

A Model for the Chemical Vapor Deposition of Poly(*para*-xylylene) (Parylene) Thin Films

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A kinetic model is developed for the chemical vapor deposition of poly(*para*-xylylene), or parylene, thin polymer films. The growth process is modeled as a multistep process that includes physisorption of monomer on the surface and subsequent chemisorption. The chemisorption step is equivalent to a propagation reaction between the monomer and a radical chain end, and each chemisorption produces a new chemisorption site. The sticking coefficient of the monomer as a function of substrate temperature is extracted from the measured data using the model and is determined to be 2.0×10^{-5} at 60 °C, increasing to 1.4×10^{-3} at -60 °C. The heat of physisorption for the monomer is also extracted from the experiment, and the value found (75 kJ/mol) is reasonable when compared to those of other similar molecules. The model fits experimental kinetic data well for a large range of pressures and temperatures, and it should be appropriate for use with all parylene-family polymers.

1. Introduction

The deposition of thin polymeric films of poly(*para*-xylylene), also known as parylene, onto a surface using a gaseous precursor was first observed by Szwarc in 1947 when he found the polymer as one of the products formed in the vacuum thermal decomposition (pyrolysis) of *para*-xylene.^{1–3} Szwarc postulated that the species produced by the decomposition in the vapor phase responsible for forming the polymer was *para*-xylylene and proved it to be so by mixing the deposition vapors with iodine vapor and finding *para*-xylylene diiodide as the only product.^{1,2} The yields of polymer film were only a few percent even at relatively high pyrolysis temperatures ranging from 700 to 900 °C.³

Gorham later found a much more efficient route to the deposition of parylene films through the vacuum pyrolysis of di-*para*-xylylene.⁴ He found that, at temperatures above 550 °C and at pressures less than 1 Torr, the dimer is quantitatively cleaved into two monomer units (*para*-xylylene), which are adsorbed onto a surface at room temperature and spontaneously polymerize, yielding high-molecular-weight, linear parylene thin films (see Figure 1).

The steps of the chemical vapor deposition of parylene consist of (1) sublimation of dimer in a sublimation furnace, (2) cracking the dimer into monomer in the pyrolysis furnace, (3) transport of the monomer into the deposition chamber, (4) diffusion of monomer from the region above the substrate through any boundary layer

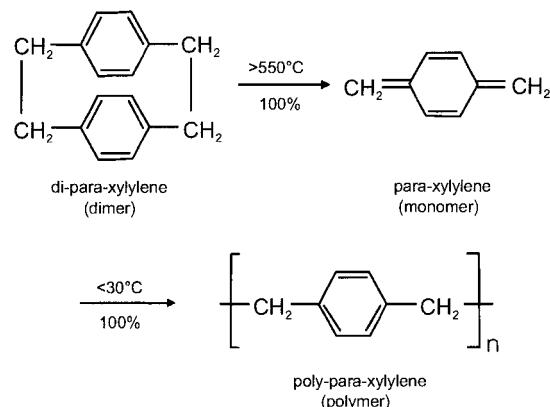
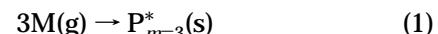


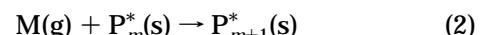
Figure 1. Polymerization route for parylene-N using the Gorham method.

that might exist, (5) adsorption of monomer onto the substrate, (6) surface migration and possibly bulk diffusion of monomer, and (7) chemical reaction (propagation or initiation). Also note that desorption of monomer can occur anytime after adsorption.

No separate initiator species is required for the polymerization to occur. The initiation reaction is believed to take place when a minimum of three monomer molecules join to form a diradical oligomer⁵ according to the equation



where M is the monomer, P is the polymer (or oligomer in this case), *m* is the number of monomer units in the chain, and * refers to a diradical. After initiation has taken place, the polymer chain can grow by propagation reaction according to the equation



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There is no termination reaction. During steady-state growth, the density of radical chain ends on the surface remains constant because the new radicals generated by initiation replace those that are buried in the growing film.

The amount of monomer consumed in propagation reactions is 2–3 orders of magnitude greater than that consumed in initiation reactions. This leads to the high molecular weight of parylene on the order of 200 000–400 000 g mol⁻¹, or about 2000–4000 units per chain length.⁵

Any model developed to describe the kinetics of the deposition process should fit the data over the appropriate range for multiple systems and be a reasonable theoretical interpretation of the process. In the case of parylene CVD, the model should fit data for deposition temperatures from around -40 °C to the temperature at which rates are no longer significant (in the range of 50–150 °C depending on parylene type) and pressures up to a few hundred millitorr. Outside these regions, the films become porous, and thus the density is lowered, and film growth rates based on the typical density of the film (about 1.11 g/cm³) are no longer valid.

A number of models have been developed to describe parylene deposition and to predict the deposition rate as a function of monomer pressure and substrate temperature.^{5–7} All of these models are based on the kinetics of the reaction process, step 7 of the CVD steps (including both initiation and propagation reactions). The models can be broken down into three types: those that define the monomer concentration at the surface of the growing film using Flory-type adsorption, Langmuir-type adsorption, or Brunauer–Emmett–Teller-type (BET-type) adsorption. Each of these types has also been presented to include either surface reaction only or surface and bulk reaction (which assumes some degree of monomer diffusion into the bulk of the film during growth).

These models have been published in three papers. Beach was the first to publish a model.⁵ His model was developed using the Flory surface concentration and assuming both surface and bulk-phase reaction. The next model was published by Gaynor.⁶ In this work, Gaynor developed a model based on the Langmuir surface concentration and only surface reaction. The third published article was by Rogojevic et al.⁷ They presented and compared six models (two for each of the surface concentration types) using Beach's approach. Rogojevic et al. presented models for each type using either surface reaction only or surface and bulk reaction. Beach's and Rogojevic et al.'s models were developed by equating the chemical potential of the monomer in the gas phase with that of the monomer at the polymer surface, which were assumed to be in equilibrium. Gaynor did not equate the chemical potentials directly. He developed an equation for the propagation reaction rate in three dimensions and then took the growth rate to scale as the propagation rate to the 1/3 power.

The models that have been presented in the literature are models of a kinetically controlled process. They are

expressed as the product of a term containing the kinetic rate constants raised to a power and an adsorption, or coverage, term raised to a power [for example, the rate equations are of the form rate = $(k_i k_p D)^{1/2}(\theta)^2$, where k_i , k_p , and D are the rate constants for initiation, propagation, and diffusion, respectively, and θ is the coverage]. The kinetic terms are complicated in that they contain the rate constants for the initiation reaction; the propagation reaction; and, in some cases, the diffusion of monomer into the bulk. The BET-based model, which allows for multilayer physisorption, seems to fit experimental data the best; however, the validity of the model was not verified by an analysis of the values of the fitting parameters.

An interesting aspect of the CVD of parylene is that the deposition rate decreases as the temperature increases. This behavior is not consistent with a typical kinetically controlled CVD reaction, which shows a deposition rate that increases with temperature as the positive activation energy for reaction is overcome.^{8–11} Errede et al. polymerized parylene in solution and saw an increase in growth rate as the temperature increased, the opposite of what is seen in the CVD case.¹²

It is apparent that, to fit the data, the existing models must be relying on the form of the surface coverage term, as the value of the kinetic term increases as the temperature increases. The surface coverage terms for all three types of adsorption that have been modeled show an increase in surface concentration of monomer as the temperature decreases and as the pressure increases. It is this coverage term that dominates the equation and allows the models to fit the experimental data approximately over the appropriate range. If these models are correct, it appears that the deposition kinetics is controlled by the surface concentration of monomer.

2. A Chemisorption Model

An alternative approach to modeling of the deposition rate is through the kinetics of the adsorption process, by modeling the rates at which the monomer impinges on the surface, is physisorbed, and is then chemisorbed (reaction with existing chain-end radicals). The model developed in this study, termed the chemisorption model, was developed on the basis of this idea, and it turns out to be very fruitful. This is a model that treats the adsorption rate as the limiting step and includes both physisorption and chemisorption.

The model is based on the fact that the maximum deposition rate for any CVD process can be given by (from refs 8, 13, and 14)

$$R_d = \frac{SPN_a V_m (60 \times 10^{10})}{(2\pi m_r R T_0)^{0.5}} \quad (3)$$

where the quantity $PN_a/(2\pi m_r R T_0)^{0.5}$ is the flux of the

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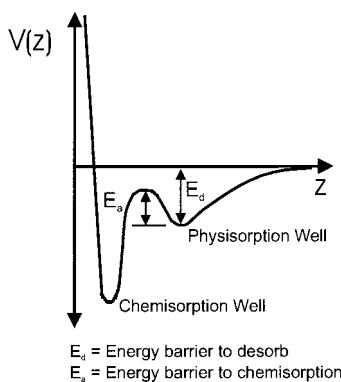


Figure 2. Lennard-Jones potential for a molecular chemisorption. E_d is the energy required for desorption from the bottom of the physisorption well, and E_a is the energy barrier for chemisorption, or in this case, polymerization, once in the physisorption well.

reactant to the substrate surface in collisions per square meter per second), P is the pressure in pascals, N_a is Avogadro's number, m_r is the molecular mass in kilograms per mole, R is the Rydberg gas constant, and T_0 is the temperature of the gas in Kelvin. The quantity V_m , which is the volume of one molecule in cubic meters, converts the flux into units of deposition rate in meters per second, and the multiplication factor of 60×10^{10} converts the units to angstroms per minute. The parameter S is the fraction of molecules that react after striking the surface, also called the sticking coefficient.¹⁵ Without the conversion factor V_m , this equation is just the rate of adsorption.¹⁴ Note that the pressure in the deposition chamber is equal to the pressure of the monomer for our system and that no dimer is present in the chamber in the vapor phase.¹⁶

The form of the sticking coefficient, which is dependent on the temperature, is determined by the energetics of the adsorption process, which can be expressed in the form of a Lennard-Jones potential.^{14,15} The Lennard-Jones potential for molecular chemisorption is shown in Figure 2. This potential energy exhibits both a deep chemisorption well and a shallow physisorption well somewhat farther from the surface. From this picture, an incoming molecule can first be trapped via physisorption in the outer well, termed a precursor state, and can then enter the deeper well at a later time via chemisorption. The sticking coefficient refers exclusively to the chemisorbed molecules.¹⁵

In the situation of parylene CVD, this can be viewed as the monomer first being physisorbed on the surface with no activation energy (which is typical of physisorption) and then surmounting an energy barrier to chemisorb. The chemisorption would be the reaction of the monomer with a chain end in a propagation reaction, and the barrier would be the activation energy for propagation.

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The term coverage needs to be clarified in this situation. In normal adsorption situations, coverage refers to the sites that are not active or that have had a molecule adsorb. In a typical chemisorption case, when a gas is led to a surface, the initial coverage is 0, and the coverage increases with time depending on the temperature, pressure, and energetics until an equilibrium is reached. In the case of parylene CVD, for every molecule that chemisorbs, a new chemisorption site, or a new radical chain end, is formed. This means that, under steady-state deposition, where the deposition rate is constant, the coverage is constant with time. It is easier to think in terms of $(1 - \theta)$, which is the fraction of the surface sites that are reactive, or are radical chain ends. Under steady-state conditions, this fraction is constant with time.

Also, in this model, $(1 - \theta)$ is taken to be a constant for all deposition conditions considered. That is, the concentration of reactive chain ends at the surface is fairly constant over the range of deposition conditions considered by the model. This assumption is based on the fact that the chain end density in the film is related to the average chain length (or molecular weight), and this has been determined to remain constant for deposition temperatures between -176 and 26 °C.¹⁷

To develop an expression for the sticking coefficient, S , as a function of coverage, a few assumptions are made.¹⁵ First, every site on the surface can support physisorption. This is true regardless of whether the chemisorption site below is occupied. Second, adsorbed molecules can roam across the surface in search of unoccupied chemisorption sites to occupy. This means that, after a molecule has physisorbed, it can chemisorb with a probability P_a , desorb back into the gas phase with a probability P_d , or migrate to an adjacent physisorption well with a probability P_m .

The limit of the sticking coefficient at zero coverage, or 100% active sites, S_0 , is defined as $P_a/(P_a + P_d)$. These probabilities are given as $P_a = V_a \exp(-E_a/RT)$ and $P_d = V_d \exp(-E_d/RT)$, where V_a and V_d are preexponential constants, E_a is the activation energy for chemisorption, E_d is the activation energy for desorption, and T is the temperature of the substrate (see Figure 2). The expression for S_0 then reduces to

$$S_0 = \frac{1}{(1 + V_e^{-(E_d - E_a)/RT})} \quad (4)$$

The typical form of the absolute sticking coefficient is $S = S_0 F(\theta)$, where $F(\theta)$ is some function of θ . The isotherm most commonly applicable to adsorption kinetics is the Langmuir isotherm. In the case of Langmuir-type adsorption, the sticking coefficient is given as $S = S_0(1 - \theta)$. Using the Langmuir isotherm, the final form of the rate equation then becomes

$$R_d = \frac{S_0(1 - \theta)PN_a V_m (60 \times 10^{10})}{(2\pi m_r RT_0)^{0.5}} \quad (5)$$

3. Experimental Section

Parylene films prepared for this study were deposited in a deposition system described elsewhere.¹⁶ The deposition pres-

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sure was controlled to within 0.1 mTorr by using a throttle valve between the sublimation furnace and the pyrolysis furnace. The chamber pressure was measured using a high-accuracy capacitance monometer heated to 100 °C. This device measured the pressure directly, unlike a thermocouple pressure gauge. The substrate temperature was controlled using a chuck equipped with a thermoelectric cooler–heater module. The temperature was measured at the substrate using a k-type thermocouple.

The data gathered in this study consist of three sets. The first data set is deposition rate as a function of pressure at 22 °C. The second data set is deposition rate as a function of pressure at -23 °C. The third data set is deposition rate as a function of temperature from -23 to 45 °C for a pressure of 4.0 mTorr (as shown in Figure 3).

The model was fit to experimental data gathered in this study using the least-squares method. The experimental data were compared to data generated from the model by changing the values of the unknown parameters and searching for the lowest value of the mean square error.

4. Results and Discussion

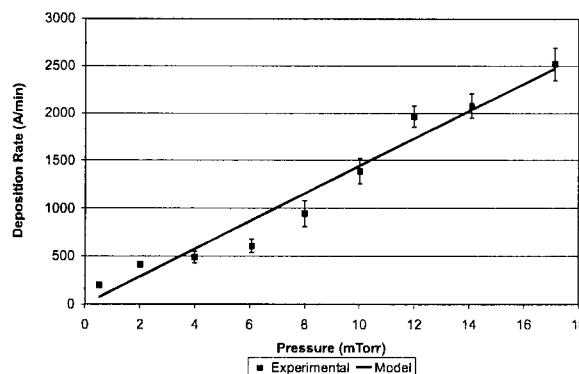
The final rate equation, eq 5, was fit to the experimental data by varying three parameters: (1) the value of $(1 - \theta)$, taken to be a constant; (2) ΔE , which is equal to $E_d - E_a$; and (3) V , which is equal to V_a/V_d . The volume occupied by one monomer was calculated from the density of the film and the molecular mass. Also, in calculating the impingement rate, the temperature of the monomer (T_0) was taken to be 298 K, or room temperature, for all deposition conditions. The best-fit values for the fitting parameters are shown in Table 1. The fit to the experimental data, which is quite good, is shown in Figure 3. The sticking coefficient as a function of temperature was extracted from the results and is shown in Figure 4. The value of $(1 - \theta)$ was found to be 1.29×10^{-3} . A value of $(6.5 - 8.6) \times 10^{-3}$ was calculated using the estimated value of the average chain molecular weight of 250 000–400 000 g/mol and considering the chain ends to be distributed evenly throughout the film.^{5,18} The best-fit value matches the calculated value within reason, especially considering that there are some sites on the surface that end up being buried in the film.

The value of $\Delta E = E_d - E_a$ can be also be checked using known data. Considering the activation energy, E_a , to be 8.7 kcal/mol as determined by Errede,¹² the value of E_d would be around 75 kJ/mol (18 kcal/mol). E_d is the heat of adsorption, the heat released during physisorption. With this in mind, a typical heat of adsorption for a small molecule such as CO or H₂O is typically on the order of 42 kJ/mol (10 kcal/mol),^{13,14} whereas, for a larger molecule, such as C₆H₆, the heat of adsorption is around 63 kJ/mol (15 kcal/mol).¹⁹ The heat of adsorption for *p*-xylene (C₈H₁₀), a solvent with a structure that is very similar to that of the monomer, has been calculated to be 82 kJ/mol (20 kcal/mol) and determined experimentally to be between 70 kJ/mol (17 kcal/mol) and 114 kJ/mol (27 kcal/mol) for adsorption onto a zeolite.²⁰ Therefore, the value for ΔE also appears to be within reason.

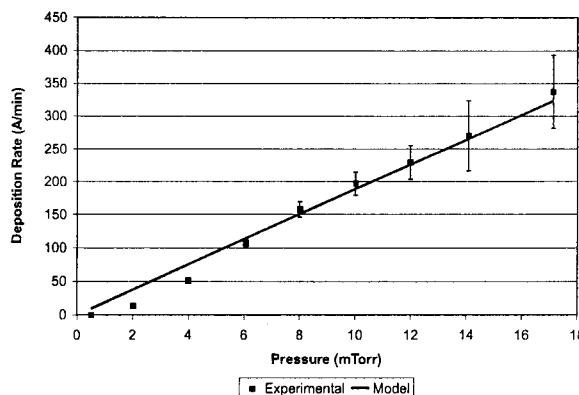
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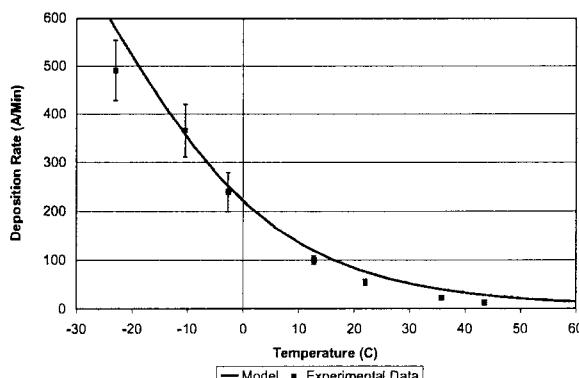
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(a) Rate vs. Pressure at $T = -23^\circ\text{C}$



(b) Rate vs. Pressure at $T = 22^\circ\text{C}$



(c) Rate vs. Temperature at $P = 4.0\text{ mTorr}$

Figure 3. Fit of the chemisorption model to this study's experimental data. The best-fit values were found to be $1 - \theta = 1.29 \times 10^{-3}$, $\Delta E = 39.4 \text{ kJ/mol}$ (9.41 kcal/mol), and $V = 1.20 \times 10^8$.

Table 1. Best-Fit Values of the Fitting Parameters for the Chemisorption Model

parameter	best-fit value
$1 - \theta$	1.29×10^{-3}
ΔE	39.4 kJ/mol (9.41 kcal/mol)
V	1.20×10^8

Finally, the sticking coefficient, shown in Figure 4, also is in a sensible range of values. Parylene is known for its excellent conformality to substrates. It has been shown to deposit deep into substrate gaps and under

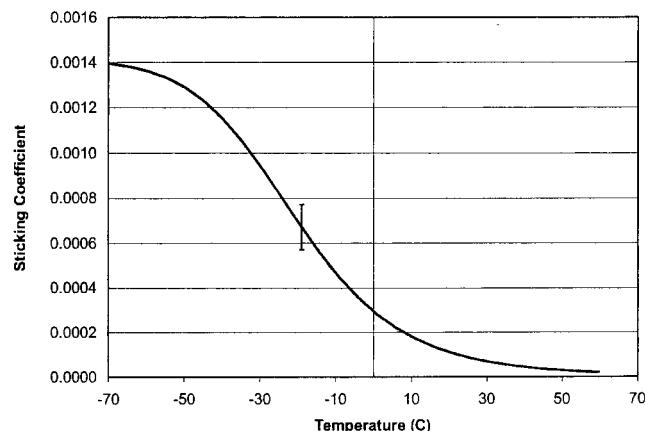


Figure 4. Sticking coefficient vs temperature from the chemisorption model. A value of 0.001 indicates that 1 out of 1000 incident monomer molecules reacts with a radical chain end and become part of the polymer. Notice that, as seen experimentally, the coefficient decreases as temperature increases.²⁴

overhanging submicron structures.^{18,21,22} This can only occur for a deposition process with a very low sticking coefficient.

The results of Errede et al.¹² for solution polymerization can now be more fully understood. In solution polymerization, there would not be a physisorbed state; there would only be a "chemisorbed" state. Therefore, there would be only one activation energy, E_a , and the result would be an increase in growth rate with an increase in temperature.

It is important to note that the chemisorption model fails to predict the correct deposition rate at very high temperatures and very low pressures. This is because, under such conditions, the initiation reaction becomes important. Parylene-family polymers are known to have a ceiling temperature above which deposition will not take place.⁴ In reality, this ceiling temperature is also dependent on pressure. This is believed to be due to the lack of initiation under these circumstances, probably resulting from a limited coverage of monomer molecules. This same concept holds true for low pressures. In this study, for example, at 25 °C, the deposition rate is 0 at 0.5 mTorr, whereas the model predicts that the rate should not go to 0 until 0 mTorr. The substrate can also play some role in this initiation reaction.²³ A model incorporating the initiation reaction would potentially be a complex one considering all of the energetics involved, but it is not necessary to incorporate the initiation reaction to account for most of depositions performed using typical deposition parameters.

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The chemisorption model does not explicitly include any parameter for diffusion of the monomer into the bulk of the film, as previous models have with limited success. This is not to say that there is not some degree of monomer diffusion into the bulk, however small. The diffusion of monomer into the bulk was found to be an important concept in the explanation of the evolution of the surface roughness of deposited parylene films.²⁴

As a final note, one aspect of using a model for a variety of different deposition systems that is important to have in mind is that there are system-to-system variations that cause pressure measurements to vary from one system to another. These variations can be caused by different deposition chamber designs and internal geometries that make it difficult to know the pressure accurately everywhere in the deposition chamber (the variation is evident by thickness nonuniformity). Another important difference between systems that leads to differences in measured pressure is the technique used to measure the pressure. Devices such as the capacitance monometer used in this study measure the pressure directly, whereas devices such as thermal conductivity and thermocouple gauges measure the pressure indirectly, by measuring the thermal properties of the gas. The indirect-measurement gauges need to be calibrated correctly for each gas that they measure, and if this calibration is not performed, significant errors can result.

The process of correctly measuring the pressure in the deposition chamber at the substrate location is a difficult one, and deviations from the true values can be large and often undeterminable. This needs to be taken into account when a model for the deposition process of a system is used.

Overall, it appears that the chemisorption model works well in predicting the deposition rate as a function of pressure and temperature for the steady-state deposition of parylene-N. It also nicely relates the chemisorption rate to the growth rate. The fact that the best-fit values for the fitting parameters are sensible further justifies this model's validity. This model should also apply to other parylene-family polymers with the values of the fit parameters adjusted on the basis of the energetics of the Lennard-Jones potential for each monomer type.

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