

Parylene Growth Rates and Temperature

We wish to explore how substrate temperature affects the growth of the three most popular Parylenes: N, C and AF4. To do this, we need vapor pressure data on the three monomers. Because of their extreme reactivity, conventional measurements of vapor pressure are impossible. Not to be deterred by such inconvenience, the next best thing is data from unreactive model compounds which otherwise closely resemble the three respective monomers. Then N monomer should closely resemble *p*-xylene in volatility, and *p*-xylene vapor pressure data is readily available in handbooks: $t_b = 138.37\text{ }^\circ\text{C}$ and $\Delta H_v = 42\text{ KJ/mol}$. My old CRC handbook lists the boiling point for 2-chloro-*p*-xylene as $187\text{ }^\circ\text{C}$. For AF4, we need to go a little further afield. An Aldrich catalog lists a boiling point of $116\text{ }^\circ\text{C}$ for the totally alpha fluorinated *p*-xylene, *p*-bis(trifluoromethyl)benzene. Neither of the latter two model compounds data sources offer heat of vaporization data, so for this discussion we will need to assume them similar to *p*-xylene's.

In my 1978 model¹ (equation 3), the concentration of monomer at the growth interface M_0 is proportional to the ratio p/p_0 , where p is the pressure of monomer gas in the adjacent gas phase and p_0 is the saturation vapor pressure of monomer, both at the temperature of the substrate. The concentration of monomer at the growth interface is the primary driver for monomer concentration within the film, and ultimately film growth rate.

Vapor pressure relationships are conveniently seen on an Arrhenius plot, in which $\log p$ is the ordinate and the abscissa is reciprocal absolute temperature, $1/T$. In this presentation, even real vapor pressure curves are relatively straight lines. For this exercise, our estimated monomer vapor pressure curves are plotted as straight lines going through the point $p = 760\text{ mm}$ (1 atmosphere) and the abscissa corresponding to the t_b , having a slope determined by the heat of vaporization. Since we assumed the same heat for all three monomers, we get three parallel lines.

Let's focus on a monomer pressure of 50 microns at two different temperatures, $+20\text{ }^\circ\text{C}$ and $-20\text{ }^\circ\text{C}$, corresponding to room temperature deposition which works so well for C, and refrigerated substrate deposition, which is needed to get acceptable rates for AF4, and N as well. That gives us an isobar **a e i** at 50 microns, and two isotherms, **a b c d** at $+20\text{ }^\circ\text{C}$ and **e f g h** at $-20\text{ }^\circ\text{C}$.

Since the vertical axis is *logarithmic*, vertical differences are *ratios*. If at $+20\text{ }^\circ\text{C}$ the concentration of N monomer in the film is proportional to **a c** and the concentration of C monomer in the film is proportional to **a b**, then we can see that C monomer concentration exceeds that of N monomer (in parallel depositions) by a factor measured by **b c**, or by about 3.7 fold. Comparing the concentration of C monomer at $+20\text{ }^\circ\text{C}$ and $-20\text{ }^\circ\text{C}$, we measure the *vertical* distance between points **b** and **f**, which corresponds to 15.7 fold. Because we initially assumed all three monomers to have the same heat of vaporization, the three monomers' vapor pressure

¹W.F.Beach, Macromolecules 11 (1978) p. 73.

curves are parallel, so we will get the same increase in concentration between +20 and -20 °C. This is of course not likely to be the case in the real world.

Point **i** is where the pressure of monomer meets the vapor pressure curve. The weatherman would call the corresponding temperature the dew point. At temperatures below this dew point, monomer spontaneously condenses on the growth surface. And polymerizes violently.

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