

# Structural Effects on Vapor Diffusivity in Rigid Polymers

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## SYNOPSIS

Sulfonated aromatic polyamide and different salts were synthesized. Water vapor diffusion in these polymers and X-ray diffraction of these polymers before and after water immersion were studied. The concentration dependence of the diffusivity is related to the morphological structure in the dry state and the change induced by absorbed water. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Poly (*p*-phenylene terephthalamide) (PPTA), a rigid polymer, has been noted for its good thermal stability but limited solubility in organic solvents.<sup>1-3</sup> Improvements in solubility were realized via *N*-substitution reactions to introduce, for example, alkyl, aralkyl, carboxymethyl,<sup>4</sup> and propane sulfonate groups.<sup>5</sup>

In our study, sulfonic acid groups were attached to the phenyl rings of PPTA to increase solubility.<sup>6-7</sup> Additionally, the proton of the sulfonic acid group was replaced by different cations, namely, Li<sup>+</sup>, K<sup>+</sup>, Zn<sup>++</sup>, and Mn<sup>++</sup> to study the effect of ionic interaction on properties. Because the backbone is rigid, microdomain formation caused by electrostatic interaction is different from the case of conventional flexible ionomers. Our study stresses the general structural effect on the sorption and diffusion of small molecules. This communication describes the use of water vapor as the diffusional probe.

## EXPERIMENTAL

### Materials

Poly [*N,N'*-(sulfo-*p*-phenylene)-terephthalamide] (PPTS) was synthesized by solution polymerization of 2,5-diaminobenzenesulfonic acid (2,5-DABSA) with terephthaloyl chloride (TPC) in dimethylacetamide containing lithium chloride, according to

the method used by Bair and Morgan<sup>8</sup> (Scheme 1). The intrinsic viscosity of PPTS was measured in concentrated sulfuric acid to be 1.69 dL/g at 25°C. The Li and K salts were synthesized from PPTS by neutralization with the respective carbonates. The degree of neutralization was determined by element analysis for the metal ion (Table I). Thin films of PPTS and the two salts were prepared by solution casting from dimethylsulfoxide on glass plates. The final drying step took place in a vacuum oven for 1 day at 150°C. The thickness range was from 0.5 to 2.2 mils. The Zn or the Mn salt was prepared by immersing a strip of the K-salt polymer in a 2% ZnSO<sub>4</sub> or MnSO<sub>4</sub> solution to allow exchange of ions to take place. The divalent cations rendered the polymers insoluble. The compositions of the two polymers are also listed in Table I.

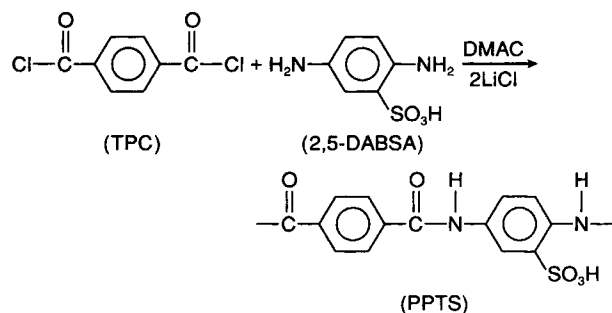
### X-Ray Diffraction

X-ray diffractometer scans were obtained using a Cu/Ni radiation source. The weighted-average wavelength was 1.542 Å. The general settings were 45 kV and 35 mA. Typical scan time was 0.02°/s. Experiments of the dried samples of PPTS and its salts were carried out in ambient environments. In order to study the effect of water swelling on polymer structure, the dried samples were immersed in water at room temperature for at least 1 day and measured again.

### Vapor Diffusion Experiments

The amount of vapor absorbed by a polymer was measured by a CAHN 2000 microbalance. The sensitivity of the microbalance was ±1 μg. The tem-

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Scheme 1

perature of the sorption chamber was controlled to  $\pm 0.2^\circ\text{C}$ . The successive sorption method was applied to study the solubility and diffusivity of water vapor. The error in the water vapor activity was attributed mostly to the error in reading the operating pressure. The sensitivity of the mercury manometer was  $\pm 1.6$  mm. The mean diffusion coefficient was calculated from the initial slope of the sorption curve (weight gain vs. square root time) according to the standard method.<sup>9</sup> The mean diffusion coefficients were used to plot versus the average vapor concentration in the following section. The "half time" method was reported to produce similar results as the "initial slope" method by several authors. We preferred the initial slope method because of the uncertainty of the experimental starting time.

## RESULTS AND DISCUSSION

The densities of PPTS and its salts were not measured so that we cannot calculate either the fractional free volume or the specific free volume. The glass transition temperature ( $T_g$ ) of PPTS was determined to be about  $320^\circ\text{C}$  and the  $T_g$  of PPTS salts are believed to be higher.

## Wide Angle X-Ray Diffraction

The X-ray diffraction data of PPTS and its salts are listed in Table I. A peak was observed at  $2\theta = 20.8^\circ$ , corresponding to a spacing of 4.3 Å. For PPTS-Li, PPTS-Zn, and PPTS-Mn, diffraction peaks appeared at  $24\text{--}25^\circ$ , (i.e., spacings of 3.5–3.7 Å). By comparing the peak positions with PPTA data, we assign the peaks to spacings controlled primarily by interchain  $-\text{C}=\text{O}\cdots\text{HN}-$  linkages.<sup>10</sup> The peak is absent in PPTS-K; the inference is that the chains are poorly organized in this polymer.

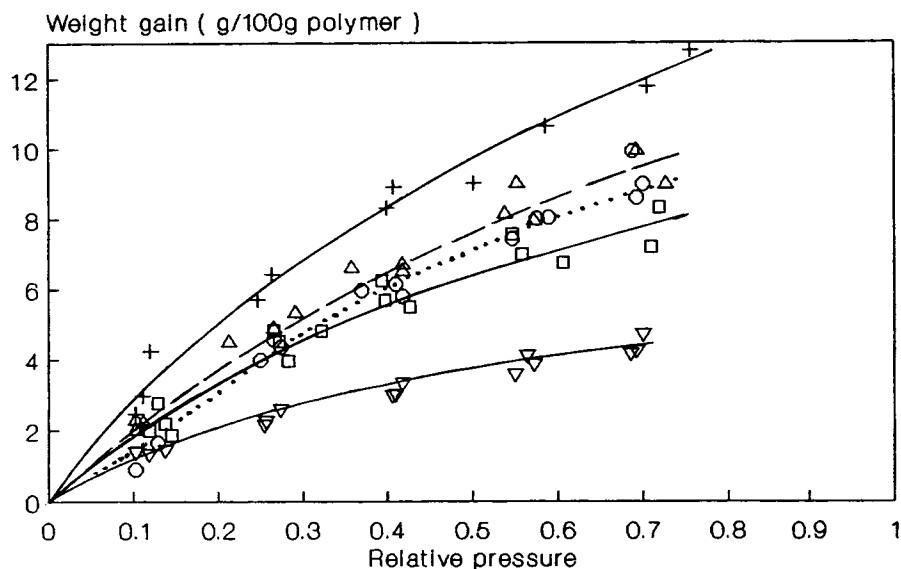
After the polymers were immersed in water for at least 1 day, the diffraction peaks at  $21\text{--}25^\circ$  were no longer observable in PPTS and the Mn, Zn polymers. In PPTS-Li, the peak was still observable but its intensity was substantially reduced. We believe that the X-ray results indicate a change in the state of chain alignment (the disappearance of the diffraction peak at  $21\text{--}25^\circ$  indicates that the regularity of interchain spacing is no longer preserved) in PPTS, PPTS-Zn, and PPTS-Mn when the polymers are immersed in water. Ionic interaction in PPTS-Li is apparently the strongest among the five polymers so that the characteristic X-ray spacing can still be seen although the diffraction intensity is weakened.

## Sorption Isotherms

The sorption isotherms of PPTS and its salts at  $50.2^\circ\text{C}$  are shown in Figure 1. The curve for PPTS-K stands out because the sorbed amount is smaller than that of PPTS although a lower molecular weight PPTS-K sample is more soluble in water than the parent polymer. The result is unexpected particularly in view of the X-ray results that indicate poor organization of chains in PPTS-K. The amount of sorption by PPTS-Zn is close to the value for

**Table I** Composition and Interchain Spacings of Polymers

	Composition					X-Ray	
	Cation (wt %)	SO <sub>3</sub> H (%)	SO <sub>3</sub> Li (%)	SO <sub>3</sub> K (%)	SO <sub>3</sub> M <sub>0.5</sub> <sup>+2</sup> (%)	2θ (°)	d-Spacing (Å)
PPTS						20.8	4.3
PPTS-Li	0.76	64.4	35.4			25.1	3.5
PPTS-K	6.78	40.8		59.2		—	—
PPTS-Mn/K	4.05/0.16	49.6		1.36	49.0	25.0	3.6
PPTS-Zn/K	4.18/0.11	56.5		0.94	42.6	23.9	3.7



**Figure 1** Sorption isotherms of PPTS and its salts at 50.2°C. (○) PPTS; (△) PPTS-Li; (▽) PPTS-K; (□) PPTS-Zn; (+) PPTS-Mn.

PPTS. The Li-polymer absorbs slightly larger quantities of water vapor than PPTS but sorption for the Mn-polymer is much larger.

Because the salt polymers are not 100% neutralized (Table I), we assess the contribution of each salt group to water vapor sorption by defining a quantity  $y$  as  $(W_{\text{salt polymer}} - W_{\text{PPTS}} \cdot \% \text{SO}_3\text{H}) / \text{mol } \% \text{SO}_3\text{M}$  (see Table I) where  $W$  is the amount sorbed at equilibrium and  $\text{SO}_3\text{M}$  stands for either  $\text{SO}_3\text{M}^+$  or  $\text{SO}_3\text{M}_0^{+2}$ . The  $y$  values can be arranged in the following order for data acquired at vapor activity of 0.2 or larger,

$$\text{Mn} > \text{Li} > \text{H} \geq \text{Zn} \gg \text{K}.$$

At lower vapor activities, for example, 0.1, the positions of H and Zn are reversed. The implications of the stated order of  $y$  values are explained in the following paragraph and are related to the capacity of the cation to form coordination compounds with water.

Generally speaking, water sorption at low pressures is governed by the number of hydrophilic or polar groups present in the polymer<sup>11</sup> and the orderliness of chain packing. The fact that PPTS-K sorbs the least amount of water vapor seems to rule out chain alignment as the dominant factor in sorption in the series of polymers studied here. We offer the tentative explanation that the amount of water vapor sorption is dependent largely on the capacity of the cation to form coordination compounds or to attract water of hydration. The  $d$ -block elements

Zn and Mn have high coordination numbers;  $\text{Li}^+$  is known to be hydrated in aqueous solutions and so does  $\text{H}^+$ . Only the K ion does not have such characteristics.

For more hydrophilic polymers the localized sorption models have been proven to be successful. Because our polymer has some hydrophilic groups (such as  $\text{C}=\text{O}$  and  $\text{NH}$ ) and water sorption is moderately high, the localized models such as the B.E.T. equation<sup>12</sup> [as eq. (1)] and "dual-mode sorption" type equation<sup>13</sup> [as eq. (2)] were employed to fit the sorption isotherms. The B.E.T. equation can be written as follows:

$$\frac{m}{m_0} = \frac{hx}{(1-x)(1+(h-1)x)} \quad (1)$$

where  $m$  is the amount of sorbed water per unit mass of polymer,  $m_0$  is the monolayer capacity,  $x$  is the relative pressure, and  $h$  is the ratio of the internal partition functions of the bound and liquid water. Enderby<sup>13</sup> proposed a "dual-mode sorption" type equation corresponding to a combined Langmuir and Henry's law isotherm as follows:

$$A = \frac{abP}{1+bP} + KP \quad (2)$$

where  $A$  is the same as  $m$  and  $P$  the same as  $x$  in eq. (1), and  $a$ ,  $b$ , and  $K$  are constants. Our experimental data will be analyzed with the use of the above models.

**Table II** Localized Model Constants of Polymers

Polymers	$m_0$	$h$	$a$	$b$	$K$
PPTS-Li	4.2	10.4	2.95	5.21	9.38
PPTS-K	1.8	23.1	1.21	16.22	4.62
PPTS-Zn	4.2	5.7	2.99	4.08	6.83
PPTS-Mn	6.5	6.1	3.72	6.02	11.67

The isotherm data of the salt polymers up to 0.6 relative pressure were used to estimate  $m_0$  and  $h$  by eq. (1). The  $m_0$  and  $h$  values of the salt polymers are listed in Table II. The rank order of the  $m_0$  values of the salt polymers seems to follow similar trends as the  $y$  values. PPTS-K has the largest  $h$  value among the salt polymers possibly resulting from low water sorption or weak water affinity of the polymer. The constants  $a$ ,  $b$ , and  $K$  in eq. (2) for the salt polymers were estimated by using the data from Figure 2 and the results of calculation are also summarized in Table II. The rank order of the Henry's law constant  $K$  follows exactly the same trend as the  $y$  values ( $Mn > Li > Zn > K$ ). The  $a$  values are roughly proportional to the  $m_0$  values. Interestingly, the  $b$  value of PPTS-K is also the biggest among the salt polymers. An inflection point at low relative pressure of the sorption isotherm of PPTS caused the poor regression of either eq. (1) or eq. (2). Therefore, the constants for PPTS are not reported in Table II.

Although Enderby's equation<sup>13</sup> is formally identical to the dual-mode sorption equation for gas sol-

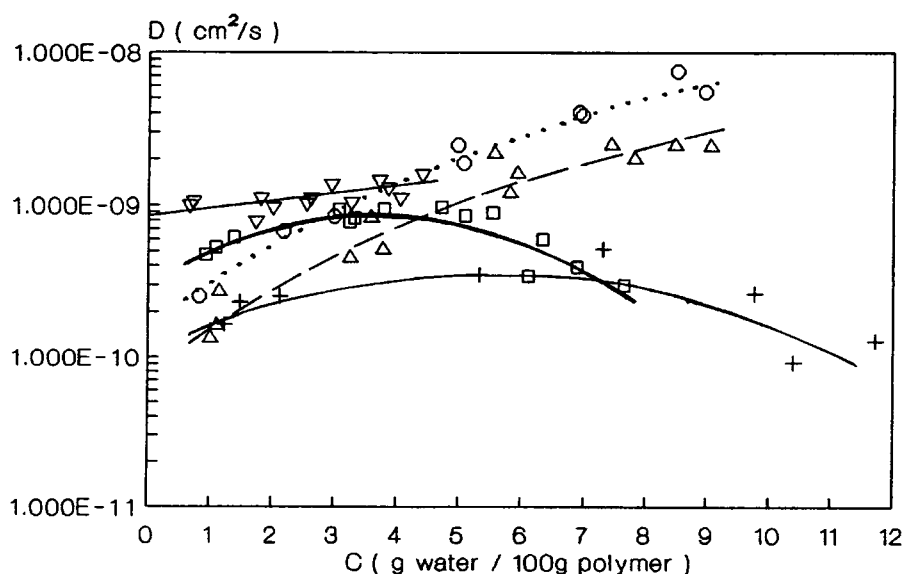
ubility in glassy polymers, water vapor sorption is different from gas sorption in that at high relative pressures the sorption isotherm will swing upward because of strong water clustering phenomenon and also the complication of structural change of the polymer caused by vapor sorption. Therefore, the localized models can only offer qualitative information about the sorption mechanism at low to moderate vapor activities.

### Diffusion Coefficient

The water vapor diffusivities of PPTS and its salts at 50.2°C are shown in Figure 2. The diffusion coefficient ( $D$ ) of water vapor in PPTS-K have only a weak dependence on concentration. However, the  $D$  values in PPTS and PPTS-Li increase with increasing diffusant concentrations. In PPTS-Mn and PPTS-Zn, the diffusivities change with concentration in a more complex manner. The diffusion coefficient increases with concentration initially but decreases when the amount of sorbed water exceeds 4–6%.

The influence of chain packing on diffusion is best analyzed by examining the magnitude of  $D_0$ , which is the value of  $D$  extrapolated to zero diffusant concentration. The  $D_0$  values are listed below.

	PPTS-K	PPTS-Zn	
$D_0 \cdot 10^{10}$ (cm <sup>2</sup> /s)	8.5	3.0	
	PPTS	PPTS-Mn	PPTS-Li
	1.7	1.1	0.83



**Figure 2** Vapor diffusivity in PPTS and its salts at 50.2°C. Data symbols as in Fig. 1.

The potassium polymer has the highest value of  $D_0$ . This is consistent with the observation that the  $2\theta$  peak at  $21-25^\circ$  is absent in this polymer and hence the lack of order in chain packing facilitates water diffusion. In contrast with PPTS-K, the Li-salt has the strongest interchain interaction as evidenced by the retention of the diffraction pattern, at least to some extent, upon immersing the polymer in water. Therefore, it is not surprising that the  $D_0$  value is the smallest for this polymer. The  $D_0$  values for the three remaining polymers, PPTS, and its Zn or Mn salt, lie in between the values for PPTS-K and PPTS-Li. Presumably, the differences among the three  $D_0$  values reflect the different degrees of accessibility of the polymers to water molecules.

Because the chains in PPTS-K are poorly packed, the presence of water molecules causes only minor perturbances to the state of chain organization; consequently, the diffusion coefficients have a very weak concentration dependence. For the rest of the polymers, the progressive disruption of interchain interaction by water molecules is believed to be responsible for the increase in  $D$ . On the other hand, the decrease in the magnitude of  $D$  in PPTS-Zn and PPTS-Mn when the diffusant concentration reaches 4–6% is probably related to water clusters assembled near the two cations that have high coordination numbers. The clusters have low diffusivities. The two opposing factors result in the maxima in the  $D$  vs.  $C$  curve.

## CONCLUSIONS

The diffusional probe method coupled with X-ray diffraction offer useful information about the influence of morphology on penetrant diffusion. The vapor diffusivities of PPTS-K has a weak dependence on concentration and is consistent with its poorly packed structure. The increasing vapor diffusivities of PPTS and PPTS-Li with increasing concentra-

tion are believed to be caused by the progressive disruption of interchain interaction by the water molecule. For PPTS-Zn or PPTS-Mn, the concentration dependence of vapor diffusivity is the result of a combination of different effects including the disruption of interchain interaction by water molecules, divalent interpolymer linkage (e.g.,  $-\text{SO}_3-\text{Zn}-\text{SO}_3-$ ) and water clustering around the cation.

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