

# Gas Transport Properties of Poly(3-Hydroxyoxetane)

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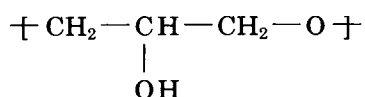
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## SYNOPSIS

Gas transport properties for poly(3-hydroxyoxetane) (PHO) were measured for five gases at 35°C. While PHO has very low gas permeability coefficients, they are larger than those reported for polyacrylonitrile (PAN), poly(vinyl alcohol) (PVAI) and copolymers of ethylene/vinyl alcohol (EVAL) for all gases tested except He. The permeability coefficients for PHO and EVAL are well correlated with the density of hydroxyl groups along the chain. Extrapolations to PVAI give values that agree well with those estimated by Salame using the Permachor method. It is suggested that some of the reported experimental values for PVAI are in error. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Wojtowicz and Polak<sup>1</sup> found that low molecular weight polymer, presumably poly(3-hydroxyoxetane) (PHO), formed spontaneously from 3-hydroxyoxetane. Later, Vandenberg established the structure of the Wojtowicz polymer as PHO and synthesized a similar polymer



from the base-catalyzed rearrangement polymerization of glycidol and its trimethylsilyl ether.<sup>2</sup> Subsequently Vandenberg et al. prepared a high molecular weight PHO by the cationic and coordination polymerization of the trimethylsilyl ether of HO and also established that PHO is usually atactic, although highly crystalline.<sup>3</sup> PHO is a close analog of poly(vinyl alcohol) (PVAI), owing to the presence of the hydroxyl group that forms strong interchain hydrogen bonding. These strong forces lead to the ability to crystallize even in the absence of stereoregularity and, of course, water solubility.

In general, highly polar polymers such as dry PVAI and polyacrylonitrile (PAN) act as excellent permeation barriers for gases because of the difficulty for diffusional jumps of the penetrant molecules from site to site amid chains held together by such strong force fields.<sup>4-10</sup> The hydrogen bonding potential of PHO suggests that the gas transport properties of this material might also be similar to that of PVAI and its copolymers. Here, we report the gas transport properties of dry PHO and briefly compare these results with other gas barrier polymers.

## EXPERIMENTAL

Poly(3-hydroxyoxetane) (PHO) was prepared as previously described in Ref. 3 (Table 1, No. 2). Films were cast from 5 wt % water solution onto glass plates at room temperature. The films were dried overnight at 60°C in a vacuum oven in order to eliminate residual water. Permeability coefficients for five gases—He, H<sub>2</sub>, O<sub>2</sub>, Ar, and CO<sub>2</sub>—were measured by transient permeation at 35°C and 2 atm upstream pressure in a modified permeation cell of the type described elsewhere.<sup>11</sup> The PHO film, 1.9 mils thick, mounted in the cell was allowed to stay under vacuum at 40°C for 3 days in order to eliminate any further moisture in the film. Apparent diffusion coefficients for the above gases were determined by the time lag method. Thermal analysis

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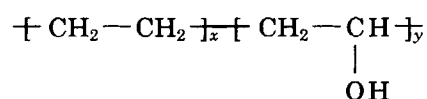
was performed using a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20°C/min under nitrogen atmosphere.

## RESULTS AND DISCUSSION

The synthesis and characteristics of the PHO used for the gas transport measurements are described elsewhere.<sup>3</sup> The thermal properties measured for the current sample are in agreement with previously reported values. Dry PHO has a  $T_g$  of 17°C and a melting peak at 140°C. The enthalpy change on melting,  $\Delta H_m$ , for the current PHO films were found by differential scanning calorimetry (DSC) to be 5.08 kJ/mol. The heats of fusion at 100% crystallinity have been reported as 6.9 kJ/mol for PVAL<sup>12,13</sup> and 7.87 kJ/mol for polyethylene.<sup>12</sup> Thus, PHO would appear to be highly crystalline as previous reports have suggested.<sup>3</sup>

Permeability coefficients for five gases in dry PHO are given in Table I along with values reported for PAN<sup>4</sup> and PVAL.<sup>5-10</sup> It should be mentioned that widely different gas permeability coefficients have been reported for PVAL. These differences could be due to several factors including variations in the level of crystallinity, degree of hydrolysis, moisture content, and errors associated with measurement of such low transmission rates. The helium perme-

ability coefficient for PHO is an order of magnitude lower than that reported for PAN,<sup>4</sup> but very similar to that reported by Kantesaria<sup>9</sup> for PVAL. For all the other gases, PHO appears to be more permeable than PVAL or PAN. A thorough comparison of the data for the latter materials reveals some apparent inconsistencies; however, this is beyond the scope of the current discussion. Because of the lower hydroxyl concentration of PHO (one per four chain atoms), it is not surprising that it is more permeable than PVAL, which has two hydroxyls per four chain atoms, not considering possible effects of crystallinity. We may compare PHO to materials of more comparable hydroxyl density by considering the family of ethylene/vinyl alcohol copolymers



available commercially under the tradename EVAL®.<sup>14</sup> This is done in Table II where the number following the EVAL acronym corresponds to the weight percentage of ethylene units in the copolymer. At this point, there is no clear explanation for the lower helium permeability of PHO than that reported for PAN, PVAL, and all the EVAL copolymers. The larger permeability coefficients for O<sub>2</sub>, Ar, and CO<sub>2</sub> in PHO as compared to the EVAL ma-

**Table I Comparison of Permeability Coefficients for PAN, PVAL, and PHO**

Polymer	Reference	$P \times 10^{15}$ [cm <sup>3</sup> (STP) cm/cm <sup>2</sup> s cmHg]				
		He	H <sub>2</sub>	O <sub>2</sub>	Ar	CO <sub>2</sub>
PHO	This work	5482	2280	375	273	1199
PAN	4	71,000		54	18	280
PVAL	5 <sup>a</sup>			6		18
	6 <sup>b</sup>			0.062		
	7 <sup>c</sup>			0.12		0.16
	7 <sup>d</sup>			294		763
	8 <sup>e</sup>			40		100
	9 <sup>f</sup>	5232	780	195	122	205
	10 <sup>g</sup>			~ 0.1		
	10 <sup>h</sup>			180		4200

<sup>a</sup> Values at 23°C.

<sup>b</sup> Permachor calculation at 25°C.

<sup>c</sup> More recent Permachor calculation for 70% crystallinity and 25°C.

<sup>d</sup> Wet polymer with no crystallinity.

<sup>e</sup> O<sub>2</sub> permeability (35°C) from an experimental system able to measure permeabilities as low as 10<sup>-14</sup>, therefore, value is at the limit of measurement. Same applies for CO<sub>2</sub> (20°C).

<sup>f</sup> Reynolon® at 26.2°C and 25% crystallinity.

<sup>g</sup> Dry Vinol 125 (25°C).

<sup>h</sup> Vinol 125 at 23°C: O<sub>2</sub> at 50% RH and CO<sub>2</sub> 75% RH.

**Table II** Permeability Coefficients for Ethylene/Vinyl Alcohol Copolymers<sup>a</sup> and PHO at 35°C

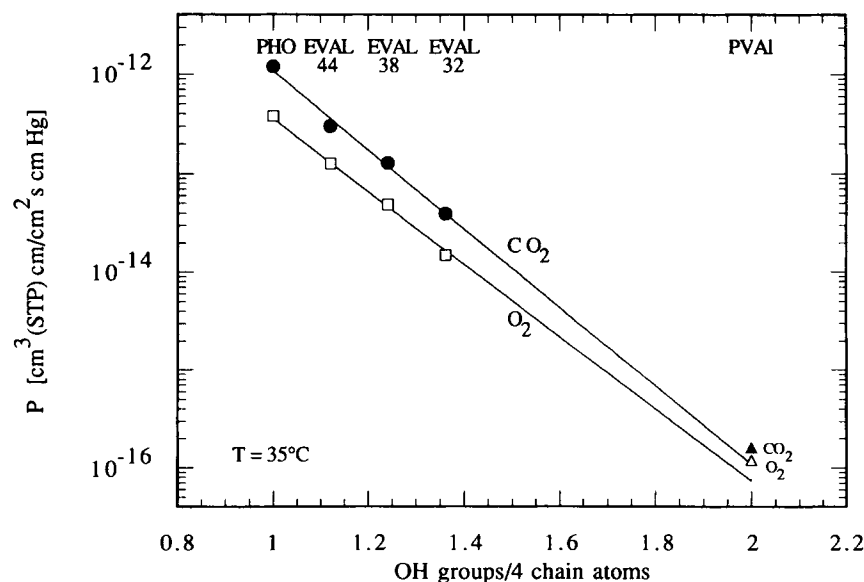
Polymer	$P \times 10^{15}$ [cm <sup>3</sup> (STP) cm/cm <sup>2</sup> s cmHg]					OH Groups/4 Chain Atoms
	He	H <sub>2</sub>	O <sub>2</sub>	Ar	CO <sub>2</sub>	
EVAL 32	8214		15		40	1.36
EVAL 38	14749		49		128	1.24
EVAL 44	21344		126		298	1.12
PHO	5482	2280	375	273	1199	1.00

<sup>a</sup> Data from Ref. 14.

materials seem to be related to its lower capacity for hydrogen bonding. To explore this hypothesis, O<sub>2</sub> and CO<sub>2</sub> permeability coefficients are compared in Figure 1 on the basis of the number of hydroxyl groups per four chain atoms. The permeability coefficients for the EVAL copolymers decreases exponentially as the number of hydroxyl groups along the backbone increases. The correlation shown in Figure 1 reveals that PHO follows closely the tendency observed for the EVAL copolymers. This suggests that the capacity to form hydrogen bonds dominates the permeation process.

Interestingly, when the correlation lines in Figure 1 are extrapolated to two hydroxyl groups per four chain atoms, estimates for the permeability coefficients for PVAL are obtained that are very close to the values predicted by Salame<sup>7</sup> using the Perma-

chor method (the triangles in Fig. 1). Sweeting<sup>10</sup> reports a comparable value for O<sub>2</sub> (see Table I) but does not elaborate on how it was obtained. These permeability coefficients are smaller by two or three orders of magnitude than experimental values reported in the literature. Some part of this difference may be attributed to differences in crystallinity of the samples. The Permachor calculations assume 70% crystallinity while the film used by Kantesaria<sup>9</sup> was stated to have 25% crystallinity. We would not expect this difference in crystallinity to amount to even one order of magnitude change in permeability. The experimental data obtained by Kantesaria were part of an investigation of the effect of relative humidity on the permeability of PVAL. It is quite likely that the films considered to be dry actually contained some residual moisture that would significantly el-



**Figure 1** Experimental permeability coefficients for O<sub>2</sub> and CO<sub>2</sub> in PHO and ethylene/vinyl alcohol copolymers as a function of hydroxyl group density along the backbone of the polymer chain. Triangles indicate Permachor calculation for PVAL from Ref. 7.

evate the gas permeability. The permeability coefficients reported by Finch<sup>8</sup> are lower than those reported by Kantesaria but are still two orders of magnitude higher than the ones shown in Figure 1. Unfortunately, Finch does not give any information about the samples, e.g., the degree of crystallinity, used in these measurements. Because of the inherent limitations in the measurement of such low gas transmission rates and possible effects of residual moisture, we believe that these experimental permeability coefficients for PVAL are in error and the predicted ones are more reliable.

Table III lists the apparent diffusion and solubility coefficients for various gases in PHO and compares them to the values reported for PAN.<sup>4</sup> The former was computed from the measured diffusion time lag,  $\theta$ , and the film thickness,  $l$ , using<sup>15</sup>

$$D_a = \frac{l^2}{6\theta} \quad (1)$$

while the later was calculated using<sup>15</sup>

$$S_a = \frac{P}{D_a} \quad (2)$$

The apparent diffusion coefficient for helium in PHO is lower than that of PAN while those for O<sub>2</sub>, Ar, and CO<sub>2</sub> are larger for PHO than PAN. These results suggest that the trends in PHO permeability relative to PAN simply reflect trends in diffusion coefficients. In general, the apparent solubility coefficients shown in Table III support this view. However, with the exception of He and CO<sub>2</sub>, the apparent

solubility coefficients appear to be slightly larger in PHO than in PAN. These results must be taken with caution because the low permeabilities exhibited by these polymers lead to some uncertainty in the time lag calculations; however, we believe the values shown generally reflect the right tendency.

## CONCLUSIONS

The gas transport properties of poly(3-hydroxyoxetane) (PHO) measured at 35°C show that PHO has higher permeability coefficients for O<sub>2</sub>, Ar, and CO<sub>2</sub> than commercial copolymers of ethylene/vinyl alcohol (EVAL) and some of the reported experimental values for PVAL.<sup>5-10</sup> The higher gas permeability of PHO is attributed to its lower hydroxyl group content, which leads to a reduced ability for hydrogen bond formation (in spite of the ether oxygen in the backbone that can serve as a hydrogen bond receptor). The permeability coefficients for O<sub>2</sub> and CO<sub>2</sub> in PHO and EVAL copolymers all fall on a single correlation with hydroxyl content. When extrapolated to the structure of PVAL, permeability coefficients are obtained that are in excellent agreement with other sources but much lower than some reported experimental measurements for PVAL. It is proposed that the latter are in error.

Even though the PHO permeability coefficients for the gases tested are larger than the ones reported for EVAL copolymers, PVAL, and PAN, they are among some of the lowest reported in the literature. Thus, in the dry state, poly(3-hydroxyoxetane) can act as an effective barrier for gases.

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**Table III** Apparent Diffusion and Solubility Coefficients for PHO and PAN at 35°C

Gas	$D_a \times 10^{10}$ [cm <sup>2</sup> /s]		$S_a \times 10^3$ [cm <sup>3</sup> (STP)/cm <sup>3</sup> atm]	
	PAN <sup>a</sup>	PHO	PAN <sup>a</sup>	PHO
He	270	70	200	59.5
H <sub>2</sub>	—	33.6	—	51.5
O <sub>2</sub>	0.14	0.68	290	414
Ar	0.042	0.28	330	741
CO <sub>2</sub>	0.023	0.54	9200	1690

<sup>a</sup> Values from Ref. 4.

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