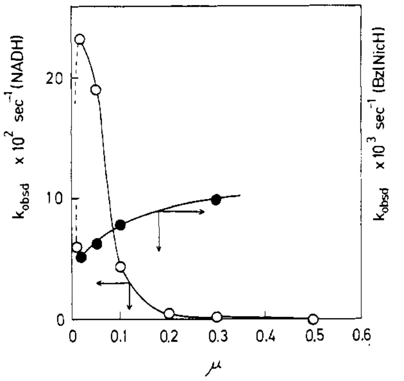

Figure 3. k_{obsd} for F-D-22 plotted as a function of ionic strength (KCl). [NADH] = 1.63×10^{-5} M, [BzlNicH] = 1.134×10^{-4} M, [flavin] in F-D-22 = 2.55×10^{-5} M.

ond-order behavior ($k_2 = 79.0\ M^{-1}\ s^{-1}$) was observed at μ = 0.3. The largest rate decrease caused by the increase in ionic strength was 342-fold. It is clear that NADH is bound onto F-D-22 mainly due to the electrostatic interaction and that the increase in ionic strength enforces the change in the reaction path from the preequilibrium binding of NADH to the simple second-order type. Strangely, the reaction rate was retarded by the further decrease in ionic strength (μ = 0.01, Figure 3). We believe that the adenine moiety of NADH is responsible for this peculiar behavior, but the details are not clear at present.

Concluding Remark. The present study established that NADH is bound to the cationic polyelectrolyte in the order of 10^{-5} M and that the efficient oxidation ensues by the immobilized flavin. The highly efficient oxidoreduction system developed is interesting not only from the standpoint of a model study of the corresponding enzymes but also in the NAD^+ recycling problem in the asymmetric synthesis of alcohol dehydrogenase.[25-27] Finally, the proposed concept may be applicable more generally to the oxidation of polyanionic species. For example, we have found that glutathione, a biological cofactor, undergoes the rapid oxidation by a flavin immobilized in cationic polyelectrolytes.

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Propagation and Depropagation Rates in the Anionic Polymerization of ε-Caprolactone Cyclic Oligomers

Koichi Ito* and Yuya Yamashita

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya, 464, Japan. *Received September 6, 1977.*

ABSTRACT: The rate of formation of ε-caprolactone cyclic oligomers has been studied in the anionic polymerization–depolymerization equilibrium system initiated by lithium *tert*-butoxide in tetrahydrofuran at 0 °C. The apparent rate constants for propagation increased with the ring size from the dimer to the hexamer, while those for depropagation remained almost constant or very slightly decreased with the ring size. This is a kinetic consequence for the cyclization equilibrium constant which decreased with increasing ring size. ε-Caprolactone monomer itself was exceedingly far more reactive than the cyclic oligomers to be hardly detected at equilibrium.

Recently[1] we have shown that the anionic polymerization of ε-caprolactone with potassium *tert*-butoxide in tetrahydrofuran provides a thermodynamically controlled, living ring-chain equilibrium system. As expected from the Jacobson–Stockmayer theory,[2-4] the product distribution was essentially determined by the entropy term, the lower cyclics being more favored over the linear polymers with increasing dilution. Although the equilibration was so fast to be complete

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Table I
Equilibrium Product Distribution at 0 °C

System[a]	$[M]_T$[f], unit M	$[I]_0$, 10^3 M	Time	Product distribution, wt %[e] $x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$	$x \geq 7$	Polymers
KO-*t*-Bu-THF[b,c]	0.21	4.0	26 s	45	10	11	9	6	19	0
KO-*t*-Bu-THF[b,c]	0.42	7.1	2 h	31	6	8	6	4	11	34
KO-*t*-Bu-Tol[b]	0.21	4.0	2 min	49	9	10	8	6	18	0
KO-*t*-Bu-Tol[b]	0.21	4.0	2 h	51	9	10	8	6	16	0
LiO-*t*-Bu-THF[b]	0.24	4.4	96 h	43	9	11	9	6	22	1
LiO-*t*-Bu-THF[d]	0.22	4.2	96 h	48	9	11	8	6	19	0
LiO-*t*-Bu-THF[d]	0.41	7.4	98 h	32	6	9	7	5	20	21

[a] THF = tetrahydrofuran. Tol = toluene. [b] Polymerization of ϵ-caprolactone monomer. [c] Previous work.[1] [d] Polymerization of cyclic dimer. [e] The monomer could not be detected in GPC. [f] $[M]_T$ = total monomer unit concentration.

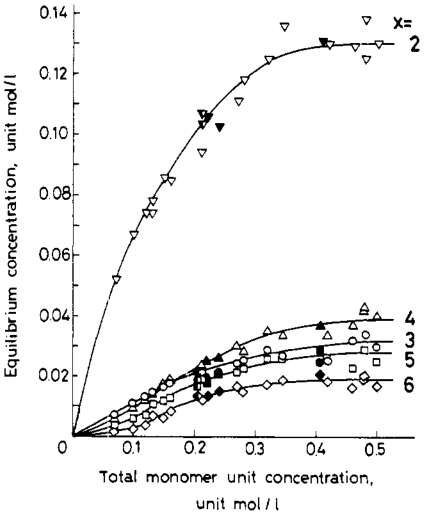

Figure 1. Equilibrium concentrations of cyclic dimer (▽), trimer (○), tetramer (△), pentamer (□), and hexamer (◇) as a function of total monomer unit concentration at 0 °C: (▽, ○, △, □, ◇) KO-*t*-Bu in tetrahydrofuran; (▼, ◐, ▲, ◧, ◆) KO-*t*-Bu in toluene; (▼, ●, ▲, ■, ◆) LiO-*t*-Bu in tetrahydrofuran.

in less than 1 min, we have also proved that the cyclic oligomers are produced by back-biting degradation from the initially formed living linear polymers.

In continuing this work with different solvent and initiator, lithium *tert*-butoxide was found to lead to a same equilibrium system, but the rate of equilibration was slow enough to be easily followed by the usual technique, permitting determination of the rate constants for propagation and depropagation of the respective cyclic oligomers. This paper describes these results to show how the propagation and depropagation rates depend on the ring size. These data should be important and interesting to examine the kinetic as well as thermodynamic polymerizability of these large ring compounds.

Experimental Section

Polymerization and depolymerization were conducted under high vacuum at 0 °C, the product distribution was determined by GPC, just as described previously.[1] Lithium *tert*-butoxide was prepared by reacting *tert*-butyl alcohol and lithium metal, and excess *tert*-butyl alcohol was completely removed by heating. It was dissolved in tetrahydrofuran and filtered to remove some metal residue, and its concentration was determined by titration of an aliquot with potassium hydrogen phthalate. Toluene was distilled over calcium hydride and then over sodium mirror. The polymer used for depolymerization experiment was prepared by polymerization of ϵ-caprolactone (ca. 1 mol/L) with potassium *tert*-butoxide in tetrahydrofuran, precipitated into methanol, and purified by reprecipitation from benzene into methanol. The number-average molecular weight was 10 400 as measured by VPO in benzene, and no fraction with molecular weight less than 2000 due to low polymers or oligomers was detected in GPC.

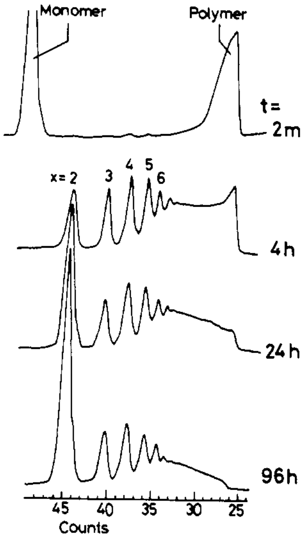

Figure 2. Change of product distribution (GPC) with polymerization time. $[M]_0 = 0.24$ M, $[I]_0 = 4.4 \times 10^{-3}$ M.

Cyclic dimer used for polymerization was isolated and recrystallized as described before.[1]

Results and Discussion

Table I shows the product distribution at equilibrium obtained with potassium *tert*-butoxide in tetrahydrofuran and in toluene and with lithium *tert*-butoxide in tetrahydrofuran. Figure 1 plots all the equilibrium data for dimer up to hexamer obtained so far as a function of total monomer unit concentration. These results clearly show the lack of the effects of solvent and initiator on the equilibrium product distribution. Therefore, the molar cyclization equilibrium constant, K_x, determined before,[1] should be taken as the one reflecting only the free-energy difference between the respective cyclic oligomer and the linear polymer, little affected by the nature of solvent and initiator.

A striking difference was a very slow equilibration rate observed with lithium *tert*-butoxide as an initiator, which required several days to get an equilibrium, in contrast to only 26 s in the case of potassium *tert*-butoxide under a similar condition. Figure 2 shows the typical GPC chromatograms of the products obtained after various polymerization times. Obviously, the monomer is first converted to the polymers, which are in turn very slowly converted to the cyclic oligomers. This is again direct evidence that the cyclic oligomers are produced by back-biting degradation from the initially formed linear polymers. In fact, an isolated polymer with a number-average molecular weight 10 400 was found to depolymerize very slowly in the presence of lithium *tert*-butoxide and give eventually the same product distribution. Figures 3 and 4

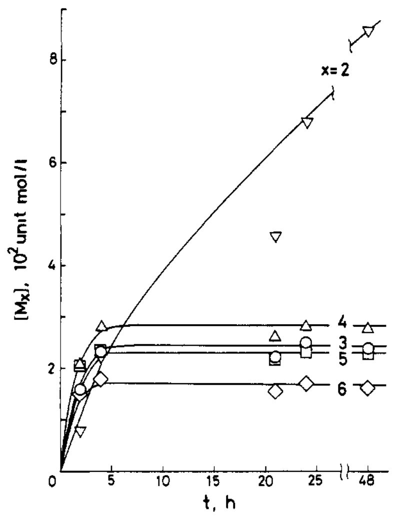

Figure 3. Formation of cyclic dimer (▽), trimer (○), tetramer (△), pentamer (□), and hexamer (◇) as a function of polymerization time. $[M]_0 = 0.24$ M, $[I]_0 = 4.4 \times 10^{-3}$ M.

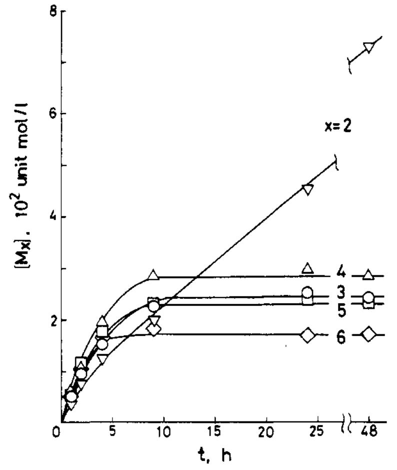

Figure 4. Formation of cyclic dimer (▽), trimer (○), tetramer (△), pentamer (□), and hexamer (◇) as a function of depolymerization time. $[M]_T = 0.23$ M, $[I]_0 = 4.5 \times 10^{-3}$ M.

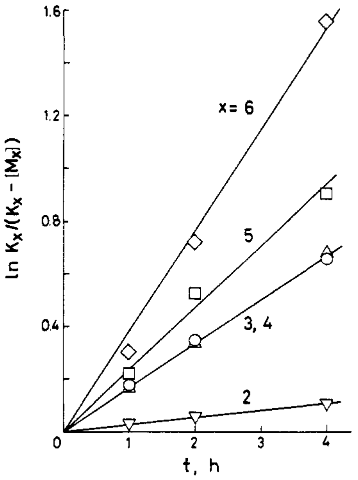

Figure 5. Plots of depolymerization data in Figure 4 according to eq 7: (▽) dimer; (○) trimer; (△) tetramer; (□) pentamer; (◇) hexamer. $[M]_T = 0.23$ M, $[I]_0 = 4.5 \times 10^{-3}$ M.

show the respective change in the cyclic oligomer concentrations with polymerization or depolymerization time. It is noted that the trimer or the higher oligomers are relatively rapidly produced to reach their equilibrium after several hours, while the dimer continues to form very slowly even after 2 days and reach its equilibrium after 4 days.

Polymerization and depolymerization in the present system should be represented as follows.

$$P_n^* + M \xrightarrow{k_{p,1}} P_{n+1}^* \qquad (1)$$

$$P_n^* \underset{k_{p,x}}{\overset{k_{d,x}}{\rightleftharpoons}} P_{n-x}^* + M_x \qquad (\text{for } x \geq 2) \qquad (2)$$

and

$$K_x = k_{d,x}/k_{p,x} \qquad (\text{for } x \geq 2) \qquad (3)$$

where P_n^* is the living linear polymer chain with a degree of polymerization n. M and M_x are monomer and cyclic x-mer, respectively. $k_{p,x}$ and $k_{d,x}$ are the rate constants for propagation and depropagation of the cyclic x-mer, respectively. $k_{p,1}$ is the propagation rate constant of the monomer, and K_x is the molar cyclization equilibrium constant. Since the monomer could not be detected in the equilibrated mixture, its final distribution is less than 1 wt % at most, indicating that $k_{d,x}$ and K_x of the monomer ($x = 1$) should be negligible under the present condition.

Now we assume for a while a living system with an instantaneous and quantitative initiation coupled with no termination and also assume $n \gg 1$, so that both $[P_n^*]$ and $[P_{n-x}^*]$ are equal to the concentration of the initiator charged, $[I]_0$. Then we have for the rate of polymerization of the monomer,

$$-\mathrm{d}[M]/\mathrm{d}t = k_{p,1}[I]_0[M] \qquad (4)$$

and for the rate of formation of the cyclic x-mer,

$$\mathrm{d}[M_x]/\mathrm{d}t = (k_{d,x} - k_{p,x}[M_x])[I]_0 \qquad (5)$$

On integration of eq 4 with the initial condition $[M] = [M]_0$ at $t = 0$, we have

$$\ln [M]_0/[M] = k_{p,1}[I]_0 t \qquad (6)$$

And integration of eq 5 with the initial condition $[M_x] = 0$ at $t = 0$, combined with eq 3, gives

$$\ln \frac{K_x}{K_x - [M_x]} = k_{p,x}[I]_0 t \qquad (\text{for } x \geq 2) \qquad (7)$$

The last equation should apply to the depolymerization experiment in Figure 4, since only the linear polymers are present at the start of the experiment and the reactions involved are only those in eq 2 not disturbed by the polymerization of the monomer.

Applying eq 6 onto the initial stage of polymerization (for example, in Figure 2 top, conversion, $1 - [M]/[M]_0 = 0.2$ at $t = 2$ min, and $[I]_0 = 4.4 \times 10^{-3}$ M), we obtained

$$k_{p,1} = 0.45 \pm 0.15 \text{ M}^{-1}\text{ s}^{-1}$$

This is only about 1/300 of the value obtained before with potassium *tert*-butoxide ($k_{p,1} = 120$ M^{-1} s^{-1})[1] but is substantially large as compared to $k_{p,x}$ of other cyclic oligomers as described below. Figure 5 shows the plots of eq 7 applied to the depolymerization data in Figure 4, using K_x determined before.[1] The plots are satisfactorily linear and go through the origin, supporting the constant concentration of the active species under these conditions. The rate constants $k_{p,x}$ and $k_{d,x}$, obtained from the slopes of the plots and K_x, are summarized in Table II. It is to be noted that $k_{d,x}$ is almost constant or very slightly decreases with increasing x, while $k_{p,x}$ sharply increases with x, $k_{p,2}$ being particularly low. It is therefore concluded that the high equilibrium concentration

Table II
Molar Cyclization Equilibrium Constant (K_x) and Apparent Rate Constants of Propagation ($k_{p,x}$) and Depropagation ($k_{d,x}$) for Cyclic x-Mer at 0 °C

		$[\mathrm{LiO}\text{-}t\text{-}\mathrm{Bu}]_0 = 4.5 \times 10^{-3}$ M		$[\mathrm{LiO}\text{-}t\text{-}\mathrm{Bu}]_0 = 8.0 \times 10^{-3}$ M	
x	K_x,[a] 10^2 M	$k_{p,x}$, 10^3 M^{-1} s^{-1}	$k_{d,x}$, 10^5 s^{-1}	$k_{p,x}$, 10^3 M^{-1} s^{-1}	$k_{d,x}$, 10^5 s^{-1}
2	6.50	1.6 ± 0.3	10 ± 2	0.73 ± 0.1	5 ± 1
3	1.07	10 ± 1	11 ± 1	4 ± 1	
4	0.98	10 ± 1	10 ± 1	4 ± 1	4 ± 1
5	0.60	14 ± 2	8 ± 1	6 ± 1	4 ± 1
6	0.34	20 ± 3	7 ± 1	9 ± 2	3 ± 1

[a] Previous work.[1]

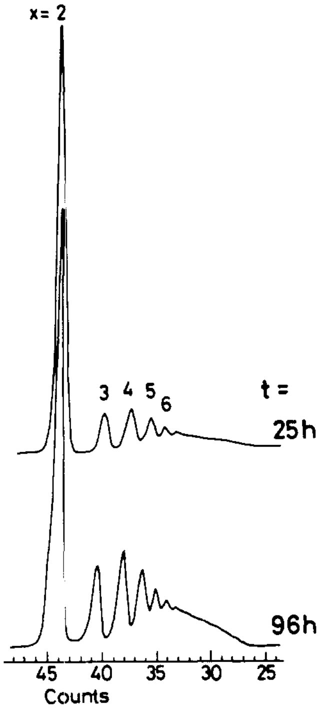

Figure 6. Product distribution (GPC) in polymerization of cyclic dimer. $[\mathrm{M}_2]_0 = 0.11$ M ($[\mathrm{M}]_\mathrm{T} = 0.22$ M), $[\mathrm{I}]_0 = 4.2 \times 10^{-3}$ M.

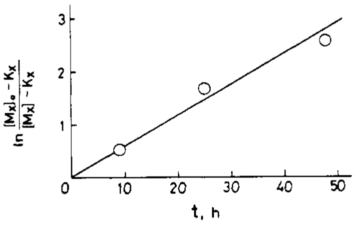

Figure 7. Plots according to eq 8 on polymerization of cyclic dimer. $[\mathrm{M}_2]_0 = 0.11$ M, $[\mathrm{I}]_0 = 4.2 \times 10^{-3}$ M.

of the dimer (high K_x) should be a kinetic consequence due to its very low reactivity to polymerize (low $k_{p,2}$) rather than due to a high rate of its formation by degradation (high $k_{d,2}$).

The low rate of polymerization of the dimer was directly checked by the polymerization of the isolated dimer, as given in Figures 6 and 7. The linear plot in Figure 7 should hold because integration of eq 5 with the initial condition $[\mathrm{M}_x] = [\mathrm{M}_x]_0$ at $t = 0$ gives for the polymerization of the cyclic x-mer,

$$\ln \frac{[\mathrm{M}_x]_0 - K_x}{[\mathrm{M}_x] - K_x} = k_{p,x}[\mathrm{I}]_0 t \qquad (\text{for } x \geq 2) \qquad (8)$$

The value of $k_{p,2}$ obtained from the slope was $(3.9 \pm 0.5) \times 10^{-3}$ M^{-1} s^{-1} which is, however, considerably higher than that determined from the depolymerization experiment (Table II, $k_{p,2} = 1.6 \times 10^{-3}$ M^{-1} s^{-1}), but still significantly lower than that for the trimer. This discrepancy appears to be related to the assumptions involved. The assumption that $n \gg 1$ in applying eq 8 seems to be invalid in the case of polymerization experiment, particularly at the initial stage of such a slow polymerization. In fact, no peak around 26 counts due to polymers was observed in GPC in Figure 6, whereas the peaks due to trimer or pentamer as well as tetramer and hexamer clearly support their formation through degradation of relatively low linear polymers. Since the living linear chains under these conditions increase their proportion with decreasing degree of polymerization, the lower cyclics would appear to be more probable to be produced than expected from the theory with $n \gg 1$. Alternatively, there may be some dependence of the kinetic parameters themselves on the chain length, n. These might also be a reason why the apparent rate of formation of the cyclic oligomers was considerably higher in the polymerization experiment (Figure 3) than that in the depolymerization experiment (Figure 4). Therefore we prefer the kinetic parameters derived from the depolymerization experiment (Table II), which would be more reliable in that they are started from the isolated high polymers ($M_\mathrm{n} = 10\,400$, $n \approx 90$) so that the condition $n \gg 1$ would be satisfactory at least in the initial stage such as plotted in Figure 5. However, we have neglected in this case the interaction between the alkoxides and the alcoholic end groups which may be present in the initial polymer used. This interaction will reduce the effective concentration of the active species, leading to an underestimation of the kinetic parameters.

Finally, we must consider the very low rate of polymerization and depolymerization observed with lithium counterion as compared to potassium counterion. $k_{p,x}$ and $k_{d,x}$ in the latter case appear to be at least an order of 10 M^{-1} s^{-1} and 0.1 s^{-1}, respectively, roughly estimated from the fact that the equilibration was complete in less than 26 s with potassium *tert*-butoxide (4×10^{-3} M). It will be pertinent here to recall the very low reactivity, coupled with the very high tendency for association, of lithium alkoxide, as reported for the epoxide anionic polymerization.[5,6] In fact, twofold increase of the initiator concentration has led to a decrease in the derived $k_{p,x}$ and $k_{d,x}$ almost by the same factor (Table II). This result indicates that the order with respect to the initiator would be near zero, suggesting a very high degree of association of the active species in the range of the concentration studied (4 to 8×10^{-3} M). Thus, the reaction appears to proceed in practice through a very minor fraction of active species that are dissociated or monomeric. Therefore $[\mathrm{I}]_0$ in eq 4 to 8 should be actually replaced by $\alpha[\mathrm{I}]_0$ where α is a fraction of true active species which decreases almost inversely with increasing $[\mathrm{I}]_0$. In this sence, the derived parameters $k_{p,x}$ and $k_{d,x}$ should not be taken as the absolute values but rather as the apparent or 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.

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

William F. Beach

Union Carbide Corporation, Chemicals and Plastics R&D,
Bound Brook, New Jersey 08805.

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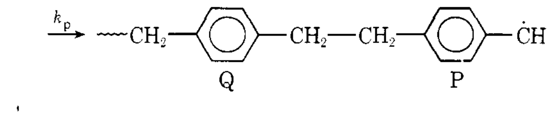
ABSTRACT: A model is developed for the vapor deposition and polymerization of *p*-xylylene which links the process variables of temperature, pressure, and rate of growth with molecular rate constants, diffusional mass transport, and molecular weight. For an important limiting case, an approximate solution 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

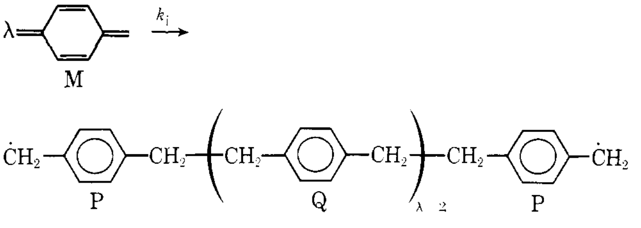
We will now discuss the chemical and physical aspects of the *p*-xylylene deposition which are essential to the development of the model. It will be assumed that the polymer propagates by the addition of monomer (M) to free radical polymer chain end propagation centers (P):



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:

$$-\left(\frac{\partial M}{\partial t}\right)_{\mathrm{p}} = \left(\frac{\partial Q}{\partial t}\right)_{\mathrm{p}} = k_{\mathrm{p}}\cdot PM; \quad \left(\frac{\partial P}{\partial t}\right)_{\mathrm{p}} = 0 \tag{1}$$

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:

$$-\frac{1}{\lambda}\left(\frac{\partial M}{\partial t}\right)_{\mathrm{i}} = \frac{1}{2}\left(\frac{\partial P}{\partial t}\right)_{\mathrm{i}} = \frac{1}{(\lambda - 2)}\left(\frac{\partial Q}{\partial t}\right)_{\mathrm{i}} = k_{\mathrm{i}}M^{\lambda} \tag{2}$$

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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