of insoluble solid was formed. After concentrated to a half volume by evaporation of DCM, the reaction mixture was filtered off and poured into excess methanol, and the precipitated product was washed with methanol several times and then dried *in vacuo* at room temperature.

Procedure II. A given amount (0.5–2.0 g) of polyimide and 1.3–6 equivalent (eq.) of NBS or DBMH were dissolved in DCM in the reaction flask. The bromination was carried out by refluxing and magnetically stirring the reaction mixture under illumination for 3–12 h. Although some precipitate was formed in many cases, the reaction was continued for a preset time. The reaction mixture, concentrated to some extent if necessary, was poured into excess methanol together with the insoluble solid, and the precipitated product was washed with methanol several times and then dried *in vacuo* at room temperature.

Procedure III. 1.5 eq. of bromine was added dropwise within 90 min to a 0.5 wt% polyimide solution (300 ml) in 1,1,2,2-tetrachloroethane at 423 K. After the addition, the reaction mixture was refluxed for additional 6 h.

Procedure IV. 2.8 eq. of bromine was added dropwise within 90 min to a 0.5 wt% polyimide solution (300 ml) in 1,2-dichloroethane at 358 K under illumination from a 500 W high pressure Hg-lamp. After the addition, the reaction was continued for additional 6 h.

Phosphorylation of Brominated Polyimides

Triethyl phosphite (TEP) and trimethyl phosphite (TMP) were used as phosphorylation reagents. They were dried over sodium and distilled under reduced pressure before use. A 5 wt% solution of the brominated polyimide in *N*-methyl-2-pyrrolidone (NMP) was added dropwise within 0.5–1 h to a refluxing mixture of equal volumes of TEP or TMP and NMP under vigorous stirring. TEP or TMP was used by 5–10 equivalent to the bromine content of the polymer. The reaction mixture was refluxed for additional 2.5–2 h (total reaction time of 3 h), cooled to room temperature, and then poured into excess of cyclohexane. The precipitated product was washed with a mixture of ethanol and cyclohexane several times, and then purified twice by dissolution in DCM and reprecipitation with a mixture of ethanol and cyclohexane.

Membrane Preparation

Membranes with thickness of 20–50 μm were prepared by casting 5 wt% DCM solutions of the phosphorylated polyimides onto glass Petri dishes and evaporating the solvent slowly at room temperature for 3 h.

They were dried at 363 K for 10 h *in vacuo*. The membranes were then crosslinked by heat treatment at 473 K for 3 h *in vacuo* and/or by immersion in a 0.5 wt% aqueous solution of 1,2-diaminoethane at room temperature for 1.5 h.

Measurements

The ^1H NMR spectra were recorded on a JEOL 270 MHz spectrometer using DCM- d_2 , chloroform- d_1 , and dimethyl- d_6 sulfoxide (DMSO- d_6) as solvents.

The inherent viscosity η of the polymers was measured at 308 K and 0.5 wt% with a Ubbelohde viscometer.

Differential scanning calorimetry (DSC) was measured with a Seiko Instruments Inc. DSC-5200 thermal analyzer at a heating and cooling rate of 10 K min^{-1} . Dynamic mechanical spectra were measured with a Reometrics mechanical spectrometer (RSAII) at 1.0 Hz and a peak strain amplitude of 0.2 or 0.1%. Thermogravimetry was carried out in flowing He at a heating rate of 5 K/ min^{-1} and the evolved gases were simultaneously determined by mass spectroscopy.

PV experiments were carried out by an ordinary method at temperatures ranging from 323 to 351 K. The effective membrane area was 20 cm^2 . The down stream pressure was maintained below 130 Pa and the permeate was collected in a liquid nitrogen trap. Feed and permeate composition was analyzed by gas chromatography.

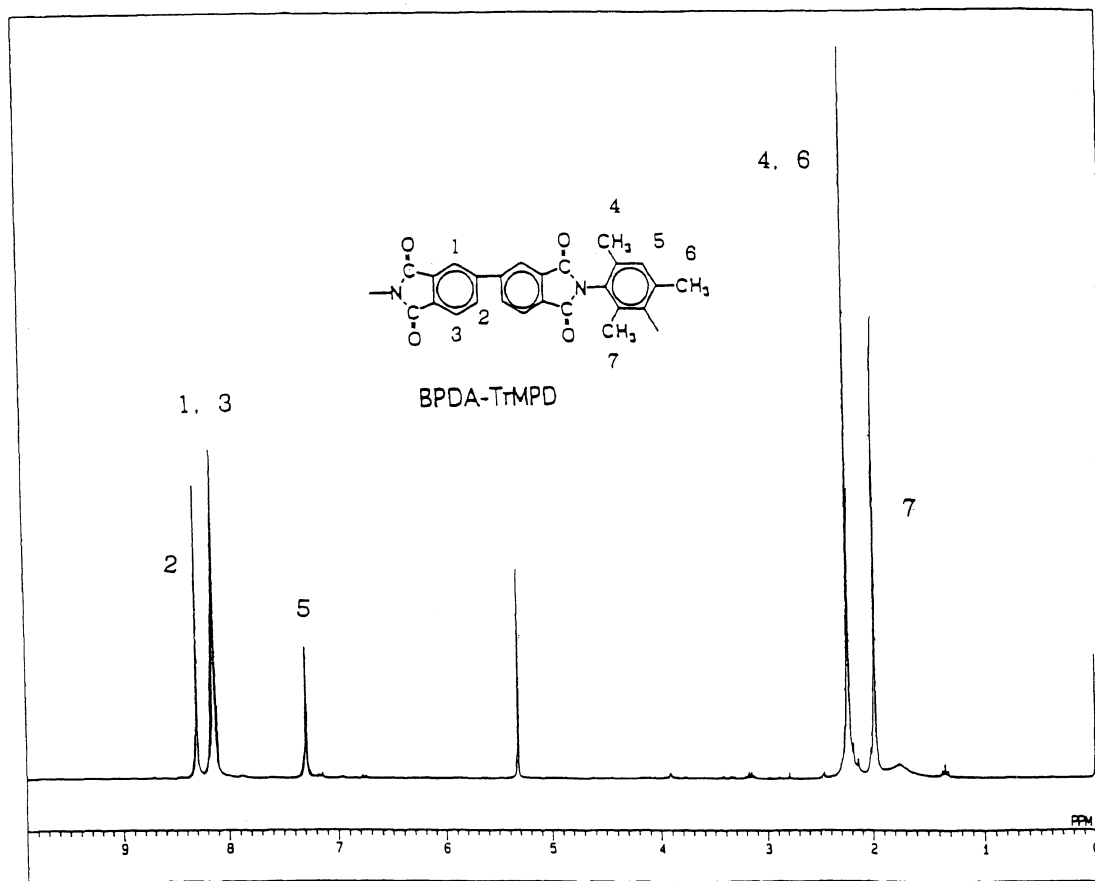
Sorption experiments were carried out by immersing membrane pieces of 0.1–0.2 g in benzene or cyclohexane at room temperature for 24 h. The membrane pieces were taken out, wiped with tissue papers, and weighed on a microbalance.

RESULTS AND DISCUSSION

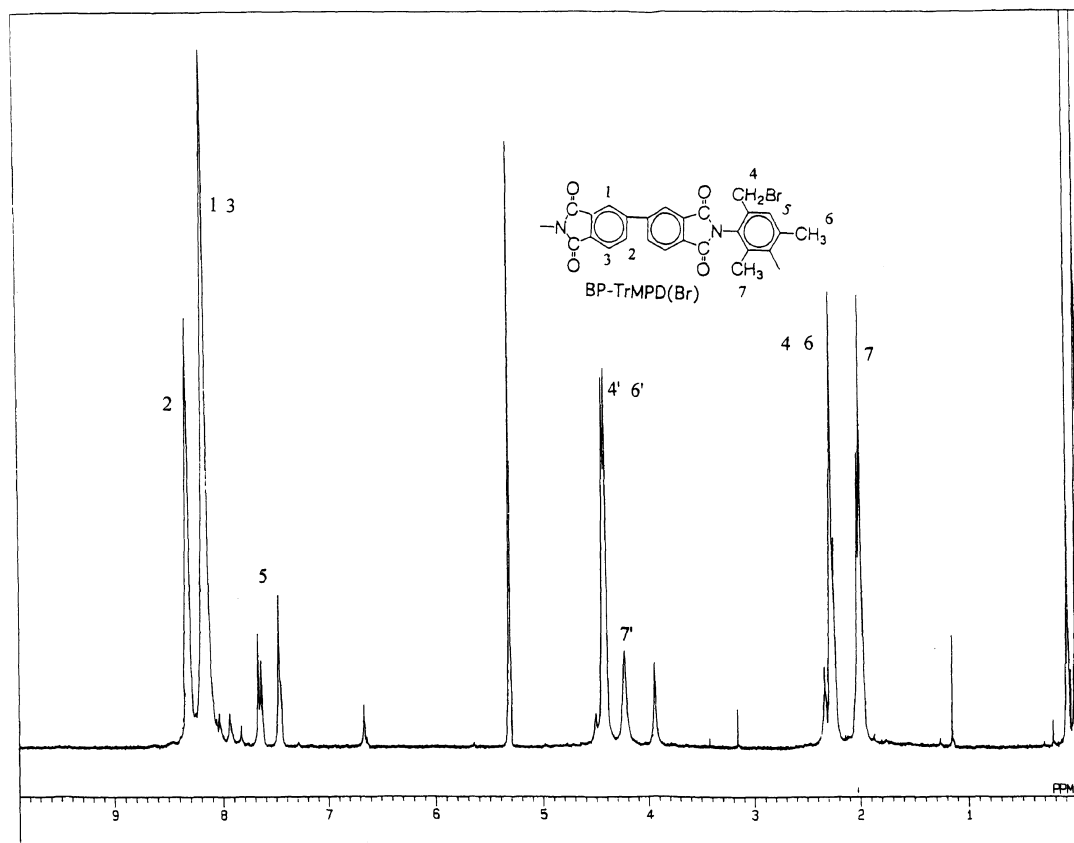
Bromination of Polyimide

The bromination conditions and results are listed in Table I. Figure 1 shows ^1H NMR spectra of BPDA-TrMPD polyimide and the brominated one (No. 2 in Table I), respectively. Each signal can be assigned as shown by the number in the figure. Methyl protons No. 4 and 6 appeared at 2.26 ppm and No. 7 at 2.03 ppm. Proton in $-\text{CH}_2\text{Br}$ No. 4' and 6' appeared at 4.45 ppm, and No. 7' at 4.25 ppm. Bromination yield was determined from the integral ratio of the signals at 4.25 and 4.45 ppm over the signals at 2.03 and 2.26 ppm. The bromination yield of 100% means that just one methyl group in a repeating unit of polyimide was brominated.

Experimental runs from No. 1 through No. 7 were done by procedure I and the other runs were done by procedure II. In the early stage of this study, we considered that the insoluble solids formed during the bromination reaction might be caused by crosslinking. Thus, in procedure I, the concentrations of polyimide and especially those of DBMH were maintained at lower levels. As a result, formation of the insoluble solids was reduced. However, the bromination yield was rather lower, in spite of larger excess of DBMH and longer reaction time, as compared with the procedure II. After the insoluble solids formed during the reaction were found to be soluble in NMP, most experiments were done by procedure II. In procedure II, the amount of



(a)



(b)

Figure 1. ^1H NMR spectra of (a) BPDA-TrMPD polyimide and (b) brominated polyimide (No. 2 in Table I) in DCM-d_2 .

Table I. Bromination and phosphorylation of polyimides^a

No.	Procedure	Bromination				Phosphorylation		
		Polymer		DBMH	Time	Yield	Yield	P-Content
		g	wt%	eq	h	%	%	wt%
BPDA-TrMPD								
1	I	0.5	0.3	3.5	7	174 ^b		
2	I	0.5	0.3	6	48	148		
3	I	0.5	0.3	1.5	15	113	104	5.9
4	I	0.5	0.3	5	37	147		
5	I	1.0	0.3	6	30	120 ^b	127	6.8
6	I	1.0	0.3	5	24		161	7.9
7	I	1.5	0.3	5	20		162	8.0
8	II	1.5	0.3	4	10	176 ^b	140	7.3
9	II	0.5	0.3	2	7		142	7.3
10	II	2.0	1.0	4	12		200	9.1
11	II	2.0	1.0	2	7		171	8.3
12	II	1.5	1.0	2	7	153	broad	
13	II	2.0	1.0	2	3		149	7.6
14	II	2.0	1.0	1.5	3	95	broad	
15	II	2.0	1.0	1.5	3	108	106	5.9
16	II	1.5	1.0	1.5	3		91	5.3
							73 ^d	4.6 ^d
17	II	1.5	1.0	3	3	157	155	7.7
18	II	1.5	0.5	2.2 ^c	5	68		
19	II	1.5	0.5	1.5	5	90		

^a The phosphorylation condition is the same as described in the experimental section. TEP was used. ^b Measured in DMSO-*d*₆ solution, because the sample was not completely dissolved in DCM-*d*₂. ^c NBS was used. ^d TMP was used.

the insoluble solid was usually 20–40%, but it reached up to 75% in No. 18. In No. 18, the inherent viscosity η values measured at 308 K and 0.5 wt% NMP solution were 0.39 and 0.97 dl g⁻¹ for the DCM soluble and insoluble products, respectively. This indicates that the slightly crosslinked product became insoluble in the reaction solution and as a result the heavy crosslinking did not occur.

The ¹H NMR spectra of the brominated polyimides prepared in procedure II were sometimes not measured, because of the insolubility in DCM-*d*₂. However, the bromination yield could be evaluated from the phosphorylation yield listed in Table I, because the phosphorylation of the brominated polyimides was almost completely achieved as mentioned below.

The bromination yield was hardly affected by the concentration of polyimide. It increased with an increase in DBMH; it ranged between 90 and 110% for DBMH of 1.5 eq. and between 140 and 170% for 2.0 eq., and reached up to 200% for 4 eq. The ratio of DBMH used effectively for bromination was the highest (~80%) around 2 eq., and decreased drastically above 3 eq. Comparison of the data among No. 9, 11, 12, and 13 shows that the reaction time of 3 h was long enough to give a high bromination yield in the case of DBMH of 2 eq. The polyimide samples having different bromination yield up to 200% (two methyl groups in one diamine moiety) were prepared by controlling the amount of DBMH.

DBMH was more effective than NBS and bromine. The thermochemical and photochemical bromination using bromine have been reported to be as effective as NBS for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).^{13,14} However, the thermochemical bromination such as procedure III gave little bromination of the

polyimide. The photochemical bromination such as procedure IV gave also much lower bromination yield than DBMH.

As can be seen from Figure 1(b), the bromination took place preferentially on methyl groups No. 4 and 6 rather than No. 7, because of the larger steric hindrance of the latter. The bromination ratio of methyl groups No. 4 and 6 over No. 7, which was evaluated from the integral ratio of the corresponding signals (4.45 ppm over 4.25 ppm), was in the range of about 3 to 5. It tended to be larger for the lower bromination yield.

Phosphorylation of Brominated Polyimides

Figure 2 shows ¹H NMR spectrum of phosphorylated polyimide No. 11. Each signal can be assigned as shown by the number in the figure. Protons in -CH₂P appeared at 3.0–3.2 ppm. Phosphorylation yield was determined from the integral ratio of the signals at 3.0–3.25 ppm over the signals at 2.03 and 2.26 ppm, and the values are listed in Table I. The signals of -CH₂Br remained slightly, indicating almost complete phosphorylation. The elemental analysis of the phosphorylated polyimides gave good agreement with the phosphorylation yields determined from ¹H NMR; for example, Calcd from ¹H NMR for No. 11: C, 59.66%; H, 4.93%; N, 4.37%; P, 8.26%; Found: C, 59.58%; H, 4.93%; N, 4.49%; P, 8.0%.

In the case of phosphorylation of active halide-containing polymers, an electron-donating polydentate etheral solvent such as diethyl carbitol is preferably used to prevent formation of insoluble gel by a crosslinking reaction.¹³ However, the brominated BPDA-TrMPD polyimides were insoluble in diethyl carbitol. Several solvents were tested. Dioxane gave a rather low conversion of about 50% because of the lower boiling point. NMP gave very high conversions without gelation. The

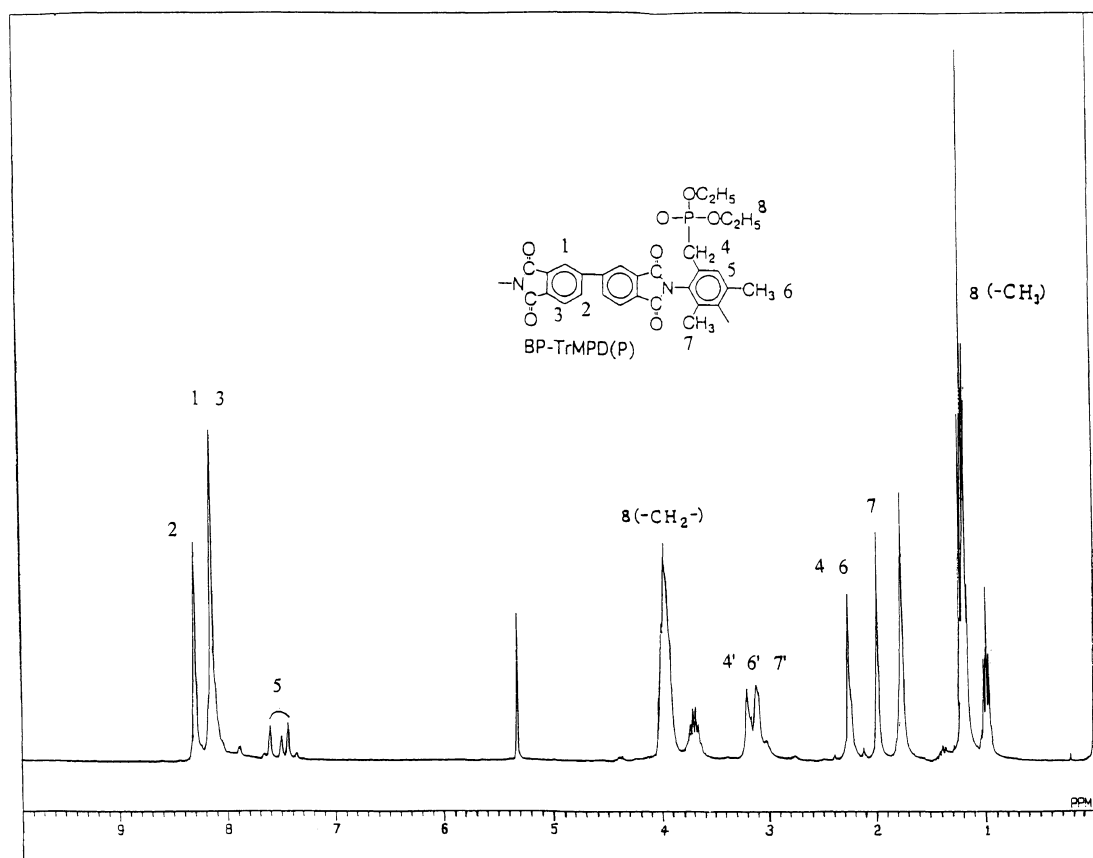


Figure 2. ¹H NMR spectrum of phosphorylated polyimide (No. 11 in Table I) in DCM-d₂.

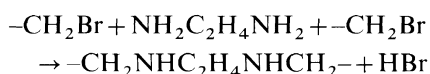
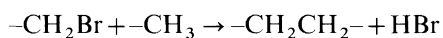
phosphorylation yields up to 200% was achieved. The η values were in the range of about 0.4 to 2 dl g⁻¹.

Characterization of Phosphorylated Polyimides

In DSC, two endothermic peaks were observed around 385 and 600 K. They were due to desorption of sorbed water and decomposition of ethyl ester group as mentioned below, respectively.

Figure 3 shows thermogravimetric (TG) curve of the phosphorylated polyimide No. 11. Weight loss took place at two stages; a sharp and large peak and a broad one in the differential TG curve were observed at 585 K and 695 K, respectively. The weight loss at the first stage amounted 17% at 623 K. The TG-MS analysis of the evolved gas gave prominent peaks at $m/z=28$ (C₂H₄), 27 (C₂H₃), 26 (C₂H₂) and weak peaks at $m/z=18$ (H₂O), 25, 31, and 45 (C₂H₅O) at the first stage, indicating the evolution of fragments from the ethyl ester group.

The phosphorylated BPDA-TrMPD polyimides (P-PIs) were soluble in many solvents such as tetrahydrofuran, NMP, DMAc, and DCM. Membranes of P-PIs were crosslinked by the reactions of unreacted -CH₂Br groups with methyl groups and/or 1,2-diaminoethane;



The crosslinking by the former reaction was achieved by heat treatment at 473 K, and hereafter is referred to as thermal crosslinking (TC). Some membranes were

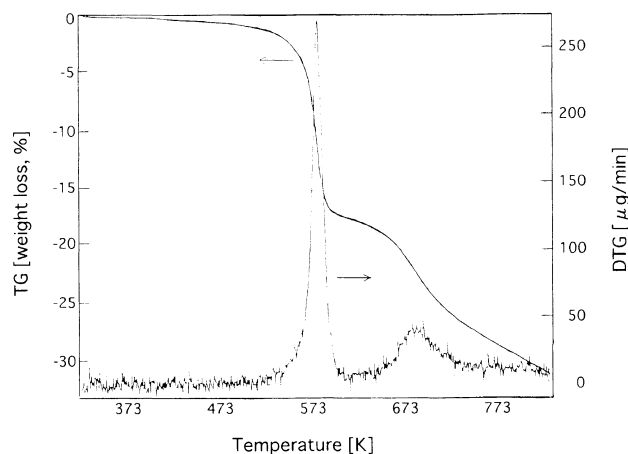


Figure 3. Thermogravimetric curves of phosphorylated polyimide No. 11 (TAC).

crosslinked thermally and then with the diamine. This is referred to as thermal and amine crosslinking (TAC). By the crosslinking, the membranes became insoluble in the solvents and their density decreased as listed in Table II because of loss of bromine. The residual amount of -CH₂Br group in P-PIs was in the range of 3% (No. 11) to 7% (No. 7), and the crosslinking level was rather low.

Figure 4 shows dynamic mechanical spectra of P-PI No. 11 (TAC). Young's modulus E' increased suddenly at about 570 K. This is probably due to a crosslinked network formed simultaneously with the decomposition of the ethyl ester group.¹³ Polyimides have three different relaxations labeled α , β , and γ in the order of decreasing

Table II. Physical properties of the phosphorylated polyimide membranes^a

Membranes	Density	δ	S_{Bz}	S_{CHx}
	$g\ cm^{-3}$			
BPDA-TrMPD	1.241	32.6	60	10
No. 15 (P=5.9%)	1.327	27.6	34	2.4
No. 15 TC	1.287			
No. 15 TAC	1.267			
No. 17 (P=7.7%)	1.319	26.2	200	3.3
No. 17 TC	1.308		40	
No. 17 TAC	1.300		14	1.0
No. 7 TC (P=8.0%)	1.300	26.1	44	2.0
No. 11 TAC (P=8.3%)	1.296	25.9	19	1.0

^a δ is solubility parameter.¹⁶

Table III. Membrane performance toward PV of Bz/CHx system

Membranes	l	X_{Bz}	T	Ql	$\alpha_{Bz/CHx}$	Ref
	μm	wt%	K	$kg\ \mu m\ m^{-2}\ h^{-1}$	—	
P-PI No. 11 (P=8.3%, TAC)	30	50	343	2.5	20	this
P-PI No. 17 (P=7.7%, TAC)	47	50	343	9.9	15	this
P-PI No. 15 (P=5.9%, TAC)	38	50	343	7.9	13.4	this
BPDA-TrMPD	44	50	323	9.1	7.1	7
BPDA-TrMPD/PD (1/1)	10	50	343	2.7	14	7
BPDA-TrMPD/PD (3/1)	31	50	343	5.4	10	7
Alloy of PS-P (P=6.1%)/CA (1/1)	20	55	351	20	12	1
Alloy of PS-P (P=10.5%)/CA (1/1)	20	55	351	24	40	1
Alloy of PPOBr P(P=10.1%)/CA (1/1)	20	55	327	4.0	9.7	2
Alloy of VC-StP (P=6.5%)/CA (1/1)	20	55	351	16	9.0	17

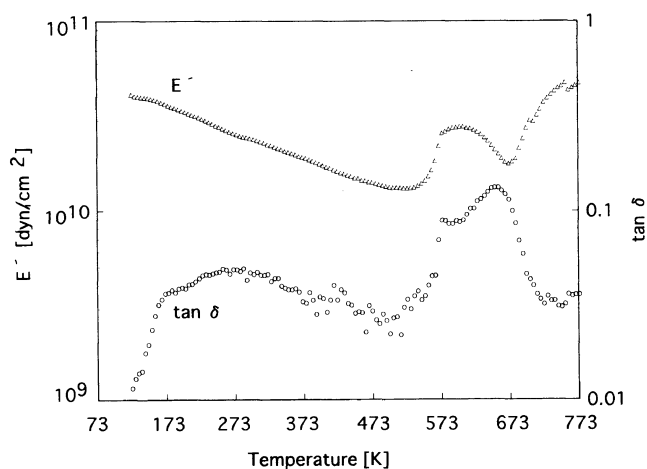


Figure 4. Dynamic mechanical spectra of phosphorylated polyimide No. 11 (TAC).

temperature.¹⁵ BPDA-TrMPD polyimide shows α , β , and γ relaxation peaks around 660, 450, and 170 K, respectively, and broad bottom between β and γ peaks. On the other hand, the phosphorylated polyimide shows a strong and broad relaxation in the temperature range below 373 K. This is most likely a composite of ordinary β and γ relaxations and another γ' relaxation superimposed between them. The γ' relaxation around 250 K is probably due to local motion of pendant phosphonate ester groups.

Pervaporation Properties

The sorption amounts of benzene and cyclohexane,

S_{Bz} and S_{CHx} , respectively, in P-PI membranes are listed in Table II. The S_{Bz} value of the uncrosslinked membrane of P-PI No. 17 was three times larger than that of BPDA-TrMPD polyimide, whereas the S_{CHx} value of the former was a third of the value of the latter. The S_{Bz} for P-PIs decreased more largely by the crosslinking, especially TAC, as compared with S_{CHx} . As a result, the ratio, S_{Bz}/S_{CHx} , decreased by the crosslinking, but it was still much larger for TAC membranes of P-PIs than for BPDA-TrMPD polyimide, indicating high affinity of phosphonate groups for benzene. The introduction of the phosphonate groups decreases the solubility parameter δ and simultaneously increases the relative contributions of hydrogen-bonding and polar forces among the solubility parameter components.¹⁶ This may be the reason of the larger solubility ratio S_{Bz}/S_{CHx} for the membranes of P-PIs.

The TAC membranes of P-PIs were conditioned by the procedure, where the PV experiment was done with benzene at 343 K until achieving the steady-state permeation. When stopping the PV experiments after the conditioning, the membranes were kept in a swollen state by keeping them in contact with a feed solution of $x_{Bz} = 10\text{--}50\%$. PV performance hardly deteriorated for a long period compared with the original fluxes and separation factors, indicating high durability of the TAC membranes to Bz/CHx mixtures.

Table III lists membrane performance toward PV at x_{Bz} of 50–60 wt% for the TAC membranes of P-PIs as compared with that of the membranes of base polyimides and alloys of other phosphorylated polymers with CA. As compared with the base polyimides such as BPDA-

TrMPD and its copolyimides with *p*-phenylene diamine (PD), BPDA-TrMPD/PD, the TAC membranes of P-PIs with P content of 5.9–8.3 wt% have higher PV performance, that is, the higher values of separation factor $\alpha_{\text{Bz/CH}_x}$ and the similar values of specific permeation flux Q_l . This is clearly due to the higher solubility selectivity judging from the sorption data. The PV performance of the P-PI (TAC) membranes is higher than that of the polymer-alloy membrane of phosphorylated PPO (PPOBrP) and CA, whereas it is rather lower than that of the membranes of PS-P and CA.

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