NOTES

A Comment on the Kinetics in a Heterogeneous Polymerization System

Studies on the catalytic polymerization have been furthered by recent advances in experimental techniques, and reasonable interpretations of the kinetics have been made (e.g., Kagiya et al.[1]), at least for polymerizations carried out in homogeneous systems. However, such kinetic treatments of homogeneous polymerization are not applicable to the polymerizations in a heterogeneous system where precipitation of the polymers takes place. For instance, Higashimura et al.[2] found that in the cationic polymerization of trioxane in nitrobenzene catalyzed by boron trifluoride etherate, the rate of polymerization was proportional to the second power of the residual monomer concentration when initial concentration of the monomer was high. Further, they pointed out that the initiation reaction, where the active species is considered to be $C_2H_5^+ \cdot (BF_3OC_2H_5)^-$, was complete at a very early stage of polymerization (occasionally after an induction period). These facts cannot be accounted for by the kinetic theory for a homogeneous system. The same authors[3] explained these peculiar phenomena in terms of the change in the dielectric constant of the system due to consumption of the monomer. However the reason seems to remain unsettled for the second power law found experimentally.

In this type of polymerization the fact that the resultant polymer precipitates in the homogeneous phase would be important, because the occlusion of the reactive chain end (or the loss of mobility of the growing chain) may well hinder the addition of the monomer molecules even if the resultant chain is "living" chemically. In fact such monomolecular termination was proposed for some polymerization reactions.[4]

In the kinetic studies of crystallization, the Avrami equation is widely used to account for the effect of the impingement of the growing crystallites. It is generally written[5] as

$$dX/dX' = 1 - (X/A) \tag{1}$$

where A is the fraction of the transformable mass in the system, X is the fraction actually transformed by the time t, and X' is the imaginary fraction transformed without any impingement of the crystallites. If the occlusion of the reactive chain end, i.e., physical termination, takes place just as the growth of the crystallites is interrupted by their mutual impingement, the application of the Avrami's equation to the polymerization kinetics will be useful. In this short note the kinetics of polymerization in a heterogeneous system will be examined along this line of argument.

Now let us assume a monomolecular reaction for the addition of monomer in a polymerizing system. The rate of the propagation of a chain is described by

$$dx_s^L/dt = k(a - x) \tag{2}$$

for the living chain consisting of x_s^L monomer units and

$$dx_s^D/dt = 0 \tag{3}$$

for the dead chain of x_s^D units, where a is the initial concentration of the monomer, $x = \Sigma x_s$, the total conversion at the time t, and k is the rate constant of the addition.

Further, the following points will be taken into account for the polymerization. At the beginning of the polymerization, the system is a homogeneous liquid of the solvent, the monomer, and a small amount of catalyst. The concentration of the last will be denoted by c_0. The activation of the catalyst takes place very rapidly, and the propaga-

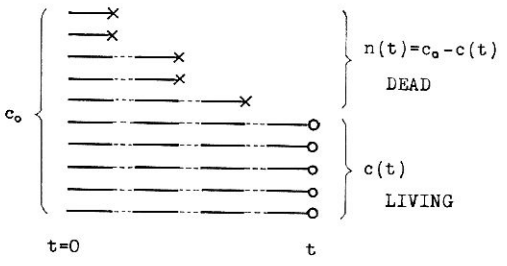

Fig. 1. Schematic illustration of the polymerization, in which all the initiation reactions takes place simultaneously at $t = 0$, followed by successive addition of the monomer; the number of reactive chain ends decreases with time due to the occlusion into the precipitate.

tion of all the chains commences simultaneously at the time $t = 0$. Neither transfer nor termination occurs chemically. However, the precipitation of the resultant polymer, which begins immediately after the initiation reaction, results in "physical" termination, i.e., occlusion of the growing chain ends. Thus the number of the dead chains $n(t)$ increases, and accordingly that of the living chains $c(t)$ decreases as the polymerization time t increases. This sort of reaction is illustrated schematically in Figure 1.

Under these conditions the apparent rate of polymerization is written by;

$$dx/dt = kc(t)(a - x) \tag{4}$$

In the case of the polymerization accompanying the precipitation of the resultant polymer, the phase change is considered a one-dimensional transformation of the growing units. In other words, the chain grows linearly during the polymerization and after the precipitation the polymer formed occupies a space which is approximately proportional to the mass of the polymer. This situation just corresponds to the one-dimensional growth of crystals, i.e., the growth of needlelike crystals. Therefore the Avrami equation, eq. (1), can be modified by using c_0 and $c(t)$ instead of dX'/dt and dX/dt, respectively.

$$c(t) = c_0[1 - (x/a)] \tag{5}$$

Thus, from eqs. (4) and (5), we obtain the expression (6) for the rate of polymerization:

$$dx/dt = kc_0a[1 - (x/a)]^2 \tag{6}$$

It can thus be derived that the rate of polymerization is proportional to the square of the residual monomer concentration. Equation (6) gives

$$a/(a - x) = kc_0t + 1 \tag{7}$$

or

$$x = a\{1 - [1/(kc_0t + 1)]\} \tag{7'}$$

Therefore, the time–conversion relationship should be similar to the usual second-order reactions.

We can also calculate the changes in the average molecular weights and the molecular weight distribution in the course of the polymerization.

The degree of polymerization of the chains which are "living" at time t or just occluded at time t, P^*, is equal to x_s^L for all of the $c(t)$ molecules. Integration of eq. (2) leads to;

$$P^* = \int (dx_s^L/dt)dt = (a/c_0) \ln (kc_0t + 1) \tag{8}$$

or

$$= (a/c_0) \ln [a/(a - x)] \tag{8'}$$

The sum of the chains which are already terminated by time t,

$$n(t) = c_0 - c(t)$$

may be written as a function of P^*

$$n = c_0(1 - e^{-(c_0/a)P^*}) \tag{9}$$

by using eqs. (5) and (8). Differentiation of eq. (9) leads to the increase dn in the number of chains whose ends are occluded when the polymer grows from the degree of polymerization P to $P + dP$;

$$dn = \frac{c_0^2}{a} e^{-(c_0/a)P} dP \tag{10}$$

Thus one can calculate the number-average molecular weight of the polymer which will be obtained by interrupting the polymerization at the time t, where the maximum molecular weight attained is P^*, as follows:

$$M_n = \frac{\int_0^{P^*} (mP)dn + mP^*c(t)}{n(t) + c(t)}$$

$$= (ma/c_0)(1 - e^{-(c_0/a)P^*}) \equiv mx/c_0 \tag{11}$$

where m is the molecular weight of the monomer unit. As can be seen, the number-average molecular weight is nothing but the ratio of the total mass polymerized to the concentration of the initial active site, the latter being the number of the chains included in the system. The total mass involves the mass of the living chains $mP^*c(t)$ and that of the dead chains (due to the occlusion) $\int_0^{P^*} (mP)dn$. Similarly the weight-average molecular weight may be written;

$$M_w = \frac{\int_0^{P^*} (mP)^2 dn + (mP^*)^2 c(t)}{\int_0^{P^*} (mP)dn + mP^*c(t)}$$

$$= \frac{2m[(a/c_0)(1 - e^{-(c_0/a)P^*}) - P^*e^{-(c_0/a)P^*}]}{1 - e^{-(c_0/a)P^*}}$$

$$\equiv (2am/c_0)\{1 - \ln[a/(a - x)]^{(a-x)/x}\} \tag{12}$$

The weight-average molecular weight, when plotted against the conversion, deviates gradually from the number-average molecular weight and is twice the latter at 100% conversion (see Fig. 6).

As mentioned just before, the weights of the living and the dead polymer at any stage of the polymerization, W_L and W_D, respectively, are written:

$$W_L = mP^*c(t) = mc_0P^*e^{-(c_0/a)P^*} \tag{13}$$

$$W_D = \int_0^{P^*} (mP)dn = ma\{1 - [1 + (c_0/a)P^*]e^{-(c_0/a)P^*}\} \tag{14}$$

In Figure 2, the two quantities given by these equations, together with the total mass, are shown as a function of P^*. The mass of the dead fraction increases monotonously and finally coincides with the total mass, whereas the living fraction increases at first and then decreases as polymerization proceeds, having a maximum at $P^* = a/c_0$, and at

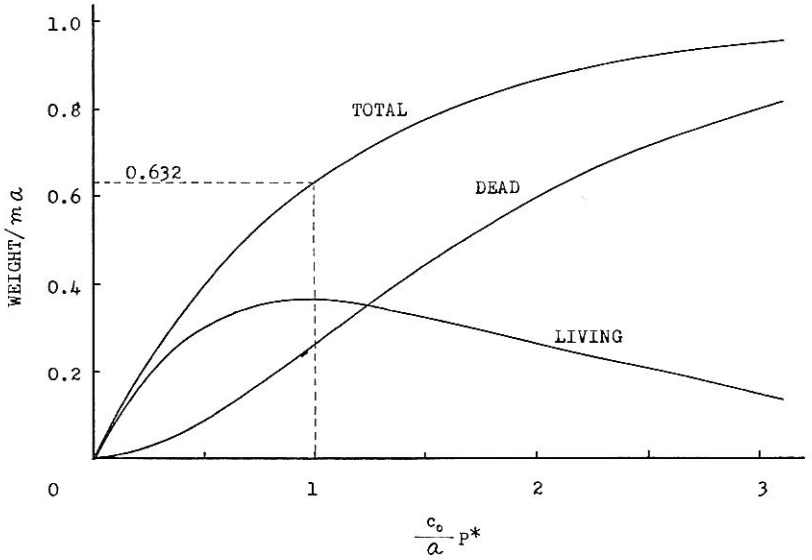

Fig. 2. Changes in the weight fractions of the living and the dead polymers as a function of the molecular weight of the living chain [calculated from eqs. (13) and (14), respectively]. The total of the two weight fractions is also shown.

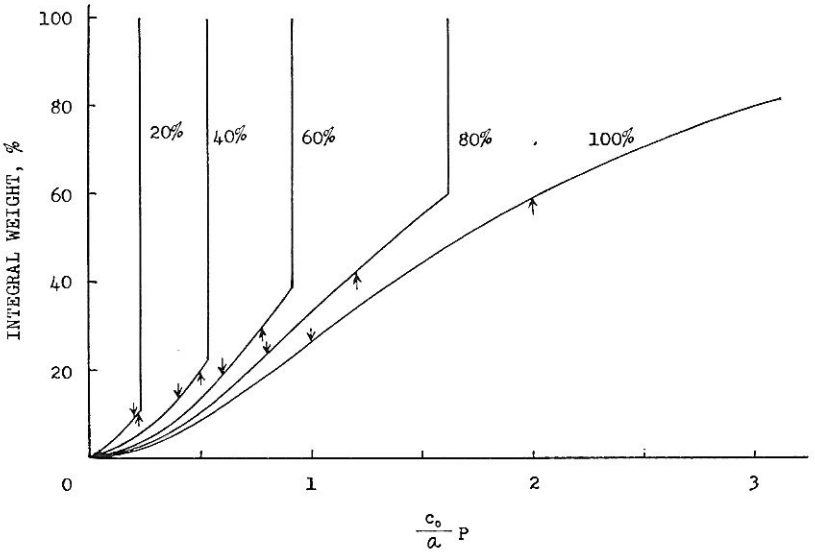

Fig. 3. Theoretical (integral weight) distribution curve for the polymers obtained by interrupting the polymerization at various conversions. The downward and upward arrows indicate the positions of the number-average and the weight-average molecular weights, respectively.

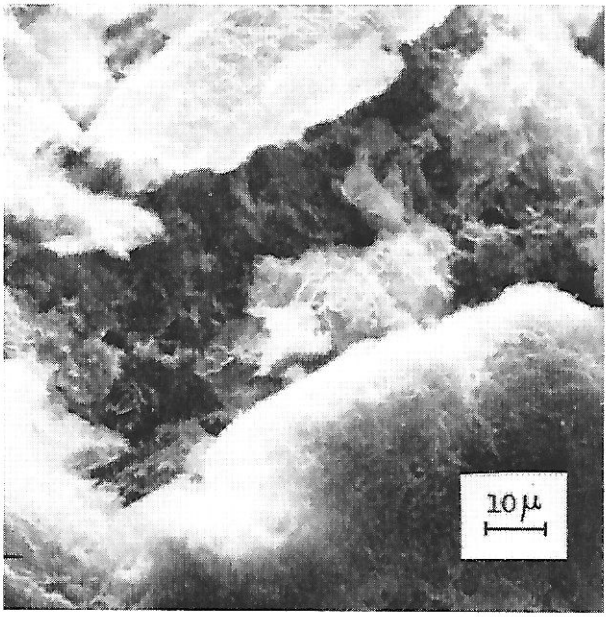

Fig. 4. Scanning-type electron micrograph of the crystalline aggregate of polyoxymethylene formed by the polymerization of trioxane in nitrobenzene.

63.2% conversion, irrespective of the various constants used in the above equations. From the curves in Figure 2, one can estimate the weight distribution of the polymers which will be obtained by interrupting the polymerization at various conversions. Figure 3 shows the integral weight distributions for five conversions, 20, 40, 60, 80, and 100%. The arrows pointing downwards and upwards in the figure indicate the positions of the number-average and weight-average molecular weights respectively.

We have repeated the experiment of Higashimura et al.[2] Our experimental conditions were: monomer, 3.3 mole/l.; catalyst, 1×10^{-3} mole/l.; temperature, 10°C. The reproducibility was good. The polymerization system became turbid on addition of the catalyst. After an induction period of a few minutes, the turbidity increased suddenly due to the precipitation induced by the polymerization, and finally the whole system apparently solidified. The precipitates observed with the use of optical and electron microscopes were made. In the very early stage of the polymerization, lamellar crystals of a size of the order of microns were suspended in the solution. However, soon after the induction period, random crystalline aggregates of the type shown in Figure 4 grew. In these stages the growing chain ends might have been buried in the crystalline aggregate so that propagation could not continue. The time–conversion plot obtained, as shown in Figure 5, is in very good agreement with the theoretical curve [eq. (7′)], for $kc_0 = 0.315$ and an induction time of 4 min. In fact, this polymerization is apparently a second-order reaction as was pointed out by Higashimura et al.[2] These authors discussed merely the relation between the relative viscosity of the polymer (at a given concentration) and the conversion. The average molecular weight was thus estimated from the intrinsic viscosity (measured in *p*-chlorophenol containing 2% α-pinene at 60°C) by using the equation of Kakiuchi et al.;[5]

$$[\eta] = 5.43\bar{M}_n^{0.66} \tag{15}$$

Average molecular weight is plotted against the conversion in Figure 6 in comparison with that obtained from the relative viscosity, measured by Higashimura et al.[2] under

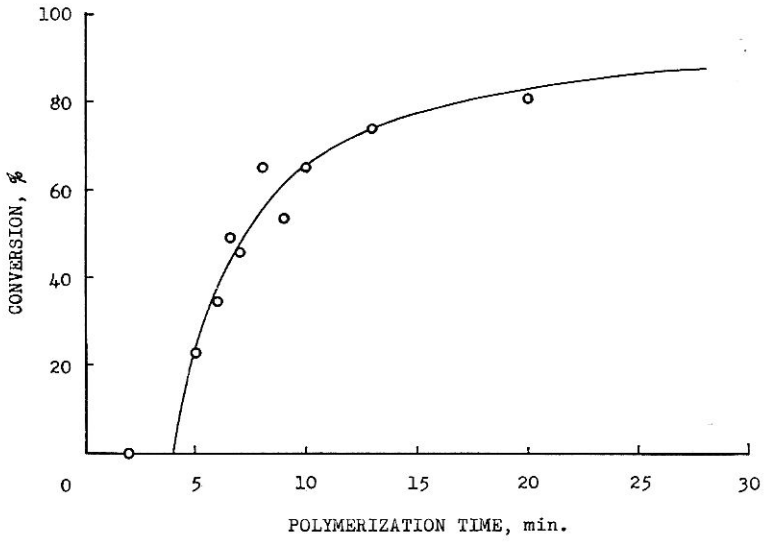

Fig. 5. Time–conversion plot for the polymerization of trioxane in nitrobenzene. Monomer, 3.3 mole/l.; catalyst, 1×10^{-3} mole/l.; temperature, 10°C. The curve is drawn by eq. (7′) for $kc_0 = 0.315$, induction time = 4 min.

the same conditions, assuming Huggins' constant $k' = 0.31$. In this figure are also included the corresponding curves calculated by eqs. (11) and (12) (for $C_0 = 1 \times 10^{-3}$ mole/l.). As can be seen, both types of plots lie approximately on a straight line and near the calulated M_n–conversion curve. Thus it may be said that the effectiveness of the catalyst was nearly 100% in this type of polymerization; i.e., no transfer reaction took place and the polymer chains propagated successively until they occluded.

As another example, the theory developed here will be applied to kinetic data obtained by Dimonie et al.[7] on the polymerization of epichlorohydrin. They carried out the polymerization in toluene at 30°C with triethylaluminum–water as catalyst and measured the rate of the polymerization by means of dilatometry. In this polymerization, the formation of the reactive sites is very fast and it is rather unlikely that new initiation or chain transfer reaction may occur during the subsequent propagation (at least when equimolar catalyst is used). Thus gellike polymers were obtained. Dimonie et al. analyzed their kinetic data on the following assumptions. Firstly there exist two types of reactive sites; one is stable throughout the polymerization; the other is unstable, so that their number diminishes as the polymerization proceeds. Secondly the addition of the monomer is a first-order reaction but the rate of the addition is different for the two kinds of the reactive sites. The kinetic data could be interpreted reasonably, but there is no direct evidence that these assumptions are valid.

In Figure 7 the reciprocal of the residual monomer fraction is plotted against the polymerization time for three different monomer concentrations. These plots were obtained from the data of Dimonie et al. (Fig. 6 in their paper[7]). As can be seen, a good linearity is obtained between the two quantities, which implies that the time–conversion relationship can be approximated by eq. (7). We have no information on the precipitation occurring in the course of the polymerization except the statement of that the polymer obtained was gellike in appearance ("had an aspect of gel"). In our experiment on the polymerization of epichlorohydrin in bulk with ferric chloride–propylene oxide as the catalyst, however, the resultant polymer was found to be a suspension of very fine precipitates of the polymer. In fact it was confirmed that the resultant polymer was insoluble in toluene and/or epichlorohydrin diluted with toluene. Therefore the poly-

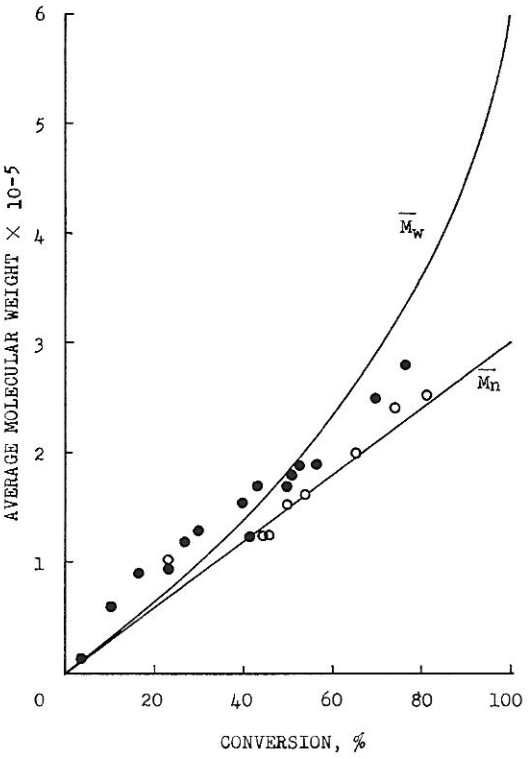

Fig. 6. Plot of the average molecular weights of the nascent polyoxymethylene against the conversion: (○) from the intrinsic viscosity, present experiment, (●) from the specific viscosity, data of Higashimura et al.[2] assuming a Huggins' constant of 0.31. The lower curve shown is the calculated $\bar{M}_n$–conversion relation; and the upper is the calculated $\bar{M}_w$–conversion relation.

merization mechanisms may be considered as follows: propagation of the chain takes place by "living" polymers, but the number of growing chains is decreased by the Avrami-type occlusion of the reactive ends into the precipitate.

The initial rate of the polymerization, i.e., the number of initial reactive sites multiplied by the addition constant, kc_0, obtained from the slope of the lines in Figure 6, is not proportional to the amount of the catalyst used, in contrast with the result of Dimonie et al.[7] However, this may not be unreasonable, because in this polymerization the catalyst is so ineffective (of the order of 10^{-2}–10^{-3}) that the quantitative discussion on the effect of its concentration is very difficult.

In this connection, the polymerization kinetics of *p*-xylylene, reported by Errede et al.[8] seems worth reconsidering. The essential points reported are as follows. The polymerization was carried out in toluene isothermally at −78°C. Initiation was caused by free radicals which were initially present in the monomer solution and no new site for the polymerization was created thereafter. Termination did not occur at this low temperature by chain-transfer reactions. Thus the propagation continued by successive addition of the monomer until the molecular weight of the linear chains reached values in excess of 2×10^5. Precipitation of the polymer was observed when the degree of polymerization exceeded about 20. The change of residual monomer concentration in the course of the polymerization was determined by a titration method.

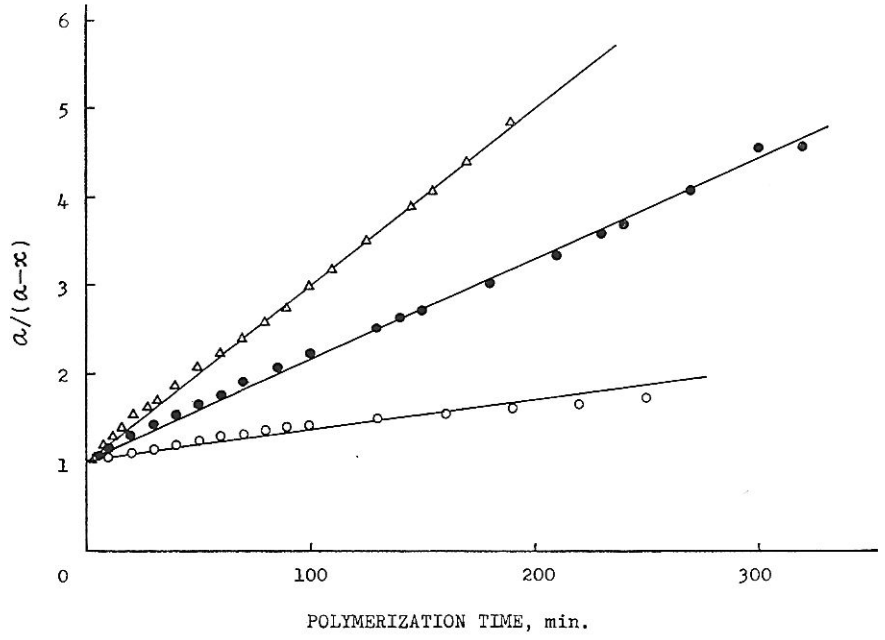

Fig. 7. Plot of the ratio of the initial monomer concentration to the residual monomer concentration against the time, for the polymerization of epichlorohydrin in toluene (data of Dimonie et al.[7]): and various catalyst concentrations: (△) 6×10^{-2} mole/l.; (●) 4.1×10^{-2} mole/l.; (○) 2×10 mole/l. Monomer concentration, 2 mole/l.

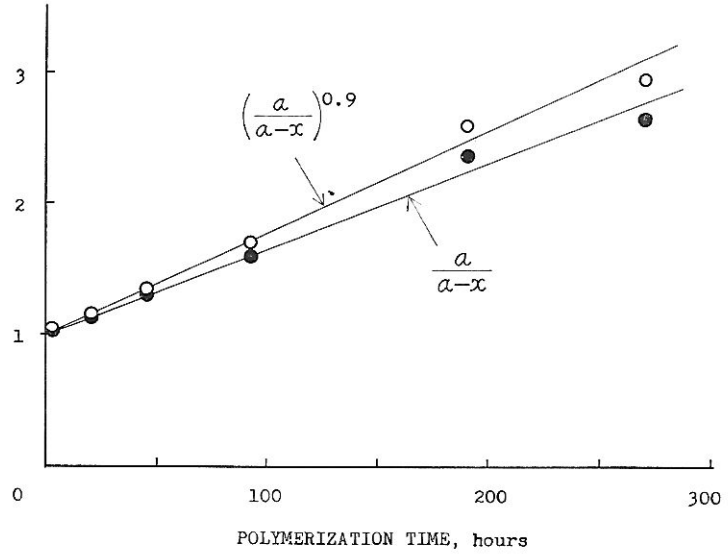

Fig. 8. Comparison of plots of (○) $[a/(a-x)]^{0.9}$ versus time and (●) $a/(a-x)$ versus time, for the polymerization of *p*-xylylene at −78°C. Data of Errede et al.[8]

In the first stage of the polymerization, which covers 10 hr, the number of sites for polymerization did not decrease appreciably, i.e., the polymerization was a first-order reaction with respect to the monomer concentration. When the polymerization proceeded further, however, deviation from first-order kinetic was found; the kinetics were described by eq. (16):

$$\left[\frac{a}{(a-x)}\right]^{2k/K} = 1 + 2Kc_0t \tag{16}$$

where K is a rate constant for the coupling between one insoluble free radical endgroup and another, which was considered to occur, despite the heterogeneous character of the system. The ratio $2K/k$ was determined experimentally as 0.9.

We do not know the details of the experiment of Errede et al., but it seems unlikely that coupling took place predominantly in the later stages of polymerization where the molecular chains should be occluded or immobilized in the precipitate. In fact this type of coupling is inconsistent with the Trommsdorf's effect[9] usually observed in bulk polymerization; the consumption of free radicals by coupling diminishes as polymerization proceeds due to the increase in the viscosity of the system. Furthermore, the coupling of the radical itself seems difficult because the mobility of the chain segments with a radical endgroup might be highly restricted at such a low temperature of polymerization, which is much lower than the glass transition temperature of the polymer (ca. 176–189°C). (This temperature was roughly estimated by taking $^2/_3$ of the melting point temperature of the polymer, 673–693°K[8], the effect of the solvent being considered to be very small at this low temperature.)

If the ratio $2K/k$ in eq. (16) were equal to 1 instead of 0.9, the equation would just coincide with eq. (7), implying that the Avrami-type occlusion of the reactive chain ends is the source of the decrease in the polymerization rate with time. As is shown in Figure 8, the linearity of plots of $[a/(a-x)]^{0.9}$ versus time obtained by Errede et al. still holds, even when the exponent was replaced by 1.

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