EXPERIMENTAL STUDY OF CONTINUOUS EMULSION POLYMERIZATION OF STYRENE

TEIJI UEDA**, SHINZO OMI AND HIROSHI KUBOTA
Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Experimental studies of the continuous emulsion polymerization of styrene were made for the purpose of examining the consistency of the authors' theory proposed previously1). Two kinds of seeders, a plug flow type and a backmixed type, were employed prior to the main reactor to analyze the formation of polymer particles, separately from their growth. Although the number of polymer particles obtained experimentally was less than that of the theoretical value due to the presence of a small amount of impurities introduced continuously in the system, the experimental results agreed well qualitatively with those predicted from the theory.

1. Introduction

It has been emphasized in the authors' previous paper1) that the kinetics of the continuous emulsion polymerization of styrene is by no means similar to that of the batch operation. One of the most peculiar consequences derived theoretically is that the number of polymer particles in the continuous operation is always less than that in the batch operation, no matter what operating condition is selected.

The authors suggested that the number of polymer particles could be controlled if the concept of the seeder was applied to the continuous operation. In this paper these theoretical proposals will be examined experimentally, using two kinds of seeders.

Review of the theory of the role of the seeder: As was discussed in the authors' paper1), the concept of the seeder is based on the fact that the seeding step of polymer particles can be separated from the growth of polymer particles already formed. The flow pattern of the reactant mixture affects significantly the formation rate of polymer particles. Two kinds of seeders, a backmixed type and a plug flow type, are used in the present experimental study. In the backmixed type seeder the following expression is obtained for the number of polymer particles as a function of the mean residence time of the reactant mixture, $\bar{t}$,

$$N = \frac{\rho N_a \bar{t}}{1 + \frac{\alpha \rho N_a}{aS_0} \bar{t}^3}$$

where,

$$\alpha = 4.36 \left( \frac{k_B k_m [M]}{1 - k_m [M]} \right)^2$$

On the other hand, in the plug flow type seeder the number of polymer particles can be assumed as identical to that obtained in the batch operation when the reaction time of the batch reactor is set equal to the mean residence time of the plug flow type seeder.

Therefore, the theory of polymer particle formation in the batch operation proposed by Smith and Ewart2) is applicable, and

$$N = 0.37 \left( \frac{\rho N_a}{\mu} \right)^{\frac{2}{5}} (aS_0)^{\frac{3}{5}}$$

2. Experimental

Experimental apparatus: The schematic diagram of the system is shown in Fig. 1. The reactant mixture is emulsified in a 680 cc stirred tank. The main reactor, which is also a stirred tank, has a capacity variable from 446 to 1030 cc.

As for the seeders, a stirred tank and a plug flow type are used. Each has a 76 cc capacity. The plug flow type seeder is a 4 mm I.D. helical tube. These tanks and seeders are all made of stainless steel and equipped with water jackets.

Reagents: Styrene monomer is purified prior to use. It is first washed with 10% sodium hydroxide.
solution, then with deionized water, dried and finally distilled under vacuum at 54°C.

Sodium oleate and potassium persulfate of reagent grade are used as emulsifier and initiator. They are used without pretreatment.

High-purity nitrogen is used after further deoxygenation by leading through reduced copper gauge at 400°C.

**Experimental procedure:** Styrene monomer, aqueous solution of the emulsifier and initiator are deoxygenated in the feed tanks by bubbling nitrogen. The reactor system is evacuated up to 30 mmHg and flushed with nitrogen. This procedure is repeated five times. Then the monomer and the aqueous solution are introduced in the emulsifier. The reactant mixture is stirred at 1,000 r.p.m. and its temperature is kept at 0°C. The emulsion is then introduced in the seeder and the main reactor successively.

When the stirred tank type seeder is used, the agitation rate is maintained at 500 r.p.m. The same rate is employed in the main reactor. The temperature of the reactant mixtures in the stirred vessel and the seeder is controlled at 60 ± 0.5°C by water jackets regardless of the type of seeder.

The atmosphere of the system is sealed with nitrogen during the polymerization.

The polymer yield is determined gravimetrically. If the effect of acceleration on the polymerization rate is negligible for each polymer particle, the rate of polymerization will be expressed as follows after steady state is attained,

\[ r_p = k_{pm}[M]^{\frac{N}{2N_A}} \]  \( (6) \)

Therefore, the number of polymer particles is determined from the observed value of \( r_p \).

The size distribution of polymer particles is measured by an electron microscope.

Experimental procedures in the batch operations are similar to those employed in the previous work4). Experimental conditions and numerical values for calculations are summarized in **Table 1**.

### 3. Effects of Particle Size on Polymerization Rate

To calculate the number of polymer particles from Eq.(5), it is necessary that the number of polymer radicals is half that of polymer particles. This condition will not be satisfied if an acceleration of the polymerization rate is observed due to the increase of polymer particle volume.

Two curves of the polymer yield vs. reaction time which are obtained from the different types of batch operation are shown in **Fig. 2**. Two curves, labeled B and B’ in the figure, are obtained from the same recipe and operations except that in the case of curve B’ additional initiator was added after 45 min. of polymerization so as to make the final initiator concentration 5.4 times as high as the initial one. According to the theoretical consideration of Stockmayer3) the average number of radicals in one polymer particle, \( \bar{n} \), is expressed as a function of \( \nu/k_p\tau_p \), where \( \nu \) and \( \tau_p \) denote the volume of a single polymer particle and the mean time interval of successive entries of radicals to the single polymer particle. This means that either increasing the initiator concentration or the particle volume gives a similar

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**Table 1 Numerical values and experimental conditions**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0°C (emulsifier)</th>
<th>60°C (seeder and main reactor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume flow ratio</td>
<td>styrene/aqueous solution = 1/4</td>
<td></td>
</tr>
<tr>
<td>Emulsifier: ( S_e )</td>
<td>( 6.17 \times 10^{-3} ) [g-mol/l]</td>
<td></td>
</tr>
<tr>
<td>Initiator: ( I_o )</td>
<td>( 2.55 \times 10^{-3} ) [g-mol/l]</td>
<td></td>
</tr>
<tr>
<td>( k_{pm} )</td>
<td>( 1.65 \times 10^9 ) [1/particle/g-mol/hr]</td>
<td></td>
</tr>
<tr>
<td>([M])</td>
<td>3.93 [g-mol/particle]</td>
<td></td>
</tr>
<tr>
<td>( a )</td>
<td>( 1.68 \times 10^4 ) [g-mol/particle]</td>
<td></td>
</tr>
<tr>
<td>( v_p )</td>
<td>1.0 [cm³/g]</td>
<td></td>
</tr>
<tr>
<td>( \nu_p )</td>
<td>1.1 [cm³/g]</td>
<td></td>
</tr>
</tbody>
</table>

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[51]: 51

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result for the value of $\bar{n}$. It is shown in Fig. 2 that the acceleration of the polymerization rate in the curve $B'$ is negligible if the monomer conversion is less than 58%. This value corresponds to the polymer yield where the zero order reaction region is terminated.

As for the size of polymer particles the situation observed in continuous operation is almost identical to that of the batch operation just discussed above. It will be suggested that the effect of the acceleration caused by the volume increase of the polymer particle can be ignored. Therefore, the volume of a single polymer particle, $v$, is proportional to the residence time after it is formed, since the polymerization is proceeding by the zero order scheme.

An observed example of the volume distribution of polymer particles when the backmixed type seeder and the main reactor are employed in series is shown in Fig. 3. This distribution curve agrees well with the residence time distribution of the polymer particle in the same system. This also demonstrates that ignoring the effect of the acceleration is justified.

4. Number of Polymer Particles Formed in the Seeder

The relation between the number of polymer particles and the mean residence time, $\bar{\theta}$, observed experimentally in the backmixed type seeder is compared with the predicted values from Eq. (1) in Fig. 4.* In Eq. (1) the rate of initiation of free radicals, $\rho$, which is effective in the formation of polymer particles is estimated from the observed value of the number of polymer particles in the batch operation with the same recipe. $1.70 \times 10^{-5}$ can be calculated from Eq. (5) for $\rho$, since the number of polymer particles in the corresponding batch run is known to be $2.8 \times 10^{17}$. The observed points do not agree with the curve predicted from the batch operation, but agrees with the other curve, which is estimated from Eq. (1) assuming that $\rho$ is equal to $5.00 \times 10^{-6}$. This value of $\rho$ represents the actual effective rate of initiation in the case of continuous operation. The result obtained from the plug flow type seeder is shown in Fig. 5. In this case the main reactor is not used. Increasing the residence time, $\bar{\theta}$, the number of polymer particles approaches to a certain constant value. This value corresponds to the calculated result from Eq. (3) if $\rho$ is assumed to be $1.95 (10^{-6})$.

At the lower value of $\bar{\theta}$, the observed values of the number of polymer particles are less than those calculated with the same value of $\rho$.

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* It is shown in the Appendix that there is no formation of polymer particles in the main reactor.
5. Discussion

It is well known that even a very small amount of impurities can have a great influence on the number of polymer particles in the batch-wise emulsion polymerization of styrene. In the present continuous operation this effect of impurities will be accelerated in the seeder, where impurities are supplied continuously though consumed steadily. Free radicals liberated from the initiator will be terminated with these inhibitors, so that the continuous operation will produce fewer polymer particles than the number predicted from the result of the batch operation.

In the batch operation, on the other hand, less effect of inhibitors will be observed because inhibitors will be easily consumed in a short period after the polymerization starts. Furthermore, it is extremely difficult to control the amount of inhibitors in each run of the continuous polymerization. These factors result in the decreasing and scattering data in Fig. 4.

When the plug flow type seeder is employed, a result similar to that in the batch operation will be obtained only if the residence time of the reactant mixture is large enough to compensate for the induction period. Contrary to this estimation, the experimental result shown in Fig. 6 clearly indicates that the monomer conversions observed in the plug flow type seeder are much less than those observed in the batch operation. This may be due to the fact that it is difficult to eliminate the dissolved gas in the reactant mixture in case of the plug flow type seeder. A small amount of oxygen in the dissolved gas will play the role of inhibitor for the formation of polymer particles, and this effect will be significantly large when residence time is small.

In conclusion, unless impurities are completely removed or controlled quantitatively, it will be difficult to predict the number of polymer particles in the continuous operation directly from the data obtained in the batch operation. It can be said, however, that there exists a certain relation of proportionality between the number of polymer particles actually formed in the seeder and the theoretical value which is predicted from the data of the batch operation. Therefore, by applying the seeder to the continuous operations of emulsion polymerization the designing aspects will become easier. Especially if one employs the plug flow type seeder, the number of polymer particles can be kept constant regardless of the residence time of the reactant mixture, \( \theta_1 \), when the considerably high value of \( \theta_1 \) is employed. In a practical operation of commercial scale the effect of dissolved oxygen as an inhibitor can be avoided and, therefore, a higher value of \( \rho \) will be expected.

Acknowledgement

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Appendix

Formation of polymer particles in the main reactor

Consider the polymer particles which are formed in the seeder and remain in the main reactor. Let \( N_1 \) denote the number of these polymer particles. The ratio of polymer particles leaving the main reactor between \( \theta \) and \( \theta + d\theta \) is expressed as

\[
\frac{dN_1}{N_1} = \frac{1}{\theta_2 - \theta_1} (e^{-\theta_1} - e^{-\theta_2}) d\theta
\]

Here, subscripts 1 and 2 denote the seeder and the main reactor. Therefore, total surface area of \( N_1 \) polymer particles, \( A_\rho(N_1) \), is expressed as

\[
A_\rho(N_1) = (36\pi)^{\frac{1}{3}} \frac{N_1}{\sqrt{\theta}} dN_1
\]

As for the polymer particles which are formed in the main reactor and remain in it, total surface area, \( A_\rho(N_2) \), will be expressed as

\[
A_\rho(N_2) = (36\pi)^{\frac{1}{3}} \frac{N_2}{\sqrt{\theta}} dN_2
\]

Therefore,

\[
A_\rho = A_\rho(N_1) + A_\rho(N_2)
\]

On the other hand the number of polymer particles formed in the main reactor, \( N_2 \), is obtained from the following expression,

\[
N_2 = \rho_2 N_0 \theta_2 \left( 1 - a_\rho^{\frac{5}{3}} \right)
\]

\( \rho_2 \) can be assumed equal to \( \rho_1 \).

From Eq.(A-4) and Eq.(A-5), the equation for \( N_2 \) is obtained as

\[
N_2 = \rho_0 N_0 \theta_2 \left( 1 - a_\rho^{\frac{5}{3}} \right) / aS_0
\]

If no polymer particles are formed in the main reactor, the bracket term of Eq.(A-6) must be negative. In the following calculation Eq.(A-6) is examined when \( \theta_2 \) takes minimum value among all the experimental conditions. In this case the formation of new polymer particles in the main reactor becomes most probable.

Experimental conditions are written as;

Volumetric flow rate 3/hr, Volume of the main reactor 1030 cc, \( \theta_1 = 0.025 \) hr, \( \theta_2 = 0.343 \) hr

At this value of \( \theta_2 \), the corresponding number of polymer particles is obtained from the curve in Fig. 4 where \( \rho_1 \) is equal to 5.0 \( 10^{-6} \).

\[
N_1 = 5.8 \times 10^{10}
\]

The second term in the bracket of Eq.(A-6) is calculated using these values and those illustrated in Table 1, and 1.29 is obtained. Therefore, the bracket term in Eq.(A-6) becomes negative, and no polymer particles are formed.

\* Details of equations discussed here can be obtained elsewhere.
in the main reactor. In this case Eq. (A-4) is simplified to

\[
A_p \frac{d}{dt} \left( \frac{1}{2} \frac{\theta_p^2}{\theta_i} \right) = \alpha A_i \frac{1}{2} \eta_i^2 \frac{\theta_p^2}{\theta_i} - \frac{1}{2} \frac{\theta_i}{\theta_p}
\]

(A-8)

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>surface area occupied by soap molecules</td>
</tr>
<tr>
<td>(A_{pi})</td>
<td>total surface area of polymer particles in (i)-th stage</td>
</tr>
<tr>
<td>(k_i)</td>
<td>specific rate constant of termination [cm(^3)/hr]</td>
</tr>
<tr>
<td>(k_0)</td>
<td>rate constant of propagation [(i)-polymer particles/mol/hr]</td>
</tr>
<tr>
<td>(k_i')</td>
<td>rate constant of propagation [cm(^3)/mol]</td>
</tr>
<tr>
<td>(M_W)</td>
<td>molecular weight of monomer [mol/(\text{cm}^3)]</td>
</tr>
<tr>
<td>(N)</td>
<td>number of polymer particles [1/l]</td>
</tr>
<tr>
<td>(N_i)</td>
<td>number of polymer particles formed in (i)-th stage [1/l]</td>
</tr>
<tr>
<td>(N_A)</td>
<td>Avogadro number [1/mol]</td>
</tr>
<tr>
<td>(r_p)</td>
<td>polymerization rate [mol/l/hr]</td>
</tr>
<tr>
<td>(S_p)</td>
<td>initial soap concentration [mol/l]</td>
</tr>
<tr>
<td>(v)</td>
<td>volume of single polymer particle [cm(^3)]</td>
</tr>
<tr>
<td>(V_m, V_p)</td>
<td>specific volume of monomer and polymer, respectively [cm(^3)/mol]</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>defined in Eq. (2)</td>
</tr>
<tr>
<td>(\theta)</td>
<td>polymerization time [hr]</td>
</tr>
<tr>
<td>(\theta_i)</td>
<td>mean residence time in (i)-th stage [hr]</td>
</tr>
<tr>
<td>(\mu)</td>
<td>volumetric growth rate of polymer particle [cm(^3)/hr]</td>
</tr>
<tr>
<td>(\rho)</td>
<td>effective initiation rate for the formation of polymer particles [mol/l/hr]</td>
</tr>
<tr>
<td>(\tau_p)</td>
<td>average interval of successive entry for radicals in single polymer particle [hr]</td>
</tr>
</tbody>
</table>

*Literature cited*


**STUDIES OF THE EFFECT OF POLYMER PARTICLES ON EMULSION POLYMERIZATION**

Makoto Harada**, Mamoru Nomura, Wataru Eguchi**, and Shinji Nagata

Department of Chemical Engineering, Kyoto University, Kyoto, Japan

Average number of radicals per polymer particle was studied theoretically, considering the process for radical to escape from particles and the retardation process in or on polymer particles. Moreover, the physical meaning of the rate coefficient of the former process was analyzed theoretically, on the assumption that radical of lower molecular weight was able to escape from particles. The validity of the above analysis was clarified, using the published data for several monomers. For the average number of radicals, the solubility of monomer in water and the reactivity of monomer are both important factors.

**Introduction**

The rate of emulsion polymerization was clarified by Smith and Ewart’s theory\(^\text{10}\), derived from Har-kins’ qualitative research\(^\text{9}\). It has been widely accepted that Smith’s theory explains well the characteristics of emulsion polymerization for highly water-insoluble monomers\(^\text{5,7}\). It is however, quite difficult to estimate by that theory the rate of emulsion polymerization for water-soluble monomers, for example, vinyl acetate. Okamura\(^\text{12}\) pointed out that the non-conformity with Smith’s theory was due to the rather high solubility of vinyl acetate in water.

Recently, many experimental results for several monomers have been reported which show the narrow applicability of Smith’s theory. Moreover, it has been reported that the theory cannot explain the characteristics of polymerization even for styrene monomer when the polymerization proceeds under the condition of a larger number of polymer particles. In emulsion polymerization, the polymer particles in the system play a great role in the course of polymerization. Therefore, it is necessary to know as a characteristic feature of emulsion polymerization the number of polymer particles generated and the effect of polymer particles on the rate of polymerization. The main reasons why Smith’s theory has only a narrow applicability are the following two. The first is the non-conformity of the generation mecha-