

The Kinetics of Condensation Polymerization

R. M. SECOR

E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware

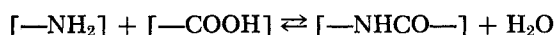
The final stages of condensation polymerization are characterized by a rapid rise in molecular weight, as the condensation product is formed and diffuses out of the polymer. The process occurring is one of desorption accompanied by a chemical reaction. The penetration theory equations for a generalized condensation polymerization reaction have been solved and some solutions are presented. The penetration theory solution, obtained by finite-difference computations, is compared with an analytical solution for the special case of no diffusional resistance.

In many instances, the rate at which a polymerization reaction proceeds is controlled or strongly affected by diffusional resistances. The high viscosities encountered in polymeric media are partly responsible for this. Even if the reaction is infinitely rapid, the diffusional processes required to bring about the reaction may be so slow as to have a dominant effect on the overall rate of polymerization. Under these circumstances, a mathematical representation is necessary if an adequate understanding of condensation polymerization is to be achieved.

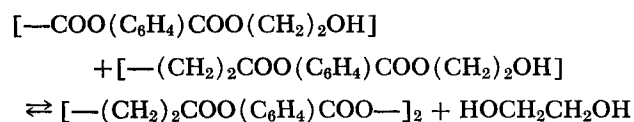
Condensation polymerization proceeds by the reaction of two functional groups, usually with the formation of a volatile by-product. This by-product must be removed in order to drive the polymerization reaction toward completion, with the formation of polymers having high molecular weights. The desorption process is often controlled by the rate at which the volatile by-product can diffuse out of the reaction medium.

The mathematical representation and analysis of problems in which a diffusing species is simultaneously consumed or produced by a chemical reaction have received considerable attention in the literature. Recently, many special cases that had previously been solved were brought together in a single mathematical model of wide applicability, that yields penetration-theory solutions by digital computation (5). The purpose of this paper is to demonstrate how the general model can be used to represent condensation polymerization.

Examples of condensation polymerizations in which diffusion is important are the synthesis of polyamides:



and the synthesis of polyesters such as polyethylene terephthalate



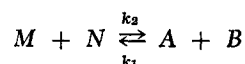
The general mathematical model that has been devel-

oped for diffusion with reaction (5) can be adapted readily to the representation of condensation polymerization. That model was developed for absorption with reaction, while we are dealing here with desorption accompanied by chemical reaction.

The Higbie penetration theory (4) is appropriate for the mathematical representation of condensation polymerization since the high viscosities encountered effectively suppress convection.

MATHEMATICAL DEVELOPMENT

A general condensation polymerization reaction can be written in terms of reactive groups as follows:



Component *A* is used here to represent the volatile condensation product. Component *B* is the repeating chain unit of the polymer.

In formulating the model, we invoke the principle of equal reactivity of functional groups (3). This principle may be stated as follows: The reactivity of every functional group is independent of the molecular weight of the polymer molecule of which it is a part. This principle is most accurate for the final stages of polymerization, when the molecular weight is high. It has been shown experimentally that changes in reactivity of a functional group are confined to the very early stages of polymerization, essentially vanishing before the polymer chain attains a length of ten atoms (3). Accordingly, it is apparent that the kinetic expression can be written in terms of functional group concentrations so long as the very early stages of polymerization are excluded. Since the mathematical model considered here is intended to represent the advanced stages of polymerization, in which the diffusional resistance is important, no significant limitation is imposed by the assumption of equal reactivity, while the simplification attained is substantial.

A second assumption is now added, namely, that the diffusion coefficient of a reactive group (which must be

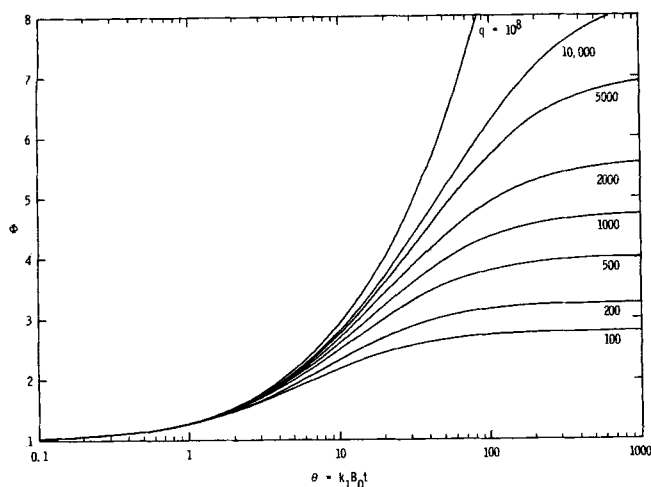


Fig. 1. Results for the condensation polymerization reaction $M + N \rightleftharpoons A + B$ in a semi-infinite medium with $K = 1$ and $A_i = 0$. For balanced ends, the parameter q is equal to Z_0^2 where Z_0 is the initial degree of polymerization in number of repeating chain units.

the same as the diffusion coefficient of the polymer molecule of which it is a part) is much smaller than that of the volatile product which is diffusing out of the reaction medium. Mathematically this assumption takes the form $(D_B/D_A) = (D_M/D_A) = (D_N/D_A) = 0$ and is the equivalent of assuming that the polymer molecules are essentially immobilized. This assumption has been suggested (1, 2) in view of the relative size of the monomeric condensation product and the polymer molecule. In addition, entanglements of the polymer chains reduce their mobility.

The differential equations representing condensation polymerization can be written:

$$\frac{\partial A}{\partial t} + (k_1 A B - k_2 M N) = D_A \left(\frac{\partial^2 A}{\partial x^2} + \frac{\lambda}{x} \frac{\partial A}{\partial x} \right) \quad (1)$$

$$\frac{\partial B}{\partial t} + (k_1 A B - k_2 M N) = 0 \quad (2)$$

$$\frac{\partial M}{\partial t} + (k_2 M N - k_1 A B) = 0 \quad (3)$$

$$\frac{\partial N}{\partial t} + (k_2 M N - k_1 A B) = 0 \quad (4)$$

where $\lambda = 0$ for a plane sheet or a semi-infinite medium

$\lambda = 1$ for a cylinder

$\lambda = 2$ for a sphere

with boundary conditions for a semi-infinite medium:

$$A = A_0, B = B_0, M = M_0, N = N_0, t = 0, x > 0$$

$$A = A_i, \frac{\partial B}{\partial x} = 0, \frac{\partial M}{\partial x} = 0, \frac{\partial N}{\partial x} = 0, t > 0, x = 0$$

$$A = A_0, B = B_0, M = M_0, N = N_0, t > 0, x = \infty$$

and for a plane sheet, cylinder, or sphere:

$$A = A_0, B = B_0, M = M_0, N = N_0, t = 0, 0 \leq x \leq x_0$$

$$A = A_i, \frac{\partial B}{\partial x} = 0, \frac{\partial M}{\partial x} = 0, \frac{\partial N}{\partial x} = 0, t > 0, x = 0$$

$$\frac{\partial A}{\partial x} = 0, \frac{\partial B}{\partial x} = 0, \frac{\partial M}{\partial x} = 0, \frac{\partial N}{\partial x} = 0, t \geq 0, x = x_0$$

The mathematical representation is similar to that of the earlier treatment (5) and is subject to the same assumptions.

The equations, in dimensionless form, that describe the condensation polymerization are:

$$\frac{\partial a}{\partial \theta} + \left(a b - \frac{q m n}{K} \right) = \frac{\partial^2 a}{\partial y^2} + \frac{\lambda}{y} \frac{\partial a}{\partial y} \quad (5)$$

$$\frac{\partial b}{\partial \theta} + \left(\frac{a b}{q} - \frac{m n}{K} \right) = 0 \quad (6)$$

$$\frac{\partial m}{\partial \theta} + \left(\frac{m n}{K} - \frac{a b}{q} \right) = 0 \quad (7)$$

$$\frac{\partial n}{\partial \theta} + \left(\frac{m n}{K} - \frac{a b}{q} \right) = 0 \quad (8)$$

It should be noted that A_i in all definitions of dimensionless quantities used earlier (5) has been changed to A_0 for the present purpose. Accordingly, for desorption, the dimensionless concentration of A is redefined as $a = A/A_0$, which gives the following dimensionless boundary conditions for a semi-infinite medium:

$$a = 1, b = 1, m = \frac{M_0}{B_0}, n = \frac{N_0}{B_0}, \theta = 0, y > 0$$

$$a = \frac{A_i}{A_0}, \frac{\partial b}{\partial y} = 0, \frac{\partial m}{\partial y} = 0, \frac{\partial n}{\partial y} = 0, \theta > 0, y = 0$$

$$a = 1, b = 1, m = \frac{M_0}{B_0}, n = \frac{N_0}{B_0}, \theta > 0, y = \infty$$

and for a plane sheet, cylinder, or sphere:

$$a = 1, b = 1, m = \frac{M_0}{B_0}, n = \frac{N_0}{B_0}, \theta = 0, 0 \leq y \leq y_0$$

$$a = \frac{A_i}{A_0}, \frac{\partial b}{\partial y} = 0, \frac{\partial m}{\partial y} = 0, \frac{\partial n}{\partial y} = 0, \theta > 0, y = 0$$

$$\frac{\partial a}{\partial y} = 0, \frac{\partial b}{\partial y} = 0, \frac{\partial m}{\partial y} = 0, \frac{\partial n}{\partial y} = 0, \theta \geq 0, y = y_0$$

It will be noted that the third boundary condition for the semi-infinite medium requires chemical equilibrium throughout at zero time, that is, when desorption begins. For a semi-infinite medium, the rate of desorption in the absence of chemical reaction is given by

$$R^0 = (A_0 - A_i) \sqrt{\frac{4D_A}{\pi t}} = (A_0 - A_i) \sqrt{\frac{4k_1 B_0 D_A}{\pi \theta}} \quad (9)$$

For desorption with reaction, the rate is given by

$$R = \frac{1}{t} \int_0^t D_A \left(\frac{\partial A}{\partial x} \right)_{x=0} dt = \frac{A_0}{\theta} \sqrt{k_1 B_0 D_A} \int_0^\theta \left(\frac{\partial a}{\partial y} \right)_{y=0} d\theta \quad (10)$$

The ratio of the rate of desorption to the physical desorption rate is

$$\Phi = \frac{R}{R^0} = \frac{\sqrt{\frac{\pi}{4\theta}} \int_0^\theta \left(\frac{\partial a}{\partial y} \right)_{y=0} d\theta}{\left(1 - \frac{A_i}{A_0} \right)} \quad (11)$$

A finite-difference approximation procedure described

in a previous paper (5) was used to compute $(\partial a / \partial y)_{y=0}$.

AVERAGE COMPOSITION AND MOLECULAR WEIGHT FOR FINITE GEOMETRIES

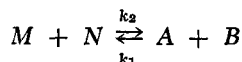
It is frequently important to obtain the average composition and molecular weight of the polymer if the material of a sheet, cylinder, or sphere is completely mixed after the polymerization is terminated. It can be shown that

$$\begin{aligned}\overline{B} &= \frac{(\lambda + 1)}{x_0^{\lambda+1}} \int_0^{x_0} B x^\lambda dx \\ \overline{M} &= \frac{(\lambda + 1)}{x_0^{\lambda+1}} \int_0^{x_0} M x^\lambda dx \\ \overline{N} &= \frac{(\lambda + 1)}{x_0^{\lambda+1}} \int_0^{x_0} N x^\lambda dx \\ \overline{Z} &= \frac{(\lambda + 1)}{x_0^{\lambda+1}} \int_0^{x_0} \left(\frac{2B}{M + N} \right) x^\lambda dx\end{aligned}$$

Equations (12) to (15) are generalizations of the expressions, representing integration under the profiles of B , M , N , and Z , respectively, for the three finite shapes.

COMPUTATIONAL RESULTS FOR A SEMI-INFINITE MEDIUM

In Figure 1, the ratio expressed by Equation (7) is plotted against dimensionless time, $\theta = k_1 B_0 t$, for the reaction



where the stoichiometry conforms to the kinetics and the equilibrium constant, K , is unity.

The extent to which Φ exceeds unity represents the increase in the desorption rate brought about by the polymerization reaction. It is evident that the rate of removal

of the volatile condensation product is always increased by the occurrence of the reaction.

The parameter $q = B_0/A_0$ shown in Figure 1 is related to the initial molecular weight of the polymer. Thus, the number of moles of polymer per cc. initially present is

$$\left(\frac{M_0 + N_0}{2} \right)$$

and the mass of polymer per cc. initially present is

$$(B_0 \mathcal{M}_B + M_0 \mathcal{M}_M + N_0 \mathcal{M}_N)$$

Accordingly, the initial number average molecular weight of the polymer is

$$\mathcal{M}_0 = \frac{2(B_0 \mathcal{M}_B + M_0 \mathcal{M}_M + N_0 \mathcal{M}_N)}{(M_0 + N_0)} \quad (12)$$

If we assume that the polymer is initially of sufficiently high molecular weight to permit neglecting the mass of the end groups in comparison to that of the entire polymer molecule,

$$\mathcal{M}_0 \cong \frac{2 B_0 \mathcal{M}_B}{M_0 + N_0} \quad (13)$$

and

$$\frac{\mathcal{M}_0}{\mathcal{M}_B} \cong \frac{2 B_0}{M_0 + N_0} = Z_0 \quad (14)$$

where Z_0 is the average initial degree of polymerization as measured by the number of repeating chain units. Since the second equality in Equation (14) does not involve an approximation, it is preferable to use Z_0 as an index of molecular weight.

When balanced ends are assumed, $M_0 = N_0$ and

$$M_0 = \sqrt{K A_0 B_0} \quad (15)$$

which gives

$$Z_0 = \frac{B_0}{\sqrt{K A_0 B_0}} = \sqrt{\frac{q}{K}} \quad (16)$$

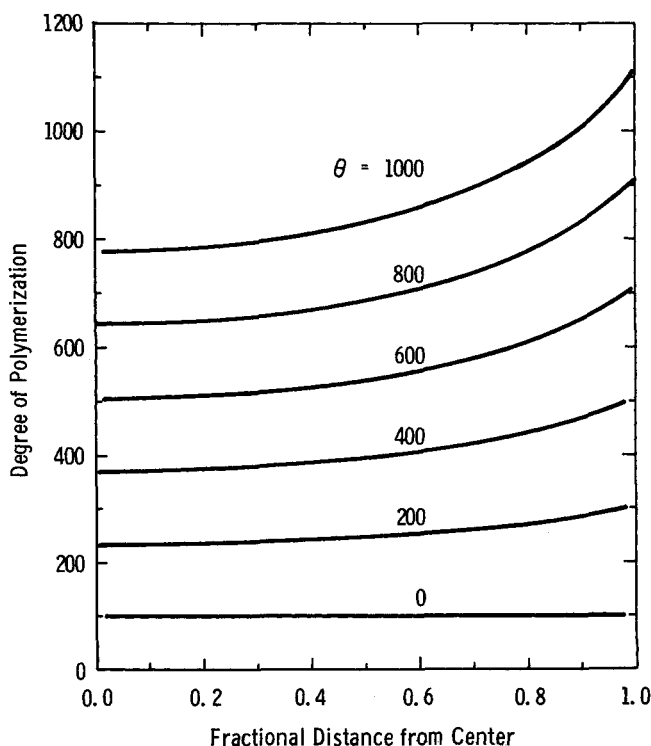


Fig. 2. Polymerization profiles through a plane sheet for $Z_0 = 100$, $K = 1$, $\gamma_0 = 1$.

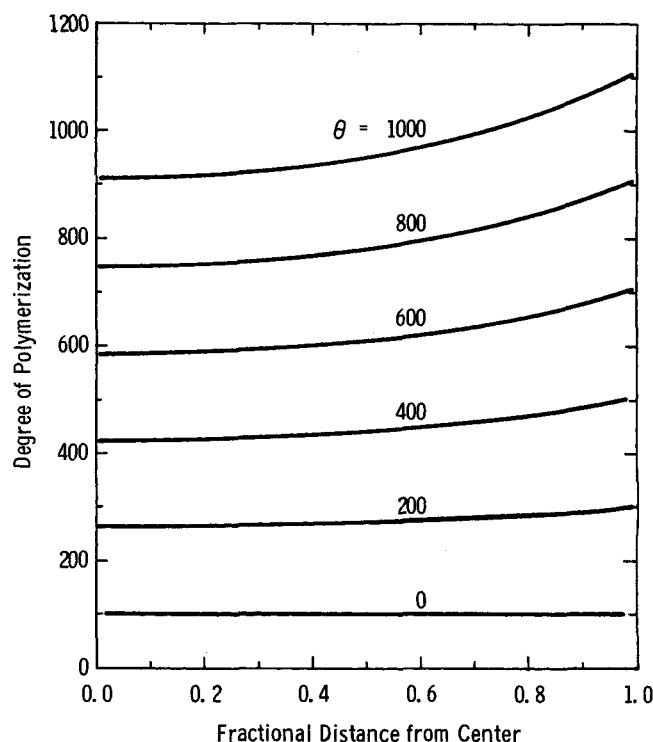


Fig. 3. Polymerization profiles through a cylinder for $Z_0 = 100$, $K = 1$, $\gamma_0 = 1$.

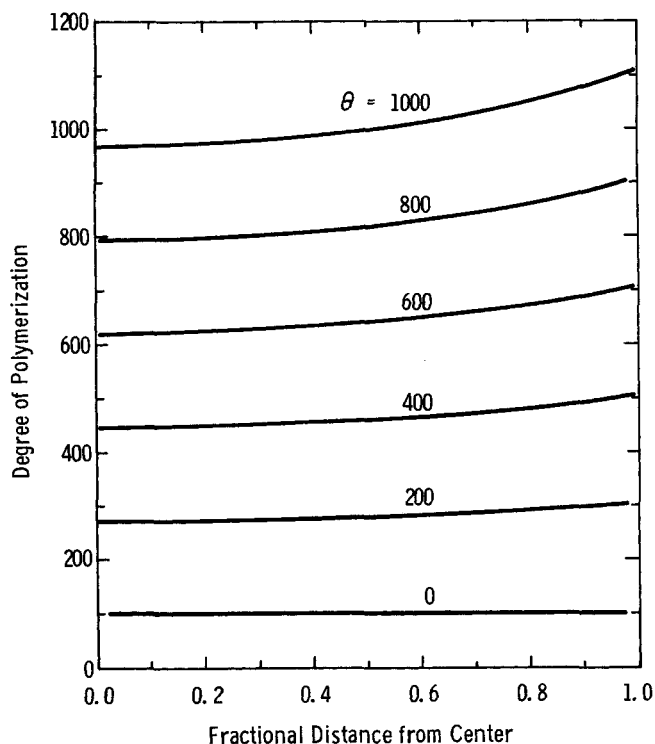


Fig. 4. Polymerization profiles through a sphere for $Z_0 = 100$, $K = 1$, $y_0 = 1$.

Since $K = 1$ in Figure 1, the parameter q is equal to Z_0^2 and the abscissa is given by $\theta = k_1 A_0 Z_0^2 t$, when $M_0 = N_0$.

At high initial degrees of polymerization (large values of q) the reaction becomes pseudo first-order in the volatile product, since little change in chain-unit concentration can occur.

At low values of θ , desorption of A occurs with little accompanying polymerization. At high values of θ , the reaction becomes infinitely rapid and Φ reaches its maximum value.

At low values of θ , the effect of the initial degree of polymerization on the desorption rate is small, since the flux of the volatile component through the interface is provided mainly by the initial concentration, A_0 , of that component present when desorption begins.

COMPUTATIONAL RESULTS FOR FINITE MEDIA

In the case of the plane sheet, cylinder, and sphere, it is easily shown from Equations (5) to (8) and the dimensionless boundary conditions that if $A_i = 0$ and $M_0 = N_0$, then

$$b = f_1(\theta, y, y_0, Z_0, K)$$

$$m = n = f_2(\theta, y, y_0, Z_0, K)$$

and

$$Z = \frac{B}{M} = \frac{b}{m} = f_3(\theta, y, y_0, Z_0, K)$$

To illustrate the kinds of results that can be obtained for the finite geometries, calculations were made for balanced ends with $A_i = 0$, $Z_0 = 100$, $K = 1$, and $y_0 = 1$. The results are shown in Figures 2 to 4. In all cases, the degree of polymerization decreases from the surface to the center, as a result of the resistance to diffusion of the condensation product toward the surface. Thus, the surface polymerizes more rapidly than any point in the interior. At any given time after the start of diffusion, the polymerization profile of the sphere is flatter than that of the cylinder, while that

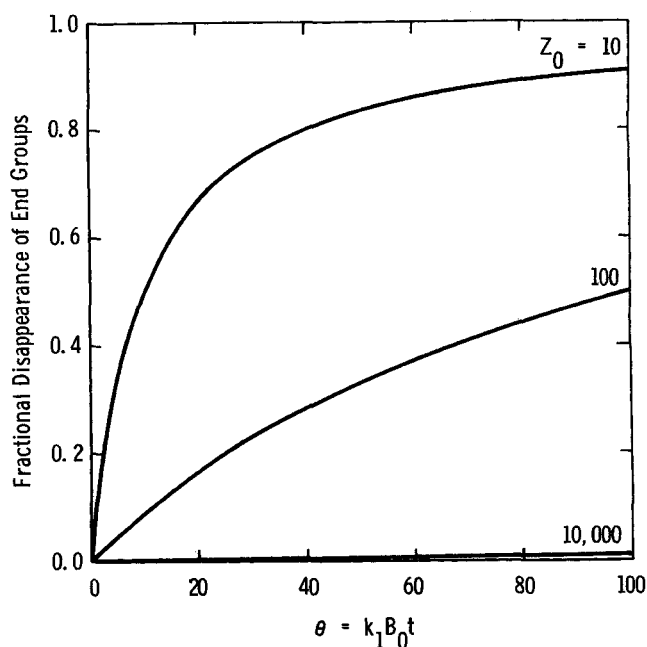


Fig. 5. Degree of completion of the reaction as a function of the dimensionless time, θ , and the initial degree of polymerization, Z_0 , for $M_0 = N_0$, $A_i = 0$, and $K = 1$. Diffusional resistance assumed zero.

of the cylinder is flatter than that of the sheet. This behavior is, of course, a result of the effect on the diffusional resistance of the distribution of mass (and therefore of the condensation product) with respect to distance from the surface. The degree of polymerization at the surface as a function of time can be computed analytically by solving the equation for the reaction kinetics with no diffusion.

LIMITING CASE OF NO DIFFUSIONAL RESISTANCE

When the volatile species experiences no resistance to diffusion from the polymerizing medium, its concentration throughout is always equal to the surface concentration, A_i . When the surface concentration is suddenly changed from A_0 to A_i , there is an instantaneous decrease in concentration throughout to A_i . Accordingly,

at time = 0

$$A = A_i$$

$$B = B_0$$

$$M = M_0$$

$$N = N_0$$

and at time = t ,

$$A = A_i$$

$$B = B_0 + X$$

$$M = M_0 - X$$

$$N = N_0 - X$$

The degree of polymerization at any time is given by:

$$Z = \frac{2B}{M + N} = \frac{2(B_0 + X)}{(M_0 + N_0 - 2X)} \quad (17)$$

and the increase in concentration of chain units is:

$$X = \frac{Z(M_0 + N_0) - 2B_0}{2(1 + Z)} \quad (18)$$

For the reaction, $M + N \rightleftharpoons A + B$, the flux of A out of

the polymerizing medium is:

$$\frac{dB}{dt} = \frac{dX}{dt} = k_2 (M_0 - X) (N_0 - X) - k_1 A_i (B_0 + X) \quad (19)$$

The solution to Equation (19) is obtained as:

$$\theta = \frac{1}{W} \ln \frac{k_2(M_0 + N_0 - 2X) + k_1(A_i + B_0W)}{k_2(M_0 + N_0 - 2X) + k_1(A_i - B_0W)} \cdot \frac{k_2(M_0 + N_0) + k_1(A_i - B_0W)}{k_2(M_0 + N_0) + k_1(A_i + B_0W)} \quad (20)$$

where

$$W = \sqrt{\left(\frac{M_0 - N_0}{KB_0} + \frac{A_i}{B_0}\right)^2 + \frac{4A_i}{KB_0} \left(1 + \frac{N_0}{B_0}\right)} \quad (21)$$

For the special case of balanced ends and zero interfacial concentration of the volatile component,

$$\frac{dX}{dt} = k_2 M_0^2 - 2k_2 M_0 X + k_2 X^2 \quad (22)$$

and the solution is

$$\theta = \frac{K Z_0 (Z - Z_0)}{(Z_0 + 1)} \quad (23)$$

or, in terms of the fractional disappearance of end groups,

$$\frac{M_0 - M}{M_0} = 1 - \frac{1}{1 + \theta/KZ_0} \quad (24)$$

This equation is plotted in Figure 5 for $K = 1$.

The fractional disappearance of end groups, as plotted in Figure 5, is equivalent to the quantity of A desorbed after time = 0. This is not true for Figure 1; when the volatile reaction product experiences a diffusional resistance, under conditions of initial equilibrium, a lag is created between desorption and polymerization, with the latter always proceeding more slowly than the former.

It is obvious from Figure 5 that the degree of approach to complete polymerization is very dependent upon the initial degree of polymerization. It is further apparent that the degree of polymerization obtained from Figure 5 or Equation (23) represents an upper limit for the conditions of Figure 1. The degree of polymerization obtained from Figure 5 is identical with the degree of polymerization at the surface of the semi-infinite medium of Figure 1.

CONCLUSIONS

The simultaneous effects of reaction and diffusion on the desorption rate for condensation polymerization have been represented by means of the penetration theory. The computer solution to the differential equations can be used to calculate concentration and molecular weight profiles and to obtain the rate of polymerization or molecular weight increase as a function of time for a plane sheet, a cylinder or a sphere as well as for a semi-infinite medium. The results for a semi-infinite medium, computed by finite-difference methods, were expressed in terms of the ratio of the rate of desorption of the volatile condensation product to the rate of physical desorption in the absence of the polymerization reaction.

Under certain conditions, the initial degree of polymerization is a critical parameter, influencing the rate of desorption to a marked degree for high reaction velocity constants or long exposure times.

An analytical solution for the limiting case of no diffu-

sional resistance was obtained. It is closely related to the general penetration theory solution, since the degree of polymerization at the surface in the latter case corresponds to the solution of the former.

ACKNOWLEDGMENT

The penetration theory was first applied to polymerization reactions by Dr. R. E. Emmert of the Du Pont Company, whose contributions are gratefully acknowledged. The author expresses his appreciation to Phyllis W. Gilmour for carrying out the machine computations.

NOTATION

A	= concentration of the volatile species leaving the medium in which reaction occurs, moles/cc.
A _i	= concentration of A at the interface, moles/cc.
A ₀	= initial concentration of A, moles/cc.
a	= A/A ₀
B	= concentration of the repeating polymer chain unit, moles/cc.
B ₀	= initial concentration of B, moles/cc.
b	= B/B ₀
D	= diffusion coefficient, subscript indicating the species, sq.cm./sec.
K	= k ₁ /k ₂ = equilibrium constant
k ₁	= reaction rate constant for depolymerization, cc./ (mole) (sec.)
k ₂	= reaction rate constant for polymerization, cc./ (mole) (sec.)
M _B	= "molecular" weight of repeating polymer chain unit
M _M	= "molecular" weight of reactive end group M
M _N	= "molecular" weight of reactive end group N
M ₀	= number average molecular weight of polymer
M	= concentration of reactive end group M, moles/cc.
M ₀	= initial concentration of M, moles/cc.
m	= M/B ₀
N	= concentration of reactive end group N, moles/cc.
N ₀	= initial concentration of N, moles/cc.
n	= N/B ₀
q	= B ₀ /A ₀
R	= average rate of diffusion of A through interface, moles/sq.cm. sec.
R ⁰	= average rate of diffusion of A through interface in the absence of reaction, moles/sq.cm. sec.
t	= time, sec.
W	= dimensionless parameter defined by Equation (21)
X	= extent of reaction at any time, moles/cc.
x	= distance in the direction of diffusion, cm.
y	= $x\sqrt{k_1 B_0 A_0 / D_A}$, dimensionless distance
Z	= degree of polymerization at any time
Z ₀	= initial degree of polymerization
γ	= stoichiometric coefficient, subscript indicating the species
θ	= k ₁ B ₀ A ₀ , dimensionless time
λ	= geometrical parameter (integer)
Φ	= k _L /k _L ⁰ = R/R ⁰

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