THE RATE OF EMULSION POLYMERIZATION OF ACYRLO NITRILE

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The rate of emulsion polymerization of acrylonitrile has been investigated under widely variable experimental conditions such as initiator concentration, emulsifier concentration and monomer-water ratio. The results obtained were interpreted reasonably well by kinetic equations, which were proposed by assuming that the reaction in polymer particles proceeds under the slow termination regime and that the surface of polymer particles alone plays a role in propagation.

1. Introduction

Quite a few experimental studies including those of the present authors5) have been presented of the emulsion polymerization of styrene, and the results are explained well by the theoretical treatment presented by Smith and Ewart7). It is known, however, that this treatment cannot be directly applied to the polymerization of acrylonitrile. This is due to the fact that the properties of acrylonitrile monomer and polymer are very different from those of styrene. Acrylonitrile monomer is highly soluble in water, and its polymer is not soluble in monomer.

In the present study, the effects of operational variables such as initiator concentration, emulsifier concentration and monomer-water ratio on the rate of polymerization have been investigated experimentally in a batchwise reactor at 50°C.

Experiments of post-addition have been also carried out from the kinetic viewpoint. On the basis of these experimental results, the kinetics of the polymerization of acrylonitrile initiated with water-soluble initiator will be discussed in relation with the authors' previous investigation4).

2. Experimental

Experimental apparatus: A flow diagram of the experimental apparatus and details of the reactor are shown in Fig. 1. The reactor was cylindrical, with a hot-water jacket, and made of stainless steel.

Reagents: Acrylonitrile monomer (supplied by Nitto Chemical Co.) was distilled under nitrogen atmosphere. Sodium lauryl sulfate as emulsifier and potassium persulfate of extra pure grade as initiator were used without further purification. Nitrogen, deoxygenated by passing through reduced copper gauze at 400°C, was used.

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Experimental procedure: An aqueous solution of emulsifier and acrylonitrile monomer was charged into the reactor. The reactor was evacuated up to 40~50 mmHg and then nitrogen was flashed. This procedure was repeated five times. Then agitation was started and simultaneously nitrogen was bubbled into the reactant mixture. The temperature was then raised to a constant reaction temperature of 50°C by the hot-water jacket. After one hour’s mixing, the initiator was added to start the polymerization reaction.

After the reaction was initiated, about 5 grs. of reaction mixture was sampled at desired time intervals. This sample was quickly weighed and then diluted with methyl alcohol. The polymer formed was precipitated and dried at 80°C overnight. The polymer yield, as weight of polymer per unit volume of reaction mixture, was determined gravimetrically, and the molecular weight was determined by viscosity measurement5). The number of polymer particles formed was counted under an electron microscope.

3. Experimental Results

3-1 Effect of emulsifier concentration: The polymerization of acrylonitrile can be carried out without emulsifier. Polymer particles deposited, however, cannot be dispersed stably in aqueous media and aggregate with each other successively as the reaction proceeds.

Polymer yield vs. time elapsed curves obtained experimentally under different monomer-water ratio of the feed are shown in Fig. 2. The curves show sigmoidal shapes. This results from the fact that in the early stage of reaction the acceleration of polymerization rate is caused by formation of polymer particles in which radicals accumulate. Rapid decrease of the polymerization rate observed is explained as the result of aggregation of polymer particles. This will be discussed later.
Fig. 1 Experimental apparatus

① Nitrogen cylinder  ② Deoxygenation column  ③ Manometer  ④ Vacuum pump  ⑤ Reservoir of initiator  ⑥ Thermocouple  ⑦ Sampling tap  ⑧ Reactor  ⑨ Circulation pump  ⑩ Baffle plates ⑪ Agitator (2 paddles) ⑫ Baffle plates (2 pieces) ⑬ Hot water jacket

Fig. 2 Polymer yield vs. time curves in absence of emulsifier.

Fig. 3 Monomer conversion vs. time curves in absence of monomer droplets at reaction outset.

When the emulsifier is added to the system, a higher rate of polymerization is observed. Conversion vs. time curves are given in Figs. 3 and 4 at different emulsifier concentrations.

The polymerization rates, obtained by graphical differentiation of the curves in Fig. 4, at a specified conversion \(x = 0.20\) under the presence of monomer droplets are plotted against emulsifier concentration in Fig. 5. The dependence of polymerization rate on emulsifier concentration is found to be around one
sixth power. A typical example of the number of polymer particles formed vs. time elapsed curve is shown in Fig. 6. The number of polymer particles is found to become constant after the conversion reaches 10%. The average number of polymer particles over the range of conversion, in which the number of polymer particles is regarded as constant, is directly proportional to emulsifier concentration over its range of 0.5g/l＜[S]＜4.0g/l. This is shown in Fig. 7.  

3-2 Effect of initiator concentration: The polymerization rates obtained at a specified conversion, \( \alpha = 0.30 \), are plotted in Fig. 8 as a function of initiator concentration. The dependence of the polymerization rate with respect to initiator concentration is estimated to be one-half power. As shown in Fig. 9, the number of polymer particles formed is independent of initiator concentration.  

3-3 Effect of monomer-water ratio: The polymer yield vs. time curves obtained for different monomer-water ratios are shown in Fig. 10. When monomer-water volume ratio is more than 150/850, monomer droplets are present at the initial stage of the polymerization, while for smaller ratios monomer is completely dissolved in water. The polymerization rates vs. unreacted monomer concentration are illustrated in Fig. 11. The dependence of monomer-water ratio on the number of polymer particles was negligibly small. The curves show marked differences from those observed in the emulsion polymerization of styrene and vinyl acetate. When excess amount of monomer above saturation is charged, the polymerization rate is sharply accelerated in the early stage of the
polymerization, followed by the periods of nearly constant rate of polymerization and then a marked decrease of polymerization rate.

3-4. Degree of polymerization: A typical example of the degree of polymerization vs. time obtained experimentally is shown in Fig. 12. As the reaction proceeds, the degree of polymerization decreases considerably.

3-5. Effect of agitation: The monomer conversion vs. time curves are shown in Fig. 13 at 450 r.p.m., 700 r.p.m. and 1000 r.p.m. As pointed out by the present authors, who discussed the stability of monomer droplets dispersed in aqueous phase with respect to the emulsion polymerization of styrene, rather strong stirring in the initial period of the polymerization, followed by mild stirring, is favorable to stable dispersion of polymer particles.

3-6. Post-addition of monomer and initiator: As shown so far, the behavior of the emulsion polymerization of acrylonitrile is very different from that of styrene.

In order to discuss the kinetics of this system, it will be worthwhile to investigate the behavior with intermittent or continuous addition of initiator and monomer in the course of the reaction. The experimental results will be shown in connection with kinetic considerations.

4. Discussion of Kinetics

4-1. Review of previous studies: In the polymerization of acrylonitrile in aqueous media with and without an emulsifier, the behavior observed is quite different from that of emulsion polymerization of styrene. Thomas et al., have observed in their experiments, in which monomer less than its saturation amount in water was initially charged, that the polymerization rate curves show a short period of acceleration followed by a constant rate period and finally a decreasing rate. Yuguchi et al. and Kiuchi et al. have performed extensive experiments on these systems and pointed out that the dependences of the polymerization rate on monomer concentration, initiator concentration and emulsifier concentration, at a low level of emulsifier, are 2nd, 0.5th and 0.4th powers, respectively. They have found that the number of polymer particles remains nearly constant during the polymerization, and they discussed the kinetics of these systems presuming that polymerization at polymer particles will be predominant after a certain period. These investigators deduced that polymerization with and without emulsifier seems to proceed according to the same mechanism. Izumi et al. have investigated the role of emulsifier and noted that the hydrophobic portion of emulsifier seems to act as a kind of nucleus around which polymer molecules precipitate and the formation of polymer particles may occur.

4-2. Analysis of the rate data: The present authors have discussed the rate of polymerization with deposition of polymer particles and derived asymptotic solutions which are applied to calculate the number of radicals in a polymer particle. As seen in the following, Eq.(12) of the authors' previous paper is applied to correlate the experimental data obtained here for emulsion polymerization of acrylonitrile. This corresponds to the fact that the termina-
radical escape from polymer particles is rather predominant, and the termination in polymer particles is very slow. A modification of Eq.(12) is made here, since acrylonitrile polymer is insoluble with its monomer and the latter will be adsorbed only on the surface of polymer particles. It is assumed, therefore, that the surface of the polymer particles alone serves as a place for propagation. The number of radicals in a polymer particle $n$ is thus in this case expressed by

$$n = \left(\frac{fkd[A][x]/k_{d}[M_a][N^1/2]}{2}\right)$$

(1)

where

$$A = \left(36\pi\right)^{1/3}[M_a]/[M_p]^{1/3}$$

(2)

The rate of polymerization is given by

$$r_p = k_p[n^1/2][M_p][x]^1/2$$

(3)

where

$$K = k_p[1/2][k_{d}N]^{1/2}$$

(4)

For convenience sake, assume that the surface concentration of monomer $[M_p]$ is related to its concentration in aqueous phase $[M_a]$ by

$$[M_p] = n[M_a]$$

(5)

As far as monomer droplets exist in the reactant mixture, $[M_p]$ is kept constant, say $[M_p1]$, because $[M_a]$ is kept as its saturated value of monomer in aqueous phase $[M_{a1}]$.

After monomer droplets disappear, mass balance of monomer leads to

$$[M_p] = \frac{M_p(1-x)}{A[M_a]^{1/2}[N^{1/3} + m(1-BM_a)x]}$$

(6)

where

$$B = M_a/[10^3\rho_p]$$

In batch operation

$$-M_p\frac{dx}{d\theta} = r_p$$

(7)

Substituting Eq.(3) with the relation between $x$ and $[M_p]$ into Eq.(7) and integrating the latter will give the relation between $x$ and $\theta$. Here it is also assumed that the number of polymer particles $N$ is constant and the consumption of initiator is negligible during the reaction. Let $x_{cr}$ denote the value of conversion at which monomer droplets disappear. At $0 \leq x \leq x_{cr}$, $[M_p] = [M_p1]$ and the integration of Eq.(7) with the initial condition of $x = x_0$ at $\theta = 0$ leads to

$$x_{cr}^2 - x_0^2 = \frac{2}{3}KA^{1/2}k_d[1/2][x][M_p1][M_a^{1/2}N^{1/4}(\theta - \theta_0)]$$

(8)

Eq.(8) shows that a straight line is obtained by plotting $x_{cr}^2$ against $\theta$. As illustrated in Fig. 14, from the value of $x$, at which this linear relation deviates, the value of $x_{cr}$ is also estimated. Substituting the values of $x_{cr}$ and the experimentally measured value of $N$ into Eq.(6) and referring to the relation of Eq.(5) gives the values of $m$ and $[M_{pi}]$. And from Eq.(8) the value of $K$ is obtained.

From the experimental data with values of $f = 0.5$ (assumed), $k_d = 4.46 \times 10^{-11}$ 1/hr and $[M_{pi}] = 1.57$ g-mol/l at 50°C the following values are obtained.

$$K = 5.8 \times 10^6$$ cm/g-mol$^{1/2}$ hr$^{1/2}$

$$[M_{pi}] = 3.1 \times 10^{-4}$$ g-mol/cm$^2$

$$m = 5 \times 10^6$$ cm$^2$/l

and

$$x_{cr} = 0.12$$ for $T = 150/800$

$$x_{cr} = 0.22$$ for $T = 200/800$

$$x_{cr} = 0.35$$ for $T = 300/700$

where $T$ is the monomer-water volume ratio of the initially charged reactant mixture.

With these values the rate of polymerization is calculated by

$$r_p = K[A][x][M_p1][N^{1/2}][M_p]$$

(9)

at $x \leq x_{cr}$,

$$r_p = KA^{1/2}k_d[1/2][x][M_p1][M_a]$$

(10)

The rate should depend on $0.5$th power of initiator concentration. This is consistent with the experimental results shown in Fig. 8. At $x < x_{cr}$, the rate is proportional to $1/6$th power of the number of polymer particles. The results shown in Fig. 5 satisfies this relation, since the number of polymer particles formed is proportional to the concentration of emulsifier added, as seen in Fig. 7. The rates of polymerization calculated from Eqs.(9) and (10) are compared with those experimentally obtained for different initial monomer concentrations in Fig. 11. The agreement between the calculated and observed values is considered reasonably good. The deviation, especially at high values of monomer conversion, may be due to the simplified assumptions, above all for the monomer distribution between polymer particles and water phase.

### 4-3 Degree of polymerization:

The number average degree of polymerization of the polymer formed at any instant of the batch operation $\bar{p}$ is given by

$$\bar{p} = \frac{r_p}{(1/2)r_d + r_{cr}}$$

(11)

where the termination is assumed to be the recombination of radicals. The value by Eq.(11) is called here
instantaneous degree of polymerization. If chain transfer only to monomer is assumed to occur,

$$r_{tr} = c_m r_p$$  \hspace{1cm} (12)$$

where $c_m$ is the transfer coefficient to monomer. And the rate of initiation is

$$r_i = 2f_k d[I]$$  \hspace{1cm} (13)$$

On the other hand, the observed value of the number average degree of polymerization of the polymer sampled in experiment $\bar{P}$, called here overall degree of polymerization, is related to the instantaneous value $\bar{p}$ as follows.

$$\bar{P} = \frac{x}{\int_0^x \left(1/\bar{p}\right)dx}$$  \hspace{1cm} (14)$$

In Fig. 12, by taking values of $f_k d = 2.32 \times 10^{-3}$ 1/hr and $c_m = 2.6 \times 10^{-4}$, the calculated values of the integral degree of polymerization $\bar{P}$ from the above equations with the experimental rate data are compared with the observed values obtained by viscosity measurement. Although the calculated curve agrees with the observed one quite satisfactorily at the initial stage of the reaction, it cannot interpret the abnormal decrease in the observed values at high monomer conversion.

4-4 Effect of post-addition of reactants: Thomas et al.\textsuperscript{8) reported that the post-addition of initiator at low monomer conversion caused a sharp increase on the rate of polymerization. They deduced that this increase of rate is due to the formation of new polymer particles. They also noted, on the other hand, that in post-addition at high monomer conversion no acceleration of the rate was observed. There remains some question, however, about their assertion, because the comparison was made on the value of monomer conversion at a fixed reaction time.

The present authors' experience indicates that the change in number of polymer particles accompanied by the addition of initiator will be negligible, although its measured value is not accurate enough, especially at low monomer conversion. From Eqs. (9) and (10) the rate of polymerization must be proportional to the square root of the total amount of initiator present in the mixture. The experimental results not quoted here, satisfy this relation reasonably well.

In the case of the post-addition of monomer, the rate of polymerization changed drastically. This is caused by the change in two factors, namely the monomer concentration on the polymer particle and the polymer yield, that is, the amount of polymer present in the reaction mixture. This will be clear from the fact that the rate of polymerization in this case was predicted by replacing $M_0 x$ and $M_0 (1-x)$ with $w M_0$ and $(w - w)/M_0$, respectively. Since Eq. (7) is also rewritten in

$$- \frac{dw(M_0)}{d\theta} = r_p$$  \hspace{1cm} (15)$$

the relation between $w$ and $\theta$ is predicted from the integration of this equation. As seen in Fig. 15, the predicted curves agree well with experimental results.

4-5 Polymerization without emulsifier: In the system without emulsifier the reaction will proceed according to the same mechanism as that of emulsion polymerization. Polymer particles aggregating successively as the reaction proceeds are responsible for the marked decrease in the rate of polymerization. The polymer particles formed, however, in this
system have totally irregular shapes, and the determination of their number is not possible. Thus, the equivalent number of polymer particles \( N_e \) is calculated from the experimentally observed polymerization rate by using Eqs. (9) and (10). The equivalent size of polymer particles \( d_{pe} \) is also obtained from

\[
w = \frac{5}{6} d_{pe}^3 \rho_p N_e
\]

(16)
The decrease in \( N_e \) and the increase in \( d_{pe} \), shown in Fig. 16, coincides qualitatively with observed results.

**Nomenclatures**

\[
\begin{align*}
A &= (36\pi)^{1/3}(M_w \rho_p)^{2/3} \quad [\text{cm}^3/\text{g-mol}^{2/3}] \\
a &= \text{surface area of a polymer particle} \quad [\text{cm}^2] \\
B &= M_w/10\rho_p \quad [\text{g-mol/cm}^3] \\
c_m &= \text{chain transfer coefficient to monomer} \quad [-] \\
d_p &= \text{diameter of polymer particle} \quad [\text{cm}] \\
f &= \text{initiator efficiency} \quad [-] \\
[f] &= \text{concentration of initiator} \quad [\text{g-mol/l}] \\
K &= \frac{k_{p_1}}{[I]} \quad [\text{cm}^3/\text{g-mol}^{1/2}\text{hr}^{1/2}] \\
k &= \text{decomposition rate constant of initiator} \quad [1/\text{hr}] \\
k_{p_1} &= \text{propagation rate constant at polymer surface} \quad [\text{cm}^3/\text{g-mol-hr}] \\
k_{p_2} &= \text{termination rate constant at polymer surface} \quad [\text{cm}^3/\text{g-mol-hr}] \\
M_w &= \text{molecular weight of acrylonitrile} \quad [\text{g-mol}] \\
[M_g] &= \text{monomer concentration at polymer surface} \quad [\text{g-mol/cm}^2] \\
[M_g^*] &= \text{monomer concentration in aqueous phase} \quad [\text{g-mol/l}] \\
[M_{g_0}] &= \text{saturated value of} \ M_w \text{with monomer} \quad [\text{g-mol/l}] \\
M_s &= \text{initial monomer concentration in reactant mixture} \quad [\text{g-mol/l}] \\
m &= \text{distribution coefficient} \quad [\text{cm}^3/l] \\
N &= \text{number of polymer particles in reaction mixture} \quad [1/l] \\
N_A &= \text{Avogadro’s number} \quad [1/\text{g-mol}] \\
\bar{n} &= \text{average number of radicals in a polymer particle} \\
\bar{P} &= \text{degree of polymerization, overall value} \quad [-] \\
\bar{p} &= \text{degree of polymerization, instantaneous value} \quad [-] \\
[r_p] &= \text{rate of polymerization, moles of monomer converted to polymer per unit volume and unit time} \quad [\text{g-mol/l-hr}] \\
r_i &= \text{rate of initiation} \quad [\text{g-mol/l-hr}] \\
r_c &= \text{rate of chain transfer} \quad [\text{g-mol/l-hr}] \\
[S] &= \text{concentration of emulsifier} \quad [\text{g-mol/l}] \\
x &= \text{monomer conversion} \quad [-] \\
x_{cr} &= \text{value of} \ x \ \text{at which monomer droplets disappear} \quad [-] \\
w &= \text{polymer yield, weight of polymer per unit volume of reaction mixture} \quad [\text{g/l}] \\
w_t &= \text{total (including monomer and polymer) mass concentration of acrylonitrile in reaction mixture} \quad [\text{g/l}] \\
\theta &= \text{reaction time in batch operation} \quad [\text{hr}] \\
\rho_p &= \text{density of polymer} \quad [\text{g/cm}^3] \\
\gamma &= \text{monomer-to-water ratio} \quad [-]
\end{align*}
\]

**Literature Cited**

6) Omi, S., Y. Shiraishi and H. Kubota: ibid., 2, 64 (1969)