Some Considerations of Suspension Polymerization of Minute Droplets

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Introduction

By the study of Hohenstein and Mark[1] on suspension polymerization, it has been established that such a polymerization is equal to a summation of individual bulk processes of many droplets of monomer which are suspended in water. But more critically Haward[2] has published his study on the effect of volume change of the monomer droplet on active centre concentration, where it is assumed that the formation of an active centre is always in pairs and it is concluded that subdividion of the system, i. e., the decrease in the volume of droplets, causes the stationary value of active centre concentration to decrease.

In this discussion, we shall reconsider the subject, introducing a new quantity which represents the yield of polymer radicals from initiator fragments which are formed by the decomposition of initiator and may produce free polymer radicals.

Stationary State

We can recognize suspension polymerization processes as probability processes concerned with the appearance and disappearance of active centres, and the following probabilities are taken into consideration:

probability of appearance of one new active centre in a droplet during a time interval Δt which is very short …… λ_1,
probability of appearance of two new active centres in a droplet during Δt …… λ_2,
probability of disappearance of two active centres during Δt by mutual termination within a droplet which has n active centres …… $\mu n(n-1)$, where μ is a constant,
probability that an arbitrarily chosen droplet has n active centres at time t …… $P_n(t)$,

and (1) is given,

$$P_n(t+\Delta t)=\{1-\lambda_1\Delta t-\lambda_2\Delta t-\mu n(n-1)\Delta t\}P_n(t)+\lambda_1\Delta tP_{n-1}(t)+\lambda_2\Delta tP_{n-2}(t)+\mu(n+2)(n+1)\Delta tP_{n+2}(t)+o(\Delta t) \qquad (1)$$

where $o(\Delta t)$ represents a higher order term of Δt. Formula (1) gives the differential equation (2).

$$dP_n/dt=-\{\lambda_1+\lambda_2+\mu n(n-1)\}P_n+\lambda_1P_{n-1}+\lambda_2P_{n-2}+\mu(n+2)(n+1)P_{n+2} \qquad (2)$$

In order to solve (2), we introduce a generating function B, i. e.,

$$B=\sum_{n=0}^{\infty}P_ns^n$$

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[1] W. P. Hohenstein and H. Mark, *J. Polymer Sci.*, **1**, 127 (1946).

[2] R. N. Haward, *J. Polymer Sci.*, **4**, 273 (1949).

and (3) is given.

$$\partial B/\partial t=\mu(1-s^2)\partial^2B/\partial s^2 -\{(\lambda_1+\lambda_2)-\lambda_1 s-\lambda_2 s^2\}B \tag{3}$$

Using a new quantity f, which is the yield of polymer radicals from initiator fragments, λ_1 and λ_2 are represented as follows, provided that Δt is sufficiengly short,

$$\lambda_1=2\varphi Vf(1-f),\quad \lambda_2=\varphi Vf^2 \tag{4}$$

where φ is the rate of formation of initiator fragments and V is the average volume of droplets. μ is proportional to $1/V$ and represented by (6), where k_t is the chain termination reaction constant.

$$\mu=k_t/V \tag{5}$$

(3), (4) and (5) give (6).

$$\partial B/\partial t=k_t(1-s^2)\partial^2B/\partial s^2/V -\varphi Vf(1-s)\{2-f(1-s)\}B \tag{6}$$

It is difficult to obtain the solution of (6) generally, and we shall discuss the stationary state only.

In the stationary state, $\partial B/\partial t=0$, and (7) is given,

$$(1-s^2)\partial^2B/\partial s^2=\varphi V^2f(1-s)\{2-f(1-s)\}B/k_t \tag{7}$$

which can be solved approximately.

Now we wish to estimate active centre concentration R. There exists a relationship (8) between R and M, where M is the average number of active centres per droplet, as represented by (9).

$$R=M/V \tag{8}$$

$$M=\sum_{n=1}^{\infty} nP_n \tag{9}$$

Using (7), (8) and (9), we can estimate the approximate numerical values of R (Appendix). Variations in f and V alter the values of R. These are shown in Table I. When

TABLE I

$f\sim V\sim R$ RELATIONSHIPS

f	V	m	P_0	P_1	P_2	M	R	$R:1/2V$
1	$\sqrt{k_t/\varphi}\times1/3.16$	0.1	0.909	0	0.091	0.182	$\sqrt{\varphi/k_t}\times0.575$	0.364
	〃 1/10	0.01	0.990	0	0.010	0.020	〃 0.200	0.040
	〃 1/31.6	0.001	0.999	0	0.001	0.002	〃 0.063	0.004
	〃 1/100	0.0001	1.000	0	0.000	0.000	〃 0.000	0.000
0.99	〃 1/3.16	0.1	0.476	0.492	0.024	0.540	〃 1.71	1.080
	〃 1/10	0.01	0.498	0.499	0.003	0.504	〃 5.04	1.008
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0.75	〃 1/3.16	0.1	0.478	0.493	0.022	0.538	〃 1.70	1.076
	〃 1/10	0.01	0.499	0.500	0.000	0.500	〃 5.00	1.000
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0.50	〃 1/3.16	0.1	0.482	0.494	0.018	0.530	〃 1.67	1.060
	〃 1/10	0.01	0.499	0.500	0.000	0.500	〃 5.00	1.000
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0.25	〃 1/3.16	0.1	0.490	0.496	0.011	0.517	〃 1.63	1.034
	〃 1/10	0.01	0.499	0.500	0.000	0.500	〃 5.00	1.000
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0.01	〃 1/3.16	0.1	0.500	0.500	0.000	0.500	〃 1.58	1.000
	〃 1/10	0.01	0.500	0.500	0.000	0.500	〃 5.00	1.000
	〃 1/31.6	0.001	0.500	0.500	0.000	0.500	〃 15.8	1.000
	〃 1/100	0.0001	0.500	0.500	0.000	0.500	〃 50.0	1.000
0	no reaction					0	〃 0	0

It is shown in this table that R, regarded as a function of f, changes discontinuously at two points, i.e., $f=0$ and $f=1$. This is a reasonable result from the difference between two boundary conditions which have been used in the course of solving (7), and completely right so far as stationary states are discussed ($t\longrightarrow\propto$). At a stationary state which has been attained after a long enough period of reaction, there exist significant differences of active centre distributions between $f=1$ and $f=0.99$ or $f=0$ and $f=0.01$.

On the other hand, it is naturally thought that at the beginning of a reaction there should be little differences of active centre distributions between $f=1$ and 0.99 or $f=0$ and 0.01. Therefore, R ought to change continuously in the whole range of $0\leqq f\leqq1$ if t takes some finite value, sometimes taking a stationary value and sometimes an unstationary one, as f varies. Actually, such a $R\sim f$ relationship at a constant finite t is the matter to be discussed. A general discussion of this would require a general solution of (6), which will not be touched on in this paper. Only the case when V is extremely small will be discussed in the next section.

f is zero, R equals zero and polymerization does not occur. When f is unity, the decrease in V causes R to decrease. When f is between zero and unity and equals neither of them, the decrease in V increases R to a maximum, $1/2V$, which is approached more and more as V decreases. The greater values of R, in this case, mean not only higher rates of polymerization reaction, but also higher degrees of polymerization of products, since the greater values of R at the same initiation rate are caused only by longer lives of molecular chains. We can know, therefore, that the subdivision of the system makes both the rate and degree of polymerization lower when $f=1$, and higher when $0<f<1$.

Of course, the above discussion is based on the assumption of a stationary state, and the length of time it takes for R to reach the stationary value is not given here.

Initial Stages of Polymerization

The usual suspension polymerization should show a very similar figure at its initial stage to bulk polymerization, if it is true that suspension polymerization is a summation of bulk polymerizations of dispersed monomer droplets. The time necessary for R to reach half of the stationary value is $(k_t\varphi f)^{-1/2}$ which is independent of V[3], provided that V is very great as compared with $1/R_\infty$[4]*.

In the case of suspension polymerization of minute droplets, on the other hand, it has been established in this paper that the stationary value of R approximately equals $1/2V$ when $0<f<1$ is satisfied. In this case the probabilities that a droplet contains no active centre and one are both 1/2. And an active centre freshly created in a droplet which contains another active centre previously created, quickly terminates together with the old one, and the probability of coexistence of two or more growing active centres in one droplet is very small as compared with unity. In this case we can make the following approximate expression,

$$v_t=4\varphi f(1-f)VR$$

where v_t is the disappearance rate of active centre (rate of chain termination reaction), and $0<f<1$ is assumed. It gives

$$dR/dt=(\lambda_1/V)-v_t=2\varphi f(1-f)(1-2VR),$$

which being integrated, gives (10).

$$R=[1-\exp\{-4f(1-f)\varphi Vt\}]/2V \qquad (10)$$

When t goes to infinity, R goes to $1/2V=R_\infty$. The time necessary to reach the half value of R_∞, or the measure of quickness with which R approaches to stationary value, is expressed by τ in (11).

$$\tau=\ln 2/4f(1-f)\varphi V \qquad (11)$$

This relationship is shown in Fig. 1.

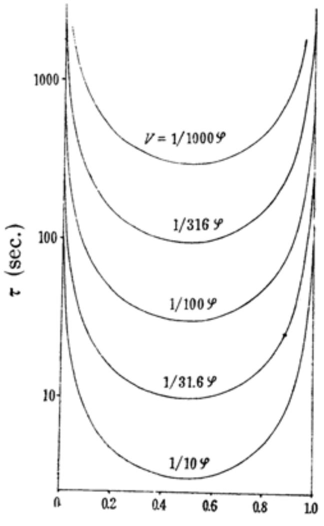

Fig. 1. Relations between τ, f and V.

If we estimate the numerical values of φ, f, and V, the numerical value of τ is known. Nozaki and Bartlett[5] have shown that the decomposition rate of benzoyl peroxide in methyl methacrylate at 60°C is 0.36×10^{-5}/sec., which means that φ is 0.72×10^{-5} (BPO) mol./l. sec. If V is smaller than $\ln 2/4f(1-f)\times0.72\times10^{-5}$ (BPO), τ is greater than one second, and the decrease in V proportionally increases τ. If V is much smaller than this, τ is much greater than unity and the decrease in V ultimately increases τ so much that the stationary state would not be reached at any late stage of reaction.

Nevertheless, R in the case of the smaller V is always greater than R in the case of the greater V at the same reaction time. This is shown in Fig. 2. The greater values of R in such cases mean not only the higher reaction rates, but also the higher degrees of polymerization of products as indicated in the previous section.

We can know, therefore, that the suspension polymerization of minute droplets should show high values in both rate and degree of polymerization than usual suspension process in either initial (unstationary) or stationary stages of reaction. In other words, a system of suspension polymerization, subdivided to smaller and smaller droplets should

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[3] W.H. Stockmeyer, *J. Chem. Phys.*, **12**, 143 (1944).

[4] This is satisfied in the case of usual suspension polymerization. Ref. 2).

* R_∞ is the stationary value of R. See the latter part of this section.

[5] K. Nozaki and P.D. Bartlett, *J. Am. Chem. Soc.*, **68**, 2377 (1946).

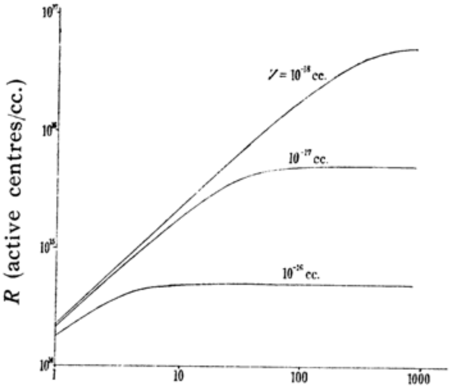

Fig. 2. $R \sim t$ relationships as for (BPO) = 0.1 mol./l.

ultimately shift to a system where both rate and degree of polymerization are greater than when undivided, provided that $0<f<1$ is satisfied. This agrees with the observation by Hohenstein and Mark[1] that the rate is increased in suspension polymerization, when agitation is done vigorously.

Emulsion Polymerization Accelerated by Oil-soluble Initiator

Following the practice that the polymerization of monomer emulsion by water-soluble initiator is called emulsion polymerization, we usually name the polymerization of monomer emulsion by oil-soluble initiator also as emulsion polymerization. These two are, indeed, common in that rate accelerating and molecular weight increasing effects are observed as compared with bulk or suspension polymerization in the same condition. But the two emulsion polymerizations cannot be the very same ones because of the difference in the modes of free radical appearance into polymerization loci, viz., one by one in the former and two at once in the latter.

There coexist in monomer emulsion two sorts of monomer dispersions, i. e., emulsified droplets and solubilized monomer in soap micelles[6]. In the case of emulsion polymerization accelerated by oil-soluble initiator, polymerization should occur in both of them. A study on BPO-initiated emulsion polymerization of methyl methacrylate, worked by Kagawa and the author[7], showed, in addition to the above mentioned rate and molecular weight increasing effects, that the turbidity decreased as reaction proceeded, which suggested that the polymerization in micelle is preferential.

The preceding authors[8] imagined some mechanisms agreeable with the characteristic figures of emulsion polymerization, accelerated by oil-soluble initiator, i. e., capture of free radicals by aqueous phase, and pre-existing of free radicals in reaction system etc. But now, these are unnecessarily essential to illustrate the characteristic figures of emulsion polymerization accelerated by oil-soluble initiator. We can do it by assuming only $0<f<1$, as follows.

Solubillzed monomer in micelles are very small crowds of monomers and can be recognized as extremely small monomer droplets. If $f=1$, the value of R should be very near to zero in micelles because of their smallness and micelles should not contribute to the reaction practically. So the reaction should proceed only in the emulsion droplets. On the other hand, when $0<f<1$, R in the micelles should be very great because of their smallness and reaction in the micelles should surpass that in droplets which in this case serve almost only as reservers of monomers, and decrease in turbidity is expected. Therefore, the above-mentioned experimental results by Kagawa and Kaichi are simply illustrated by assuming $0<f<1$. This condition $(0<f<1)$ is perhaps satisfied in all oil-soluble initiators because the mutual reaction between two decomposition fragments can always be considered[9].

Thus we can understand suspension polymerization and emulsion polymerization accelerated by oil-soluble initiator on a simple common basis that there is no essential difference in mechanisms and only volume difference of reaction loci between these two.

Conclusion

Systems of suspension polymerization, subdivided into smaller and smaller droplets, should shift ultimately to those where both the rate of reaction and the degree of polymerisation are greater than the initial, provided that the yield of polymer radicals from initiator fragments equals neither zero nor unity. The characteristic figure of emulsion polymerization accelerated by oil-soluble initiator can be understood on this basis.

Appendix

Estimation of R from Formulae (7), (8) and (9)

The stationary state assumption gives (i), when we represent the numbers of droplets which contain odd and even numbers of active centres by N_o and N_e, respectively,

$$dN_o/dt = \lambda_i(N_e - N_o), \quad dN_e/dt = \lambda_i(N_o - N_e) \qquad \text{(i)}$$

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[6] W. d. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).

[7] S. Kaichi and I. Kagawa, *J. Chem. Soc., Japan* (Ind. Chem. Section), **58**, 509 (1955).

[8] Ref. 2); Ref. 7).

[9] M.S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

which gives (ii).

$$(N_e-N_o)/(N_e+N_o)=\exp(-2\lambda_1 t) \qquad \text{(ii)}$$

(A) $\lambda_1=0$

This means $f=0$, or $f=1$.

a) $f=0$ No reaction.

b) $f=1$ This means the formation of active centers exclusively in pairs.

(ii) gives (iii).

$$\left.\begin{array}{l} \left.\begin{array}{l} N_o=0 \\ \quad \therefore \sum P_{2i+1}=0 \\ N_e=N_e+N_o \\ \quad \therefore \sum P_{2i}=1 \end{array}\right\} \quad \therefore \quad B_{s=-1}=1 \\ N_e+N_o=\text{const.} \\ \quad \therefore \sum P_n=1 \qquad \therefore \quad B_{s=1}=1 \end{array}\right\} \qquad \text{(iii)}$$

Using (iii) as boundary conditions, we obtain (iv) from (7), (8) and (9), which gives the approximate numerical values of R, neglecting higher order terms of m, where m is the abbreviation of $\varphi V^2/k_t$. (iv) is applicable to small values of V.

$$\left.\begin{array}{ll} P_0=1/1+m, & P_1=0, \\ P_2=m/1+m, & P_3=0,\cdots\cdots. \\ R=2m/(1+m)V. & \end{array}\right\} \qquad \text{(iv)}$$

(B) $\lambda_1 \neq 0$

The means $0<f<1$.

(v) is given by (ii).

$$\left.\begin{array}{ll} N_e=N_o & \\ \quad \therefore \sum P_{2i}=\sum_{2i+1} & \therefore \quad B_{s=-1}=0 \\ N_e+N_o=\text{const.} & \\ \quad \therefore \sum P_n=1 & \therefore \quad B_{s=1}=1 \end{array}\right\} \qquad \text{(v)}$$

Using (v) as boundary conditions, we obtain (vi) from (7), (8) and (9), neglecting higher order terms of m, which is applicable to small values of V.

$$\left.\begin{array}{l} P_0=1/2[1+mf(2-f)/2-0.032\,mf(1-f)] \\ P_1=1/2[1+mf(2-f)/6-0.010\,mf(1-f)] \\ P_2=mf(2-f)/4[1+mf(2-f)/2-0.032\,mf(1-f)] \\ R=(P_1+2P_2)/V \end{array}\right\} \text{(vi)}$$

Above P_3 are not given because of their extreme smallness. Fig. 1 is the result of the abovementioned numerical estimations of P_0, P_1, P_2 and R by inserting several values of m and f into (iv) and (vi).

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