overall rate constants involving the dissociation constants of the alkoxide species. They are, however, clearly most significant as the relative values to reflect the dependence on the ring size, as far as we compare the parameters at a constant initiator concentration which means a constant α.

In summary, we can conclude from both the kinetic and thermodynamic points of view that the cyclic dimer is the least reactive among the cyclic oligomers to reach the highest equilibrium concentration and that the higher the ring size of the cyclic oligomer the higher is its reactivity and the lower its equilibrium concentration. ϵ-Caprolactone monomer is exceedingly far more reactive than the other cyclic oligomers so that it can be hardly detected in the equilibrated mixture.

References and Notes

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A Model for the Vapor Deposition Polymerization of *p*-Xylylene

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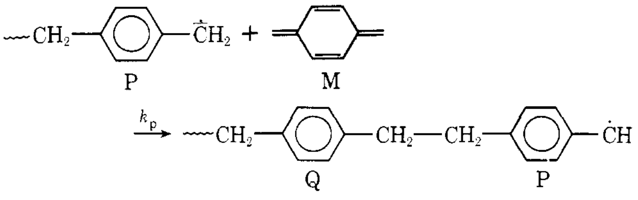
ABSTRACT: A model is developed for the vapor deposition and polymerization of *p*-xylylene which links the process variables of temperature, pressure, and rate of growth with molecular rate constants, diffusional mass transport, and molecular weight. For an important limiting case, an approximate solution is extracted which predicts the interdependence of process variables and polymer properties. Data from the literature regarding the polymerization of *p*-xylylene are used to set up exemplary model parameters to describe the conditions present in a typical vapor deposition polymerization. The picture which emerges is that the polymer is formed within a few thousand ångströms of the growth surface in a medium which is best described as a slightly swollen solid.

The poly(*p*-xylylenes) are of modest but growing commercial importance, finding applications as plastic coatings in particular with the electronics industry. The key to their acceptance lies not so much in their excellent properties as materials, but rather in the uniqueness of the process by which they are formed, and particularly in the results that process can alone provide.[1] Typically, a substrate to be coated is exposed at room temperature to low-pressure (<0.1 torr) gaseous *p*-xylylene monomer. Condensing monomer polymerizes spontaneously to grow the coating outward from the substrate surface at rates typically in the vicinity of 50 Å s^{-1}. Solid polymer grows from gaseous monomer directly, without a discernible intervening liquid phase. No polymer is formed in the gaseous phase.

Little has been added to the general body of open knowledge regarding the mechanism of formation of poly(*p*-xylylenes) from the vapor phase since Errede and Szwarc prepared their review article in 1958.[2] Their qualitative picture of the polymerization mechanism still seems valid. In the work reported here, a framework is erected for the quantitative understanding of *p*-xylylene vapor deposition polymerization.

Deposition Chemistry

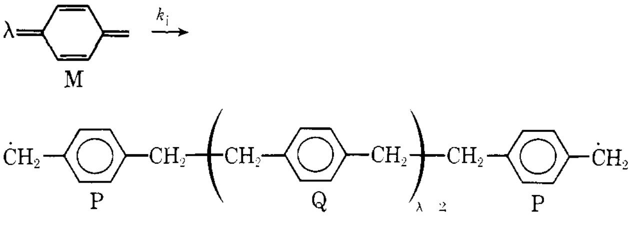
We will now discuss the chemical and physical aspects of the *p*-xylylene deposition which are essential to the development of the model. It will be assumed that the polymer propagates by the addition of monomer (M) to free radical polymer chain end propagation centers (P):



Each event results in the consumption of one monomer molecule and the production of one polymer repeat unit (Q), with no net change in the number of propagation centers. Using the symbols *P*, *Q*, and *M* to represent the mass concentrations (g cm^{-3}) of the respective species:

$$-\left(\frac{\partial M}{\partial t}\right)_p = \left(\frac{\partial Q}{\partial t}\right)_p = k_p \cdot PM; \quad \left(\frac{\partial P}{\partial t}\right)_p = 0 \qquad (1)$$

where the subscript p specifies the propagation reaction. The propagation reaction is responsible for building essentially all high molecular weight polymer. However, the chains must be started before propagation is possible. It will be assumed here, as Errede and Szwarc[2] and Kubo[3] have proposed, that the free-radical propagation centers are created by an initiation reaction which is of order two or greater with respect to monomer, the actual order, λ, being otherwise unspecified at this time:



$\lambda \geqslant 2$

Each initiation event results in the consumption of λ monomer units and the production of two free-radical propagation centers and ($\lambda - 2$) polymer repeat units:

$$-\frac{1}{\lambda}\left(\frac{\partial M}{\partial t}\right)_i = \frac{1}{2}\left(\frac{\partial P}{\partial t}\right)_i = \frac{1}{(\lambda - 2)}\left(\frac{\partial Q}{\partial t}\right)_i = k_i M^\lambda \qquad (2)$$

where the subscript i specifies the initiation reaction. Again following Errede and Szwarc,[2] it will be assumed that polymer chains continue to propagate as long as monomer is in their

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vicinity, ceasing to grow when they are "buried" (isolated from the influx of fresh monomer). It will be unnecessary to invoke a specific chemical event which ends chain growth. This model will assume that the polymer is truly living.

The process model requires a relation linking the pressure of monomer gas and concentration of monomer at (near) the growth surface. Flory[4] gives an expression for the limiting form of Henry's law when the concentration of diluent is expressed as volume fraction. Neglecting volume change on polymerization, Flory's expression becomes:

$$M_0 = \frac{\rho}{K_H}\frac{p}{p_0} \tag{3}$$

Where ρ is the mass density of the polymer film and M_0 is the mass concentration of monomer at the growth surface (both in g cm^{-3}); p_0 is the equilibrium vapor pressure of monomer and p is the process pressure of monomer gas in the vicinity of the growth surface (in the same suitable pressure units such as millitorr); and K_H is the dimensionless constant for Henry's law which should have a value near 3.[4] Under typical conditions of vapor deposition polymerization, it can be shown that the rate at which molecules strike the growth surface exceeds that at which molecules of monomer are incorporated into the coating by about three or four orders of magnitude. Thus, the equilibrium approximation inherent in eq 3 is normally justified.

The crystallinity of the poly(*p*-xylylene's) is a major factor influencing their properties as coatings materials and has been studied extensively by Wunderlich[3b,5] and Niegisch.[6] While crystallization proceeds in close temporal proximity to polymerization, it is generally accepted that polymerization precedes crystallization. It will be assumed in this model that crystallization processes do not affect the rate of deposition.

Formulating the Model

In the absence of temperature and pressure gradients and external force fields, the expression[7] for mass transport within a two-component fluid is:

$$\mathbf{j}_A = \rho_A \mathbf{V}_A = -D_{AB}\nabla\rho_A \tag{4}$$

where $\mathbf{j}_A$ is the mass flux resulting from diffusion (g cm^{-2} s^{-1}), ρ_A is the mass concentration of component A (g cm^{-3}), $\nabla\rho_A$ is the gradient in mass concentration of component A (g cm^{-4}), and D_{AB} is the diffusivity for the pair A–B. $\mathbf{V}_A$, the diffusion velocity of component A (cm s^{-1}), is the velocity of component A, $\mathbf{v}_A$, with respect to the local mass average velocity of the fluid, $\mathbf{v}_0$: $\mathbf{V}_A = \mathbf{v}_A - \mathbf{v}_0$. Thus, diffusivity is defined with respect to a stationary fluid.

At any point in the fluid, the flux of A (g cm^{-2}s^{-1}) is $\rho_A\mathbf{v}_A$. The divergence of the flux of component A is the net rate per unit volume at which A leaves an infinitesimally small volume containing the point of interest. Therefore, at any point within the fluid, the time rate of change of mass density, $(\partial\rho_A/\partial t)$, is equal to the rate r_A at which A is being generated by chemical reaction within an arbitrarily small volume containing that point, less the rate A is being lost from that volume, all per unit volume:

$$(\partial\rho_A/\partial t) = r_A - \nabla\cdot\rho_A\mathbf{v}_A = r_A - \nabla\cdot\rho_A\mathbf{V}_A - \nabla\cdot\rho_A\mathbf{v}_0$$

$$(\partial\rho_A/\partial t) = r_A + \nabla\cdot D_{AB}\nabla\rho_A - \nabla\cdot\rho_A\mathbf{v}_0 \tag{5}$$

The three terms on the rhs of eq 5 resolve the time rate of change of mass density of component A into chemical reaction, diffusion, and convection effects, respectively.

In the case of macroscopic diffusion of monomer within a poly(*p*-xylylene) film, we will regard the medium as a homogeneous fluid, comprising monomer (M) and polymer (P + Q). Since P and Q are covalently bonded, the only diffusivity term of concern is that between monomer and polymer, which we shall call D. It will be further assumed that D is independent of the composition of the medium.

The case of vapor deposition polymerization coating growth is a one-dimensional problem, the coordinate of interest being that normal to the plane of the substrate surface. All profiles of composition within the coating will be expressible in terms of such a single space coordinate (x) and time and will be solutions to:

$$(\partial\rho_A/\partial t) = r_A + D(\partial^2\rho_A/\partial x^2) - (\partial/\partial x)(\rho_A\mathbf{v}_0) \tag{6}$$

For the special case in which the mass average velocity of the medium ($\mathbf{v}_0$) is zero everywhere in the coordinate system selected,

$$(\partial\rho_A/\partial t) = r_A + D(\partial^2\rho_A/\partial x^2) \tag{7}$$

This will be recognized as Fick's second law of diffusion, modified for chemical formation of A.

Consider the case of a poly(*p*-xylylene) coating growing under constant process conditions, after sufficient time has elapsed that steady state growth is achieved. If a coordinate system z is selected in which the growth interface is stationary at $z = 0$ and the polymer is entirely at $z > 0$, time independent steady state profiles of composition are the solutions to equations of the type:

$$(\partial\rho_A/\partial t) = 0 = r_A + D(\partial^2\rho_A/\partial z^2) - (\partial/\partial z)(\rho_A v_0) \tag{8}$$

Whereas it would be possible to include change in molar volume with polymerization in the model, the present state of knowledge of the poly(*p*-xylylene) polymerization does not justify the resulting complications. Invoking zero shrinkage on reaction, momentum conservation leads us to the conclusion that $\mathbf{v}_0$ is independent of z and in fact equal to the growth rate γ (cm s^{-1}) of the poly(*p*-xylylene) coating, the rate at which the substrate–polymer interface is advancing to higher z. Thus, the zero shrinkage on polymerization assumption adds further simplification:

$$0 = r_A + D(\partial^2\rho_A/\partial z^2) - \gamma(\partial\rho_A/\partial z) \tag{9}$$

The convection term $-\gamma(\partial\rho_A/\partial z)$ has the following physical meaning. Monomer (A = M) decreases in mass concentration with increasing z. Thus, $(\partial\rho_A/\partial z) < 0$. The convection of monomer from lower z by the positive mass average velocity γ tends to increase the mass concentration of a given z, adding to that created by chemical reaction r_A.

Using the symbols M, P, and Q to represent the appropriate mass concentrations and incorporating (1) and (2) in r_A, we arrive at a set of differential equations which describe the time-independent profiles of mass concentration within the steadily growing poly(*p*-xylylene) film:

$$0 = -\lambda k_i M^\lambda - k_p PM + D\left(\frac{\partial^2 M}{\partial z^2}\right) - \gamma\left(\frac{\partial M}{\partial z}\right) \tag{10a}$$

$$0 = 2k_i M^\lambda + D\left(\frac{\partial^2 P}{\partial z^2}\right) - \gamma\left(\frac{\partial P}{\partial z}\right) \tag{10b}$$

$$0 = (\lambda - 2)\, k_i M^\lambda + k_p PM + D\left(\frac{\partial^2 Q}{\partial z^2}\right) - \gamma\left(\frac{\partial Q}{\partial z}\right) \tag{10c}$$

An Approximate Solution

Because the sum of the mass concentrations ρ_P, ρ_Q, and ρ_M equals the polymer density ρ and it is assumed that there is zero volume change on reaction, it is sufficient to solve for only two profiles:

$$D\left(\frac{\partial^2 M}{\partial z^2}\right) - \gamma\left(\frac{\partial M}{\partial z}\right) = k_p PM + \lambda k_i M^\lambda \tag{10'a}$$

$$D\left(\frac{\partial^2 P}{\partial z^2}\right) - \gamma\left(\frac{\partial P}{\partial z}\right) = -2k_i M^\lambda \tag{10'b}$$

While it will in general be possible to obtain solutions to this coupled set by numerical techniques for any specific set of model parameters (D, γ, k_p, k_i, and λ), more insight is to be gained by making the following three further assumptions, which, although they place restrictions on the acceptable values of the model parameters, decouple and simplify the DE's to the point where they are easily integrated analytically.

Assumption A, $k_pPM \gg \lambda k_iM^\lambda$. This is equivalent to saying that virtually all monomer is consumed by propagation and that high molecular weight polymer is formed. It will be developed that because M is greatest at $z = 0$, if compliance to this assumption is tested there, compliance over all z is implied.

Assumption B, $|D(\partial^2M/\partial z^2)| \gg |\gamma\ (\partial M/\partial z)|$ and $|D(\partial^2P/\partial\ z^2)| \gg |\gamma(\partial P/\partial z)|$. This is equivalent to saying the deposition is conducted sufficiently slowly that convection effects are unimportant. It will be shown that both conditions B hold if $aD/\gamma \gg 1$.

Assumption C, $P \simeq P_\infty$ over all z. This, it will be shown, will be true if $P_\infty \gg 2k_iM_0^\lambda/a^2\lambda^2D$. It should be noted that assuption C does not imply that $(\partial^2P/\partial z^2)$ and $(\partial P/\partial z)$ are zero for all z, merely that they are not sufficiently large to appreciably affect $P(z)$. Under these restrictions on the model parameters eq 10′ simplify to:

$$D\ (\partial^2M/\partial z^2) = k_pP_\infty M \tag{11a}$$

$$D\ (\partial^2P/\partial z^2) = -2k_iM^\lambda \tag{11b}$$

These equations will be the basis of the approximate solution.

Equation 11a is a simple DE in one variable which has solutions of the form:

$$M = M_0 \exp[(k_pP_\infty/D)^{1/2}\cdot z] = M_0\exp(-az) \tag{12}$$

The reciprocal of the logarithmic decrement $a = (k_pP_\infty/D)^{1/2}$ is a measure of the depth of penetration of monomer into the growing polymer and therefore the depth of the reaction zone behind the growth surface. The solution to (11b) is obtainable by integration after substituting (12) for M:

$$P = P_\infty - \frac{2k_i\mathrm{M}_0{}^\lambda}{\mathrm{a}^2\lambda^2\mathrm{D}}\exp(-a\lambda z) \tag{13}$$

Two constraints on the deposition-polymerization system are necessary from physical considerations. First, monomer must cross the growth surface ($z = 0$) at a flux sufficient to supply the growth of the film at γ cm s^{-1}. At the growth surface, before any monomer can be consumed, Fick's first law establishes the concentration gradient:

$$-D\left(\frac{\partial M}{\partial z}\right)_{z=0} = \gamma\cdot\rho \qquad (\mathrm{g\ cm^{-2}\ s^{-1}})$$

Substituting the first derivative of (12):

$$-D(-aM_0\exp(-az))_{z=0} = aDM_0 = \gamma\rho$$

or

$$M_0 = \gamma\rho/aD \tag{14}$$

The same relation can also be derived by a somewhat different argument. Under steady state conditions, the total quantity of unreacted monomer within the film is time invariant. Therefore, the rate at which monomer enters the film from the vapor phase ($\gamma\rho$) must exactly equal the rate at which it is consumed within the growing medium:

$$\gamma\rho = \int_{\mathrm{film}}\left(\frac{\mathrm{d}M}{\mathrm{d}t}\right)_x \mathrm{d}x = \int_0^\infty k_pP_\infty M\ \mathrm{d}z$$

$$= k_pP_\infty\int_0^\infty M_0\exp(-az)\ \mathrm{d}z = \frac{k_pP_\infty M_0}{a} = aDM_0$$

$$M_0 = \gamma\rho/aD \tag{14′}$$

For the last step, it will be recalled that $a^2D = k_pP_\infty$.

Second, it is necessary that the rate at which P is formed be equal to the rate at which P is buried.

$$\text{Rate of burying } P = \gamma P_\infty\ (\mathrm{g\ cm^{-2}\ s^{-1}})$$

$$\text{Rate of generating } P = \int_{\mathrm{film}}\left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)\mathrm{d}x = \int_0^\infty 2k_iM^\lambda\ \mathrm{d}z$$

$$= 2k_i\ M_0{}^\lambda\int_0^\infty \exp(-a\lambda z)\mathrm{d}z = \frac{2k_iM_0{}^\lambda}{a\lambda}$$

$$\gamma P_\infty = 2k_iM_0{}^\lambda/a\lambda$$

$$\lambda a\gamma P_\infty = 2k_iM_0{}^\lambda \tag{15}$$

At this point, it is possible to select three independent equations which interrelate four process parameters: the growth rate γ (cm s^{-1}); the logarithmic decrement a (cm^{-1}); the bulk concentration of free-radical chain ends P_∞ (g cm^{-3}), which can be in turn related to number average molecular weight; and the growth surface concentration of monomer M_0 (g cm^{-3}), which can be in turn related to the pressure of monomer gas in the adjacent phase. From eq 14, 15, and the relation defining a we have:

$$a/\gamma = P/M_0D \tag{16a}$$

$$a\gamma Pb = 2k_iM_0{}^\lambda/\lambda \tag{16b}$$

$$a^2/P_\infty = k_p/D \tag{16c}$$

Taking logarithms of both sides and solving the three resulting simultaneous linear equations for a, γ, and P_∞:

$$a = \left(\frac{2\rho}{\lambda}\right)^{1/4}\left(\frac{k_ik_p}{D^2}\right)^{1/4} M_0{}^{((\lambda-1)/4)} \tag{17a}$$

$$\gamma = \left(\frac{2}{\gamma\rho^3}\right)^{1/4}(k_ik_pD^2)^{1/4}M_0{}^{((\lambda+3)/4)} \tag{17b}$$

$$P_\infty = \left(\frac{2\rho}{\lambda}\right)^{1/2}\left(\frac{k_i}{k_p}\right)^{1/2}M_0{}^{((\lambda-1)/2)} \tag{17c}$$

The surface and bulk concentrations of monomer and free-radical chain ends, M_0 and P_∞, can be related to monomer gas pressure and poly(p-xylylene) number average molecular weight, p and $\overline{M}_n$, by relations previously discussed:

$$M_0 = \frac{\rho}{K_H}\frac{p}{p_0} \tag{3′}$$

$$P_\infty = 2\rho w/\overline{M}_n \tag{18}$$

where w is the polymer repeat unit (monomer) molecular weight, g mol^{-1}. Therefore:

$$a = \left(\frac{2\rho}{\lambda}\right)^{1/4}\left(\frac{k_ik_p}{D^2}\right)^{1/4}\left(\frac{\rho}{K_Hp_0}\right)^{((\lambda-1)/4)}p^{((\lambda-1)/4)} \tag{19a}$$

$$\gamma = \left(\frac{2}{\lambda\rho^3}\right)^{1/4}(k_ik_pD^2)^{1/4}\left(\frac{\rho}{K_Hp_0}\right)^{((\lambda+3)/4)}p^{((\lambda+3)/4)} \tag{19b}$$

$$\overline{M}_n = w(2\rho\lambda)^{1/2}\ (k_p/k_i)^{1/2}\left(\frac{K_Hp_0}{\rho}\right)^{((\lambda-1)/2)}p^{-((\lambda-1)/2)} \tag{19c}$$

Before utilizing the results of the approximate solution (eq 17 or 19) it will be essential to establish that all three of the approximate solution assumptions (A, B, and C) are valid for the set of model parameters (D, γ, k_p, k_i, and λ) being considered.

Temperature Dependence

Chemical reactions, diffusion, and vaporization are each activated processes, obeying a temperature-dependence law of the Arrhenius form:

$$(\partial\ln K/\partial(1/T)) = -E_K/R$$

where K is the rate or equilibrium constant, E_k is the energy of activation or process heat, and R is the universal gas constant. The temperature dependence of such activated processes is usually far in excess of that for, for example, density. The expressions for temperature dependence of a, γ, and $\overline{M}_n$ can be derived from the approximate solutions, eq 19, by assuming Arrhenius behavior of k_i, k_p, D, and p_0 with activation energies E_i, E_p, E_D, and heat of vaporization of monomer ΔH_v, ignoring any temperature dependence of other parameters:

$$\frac{\partial \ln a}{\partial(1/T)} = \frac{-E_i - E_p + 2E_D + (\lambda - 1)\Delta H_v}{4R} \tag{20a}$$

$$\frac{\partial \ln \gamma}{\partial(1/T)} = \frac{-E_i - E_p - 2E_D + (\lambda + 3)\Delta H_v}{4R} \tag{20b}$$

$$\frac{\partial \ln \overline{M}_n}{\partial(1/T)} = \frac{-E_p + E_i - (\lambda - 1)\Delta H_v}{2R} \tag{20c}$$

Discussion

The model makes testable predicitons. The approximate solutions, eq 19, within their range of validity, predict that at constant temperature, growth rate γ and $\overline{M}_n$ have specific functional relationships with the pressure of monomer gas. It has been reported that the deposition rate is proportional to the square of monomer pressure.[3b,8] In retrospect, however, the fractional orders which may be predicted by this model might not have been anticipated by the earlier workers. Studies of growth rate as a function of monomer pressure may be the most direct route to obtaining experimental evidence for λ, the order of the initiation reaction. Studies of $\overline{M}_n$ as a function of monomer pressure might be expected to be more difficult but will provide corroborative support for the model and its λ. Equations 20 predict the temperature dependence of growth rate λ and $\overline{M}_n$ in terms of the activation energies for initiation, propagation, and diffusion and the latent heat of vaporization of monomer, when the approximate solution is valid. If reliable estimates for E_D and ΔH_v could be obtained, the temperature dependence of $\overline{M}_n$ and γ together would be sufficient to provide independent values for the activation energies for initiation and propagation, E_i and E_p. Some reference to the temperature dependence of $\overline{M}_n$ and γ is already in the literature. Gorham[9] presents relative rates of growth at three temperatures which may be interpreted as an "activation energy" for growth, $E_\gamma = -R\cdot(\partial \ln \gamma/\partial(1/T))$, of −9 kcal/mol. The deposition rate law given by Cariou, Valley, and Loeb[3b,8] implies that $E_\gamma = -6.22$ kcal/mol. The negative "activation energy" means that growth rate γ decreases with increasing temperature. Errede and Szwarc[2] site unpublished work of Szwarc and Roper in which polymer prepared over the temperature range 0–80 °C exhibited a molecular weight ("or degree of cross-linking") decrease with increasing temperature.

The model and its approximate solutions, where they can be shown to hold, allows us to understand a little more about the events occurring within the growing *p*-xylyene film. We shall now select a set of exemplary parameters to illustrate what happens during a typical polymerization. According to an empirical growth rate equation of Cariou, Valley, and Loeb, *p*-xylyene gas at a pressure of 50 mTorr results in a film growth rate of 18.2 Å/s at 20 °C.[3b,8] The vapor pressure of *p*-xylylene at 20 °C is estimated to be 6.66 Torr. Thus, p/p_0 is 7.51×10^{-3}, and by eq 3, using $K_H = 3$ and $\rho = 1.11$ g cm^{-3}, $M_0 = 2.78 \times 10^3$ g cm^{-3} (about 0.25 wt %). Since the growth surface monomer concentration M_0 is greater than M at any other point in the polymer, the medium in which the polymerization occurs is accurately described as a slightly swollen solid. Noting that molecular weights of the poly(*p*-xylylenes) are typically on the 200 000 to 400 000 range,[9,10] a value of $\overline{M}_n$ = 300 000 g mol^{-1} is assumed, implying $P_\infty = 7.70 \times 10^{-4}$ g cm^{-3}.

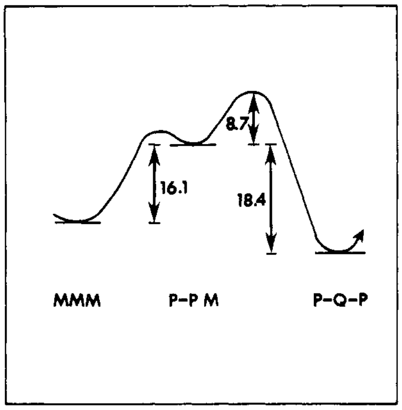

Figure 1.

From the data of Errede,[10] one can extrapolate to 20 °C to obtain a value for the propagation rate, $k_p = 6.11 \times 10^3$ cm^3 g^{-1} s^{-1}. Two remaining parameters are needed: k_i and D. We have no satisfactory way of estimating them at this time. However, values can be selected for each which best satisfy the assumptions of the approximate solution. These are the values for k_i and D which one obtains by assuming the approximation valid, and working back through eq 19b and 19c. The results are: $k_i = 6.34 \times 10^2$ cm^6 g^{-2} s^{-1} and $D = 1.13 \times 10^{-9}$ cm^2 s^{-1}. This D is in line with the results of equilibrium swelling experiments, in which a 1 mil poly(*p*-xylylene) film immersed in *p*-xylene at room temperature reached an equilibrium increase in thickness of 1.4% in about 1 h. It is also consistent with values reported for other polymers,[11] considering the superior barrier properties of the poly(*p*-xylylenes).

In order to establish the reasonability of $k_i = 6.34 \times 10^2$ cm^6 g^{-2} s^{-1}, the following line of reasoning is constructed from available observations. The activation energy for the propagation reaction E_p was measured by Errede[10] to be 8.7 kcal/mol. Quite similar activation energies have been observed in the polymerizations of quite different xylylene monomers.[12] No similar measure of the activation energy for initiation exists. Errede's experience[10] suggests that it is considerably larger than E_p. Figure 1 illustrates the potential energy of a system of three xylylene molecules undergoing initiation. According to Kubo's calculation, the dimer diradical P–P lies 16.1 kcal/mol above the starting monomers, and the addition of a monomer unit in a propagation step is an exothermic process by 18.4 kcal/mol.[3] Assuming that there is nothing peculiar about the addition of a monomer to the dimer diradical, the activation energy should be that for propagation, $E_p = 8.7$ kcal/mol. The activation energy for the decomposition of dimer diradical should be very low compared to E_p. Furthermore, the addition of a fourth monomer to the trimer diradical P–Q–P should proceed with an energy of activation of $E_p = 8.7$ kcal/mol. Thus it can be estimated that the activation energy for initiation (the highest potential energy above the starting energy of the monomers) is $E_i = 16.1 + 8.7 = 24.8$ kcal/mole. This line of reasoning also presents the chemical evidence for expecting the order of the initiation reaction, λ, to be three.

In Figure 2 is a plot of monomer consumption rate due to initiation and propagation, separately, based on the above, so that the maximum propagation and initiation rates (the rates at the growth surface) might be compared as a function of temperature. By this plot, at the highest temperature Errede took kinetic data (−36 °C), the rate of consumption of monomer by initiation is in excess of 100 000 times slower than

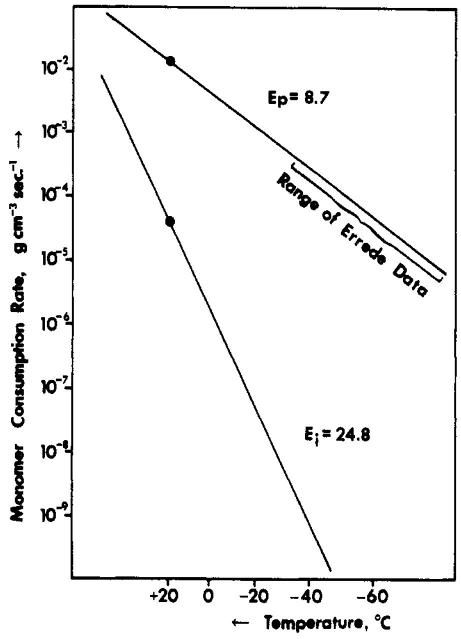

Figure 2. *p*-Xylylene polymerization ($\lambda = 3$) illustrating temperature dependence of initiation and propagation reactions.

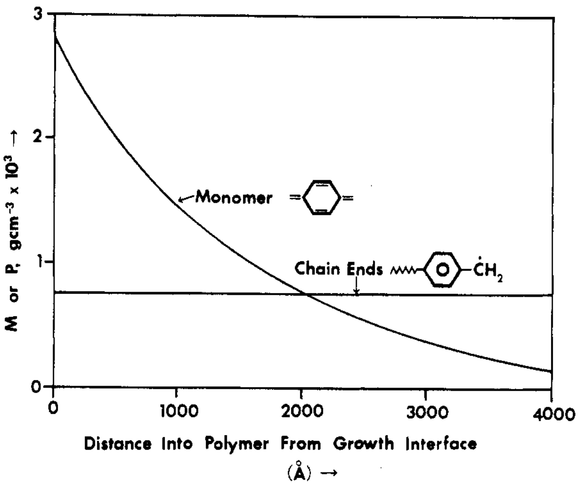

Figure 3. Concentration profiles of monomer and chain ends as function of distance from the growth interface. Examplary case of Table II.

Table I
Exemplary Parameters for *p*-Xylylene Polymerization

$\lambda = 3$
$T = 20\ ^\circ\mathrm{C}$
$p = 50\ \mathrm{mTorr}$
$\rho = 1.11\ \mathrm{g\ cm^{-3}}$
$p_0 = 6.66\ \mathrm{Torr}$
$\gamma = 18.2\ \mathrm{Å\ s^{-1}}$
$K_\mathrm{H} = 3$
$M_0 = 2.78 \times 10^{-3}\ \mathrm{g\ cm^{-3}}$
$\overline{M}_\mathrm{n} = 300\,000\ \mathrm{g\ mol^{-1}}$
$P_\infty = 7.70 \times 10^{-4}\ \mathrm{g\ cm^{-3}}$
$k_\mathrm{p} = 6.11 \times 10^3\ \mathrm{cm^3\ g^{-1}\ s^{-1}}$
$k_\mathrm{i} = 6.34 \times 10^2\ \mathrm{cm^6\ g^{-2}\ s^{-1}}$
$D = 1.13 \times 10^{-9}\ \mathrm{cm^2\ s^{-1}}$
$a = 6.46 \times 10^4\ \mathrm{cm^{-1}}$
$1/a = 1550\ \mathrm{Å}$
$w = 104\ \mathrm{g\ mol^{-1}}$

by propagation,[10] coinciding with his observation of pure propagation in his experiments.

The growth model parameters for *p*-xylylene at 20 °C and 50 mTorr developed above are summarized in Table I. It will now be demonstrated that they as a set meet the criteria stated earlier for the validity of the approximate solution: (A) $k_\mathrm{p}P_\infty M_0 = 1.31 \times 10^{-2}\ \mathrm{g\ cm^{-3}\ s^{-1}} \gg \lambda k_\mathrm{i} M_0{}^\lambda = 4.09 \times 10^{-5}\ \mathrm{g\ cm^{-3}\ s^{-1}}$. The factor of 320 in rates of consumption of monomer by propagation over initiation, even at the growth interface, is satisfactory. (B) $aD/\gamma = 400 \gg 1$. Convection effects are insignificant. (C) $P_\infty = 7.70 \times 10^{-4}\ \mathrm{g\ cm^{-3}} \gg 2k_\mathrm{i}M_0{}^\lambda/a^2\lambda^2 D = 6.42 \times 10^{-7}\ \mathrm{g\ cm^{-3}}$. $P(z)$ drops only 0.08% below P_∞ at the growth interface, $z = 0$. Until better data become available on the deposition polymerization of *p*-xylylene, the set of exemplary model parameters developed above will serve to aid our understanding of the process through the model developed here.

Figure 3 is a plot of the concentration profiles deduced from the model using eq 12 and 13, using the parameters of Table I. Note that monomer concentration drops off rapidly from a growth interface value of ca. 0.3% to reach less than one-tenth of the surface concentration at less than 4000 Å from the surface. Note also that the concentration of free-radical propagation centers is invarient with distance and exceeds the monomer concentration at about 2000 Å from the growth surface.

References and Notes

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