

Penetration of *p*-xylylene Vapor into Small Channels Prior to Polymerization

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Synopsis

The penetration of *p*-xylylene gas into small rectangular channels has been studied by measuring the thickness of the formed poly(*p*-xylylene) films as a function of penetration distance. The experimental values are related to the theoretical penetration curves under various process conditions. At low monomer and residual gas pressures, meeting the Knudsen conditions for wall-to-wall collisions of the monomer, a molecular flow model is valid which shows large penetration distances and a gradual decrease in film thickness. At increasing monomer pressures and corresponding deposition rates the molecular flow at the entrance is disturbed in favor of a more viscous type of flow. Consequently an accumulation of poly(*p*-xylylene) has been observed in the first part of the channel. At increasing residual gas pressures the penetration can be described by a mass transfer model. Under our process conditions however, its ideal penetration characteristics could not be realized due to a viscous flow transition at the entrance of the channel. Polymerization of chloro-*p*-xylylene at low residual gas pressures showed a molecular flow controlled penetration, also at high deposition rates. Owing to its higher reactivity the penetration is less favorable than for *p*-xylylene.

INTRODUCTION

Since the introduction of poly(*p*-xylylene) in the electronics industry it has been shown to possess remarkable chemical and physical properties in a broad field of applications.^{1,2} Rather unique is the process by which the polymer coatings are formed from the monomeric vapor phase.³ A substrate to be coated is exposed at room temperature to low pressure *p*-xylylene vapor. The condensing monomer polymerizes spontaneously at the substrate surface, while no polymer is formed in the gaseous phase. The mean free path of the monomer molecules is small compared to the dimensions of the apparatus, which results in a random distribution of the molecular motions. Besides the sticking coefficient of the collision monomer-substrate is low (10^{-4} – 10^{-5}), enabling the monomer to penetrate into small pores to form polymer coatings in areas where other coating processes fail. As little is known about the optimum penetration conditions, the aim of our work is to relate process variables such as monomer pressure, residual gas pressure, growth rate, and monomer type with the film thickness distribution in standardized small channels. The experimental results are compared with theoretical transport models, which describe the penetration of the *p*-xylylene monomer either as caused by a total pressure gradient at low residual gas pressures or as caused by a concentration gradient at high residual gas pressures.

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EXPERIMENTAL

The polymer deposition technique consists of three steps: (i) sublimation under vacuum (0.1 or 0.01 Torr residual gas pressure) at 80 to 200°C of 10 g of stable crystalline dimer, the cyclic di(*p*-xylylene); (ii) pyrolysis of the vapor at 600°C to form gaseous *p*-xylylene, the reactive monomer; and (iii) deposition and polymerization of the monomer at room temperature. The experiments were carried out with cyclic di(*p*-xylylene) and cyclic di(chloro-*p*-xylylene) as supplied by Union Carbide Corp. The polymer deposition rates were measured with a quartz crystal oscillator, the monomer and residual gas pressures with a capacitance manometer. Under our experimental conditions we found the reaction rate constants as defined in eq. (2) to be 2.6×10^{-5} and 4.4×10^{-4} cm sec⁻¹Torr⁻² for the polymerization of *p*-xylylene and chloro-*p*-xylylene, respectively.

Penetration measurements were carried out in 70 mm long rectangular flow channels. The gap between the two parallel glass side walls was maintained at values of 56, 28, or 14 μm respectively, using aluminium spacers. The width of the channels was taken large (20 mm) compared to the distance between them. The film thickness distributions in the channels were measured with a Dektak surface profile measuring system with a stylus diameter of 50 μm by partial removal of the poly(*p*-xylylene) coating along the longitudinal axis of the glass side walls.

RESULTS AND DISCUSSION

In order to study the penetration of *p*-xylylene vapor into the channels, the thickness of the formed poly(*p*-xylylene) films is measured as a function of the penetration distance x . To achieve comparable values in different experiments, the film thickness in the channel is related to the thickness at $x = 0$. As this relative film thickness (l_x/l_0) is independent of time, the following equation is valid:

$$l_x/l_0 = r/r_0 \quad (1)$$

where r and r_0 represent the growth rates at the penetration distance x and $x = 0$, respectively. According to the empirical growth rate equation of Cariou et al.⁴ the deposition rate is proportional to the square of monomer pressure P_M ,

$$r = k' P_M^2 \quad (2)$$

Substitution of eq. (2) in eq. (1) yields

$$l_x/l_0 = (P_M/P_{M_0})^2 \quad (3)$$

To find the variation of monomer pressure in the x direction, the law of conservation of mass can be used. The quantity of monomer which is polymerized on a length x of the walls of the channel equals the difference in molar rate N_M over the same length, thus

$$\frac{\partial N_M}{\partial x} = 2\rho(a+b)(ab)^{-1} M^{-1}r \quad (4)$$

where ρ is the polymer density, a and b are the gap dimensions, and M is the molecular weight of the *p*-xylylene monomer. Substitution of eq. (2) gives

$$\frac{\partial N_M}{\partial x} = 2\rho(a+b)(ab)^{-1} M^{-1} k' P_M^2 \quad (5)$$

The relation between the monomer molar rate N_M and the monomer pressure P_M is determined by the transport mechanism, which can be (i) a momentum transport caused by a pressure gradient in the x direction, which in steady state must be accompanied by an equimolecular counter transport of the residual gas A ($\partial P_A/\partial x = 0$), or (ii) a mass transfer through stationary, residual gas due to a concentration gradient of the monomer in the x direction [$\partial(P_A + P_M)/\partial x = 0$].

In general a steady-state momentum transport is expected to occur at low residual gas pressures P_A and a steady-state mass transfer at higher residual gas pressures.

Polymerization at Low Residual Gas Pressures

At low residual gas pressures the gas flow into the gap is expected to be caused by the pressure gradient in the x direction. In order to specify the transport mechanism the Knudsen number has to be taken into account, which gives the relation between the mean free path of the *p*-xylylene molecules and the gap dimensions. At low monomer pressures (<0.5 Torr), the mean free path of the gas molecules is large compared to the gap distance b and the gas flow is limited by molecular collisions with the walls of the channel (molecular flow). At higher monomer pressures or large gap values the monomer flow will become determined by intermolecular collisions and can be described in terms of hydrodynamics (viscous flow). To characterize the gas-carrying ability of channels the conductance F is commonly used,⁵ which relates the flow rate to the difference in pressure over the length dx according to

$$(N_M + N_A) = \frac{F}{abRT} \frac{\partial(P_A + P_M)}{\partial x} \quad (6)$$

Since the ratio between the molar rates of the monomer N_M and the residual gas N_A is equal to the ratio between the partial pressures at any point x and $\partial P_A/\partial x = 0$ to satisfy the steady state, then

$$N_M = \frac{F}{abRT} \frac{P_M}{P_A + P_M} \frac{\partial P_M}{\partial x} \quad (7)$$

In general for a molecular type of flow and a channel of uniform rectangular cross section, the conductance by unit of length F_{mol} can be written⁵

$$F_{\text{mol}} = \frac{2(ab)^2}{3(a+b)} \left(\frac{8RT}{\pi M} \right)^{1/2} \alpha \quad (8)$$

where α is a proportionality constant, depending on the relative dimensions of the cross section. It can either be found in literature⁶ or can be deduced from transmission probabilities as given by Holland et al.⁵ By substituting N_M from eq. (7) and F from eq. (8), eq. (5) can be transformed into

$$\frac{\partial}{\partial x} \left(\frac{P_M}{P_M + P_A} \right) \frac{\partial P_M}{\partial x} = \frac{3\rho(a+b)^2 k'}{\alpha(ab)^2} \left(\frac{\pi RT}{8M} \right)^{1/2} P_M^2 \quad (9)$$

with boundary conditions

$$P_M = P_{M_0} \quad \text{at } x = 0 \quad (10)$$

$$P_M = 0 \quad \text{as } x \rightarrow \infty \quad (11)$$

Equation (9) can be solved numerically which, after substitution in eq. (3), yields the theoretical penetration curves. For the experiments carried out at a *p*-xylylene gas pressure and a residual gas pressure both of 0.01 Torr, the thickness distribution in channels with gaps of 14, 28, and 56 μm fit well with the theoretical penetration curves. When the *p*-xylylene pressure is raised to 0.05 Torr the experimental and the theoretical results differ slightly at a gap distance of 56 μm while with 14 and 28 μm gaps they are still in accordance with each other (Fig. 1). At increasing monomer pressures the intermolecular collisions become more important and the molecular flow model is not suitable for a description of what takes place at the channel entrance. This effect is even more pronounced at a *p*-xylylene pressure of 0.07 Torr, which yields strong deviations from the model at the entrance of the 28 and 56 μm gaps as can be seen in Figure 2. As the in-

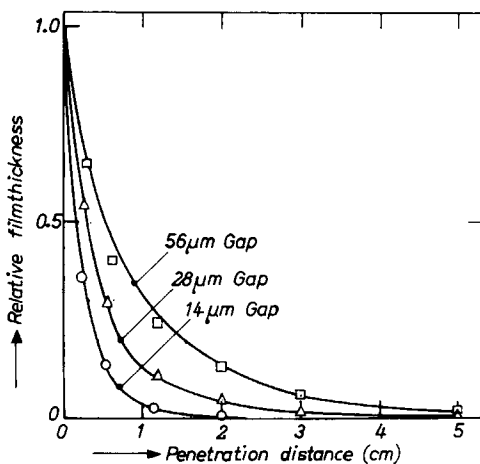


Fig. 1. Film thickness distribution of poly(*p*-xylylene) polymerized under conditions of medium monomer pressure (P_M) ($P_{M_0} = 0.05$ Torr) and low residual gas pressure (P_A) ($P_A = 0.01$ Torr) determined experimentally (points) and calculated for the molecular flow model (curves).

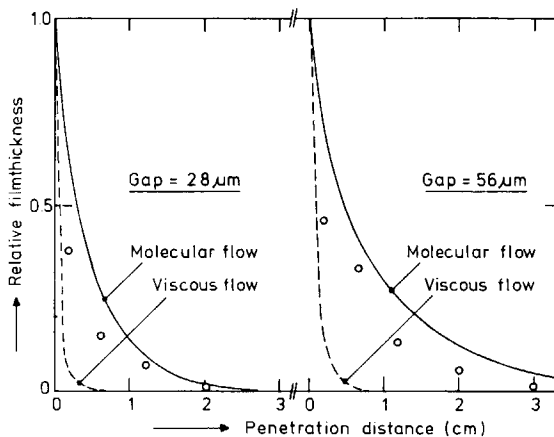


Fig. 2. Film thickness distribution of poly(*p*-xylylene) polymerized under conditions of low residual gas and high monomer pressure determined experimentally (points) and calculated for the molecular flow and the viscous flow models (curves). $P_{M_0} = 0.07$ Torr; $P_A = 0.01$ Torr.

termolecular collisions cause a strong decrease in monomer pressure due to an enhanced deposition rate, the mean free path of the gas molecules again meets the Knudsen conditions for molecular flow after a penetration distance ≥ 0.2 cm (Fig. 3). At a gap distance of $14 \mu\text{m}$ and a *p*-xylylene pressure of 0.07 Torr the mean free path of the gas molecules satisfies the Knudsen conditions for molecular flow over the whole length of the gap and a deviation from this model at the entrance can be seen only at higher monomer pressures up to 0.10 Torr. Combining these data yields Figure 4, which shows the maximum monomer pressure, at which a molecular flow is maintained over the entire gap length, to be inversely proportional to the gap distance according to Knudsen's theory. Furthermore *p*-xylylene shows better penetration characteristics at decreasing monomer pressures (Fig. 5), in agreement with our theoretical expectations.

In the case of a unidirectional laminar viscous flow of a gas with viscosity η ,

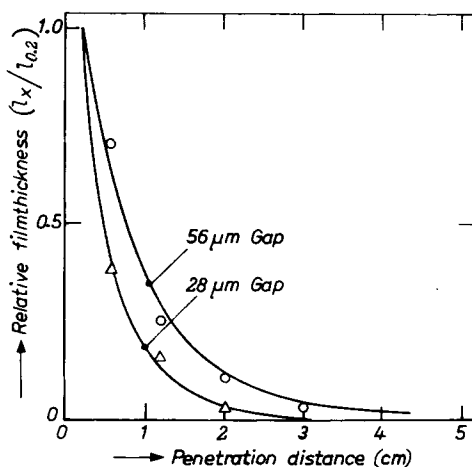


Fig. 3. Relative film thickness distribution of poly(*p*-xylylene) polymerized under conditions of low residual gas and high monomer pressure determined experimentally (points) and calculated for the molecular flow model (curves) taking into account an entrance transition of 0.2 cm. P_{M_0} and P_A as in Figure 2.

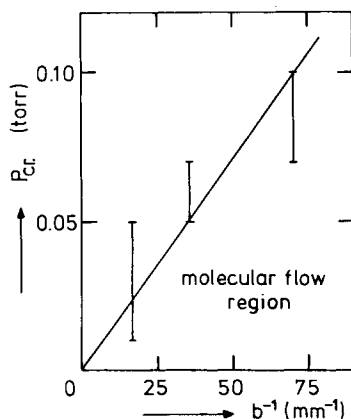


Fig. 4. Critical monomer pressure, above which molecular flow is disturbed by intermolecular collisions, as a function of the reciprocal gap distance. The gap width is 20 mm and the residual gas pressure 0.01 Torr.

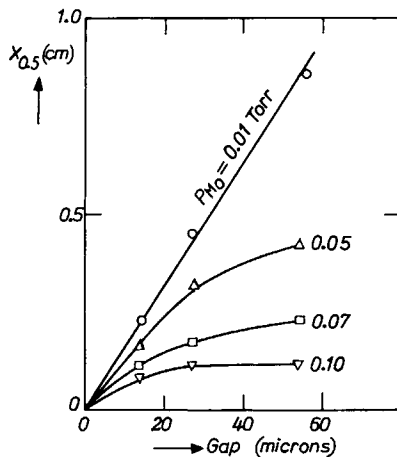


Fig. 5. Penetration distance meeting the condition $l_x/l_0 = 0.5$ as a function of gap distance and monomer pressure.

the conductance F_{visc} of a channel with a rectangular cross section can be derived from literature data⁷:

$$F_{\text{visc}} = (ab^3/12\eta) (P_M + P_A) \quad (12)$$

After substitution of N_M from eq. (7) and F from eq. (12), eq.(5) yields

$$\frac{\partial^2 P_M}{\partial x^2} = \frac{48\rho\eta(a+b)k'RT P_M^2}{Mab^3} \quad (13)$$

When the boundary conditions (10) and (11) are satisfied, eq. (13) can be solved to give

$$P_M^2 = P_{M_0}^2 \exp\left[-\left(\frac{48\rho\eta(a+b)k'RT}{Mab^3}\right)^{1/2} x\right] \quad (14)$$

The viscosity of the *p*-xylylene vapor was calculated at 7.56×10^{-6} Pa sec using the model of molecular interaction due to Chapman and Cowling.⁸ Substitution of eq. (14) in eq. (3) yields the theoretical penetration curves shown in Figure 2. Under our experimental conditions relative poly(*p*-xylylene) thickness values, which agree with the viscous flow model were found only at very small penetration distances and high monomer pressures.

Owing to its higher reaction rate constant, polymerization of chloro-*p*-xylylene generally takes place at lower monomer pressures than those used for *p*-xylylene. Even at high deposition rates, for instance 25 Å/sec, its monomer pressure satisfies the condition for molecular flow at gap values $\leq 56 \mu\text{m}$, given in Figure 4. Experiments were carried out at chloro-*p*-xylylene pressures of 0.01 to 0.025 Torr and a residual gas pressure of 0.01 Torr. In all cases the experimental penetration data fit with the theoretical curves calculated according to the molecular flow model. As is the case with *p*-xylylene the penetration can be improved by lowering the monomer pressure. However, mainly as a result of the higher reaction rate constant, chloro-*p*-xylylene shows a less favorable penetration than does *p*-xylylene under molecular flow conditions, in agreement with eq. (9).

Polymerization at High Residual Gas Pressures

At higher residual gas pressures the monomer molecules are unable to collide from wall to wall without being disturbed by the residual gas molecules. As soon as the monomer pressure outside the gap has reached a constant value the total pressure gradient in the gap is expected to be zero. In the mixture of monomer vapor and residual gas only the monomer reacts at the walls of the channel. Therefore a partial pressure gradient will be set up, causing the monomer to diffuse in the x direction and the residual gas in the opposite direction. To prevent the formation of a gradient in total pressure, a bulk motion of monomer and residual gas in the x direction arises. Since we assume no net motion of residual gas, its bulk rate of flow must balance its transfer by diffusion. The total rate of transfer of the monomer is obtained by summing the transfer by diffusion and bulk flow and is according to Stefan's law of diffusion

$$N_M = \frac{D}{RT} \left(\frac{P_M + P_A}{P_A} \right) \frac{\partial P_M}{\partial x} \quad (15)$$

The diffusivity D of *p*-xylylene vapor in residual gas is pressure dependent and has been calculated from Maxwell's empirical equation, modified by Gilliland.⁹ The calculated values are in good accordance with those found in literature for *p*-xylene, the molecule most resembling *p*-xylylene. Substituting eq. (15) in eq. (5) gives

$$\frac{\partial}{\partial x} \left(\frac{P_M + P_A}{P_A} \right) \frac{\partial P_M}{\partial x} = \frac{2\rho(a+b)k'RT P_M^2}{abMD} \quad (16)$$

Subjecting eq. (16) to the boundary conditions (10) and (11), the solution can be found numerically. Figure 6 shows the mass transfer based penetration curves, which however disagree with the experimental data. The high residual gas experiments show an entrance transition which causes a rapid drop in monomer pressure and accordingly a decrease in film thickness similar to a viscous type of flow. At increasing penetration distances, where the monomer pressure has been decreased and the condition $\partial(P_A + P_M)/\partial x = 0$ becomes more

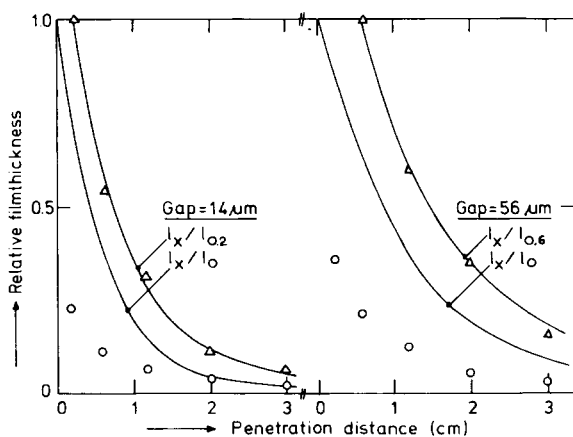


Fig. 6. Film thickness distribution of poly(*p*-xylylene) polymerized under high residual gas pressure conditions, related to the film thickness at $x = 0$ and $x = 0.2$ or 0.6 cm, respectively, as measured (points) and as calculated for the mass transfer model (curves). $P_{M_0} = 0.10$ Torr; $P_A = 0.10$ Torr.

likely, the observed and calculated film thickness distributions are in good agreement.

CONCLUSIONS

In order to obtain good penetration characteristics of *p*-xylylene vapor into channels with spacings $\leq 56 \mu\text{m}$ prior to its polymerization, viscous flow conditions must be avoided. Low residual gas pressures and low monomer pressures satisfying the Knudsen conditions for wall to wall collisions, result in a molecular flow controlled penetration and a gradual decrease in film thickness at increasing penetration distances. Apparently there is no net flux of residual gas under these conditions. Decreasing monomer pressures with corresponding low deposition rates result in increasing penetration properties. An increase of the residual gas pressure yields a diffusion controlled penetration and large penetration distances. It is difficult, however, to prevent a sharp decrease in film thickness at the entrance of the channel under these process conditions. The entrance transition is probably caused by a viscous type of flow. Again the best penetration properties are obtained at low deposition rates. Polymerization of chloro-*p*-xylylene at low residual gas pressures showed a molecular flow controlled penetration, even at high deposition rates, as a result of a higher reactive rate constant. However, owing to the high reactivity of the chloro-*p*-xylylene monomer, a considerable less favorable penetration is observed than for *p*-xylylene.

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