Notes

Water Permeation in Polymer Films.   V.   Parylene D

In the previous paper in this series,[1] Teflon FEP was found to have a time-dependent Langmuir-like layer on its surface when water was used as the permeant. Because oxygen did not form such a layer[2]; it was speculated[1] that layer formation may be due to specific interaction between penetrant and polymer. The present note reports on water permeation in Parylene D, and the reason why no such Langmuir-like water layer was detected.

Parylene D, a product of Union Carbide, is the common name for poly(p-2,6-dichloroxylene). [So identified in the vendor literature. Space-filling molecular models suggest that steric hindrance will cause head-to-tail addition to predominate, based on similar monomeric radical reactions.[3]] It, and other members of the family, are made[4,5] by the pyrolysis of the appropriate di-p-xylylene (p-cyclophane) to give the p-xylylene diradical, followed by radical addition to give the polymer. The Parylene D films were obtained after having been deposited onto glass; they ranged from 20 to 50 μm in thickness. After demounting in warm water, the films were dried under vacuum before use.

The data were obtained on a modified Dohrmann Envirotech Polymer Permeation Analyzer model PPA-1,[6] in the temperature range 30–80°C and in the relative humidity range 20–95%. The permeation coefficient P was obtained from the total instrument signal,[7] while the diffusion coefficient D was obtained at two stages during the permeation process: 10–40% and 40–70%. The solubility coefficient S and concentration of sorbed water, C, were calculated from P and D. Although only data for the 33-μm sample are reported here, they are typical of data obtained at the other thicknesses.

In no case were values obtained at the earlier stage of the process found to differ from those obtained at the later stage. All the data fit the Arrhenius equation, and the permeation parameters so obtained are found in Table I. The entropy of activation for the diffusion process, $\Delta S_D^{\ddagger}$[8(a)], was found to be 8.84 J/mol K, and positive in sign, as expected for the diffusion process.[1,8(b)]

The concentration of sorbed gas was determined over the full relative humidity range only at 55°C. It was well represented by a Henry's law plot, of C vs. % RH, which intersected the origin. This indicates that there is no contribution from a Langmuir-like adsorption layer, since such behavior would intersect the C axis at some finite value, as previously shown.[9] It fit the equation

$$C = (3.786 \pm 0.320) \times 10^{-6} \times \% \text{ RH-}2.298 \times 10^{-5} \text{ g water/g polymer} \tag{1}$$

with a statistical significance of >0.9995. At 100% RH, this translates to 3.42×10^{-3} mol water/mol polymer repeat unit. The reason for this low value appears to be, as with Teflon FEP,[1] the short residence time of the permeant on the surface, although the lack of dipole–dipole interaction, to be demonstrated shortly, may also contribute. In the present case, this time is calculated[10] to be 7.7 $\times 10^{-10}$ s at 25°C; this is slightly longer than the residence times for Teflon FEP,[1] giving slightly larger C values.

TABLE I
Values of Permeation Parameters for 33-μm Parylene D at 50% RH

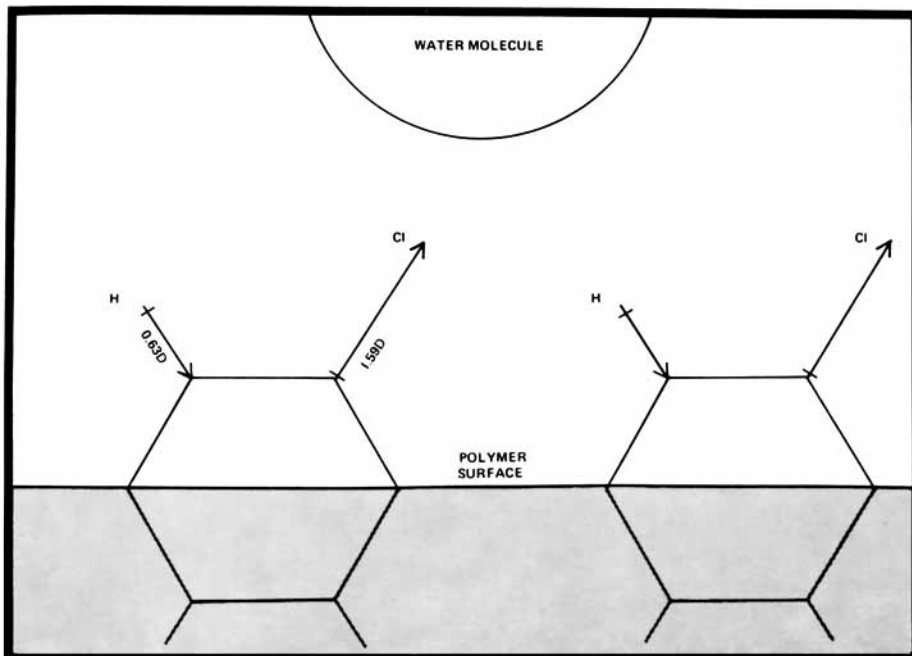|	
P_0 (std cc cm/cm²·s·cm Hg)	1.726×10^{-6}
E_P (kJ/mol)	19.46 ± 2.22
Statistical significance[a]	>0.9995
D_0 (cm²/s)	1.194×10^{-2}
E_D (kJ/mol)	35.96 ± 2.98
Statistical significance[a]	>0.9995
S_0 (std cc/cm·cm Hg)	1.457×10^{-4}
E_s (kJ/mol)	-16.47 ± 3.90
Statistical significance[a]	>0.9995

[a] Both t-test and correlation coefficient.

Fig. 1. The interactions of water and exposed Parylene D repeat units lying perpendicular to the surface. The structures are drawn to scale, using standard bond angles and bond lengths, with dipole moments taken from the literature.[14] The direction of the dipolar arrow is from the positive to the negative end.

of the film. Parylene C (monochloro-substituted Parylene) exhibits a substantially lower preferred orientation,[4] and molecular models suggest a reason for this: three dimerization products seem possible. There are the 2,6' head-to-head and the 2,2' and 2,6' head-to-tail configurations. (The 2,2' head-to-head configuration is rejected on steric grounds.) This multiplicity of configurations will make packing difficult during deposition. This difficulty may also be seen in the crystal densities: 1.176 g/cc for Parylene N[4,11,12] and 1.320 g/cc for Parylene C[4]; note the 12% increase in density for a 33% increase in monomer molecular weight.

While Parylene D will probably exist predominantly in the head-to-tail configuration, as mentioned earlier, the use of space-filling models shows that the larger van der Waals radius of the Cl (1.80 Å, compared with 1.00 Å for H[13]) will cause difficulty in amorphous packing, especially since adjacent chains may be opposite in direction or offset. From this, one may conclude that Parylene D, too, will exhibit a lower preferred orientation than Parylene N. Thus, since the rings are not confined to the plane of the film, molecules at the surface will have components of the dipole moment which will lie perpendicular to the plane of the film.

Consider the extreme case of Fig. 1; a phenylene ring lying perpendicular at the surface has its exposed dipoles and, therefore, any dipole–dipole interactions with permeant molecules only partly neutralized by the dipoles on the other side of the ring, because they are farther away from the permeant molecules. Thus, interactions with water may be possible. However, as seen in Figure 1, not only do the ϕ–H and ϕ–Cl dipoles tend to counteract each other but a water molecule of some 3.50 Å diameter cannot interact exclusively with any one of them (especially in view of offset or oppositely directed adjacent chains). Based on this, it seems evident that no Langmuir-like layer is formed because the dipole–dipole interactions necessary to form it cannot occur.

Compare this with the case of Teflon TFE: the van der Waals radius of the F causes a shift from planar zigzag to helix (about 24° for every C_2F_4 group[15]. While this conformation turns a given C—F bond away from the surface, it turns another toward the surface, always presenting a C—F dipole to the permeant.

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