

# Dehydration of Benzene Through Fluorine Containing Aromatic Polyamide Membrane by Pervaporation

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**ABSTRACT:** A series of soluble polyamides were synthesized by direct polycondensation of the 5-*tert*-butyl isophthalic acid with different diamines. Solution (20%) of the polymers in suitable solvents was used to cast the membranes. The membranes showed selectivity toward the benzene (Bz) in a mixture of Bz/water (H<sub>2</sub>O). Water affinity of the membrane was found to be lower than that of Bz. The polyamide incorporating hexafluoro isopropylidene moiety was promising for the dehydration of Bz and breaking of Bz/H<sub>2</sub>O azeotrope. The polymers exhibited inherent viscosities, ranging from 0.40 to 0.92 dL/g

and 10% weight loss in synthetic air up to 474°C. Glass transition temperature measured by DSC and DMA reached up to 258°C. The membranes were pale yellow in appearance having tensile strength up to 85 MPa, modulus of elasticity up to 2.6 GPa, and elongation at break up to 9.5%, depending upon the exact repeating unit structure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 203–209, 2008

**Key words:** polyamides; membranes; pervaporation; azeotropes; thermal stability

## INTRODUCTION

Benzene (Bz) is an important solvent and raw material. It is used not only as a component or a solvent of fuels, but also as a raw material in the production of fuels, medicines, and fine chemicals.<sup>1</sup> During the application of Bz, it is often necessary to remove water from it to avoid deactivation of catalyst or/and corrosion of equipment. For example, in the production of isopropyl benzene with Bz and propylene, the water content in Bz must be reduced to lower than 50 ppm for either aluminum trichloride or solid-acid as catalyst.<sup>2</sup> Another example is the production of long straight chain alkylbenzene (C10–C14) with Bz and dodecene. In this process, it is necessary to reduce the water content to lower than 20 ppm for either hydrogen fluoride or crystalline silica aluminate as catalyst.<sup>3</sup> The present processes for dehydration are still distillation or absorption. However, these processes show some disadvantages. For example, the still distillation needs high-energy consumption, and the absorption has operation difficulty, high-energy consumption as well as environmental pollution.

In the recent years, pervaporation (PV) has emerged as an economical and easy-to-operate replacement of the traditional processes for the re-

moval of organics from water and organic–organic separations azeotrope separation.<sup>4–7</sup>

This process is especially attractive in the azeotropic and close-boiling point-mixture separations and the removal of small amount of water from organics. The separation mechanism in PV is not based on the relative volatility of components as distillation process, but the difference in the sorption and diffusion properties of the feed substances in PV membranes.

The efficiency of the PV process depends mainly on the intrinsic properties of the polymer used to prepare the membrane. Therefore, designing membranes with a high permeation rate and separation factor is an important issue. Wholly, aromatic polyamide is a potential thermoplastic material for PV because of its attractive combination of chemical, physical, and mechanical properties. However, the poor solubility and high softening or melting temperatures caused by their high crystallinity and high stiffness of the polymer backbone makes them difficult to process into membranes of these aramids. Attempts to increase the solubility of aromatic polymers have been made through the incorporation of flexible links to the main chain<sup>8</sup> or by the replacement of symmetrical aromatic rings by the unsymmetrical ones,<sup>9,10</sup> which leads to the decrease in crystallinity. Considerable attention has been devoted to the preparation of fluorine-containing condensation polymers because of their unique properties and high performance.<sup>11,12</sup> Several researchers<sup>13–15</sup> reported that solubility is improved with the incor-

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poration of hexafluoroisopropylidene groups between two rigid phenyl rings in the polymer backbone.<sup>16,17</sup> The introduction of the fluorine into polymers can affect many properties, in technologically desired directions. This includes higher thermal stability,<sup>18</sup> low moisture absorption,<sup>19</sup> optical transparencies, and low dielectric constant.<sup>20</sup>

The increase of the solubility by the introduction of bulky pendant group into the polymer backbone<sup>21</sup> such as 5-*t*-butyl isophthalic acid is also reported. These reports prompted us to synthesize a series of polyamides by the polycondensation of 5-*t*-butyl isophthalic acid with various diamines containing moieties such as hexane, bisphenol-A, hexafluorobisphenol-A, diphenyl sulfone, diphenyl ether, and hydroquinone. A detailed characterization of the readily soluble polyamides has been done, and PV properties of the polymers were evaluated for Bz/H<sub>2</sub>O system.

Dehydration by the PV has become an important industrial application for PV. The pervaporative characteristics of poly(ethylene)-*co*-vinyl acetate were examined using acetone/chloro hydrocarbon mixtures.

In this article, we have also studied the pervaporative characteristics of synthesized poly(etheramide)s membranes with special reference to hexafluoroisopropylidene-based polyamide membrane for the separation of Bz from Bz/H<sub>2</sub>O system at variable concentration and at azeotropic composition also.

## EXPERIMENTAL

### Characterization of the polymers

Elements, carbon and hydrogen, were analyzed by Prejel method, and nitrogen was analyzed by Kjeldahl method. <sup>1</sup>H NMR was recorded on 400 MHz Bruker Avance DPX NMR instrument, reference 0 ppm with TMS. IR spectra were recorded with a Bruker IFS 55 spectrophotometer with KBr pellets. DSC measurements were made on a TA Instruments DSC-2920 instrument at a heating/cooling rate of 20°C/min under nitrogen. Glass transition temperature ( $T_g$ ) was taken at the midpoint of the step transition in the second heating run. Thermogravimetry was measured on a TA Instruments thermogravimetric analyzer, Model TGA-2950. A heating rate of 10°C/min was used for the determination of the decomposition temperature ( $T_d$ ) at 5% weight loss under synthetic air. Dynamic mechanical analysis (DMA) was performed on a Netzsch, DMA-242 instrument in the tension mode on thin film (80–100 μm) samples with a heating rate of 5°C/min (10 Hz). Mechanical properties of thin polymer membranes were evaluated at room temperature on a Miniature Materials Tester, Rheometric Science, under a strain rate of 5%/min.

### Materials

All reagents were purchased from Lancaster, Acros, Aldrich, or Fluka Chemical Company and used as received unless otherwise noted. NMP (Fluka) and DMF (E. Merck, India) was purified by stirring with NaOH and distilled twice from P<sub>2</sub>O<sub>5</sub> under reduced pressure. The diamino monomers were prepared according to the reported literature procedure.<sup>22</sup> The reagents used for PV and sorption such as Bz used in this study was of HPLC grade.

### Preparation of the polymers

The polyamides were prepared by direct polymerization of 5-*tert*-butyl isophthalic acid with various diamines in NMP by using triphenyl phosphate as condensing agent and pyridine as base. A mixture of 5-*t*-butyl isophthalic acid (0.555 g, 25 mmol), diamines (25 mmol), calcium chloride (0.36 g), NMP (5 mL), pyridine (1.4 mL), and triphenyl phosphite (TPP, 1.4 mL) was heated at 80–90°C for 5–6 h under nitrogen atmosphere with stirring. The viscous polymer solution was precipitated in excess of methanol with stirring. The precipitated polymer was washed thoroughly with methanol and hot water and then dried at 100°C under vacuum.

### Preparation of membranes

Solution (20%) of individual polymer in suitable solvent was cast onto a glass petridishes at ambient conditions, followed by drying under vacuum at 80°C to complete the evaporation of solvent. The membrane was gently peeled off from the mold after cooling to 10°C.

### Determination of sorption

Dry membranes of predetermined weight ( $W_d$ ) were immersed in Bz and water separately at 30°C ± 1°C for 72 h to allow them to attain equilibrium sorption. The specimens were removed from the container and quickly wiped with tissue paper to remove the superfluous liquid. The weight of swelled membrane,  $W_s$  was recorded on Shimadzu balance with an accuracy of  $1 \times 10^{-4}$  g. The average of three measurements was taken to determine the extent of sorption<sup>4–7</sup> also called swelling index ( $Q$ ) as per the equation given below.

$$Q = (W_s - W_d) \times 100/W_d \quad (1)$$

where  $W_s$  is the weight of the membrane swelled in Bz or water and  $W_d$  is the dry weight of the membrane.

### Sorption isotherms

The sorption isotherms for Bz and H<sub>2</sub>O were determined using an automated sorption analyzer termed intelligent gravimetric analyzer (IGA) procured from M/s Hiden Analytical, England. The instrument (Hiden Analytical, document number HA-085-060 issue A) is based on the principle of mass relaxation in the polymer accompanying vapor sorption. The concentration ( $P/P_0 \sim$  activity or concentration) of the vapors was increased in 14–16 equal steps at constant temperature of 30°C + 1°C, and the corresponding increase in weight of the sample was monitored to obtain the sorption, which were fitted into appropriate sorption models<sup>23</sup> and converted to the isotherms by the system software.

### PV studies

The pervaporation (PV) experiments were carried out at 30°C + 1°C using a batch-stirred reactor described by Natke et al.<sup>24</sup> The effective membrane area was 29.40 cm<sup>2</sup>. The membrane was supported on a filter paper over a porous-sintered steel disc 6.4 cm in diameter. Before PV, the membrane was allowed to equilibrate with the feed solution for 24 h. After the attainment of steady state, the permeate was condensed in cold traps immersed in liquid nitrogen. The permeate composition was determined by gas chromatography equipped with thermal conductivity detector maintained at a temperature of 90°C and OV-17 (3 wt %, 100–120 meshes) stainless steel column [1.8288 m (6 ft) × 0.3175 mm (1/8 in) × 2 mm] at a temperature of 30°C. The injector was kept at 90°C. The downstream pressure was maintained at 1 mm Hg in all experiments. The flux ( $J$ ) was determined by measuring the weight of the permeate, and using the equation<sup>4–7</sup>

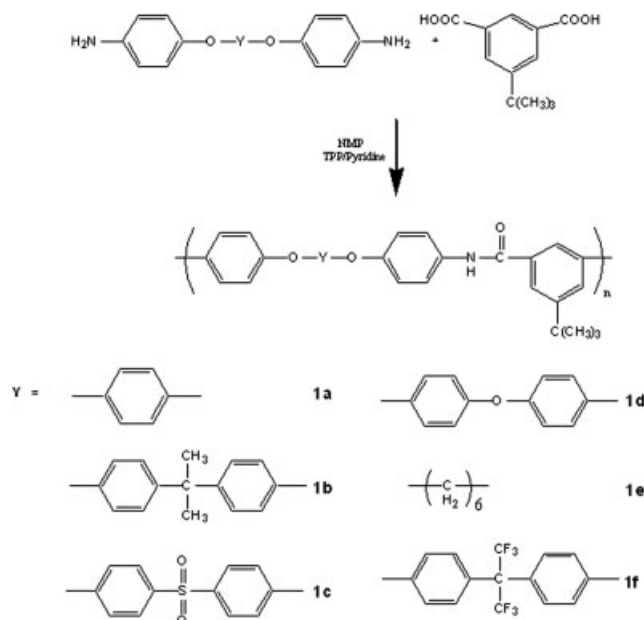
$$J = w/Ah \quad (2)$$

where  $A$  is the effective membrane area and  $h$  is the time for the PV. The normalized flux ( $J'$ ) was obtained from the product of flux and thickness (in micrometer) of the membrane.<sup>25</sup>

The permeation selectivity ( $\alpha_p$ ) was calculated using the following equation

$$\alpha_p = \frac{Y_{\text{benzene}}/Y_{\text{water}}}{X_{\text{benzene}}/X_{\text{water}}} \quad (3)$$

where  $Y$  and  $X$  are the weight of water and species in the feed and permeate, respectively.



Scheme 1 Synthesis of polyamides.

## RESULTS AND DISCUSSION

### Characterization of the fluorine-containing polyamides

Various poly(etheramide)s were synthesized as per reported method.<sup>22</sup> Two synthetic methods are available for the preparation of polymers of a moderate or large molar mass: polycondensation at low temperature (< 100°C) and direct polycondensation in solutions using phosphates, especially in the presence of metal salts.<sup>26</sup> Most aramids are synthesized by solution polycondensation, at low temperatures by reacting aromatic diacid chloride with aromatic diamine in polar aprotic solvents. Direct polycondensation of aromatic diamines with aromatic dicarboxylic acids in the presence of TPP and pyridine as condensation agent is a convenient method for the preparation of aromatic polyamides.<sup>9,10,27</sup> We used this method in present synthesis. The reaction scheme and the structures of the polymers are shown in following Scheme 1.

#### Polymer 1a

Analysis: Calculated for (C<sub>30</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub>), (478 g/mol); C, 75.31; H, 5.43; N, 5.85; found: C, 75.20; H, 5.39; N, 5.79; IR (KBr): 3352 (N—H), 1659 (C=O) <sup>1</sup>H NMR: (DMSO-*d*<sub>6</sub>): δ(ppm) 10.47 (2H, s, —NH); 7.0–8.6 (15H, m), 1.29 (9H, s, —CH<sub>3</sub>). Yield 96–97%.

#### Polymer 1b

Analysis: Calculated for (C<sub>39</sub>H<sub>36</sub>O<sub>4</sub>N<sub>2</sub>), (596 g/mol); C, 78.52; H, 6.06; N, 4.69; found: C, 78.31; H, 6.10; N,

**TABLE I**  
Inherent Viscosities, Film Quality, and Water Absorption of Polyamides

Polymer	Yield	$\eta_{inh}$ (dL/g)	Film quality	Thickness of the membrane ( $\mu\text{m}$ )
1a	98	0.574	Flexible	88.0
1b	95	0.406	Flexible	98.0
1c	96	0.590	Flexible	83.0
1d	95	0.480	Flexible	94.0
1e	98	0.920	Flexible	84.0
1f	97	0.612	Flexible	82.0

4.53; IR (KBr): 3359 ( $N-H$ ), 1653 ( $C=O$ )  $^1H$  NMR: (DMSO- $d_6$ ):  $\delta$ (ppm) 10.50 (2H, s,  $-NH$ ); 6.7–8.5 (19H, m), 1.43 (9H, s,  $-CH_3$ ), 1.48 (6H, s,  $CH_3$ ).

#### Polymer 1c

Analysis: Calculated for ( $C_{36}H_{30}O_6N_2S$ ), (618 g/mol); C, 69.90; H, 4.85; N, 4.53; found: C, 69.78; H, 4.71; N, 4.50; IR (KBr): 3354 ( $N-H$ ), 1653 ( $C=O$ )  $^1H$  NMR: (DMSO- $d_6$ ):  $\delta$ (ppm) 10.52 (2H, s,  $-NH$ ); 6.7–8.3 (19H, m); 1.35 (9H, s,  $-CH_3$ ).

#### Polymer 1d

Analysis: Calculated for ( $C_{36}H_{30}O_5N_2$ ), (570 g/mol); C, 75.78; H, 5.26; N, 4.91; found: C, 75.67; H, 5.18; N, 4.73; IR (KBr): 3357 ( $N-H$ ), 1665 ( $C=O$ )  $^1H$  NMR: (DMSO- $d_6$ ):  $\delta$ (ppm) 10.52 (2H, s,  $-NH$ ); 6.8–8.6 (19H, m); 1.31 (9H, s,  $-CH_3$ ).

#### Polymer 1e

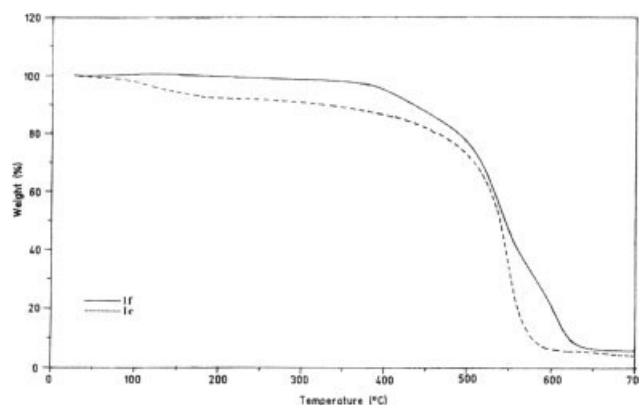
Analysis: Calculated for ( $C_{30}H_{34}O_4N_2$ ), (486 g/mol); C, 74.00; H, 6.99; N, 5.76; found: C, 73.86; H, 6.88; N, 5.69; IR (KBr): 3359 ( $N-H$ ), 1651 ( $C=O$ )  $^1H$  NMR: (DMSO- $d_6$ ):  $\delta$ (ppm) 10.32 (2H, s,  $-NH$ ); 6.7–8.1 (11H, m); 3.9 (4H, t, 1.31), (9H, s,  $-CH_3$ ), and 1.8 (m, 8H,  $CH_2$ ).

#### Polymer 1f

Analysis: Calculated for (704 g/mol)  $C_{39}H_{30}N_2O_4F_6$ : C, 66.48; H, 4.29; N, 3.98. Found: C, 64.89%; H, 4.31%; N, 3.94%; IR (KBr): 3314 ( $N-H$ ), 1659 ( $C=O$ )

**TABLE II**  
Thermal Properties of the Polyamides

Polymer	$T_g$ ( $^{\circ}C$ )		10 % weight loss temp. ( $^{\circ}C$ )
	DSC	DMA (tan $\delta$ )	
1a	191	200	391
1b	195	207	433
1c	224	241	432
1d	220	240	392
1e	157	175	358
1f	253	258	474



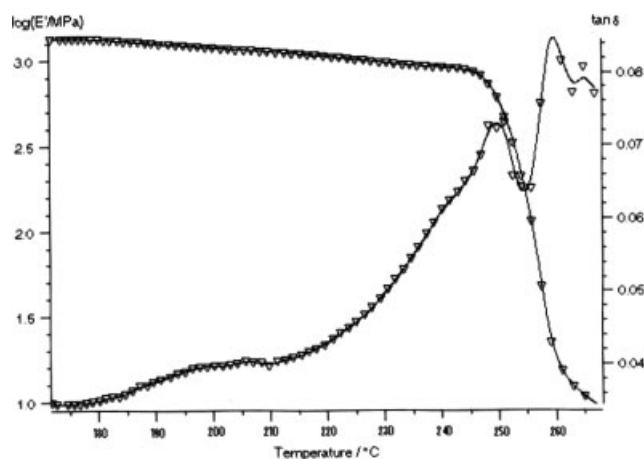
**Figure 1** TGA plot of polymer 1e and 1f.

$^1H$  NMR: (DMSO- $d_6$ ): 10.52 (2H, s,  $-NH$ ); 7.1–8.5 (19H, m); 1.31 (9H, s,  $CH_3$ ).

The polyamides were obtained in almost quantitative yield with inherent viscosities 0.406–0.92 dL/g (Table I). The polymers synthesized were analyzed by FTIR,  $^1H$  NMR, and elemental analysis. The IR spectra showed characteristic amide absorptions  $\sim 3310$  and  $1660\text{ cm}^{-1}$ , corresponding to amino and carbonyl groups, respectively. The  $^1H$  NMR spectra showed a sharp singlet around 10.5 ppm corresponding to the amide proton. Detailed analytical data are provided in the Experimental section.

#### Polymer properties

The solubility of polyamides was tested in various solvents at room temperature. All polyamides were soluble in polar aprotic solvents such as DMF, DMAc, NMP, and DMSO. Their highly soluble nature is attributed to the introduction of bulky *t*-butyl group in polymer backbone.<sup>9,10,28</sup> This pendant bulky *t*-butyl group is also responsible for enhanced solubility.



**Figure 2** DMA plot of polymer 1f.

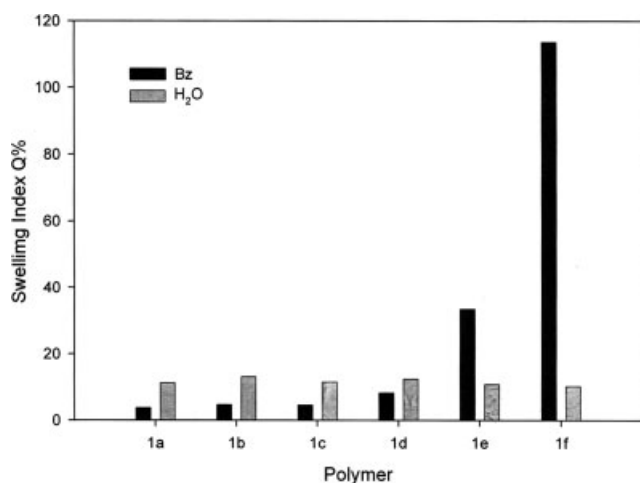
**TABLE III**  
Mechanical Properties of the Polyamides

Polymer	Tensile strength (MPa)	Initial modulus (GPa)	Elongation at break (%)
1a	66	1.35	6.6
1b	62	1.80	5.0
1c	78	1.80	9.5
1d	85	2.6	4.0
1e	48	1.9	5.2
1f	63	1.9	8.0

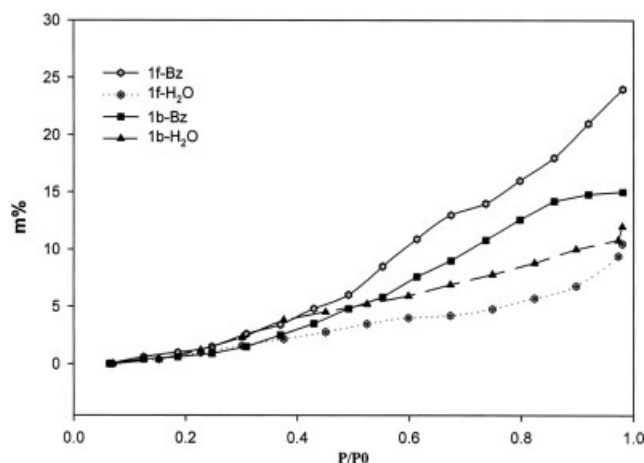
Thermal behavior and glass transition temperatures ( $T_g$ ) of the polymers were evaluated by TGA, DMA, and DSC means, respectively. The values are summarized in Table II. The TG curves of these polymers indicated that no loss of mass of polymers occurs below 358°C. Representative TGA plot for polymers 1e and 1f is shown in Figure 1. The lowest thermal stability of 1e is due to the presence of oxidizable aliphatic unit in the polymer backbone.

DSC measurements were conducted at 20°C/min heating rate in nitrogen atmosphere, and second heat scans were used to evaluate glass transition temperature (Table II). In general, the polymers exhibited high glass transition temperature. Highest glass transition temperature was observed for 1f, which may be due to its rigid structure.

Glass transition temperature of the series was also evaluated by DMA. The  $\tan \delta$  peak values at 10 Hz for these polymers are 5–25°C higher than the DSC  $T_g$  values. Representative DMA plot for polymer 1f is shown in Figure 2. Transparent, tough, and flexible polymeric membranes were obtained by casting from their DMF solutions. Tensile properties of the polymers are summarized in Table III. The polymers showed a tensile strength up to 85 MPa, initial modulus 2.3 GPa, and elongation at break up to 9%



**Figure 3** Swelling index of different polymers in Bz and H<sub>2</sub>O.



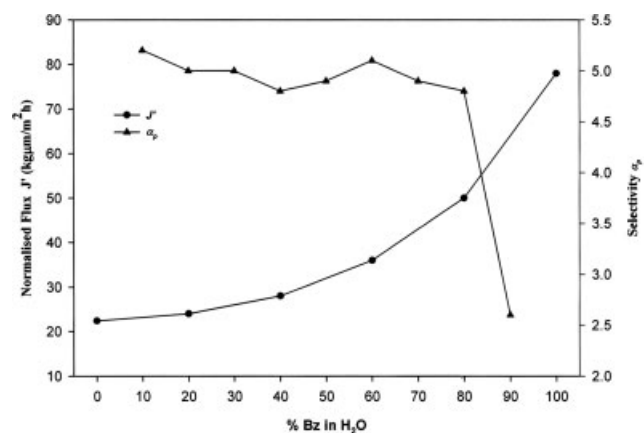
**Figure 4** Sorption isotherm for Bz and H<sub>2</sub>O vapors on 1f and 1b at 30°C. Sorption data is shown in the table;  $P$ , pressure (mbar);  $P_0$ , saturation vapor pressure (mbar);  $P/P_0$ , relative pressure  $\approx$  activity or concentration;  $w$ , weight of sample;  $m$ , mass uptake of vapors (%).

ulus 2.3 GPa, and elongation at break up to 9% depending on the exact repeat unit structure.

#### PV characteristic of membranes

The degree of sorption calculated using eq. (1) indicated that the membrane 1f has highest sorption of Bz and lowest sorption of water when compared with other membranes (Fig. 3). This might be due to the higher fluorine content in 1f, which increases the hydrophobic character of the polymer.

The above observations on the sorption characteristics of 1f membrane are also supported by vapor sorption isotherms for Bz and water using the automated sorption analyzer IGA. The isotherms plotted in Figure 4 provide the dynamics and magnitude of sorption over entire  $P/P_0$  (corresponding to concen-



**Figure 5** Normalized flux and selectivity at 30°C + 1°C as a function of feed composition.

**TABLE IV**  
**Solubility Parameter ( $\delta$ ), Molar Free Volume ( $\Sigma V$ ), Fedor Free Volume ( $\Sigma F$ ) and Density ( $\rho$ ) of Polymers and Permeants**

Code	$\delta$ ( $\text{cal}^{1/2}/\text{cm}^{3/2}$ )	$\Sigma V$ (cc/mol)	$\Sigma F$ (cc/mol)	$\rho$ at 25 °C	$\Delta\delta_1 =$ $\delta_{1f} - \delta_{\text{permeant}}$	$\Delta\delta_2 =$ $\delta_{1f} - \delta_{\text{permeant}}$
1b	14.79*	–	291.3	0.81**	–	–
1f	11.76*	–	436.0	0.78**	–	–
Bz	9.17	89.4	–	0.87	2.59	5.62
H <sub>2</sub> O	23.4	18.0	–	0.9970	11.64	8.61

\* Calculated by the small method.

\*\* Estimated by froth floatation method.

tration or activity) ranges from 0.06 to 0.98. The isotherm for pure Bz lies toward the ordinate and for water toward the abscissa, implying that 1f-Bz interaction is higher than those of 1f-water for any concentration. This results in almost 2–2.5 times higher vapor sorption of water than Bz.

1f membrane was also investigated for Bz flux and selectivity in the entire range of Bz/water feed compositions (Fig. 5). The normalized flux values increased with amount of Bz in the feed, varying from 22.4 kg  $\mu\text{m}/(\text{m}^2 \text{ h})$  for pure water to 50.0 kg  $\mu\text{m}/(\text{m}^2 \text{ h})$  for 80% Bz. For pure Bz, the flux reached a value of 78.0 kg  $\mu\text{m}/(\text{m}^2 \text{ h})$ . The separation factor varied in between 5.2 and 4.8 with the feed Bz concentration up to 80% and then decreased to 2.6 at 90% Bz. This might be due to its swelling-induced plasticization or azeotrope formation in this region. Bz tends to plasticize the 1f membrane, the relaxed polymer chains, thus becoming accessible to water molecules as well, thereby reducing the selectivity.

To discuss the PV performance of 1f membrane in more detail, the solubility parameter and molar volume of each component were calculated, and the relationship between the Bz/water selectivity was investigated. The solubility parameter of each component calculated by the group contribution method<sup>29</sup> and the difference in the solubility parameter between the membrane and the permeants are

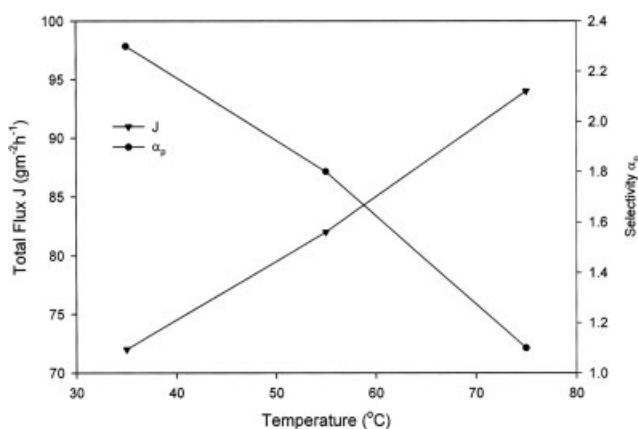
shown in Table IV. The difference in the solubility parameter ( $\Delta\delta$ ) was calculated from the solubility parameter of permeant (Bz or H<sub>2</sub>O) and the membrane ( $\delta_{\text{membrane}}$ ) using eq. (4):

$$\Delta\delta = |\delta_{\text{membrane}} - \delta_{\text{permeant}}| \quad (4)$$

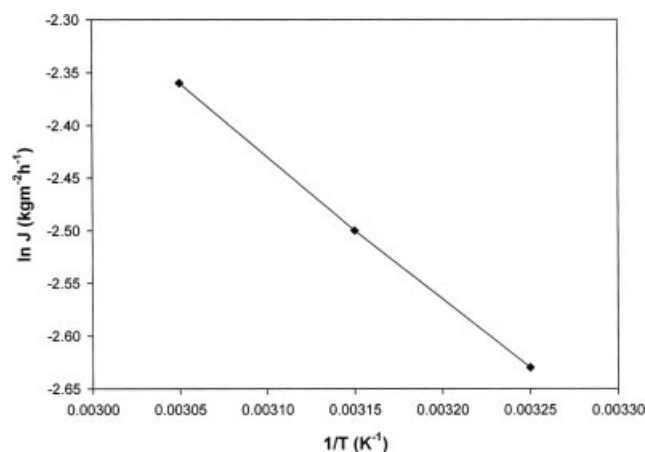
A small  $\Delta\delta$  means that the membrane has a strong affinity for the species. From the table, it is clear that membrane 1f has stronger affinity towards Bz when compared with H<sub>2</sub>O.

#### Temperature dependence of flux and selectivity

The PV process is known to be temperature dependent<sup>29–31</sup> as both flux and selectivity are influenced by the change in temperature. As a representative study, the dependence of PV of Bz/H<sub>2</sub>O binary mixture (90 : 10% (w/w)) was investigated at a temperature ranging from 35 to 75°C. From the results depicted in Figure 6, it is observed that the total flux increases from 72 to 94  $\text{g}^{-2} \text{h}^{-1}$  with the concomitant decrease in selectivity from 2.3 to 1.1. The increase in flux may be attributed to the increased kinetic energy of the permeants, which assist their diffusivity through matrix of the membrane.



**Figure 6** Temperature dependence of  $J$  and  $\alpha_p$ .



**Figure 7** Arrhenius plot for PV of Bz/H<sub>2</sub>O (90 : 10% (w/w)) through 1f membrane.

To determine the kinetic energy of activation ( $E_j$ ) for the PV process,  $\ln J$  was plotted against the inverse of temperature (in Kelvin) in accordance with the extensively used Arrhenius type of relationship.<sup>28,29</sup>

$$J = J_0 \exp(-E_j/RT) \quad (5)$$

$E_j$  as determined from the slope of the plot in Figure 7 was 10.8 kJ/mol.  $E_j$  thus calculated is a compounded parameter characterizing the overall temperature dependence of permeation flux.

### CONCLUSIONS

Several substituted polyamides with satisfactory thermal stability, mechanical properties were synthesized. These materials may find application as membranes for the dehydration of Bz or breaking of Bz/H<sub>2</sub>O azeotropes. Substantially high-normalized flux (upto 78 kg  $\mu\text{m}/\text{m}^2\text{h}$ ) and lower activation energy ( $E_j$ ) of 10.8 kJ/mol is indicative of the potential of 1f membrane for the dehydration of Bz and breaking of Bz/H<sub>2</sub>O mixture.

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