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### **Kinetics of Living Polymerization with Propagation Rate Constants Depending on Degree of Polymerization**

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## Kinetics of Living Polymerization with Propagation Rate Constants Depending on Degree of Polymerization

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### SUMMARY

A study is presented on the kinetics of living polymerization in which the propagation rate constants decrease to zero at a certain degree of polymerization of the propagating chain. The general solution for the distribution function and the rate of polymerization is given and two special cases are discussed. When all the propagation rate constants are the same up to a critical degree of polymerization and null beyond it, the polymerization proceeds approximately as a normal living polymerization until the number-average degree of polymerization reach 85 to 90% of the critical value. When the propagation rate constants decrease linearly with the degree of polymerization, the distribution of living polymer is narrower than the usual Poisson distribution and the reaction order of the rate of polymerization with respect to monomer concentration is between first and second and is affected by the initial monomer and catalyst concentrations.

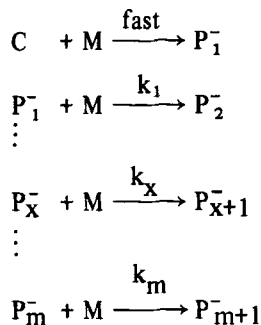
This work presents the kinetics of living polymerization without termination in which the rate constants of propagation decrease to zero at a certain degree of polymerization.

In a series of studies on the anionic polymerization of aldehydes [1, 2], we have shown that the polymerization is living but when the polymer precipitates, the polymerization does not proceed beyond a certain degree because of occlusion of the active chain ends in the precipitate. When the temperature of the system is raised, the living polymer is depolymerized and the precipitate disappears whereas the end capped polymer does not. These facts show that the polymerization stops due to the slowing down of the propagation rate and not because of the termination reaction.

In the case of radical polymerization accompanied by precipitation, it is often said that in addition to the usual second-order termination, a first-order termination is operative. But this concept is rather ambiguous and must be elaborated further. The propagation of chain radical must stop either by second-order termination or by occlusion, but the concurrent occurrence of the two phenomena is rather unlikely. In the media or precipitate where the former reaction is going on, the polymer chain is sufficiently mobile and occlusion cannot be anticipated. For a chain end to be occluded, the media must be a glassy state where not only the second-order termination but also the propagation reaction must cease. Stoppage of polymerization due to glassification of the media has been shown in our works on diffusion controlled polymerization [3, 4]. In radical polymerization, a so-called gel effect makes the kinetics very complex. Consequently, in the present work we confine ourselves to the problem of a living anionic polymerization in which chemical termination can be excluded. There are many theoretical works on the kinetics of living polymerization and that of Coleman et al. [5] is especially very elegant. However, none of them has studied the cases where the propagation rate constants vary with the degree of polymerization.

## RESULTS AND DISCUSSION

We assume: 1) propagation rate constants are dependent only on the degree of polymerization of the growing chain, 2) polymer does not grow beyond  $(m + 1)$ -mer, 3) chemical termination and side reaction are excluded, and 4) initiation is instantaneous. Then the reaction scheme is expressed by



$P_{m+1}^-$  does not propagate further.

Two notations,  $\theta$  and  $p_x$ , are introduced. The former is defined as

$$\theta = \int_0^t (M) dt \quad (1)$$

or

$$d\theta/dt = (M) \quad (2)$$

and

$$p_x = (P_x^-)/(C)_0 \quad (3)$$

where  $(C)_0$  is the initial catalyst concentration or, because the initiation is instantaneous, it is equal to  $(P_1^-)_0$ . Consequently,  $p_x$  represents a concentration fraction of living  $x$ -mer.

The rate equations corresponding to the above mechanism are given by

$$dp_1/d\theta = -k_1 p_1 \quad (4)$$

$$dp_x/d\theta = k_{x-1} p_{x-1} - k_x p_x \quad (2 \leq x \leq m) \quad (5)$$

$$dp_{x+1}/d\theta = k_m p_m \quad (6)$$

At  $\theta = 0$ ,  $p_1 = 1$  and  $p_x = 0$  ( $x \neq 1$ ).

The above series of differential equations can be solved by application of Laplace transformation. The results are

$$p_1 = a_1^1 e^{-k_1 \theta} = e^{-k_1 \theta} \quad (7)$$

$$p_2 = a_1^2 e^{-k_1 \theta} + a_2^2 e^{-k_2 \theta} = \frac{k_1}{k_2 - k_1} e^{-k_1 \theta} + \frac{k_1}{k_1 - k_2} e^{-k_2 \theta}$$

$\vdots$

$$p_x = \sum_{i=1}^x a_i^x e^{-k_i \theta} \quad (1 \leq x \leq m) \quad (8)$$

where  $a_i^x$  is given by

$$a_i^x = \frac{k_1}{k_1 - k_i} \frac{k_2}{k_2 - k_i} \cdots \frac{k_{i-1}}{k_{i-1} - k_i} k_i \frac{k_{i+1}}{k_{i+1} - k_i} \cdots \frac{k_{x-1}}{k_{x-1} - k_i} \frac{1}{k_x - k_i}$$

$$= \prod_{n=1}^{x-1} k_n \prod_{n \neq i}^x \frac{1}{k_n - k_i} \quad (2 \leq x \leq m) \quad (9)$$

and

$$p_{m+1} = 1 - \sum_{i=1}^m a_i^{m+1} e^{-k_i \theta} \quad (10)$$

where

$$a_i^{m+1} = \prod_{n=1}^m k_n \prod_{n \neq i}^m \frac{1}{k_n - k_i} \quad (11)$$

As for the rate equation of monomer consumption, it is given by

$$-d(M)/d\theta = (C)_0 \sum_{x=1}^m k_x p_x = (C)_0 \sum_{i=1}^m (e^{-k_i \theta} \sum_{x=1}^m k_x a_i^x) \quad (12)$$

and by integration

$$\bar{x}_n = \frac{(M)_0 - (M)}{(C)_0} = \sum_{i=1}^m \frac{(1 - e^{-k_i \theta})}{k_i} \sum_{x=1}^m k_x a_i^x \quad (13)$$

Equations (7) through (13) are the general solution for the distribution of living  $x$ -mer and for the rate equations of a polymerization with different propagation rate constant at each propagation step.

These equations are, however, too general to know any characteristic

feature of the polymerization. Consequently, two special cases will be treated in the following, i.e., a case where all the propagation constants are equal up to  $m$ -mer and a case where the rate constants are linearly decreasing with the degree of polymerization.

### Case 1

The conditions are given by two equations,  $k_x = k$  ( $m \geq x \geq 1$ ) and  $k_{m+1} = 0$ . In this case, the original differential equations up to  $x = m$  are reduced to those of normal living polymerization leading to Poisson distribution. Consequently  $p_x$  is given by

$$p_x = e^{-k\theta} \frac{(k\theta)^{x-1}}{(x-1)!} \quad (m \geq x \geq 1) \quad (14)$$

and  $p_{m+1}$  is given by the remaining fraction

$$p_{m+1} = 1 - \sum_{x=1}^m p_x = \sum_{x=m+1}^{\infty} e^{-k\theta} \frac{(k\theta)^{x-1}}{(x-1)!} \quad (15)$$

Equations (14) and (15) can also be obtained from Eqs. (7) to (10) by putting all the  $k_x$  identical. But it can not be done directly and it is necessary to put  $k_x = k + \delta_x$ , expand  $e^{\delta_x}$  with  $\delta_x$ , and calculate the limiting value at  $\delta_x \rightarrow 0$ .

As is well known, the Poisson distribution is very narrow and  $p_{m+1}$ , given in Eq. (15), must be very small until the degree of polymerization of the living polymer comes near to  $m + 1$ . It can be evaluated as follows:

$$\begin{aligned} p_{m+1} &= e^{-k\theta} \frac{(k\theta)^m}{m!} \left( 1 + \frac{k\theta}{m+1} + \frac{(k\theta)^2}{(m+1)(m+2)} + \dots \right) \\ &< e^{-k\theta} \frac{(k\theta)^m}{m!} (1 + t + t^2 + t \dots) = e^{-k\theta} \frac{(k\theta)^{m+1}}{(m+1)!} \cdot \frac{1}{t(1-t)} \end{aligned} \quad (16)$$

where

$$t = \frac{k\theta}{m+1}$$

Using as an approximation  $(m+1)! \approx [(m+1)/e]^{m+1} [2\pi(m+1)]^{\frac{1}{2}}$  we obtain

$$p_{m+1} \lesssim (te^{1-t})^{m+1}/t(1-t) [2\pi(m+1)]^{\frac{1}{2}} \quad (17)$$

For a polymer with a normal Poisson distribution, the number-average degree of polymerization is given by  $\bar{x}_n = k\theta + 1$ , and this also holds approximately for our case provided that  $p_{m+1}$  is small. Accordingly,  $t \approx \bar{x}_n/(m+1)$ , or in other words  $t$ , is a ratio of the number-average degree of polymerization to its final value. Using Eq. (17), we can evaluate numerically the value of  $p_{m+1}$  for arbitrary  $t$  and  $m$ . For example, for the  $p_{m+1}$  to be more than 0.01 or 1%,  $t > 0.93$  for  $m = 10^3$  and  $t > 0.85$  for  $m = 300$ . This means that most of the polymerization proceeds as a usual living polymerization until  $\bar{x}_n$  is near its final value. Consequently the rate of polymerization is first-order with respect to monomer concentration and the distribution is approximately of the Poisson type. At the final stage of polymerization the rate decreases gradually because of a decrease in active chain ends, and the distribution becomes sharper than Poisson distribution and reaches a monodispersed  $(m+1)$ -mer at the completion of the reaction.

### Case 2

The rate constants of propagation decrease linearly with the degree of polymerization and  $k_{m+1} = 0$ . This condition is expressed by

$$k_x = k_0 \left(1 - \frac{x-1}{m}\right) \quad (18)$$

Then  $a_x^i$ , given by Eqs. (8) and (10), can be cast into a very compact form.

$$\begin{aligned} a_i^x &= \frac{m}{i-1} \frac{m-1}{i-2} \cdots \frac{m-i}{1} (m-i+1) \frac{m-i+2}{(-1)} \cdots \frac{m-x}{i-x+1} \frac{1}{i-x} \\ &= (-1)^{x-i} {}_m C_{x-1} {}_{x-1} C_{i-1} \quad (m \geq x \geq 1) \end{aligned} \quad (19)$$

and

$$a_i^{m+1} = (-1)^{m-i} {}_m C_{i-1} \quad (x = m+1) \quad (20)$$

where  ${}_s C_t = s!/(s-t)!t!$ .

By using Eqs. (19) and (20) and the simplifying notation  $r = e^{k\theta/m}$ , Eqs. (8) and (10) are reduced to a single distribution function of very simple form.

$$p_x = r^{-m} {}_m C_{x-1} (r-1)^{x-1} \quad (m+1 \geq x \geq 1) \quad (21)$$

This is a sort of binominal distribution.

From the distribution function thus obtained, each moment of distribution can be calculated easily.

$$\text{0th moment} \quad L_0 = \sum_{x=1}^{m+1} p_x = 1 \quad (22)$$

$$\text{1st moment} \quad L_1 = \sum_{x=1}^{m+1} x p_x = [(m+1)r - m]/r \quad (23)$$

$$\begin{aligned} \text{2nd moment} \quad L_2 = \sum_{x=1}^{m+1} x^2 p_x &= [(m+1)^2 r^2 - (2m^2 + m)r \\ &+ (m^2 - m)]/r^2 \end{aligned} \quad (24)$$

Number- and weight-average degrees of polymerization are

$$\bar{x}_n = L_1/L_0 = [(m+1)r - m]/r \quad (25)$$

$$\bar{x}_w = L_2/L_1 = [(m+1)^2 r^2 - (2m^2 + m)r + (m^2 - m)]/[(m+1)r^2 - mr] \quad (26)$$

From Eq. (25) the parameter  $r$  can be visualized as a function of number-average degree of polymerization

$$r = m/(m+1 - \bar{x}_n)$$

The dispersity parameter  $U$  is given either as a function of  $r$  or of  $\bar{x}_n$ :

$$U = (\bar{x}_w/\bar{x}_n) - 1 = m(r-1)/[(m+1)r - m]^2 = (m+1 - \bar{x}_n)(\bar{x}_n - 1)/m\bar{x}_n^2 \quad (27)$$

As is well known, the dispersity parameter of a normal Poisson distribution is given approximately by  $U = 1/(\bar{x}_n - 1)$ . Accordingly, the above distribution is narrower than the usual Poisson distribution by a factor of approximately  $1 - \bar{x}_n/m$ .



Now let us calculate the rate Eq. (12). By using the initial condition (18) and with the aid of Eqs. (22) and (23), it is simplified as

$$\begin{aligned} -d(M)/d\theta &= (C)_0 \sum_{x=1}^{m+1} k_x P_x = (C)_0 k_0 [(m+1)L_0/m + L_1/m] = (C)_0 k_0/r \\ &= k_0 (C)_0 e^{-k_0 \theta/m} \end{aligned} \quad (28)$$

By integration

$$(M)_0 - (M) - (C)_0 = (C)_0 m (1 - e^{-k_0 \theta/m}) \quad (29)$$

By substituting  $e^{-k_0 \theta/m}$  obtained from Eq. (29) into Eq. (28) and replacing  $d(M)/d\theta$  by  $d(M)/(M) dt$ , a rate equation in terms of monomer concentration and time can be obtained:

$$-d(M)/dt = (k_0/m)(M)[(C)_0(m+1) - (M)_0 + (M)] \quad (30)$$

Its integrated form is given by

$$(M) = s[(M)_0 - (C)_0] / [(C)_0 m e^{st/m} + (C)_0 - (M)_0] \quad (31)$$

where

$$s = (C)_0(m+1) - (M)_0$$

When  $s > 0$  or  $m+1 > (M)_0/(C)_0$ ,  $(M) = 0$  at  $t \rightarrow \infty$ , i.e., monomer is consumed completely before  $\bar{x}_n$  reach the critical value  $m+1$ . When  $s < 0$  or  $m+1 < (M)_0/(C)_0$ ,  $(M)_{\text{final}} = (M)_0 - (C)_0(m+1)$  at  $t \rightarrow \infty$ , i.e., all the living chains will have their maximum degree of polymerization and the remaining monomer cannot react further. Equation (30) shows that the reaction is externally first-order with respect to monomer concentration because  $(M) = (M)_0$  at the initial stage. But the internal consumption of monomer during polymerization is between first- and second-order, and it can be approximated as first-order only when  $|s| \gg (M)$ , and when  $s \ll (M)$  the reaction is approximately a second-order reaction.

Internal second-order consumption of monomer has been reported by Higashimura et al. [6] for heterogeneous cationic polymerization of trioxane in nitrobenzene. They have attributed the behavior to the change in dielectric constant of the media. The second-order nature of the reaction was

confirmed by Iguchi and interpreted by a concept that the rate of formation of precipitate is expressed as an Avrami's crystallization equation, and that the polymerization proceeds only outside of precipitate [7]. In the case of precipitation of crystals during polymerization, this interpretation might hold, but in the case of precipitation of amorphous polymer, the polymer may be swelled with monomer and the polymerization may proceed in the precipitate until the system becomes glass and propagation is no longer allowed.

Only two special idealized cases are treated in this work. Real polymerizations accompanied with precipitation or glassification may be much more complex. Nevertheless, the results of our calculations show some characteristic features of the polymerization.

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