PROGRESS IN UNDERSTANDING THE FORMATION OF POLY(P-XYLYLENE) COATINGS

William F. Beach

933 E. Josephine Saddle Place
Green Valley AZ 85614

It is now thirty years since I presented my first model of the formation of poly(p-xylylene) or Parylene films[1]. A detailed model for Parylene film formation is of vital importance in engineering and troubleshooting real life Parylene applications.

The ultimate test of any model is how its predictions match real-life experience. In this case, the predicted non-integral order of pressure dependence was later verified experimentally[2]. The model connects the 1.5 order of pressure dependence observed to the third order of the initiation reaction. Furthermore, the compressive stress observed in freshly deposited films[3] is also consistent with the model.

But there is much more to be learned. The first model describes steady state growth, once the coating formation process is well underway. It does not address what happens in the earliest stages of film formation. It also contains a number of approximations that tend to distort some details of interest. More importantly, it fails to recognize explicitly that, while the monomer p-xylylene **M** is free to diffuse anywhere in the film, the polymeric elements (chain links **Q** and end groups **P**), once formed, are immobilized by surrounding polymer chains and maintain their positions relative to their neighboring polymer elements throughout the entire coating process.

For impermeable substrates, prior to the steady state regime of the first model, the coating is thin enough that at least some monomer **M** diffuses all the way to the substrate surface at $z=L$. An added requirement on the function describing $M(z)$ for this intermediate regime is that its slope dM/dz at $z=L$ is zero, since no monomer can cross into the substrate. A function that has all the right properties is:

$$
\begin{aligned}
M(z) &= M_0\left(\cosh az - \tanh aL \sinh az\right) \\
&= M_0\left(\frac{\cosh a(L-z)}{\cosh aL}\right)
\end{aligned}
$$

As coating thickness L goes from very small to very large, this function changes neatly from $M(z)=M_0$ to $M(z)=M_0\exp(-az)$. Whereas this function is defined mathematically down to $L=0$, it looses its ability to describe what is going on in real world coatings in the vicinity of a few monolayers (~10-20Å or 1-2nm). Even though we might use this function to find an analytical solution to the necessary D.E.s, we would still have to resort to other methods to describe the very beginning of the coating process on impermeable substrates.

Unfortunately, the monomer p-xylylene is so highly reactive that most conventional measurements of its properties are impossible. Hence, we must often rely on analogies with similar but not-so-reactive substances. In 1946, Kemball[4] reported studies of the adsorption of three substances on purified mercury. From his adsorption data for benzene, an experimental adsorption entropy was obtained for benzene's adsorbed state. The result is consistent with a loss of a single translation and the retention of only one rotation – that in the plane of the ring. Thus benzene absorbed on mercury appears to be scooting about the surface, spinning – a two dimensional gas with velocities similar to those in the gas phase (at the same temperature). p-Xylylene is also a planar molecule, albeit not as highly symmetrical as benzene. We can therefore reasonably suggest that it behaves similarly to benzene when in its adsorbed state.

In order to explore further, we turn to numeric methods. For deposition parameters, we use the exemplary parameters of table 1 in the 1978 paper. We start with a 2-dimensional gas of adsorbed monomer. During this *monolayer regime*, the reaction volume is a slab of the thickness of an adsorbed monomer molecule, 4 Ångstroms (0.4 nm). Stepping forward in time at a convenient interval, we first compute the amount of additional initiation and propagation that has occurs in each interval, and then compute the resulting average polymer coating thickness using molecular volumes for M, P and Q. When the computed average thickness passes the adsorbed monomer molecule thickness, we pass into a new regime.

During the *homogeneous regime*, reactive monomer has equal access to all end groups throughout the thickness of the film. The computation here is similar to that of the monolayer regime, except that the reaction volume is the thickness of the film. Stepping forward at convenient time intervals, we first compute the amount of additional initiation and propagation that has occurred in the interval, and then expand the film to the new thickness using the same molecular volumes. The growth rate of the film increases exponentially during this homogeneous regime.

When a certain thickness is reached, monomer transport by diffusion from the growth interface begins to restrict its availability for reaction with the polymer chain ends toward the back of the film at the substrate interface. Here we enter the *intermediate regime*, in which we must additionally consider transport of monomer by diffusion. This computation starts by dividing the film up into a large number of slabs. As we step forward in time, attention must be given to each of these slabs in turn. For each slab, we compute monomer diffusion into the slab, monomer diffusion out of the slab, and monomer lost by reaction within the slab, as well as the additional polymer elements P and Q generated within the slab during the time interval. Then we are in a position to compute a new volume for each slab and thus determine how much each slab expands in thickness during the time interval. The total thickness of the film is the sum of the thicknesses of all slabs. What we have established here is an "oozing" coordinate system, in which the polymer is stationary once it is created. It allows us to avoid polymer transport and monomer convection complications that plague the more conventional computations using static or moving coordinate systems.

The Stages of Parylene Coating Growth on Substrates which are Impermeable to Monomer

This important class of substrates includes glass, mercury, silicon or silica, and metals, including conductors and metallic components and fixtures on a printed wiring board. The formation of a coating on an impermeable substrate passes through a sequence four growth stages or regimes.

1. The **MONOLAYER REGIME** starts out with the physical adsorption of monomer at a coverage in the range 0.1-1.0%. Even at such low coverage, the effective concentration of monomer in the monolayer is much greater than that in the gas phase from whence it came, greatly favoring initiation chemistry. After initiation events occur, propagation to high molecular weight polymer chains proceeds quickly. The polymer strands on the substrate surface have very little organization, but are held to the surface and ultimately to one another by vanderWaals dispersion forces. The disorder includes the crossing of chains over one another well before the average thickness reaches one monolayer (~4 Å). Hence, the continuity (pinhole freeness) of the deposit is not achieved until the average thickness reaches at least several monolayers (perhaps 20-50 Å). The average thickness of one monolayer is passed about one minute after the start of exposure to gaseous monomer.

2. The **HOMOGENEOUS REGIME**, in which the film is thin enough and growth slow enough that monomer (**M**) diffusion is unrestricted and consequently its concentration substantially uniform throughout, as is the concentration of reactive free radical polymer chain ends (**P**). Under these conditions, the rate of film growth increases exponentially, which is to say that film growth rate is proportional to film thickness (L).

$$
\frac{dL}{dt} = kL; \quad L = \exp(+kt)
$$

This regime is in effect for a short time after the completion of the monolayer, during which time the film experiences a substantial increase in thickness.

3. The **INTERMEDIATE REGIME**, in which the flux of monomer through the growth interface to supply the growing film is large enough, and the film is sufficiently thick, that free radical polymer chain end groups (**P)** located deeper in the film begin not to have the same availability of monomer as those nearer the surface. The result is that the growth rate acceleration experienced in the homogeneous regime is gradually throttled back to the steady growth rate of the steady state regime. In another five minutes or so, the film thickness is 3000-5000 Angstroms, and the characteristics of the steady state regime achieved. Interestingly, without the moderating effect of diffusion, the growth rate would continue to increase without limit.

It is during this Intermediate Regime that the coating becomes sufficiently thick to exhibit the famous rainbow effect. A lot happens before you see the first signs of the coating.

4. The **STEADY STATE REGIME** is much as described by the old model.

The Stages of Parylene Coating Growth on a Substrate Which is Permeable to Monomer.

This important class of substrates includes Parylene itself (as experienced in restarting a coating process or overcoating), as well as rubber and plastic materials in general, including the cured epoxy gel coat of a printed wiring board.

Upon exposure to gaseous monomer under typical deposition conditions, availability of monomer from the gas and diffusivity of monomer within the substrate are sufficient that a growth zone of a few thousand Angstroms depth will be developed essentially instantly (<1 second). The chemistry, however, is a little slower. In the case of a Parylene substrate, if free radical chain ends are present, even if they are peroxides as a result of momentary exposure to atmospheric oxygen, the chains will continue to grow by the reaction with incoming monomer. In the absence of such radicals, which is usually the case when the substrate is other than Parylene, chain propagation must await initiation events. Because the initiation chemistry is third order in monomer, the region in which initiation occurs is one-third the depth of the zone in which the bulk of the polymer is formed by propagation.

Nevertheless, new parylene chains are initiated and grow in length in the midst of the substrate polymer, offering a unique mechanism for adhesion via chain entanglement unavailable to any other polymer system. One of the requirements for this entanglement adhesion mechanism to be successful is that the substrate polymer have good physical strength right out to the growth interface. A 500 Å layer of undercured material or mold release deposit on the substrate might defeat the adhesion process and produce a blistering coating.

Parylene coating growth on a permeable substrate starts out faster than on an impermeable substrate, and quickly develops into steady state growth. In the early stages, when both types of surfaces are present in applications such as circuit board coating, the thickness of the Parylene layer on the permeable substrate gets ahead of that on an impermeable substrate. This small differential is maintained after steady state growth is achieved over the two different substrate types.

An additional feature in the case of non-Parylene substrates is that the composition in the vicinity of the original substrate interface moves gradually from totally substrate material to totally Parylene over a distance of several growth zone depths bracketing the original interface position.

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