EMULSION POLYMERIZATION OF STYRENE IN THE VICINITY OF CRITICAL MICELLE SOAP CONCENTRATION*

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Emulsion polymerization of styrene with soap concentration chosen in the vicinity of critical micelle concentration (CMC) has been investigated. The rate of polymerization and the number of polymer particles correlated with initial monomer, soap and initiator concentrations, are explained qualitatively. An analysis of the gel effect observed at later stage of the reaction has been also carried out. The accumulation of polymeric radicals in polymer particles is considered to be due to the decrease in the termination rate constant $k_t$ as monomer conversion increases. An empirical equation for $k_t$ as a function of viscosity in polymer particles is derived.

1. Introduction

In the history of the emulsion polymerization of vinyl monomers, that with styrene has been studied most frequently because it has so many advantages in experimental procedures for basic researches. Since Smith and Ewart proposed a quantitative theory of emulsion polymerization, many papers have been published with respect to this system. Several interesting results have been also reported by the present authors concerning the general kinetics, the effect of agitation, and continuous operations. These investigations have been carried out under conditions where initial soap concentrations are usually selected above the CMC. The Smith and Ewart theory predicts that the number of polymer particles is related to the soap and initiator concentrations as follows.

$$N \propto S^{0.6}I^{0.4}$$

Eq. (1) is only valid at soap concentrations rather higher than the CMC. On the other hand, van der Hoff has reported that the number of polymer particles changes drastically with soap concentration in the vicinity of the CMC. The observation and explanation of this peculiar phenomenon is one of the main interests of this work.

According to the Smith-Ewart theory, the expression for the rate of polymerization can be written as

$$r_p = k_p [M_p] \frac{\bar{n}N}{N_A}$$

Eq. (2) holds in the so-called zeroth-order reaction region where the number of polymer particles is fixed after the depletion of all soap micelles, and the monomer concentration in polymer particles is kept constant in the presence of monomer droplets. They propose that the average number of radicals per polymer particle $\bar{n}$ can be calculated, and is one half.

This prediction for $\bar{n}$ is experimentally supported in the zeroth-order reaction region, but it is no longer constant after monomer droplets are consumed since the autocatalytic effect is enhanced in the case of a lower soap concentration recipe. It is another interest of this work to obtain some quantitative knowledge of this effect induced by the accumulation of active radicals in polymer particles, i.e. the increase in $\bar{n}$.

2. Experimental Procedures

2.1 Apparatus

The reactor used is a stirred-tank type with a hot water jacket, and is made of stainless steel. The detailed sketch of the reactor is shown in Fig. 1.

2.2 Reagents

Styrene monomer of commercial grade is distilled with a reduced pressure of 30 mmHg and is stored in a refrigerator prior to use. Potassium persulfate of reagent grade as an initiator and sodium lauryl sulfate of commercial grade as an emulsifier are used without further purification. Deionized water and extremely pure nitrogen gas are used, and hydroquinone as an inhibitor is added to polymer samples to prevent...
monomer and soap solution is charged in the reactor, and the inner atmosphere is sealed with nitrogen by the repeated procedure of nitrogen flush and evacuation. After starting the agitation, the reactant mixture is heated to the reaction temperature by a hot water jacket. Meanwhile, dissolved oxygen in the reactant mixtures is removed by introducing nitrogen. After precisely one hour’s agitation and temperature elevation, an initiator solution is added to the reactant mixtures. Samples are withdrawn at successive intervals, and the atmosphere in the reactor is sealed with nitrogen during the reaction.

Monomer conversion vs. reaction time curves are determined gravimetrically, and the number of polymer particles is determined by an electron microscope. The average molecular weight is determined by viscometric measurements using the equation proposed by Goldberg et al.⁹.

3. Results and Discussion

According to the authors’ previous work⁹, there exist three reaction regions in the batchwise emulsion polymerization of styrene;

(i) **Induction reaction region**, in which polymer particles are formed and free soap micelles disappear at the end of this reaction region. From this instant, the number of polymer particles is kept constant throughout the reaction.

(ii) **Zeroth order reaction region**, in which the reaction proceeds apparently with zeroth-order in respect to the monomer concentration. This region terminates at the instant when monomer droplets are all consumed.

(iii) **First-order reaction region**, in which the reaction is first-order with respect to monomer concentration since monomer molecules are no longer supplied from the aqueous phase to polymer particles due to the depletion of monomer droplets. The gel-effect is more or less observed in this region.

At first the authors will report how the zeroth-order reaction rate and the number of polymer particles are affected by various experimental conditions, and then will follow with an analysis of the gel-effect induced by the accumulation of active radicals in polymer particles.

3.1 Investigation for zeroth-order reaction region

The behaviour of the rate of polymerization and the number of polymer particles are affected by various experimental conditions, and then will follow with an analysis of the gel-effect induced by the accumulation of active radicals in polymer particles.

Fig. 1 Details of the stirred-tank reactor

![Fig. 1](image1)

Fig. 2 Relation between rate of polymerization and number of polymer particles

![Fig. 2](image2)

Fig. 3 Polymer yield vs. reaction time (1) Effect of initial monomer concentration (for keys see Fig. 2)

![Fig. 3](image3)

Further polymerization.

2.3 Procedures

Reactant mixture with a desired composition of
Effect of initial monomer concentration: Polymer yield vs. reaction time curves with initial monomer concentration as a parameter are shown in Fig. 3, and the number of polymer particles is related with initial monomer concentration in Fig. 4. It is shown that the number of polymer particles depends remarkably on initial monomer concentration. This observation will be discussed in a later section together with the effect of soap concentration on the number of polymer particles.

Effect of initiator concentration: Polymer yield vs. reaction time curves with charged initiator concentration is shown in Fig. 5, and the number of polymer particles is plotted against initiator concentration in Fig. 6. As is proposed by Smith and Ewart\(^9\), the number of polymer particles is regarded to be proportional to 0.4-th power of initiator concentration. However, it does not hold in the case of lower soap concentration, and its dependence is of much higher order than 0.4.

Effect of soap concentration: Polymer yield vs. reaction time curves with different soap concentration are shown in Fig. 7. The number of polymer particles vs. soap concentration relation is shown in Fig. 8 as a solid curve. In the region of relatively higher soap concentration, the experimental result agrees well with the Smith and Ewart theory, but the number of polymer particles declines sharply as soap concentration is lowered. If soap molecules adsorbed on the surface of monomer droplets are not taken in account, effective soap concentration for the creation of polymer particles will be \(S_0 - S_{oc}\), where \(S_{oc}\) denotes the CMC based on the unit volume of the total reaction mixture. As \(S_0\) approaches \(S_{oc}\), \(S_0 - S_{oc}\) will be getting smaller and the number of polymer particles generated will change.
remarkably even if the change in $S_0$ is by no means notable. Van der Hoff\(^4\) has reported similar behaviour for the change of number of polymer particles shown as a solid curve in Fig. 8. On the other hand, consider the experimental result reported in Fig. 4, where initial monomer concentration is a variable, from the point of the discussion proposed above. $S_{oc}$ will be related with the CMC based on the unit volume of the aqueous phase $S_{wc}$ in the equation

$$S_{oc} = S_{wc} \phi_w$$

Here, $\phi_w$ denotes volume fraction of the aqueous phase with respect to the total reaction mixture. It will be understood from Eq. (3) that $S_0 - S_{oc}$ varies as initial monomer concentration is changed. If initial monomer concentration is lowered, $\phi_w$ is getting larger and so is $S_{oc}$. This means that the number of polymer particles generated declines even if $S_0$ is kept constant. This decline is particularly emphasized when initial soap concentration is selected near the CMC as in the case shown in Fig. 4. This qualitative consideration is shown as illustrative curves in Fig. 8, where the shift in $S_0 - S_{oc}$ with the change of initial monomer concentration $M_0$ is clearly seen.

Effect of agitation: Polymer yield vs. reaction time curves are shown in Fig. 9 with different agitation rate, and the number of polymer particles is related to agitation rate in Fig. 10. The number of polymer particles decreases slightly as the agitation rate becomes higher due to the decrease of soap molecules in the aqueous phase, since the surface of monomer droplets increases and more soap molecules are adsorbed on it.

3.2 Analysis of gel-effect

An unexpectedly higher rate of polymerization is often observed in the first-order reaction region, and this is caused by the increase in average number of polymeric radicals in a polymer particle $\bar{n}$ beyond the constant value of one half observed in the zeroth-order reaction region. This increase in $\bar{n}$ can be connected with the decrease in the termination rate constant $k_t$.

Average number of radicals in a polymer particle $\bar{n}$: $\bar{n}$ can be calculated from expressions for the rate of polymerization shown in Eqs. (4) and (5)

$$r_p = k_p \left[ M_p \right] \frac{nN}{N_A} \quad x \leq x_{cr} \quad (4)$$

$$r_p = k_p \left[ M_p \right] \left( \frac{1 - x}{1 - x_{cr}} \right) \frac{nN}{N_A} \quad x \geq x_{cr} \quad (5)$$

The rate of polymerization in Eq. (5), which is applicable after monomer droplets are consumed, is based on monomer concentration in the total reaction mixture. Details are shown elsewhere\(^5\).

Constant value of $8.22 \times 10^6 \text{ hr}^{-1}$ modified slightly from the author’s previous report\(^5\) is taken for $k_p [M_p]$ and $x_{cr}$ is assumed to be 0.575 observed experimentally.

Calculated values of $\bar{n}$ from Eq. (4) using these values fall around one half, and the Smith-Ewart theory is justified. $\bar{n}$ increases with increasing monomer conversion after monomer droplets are consumed, and the result is shown in Fig. 11.

Termination rate constant $k_t$: Since there is no escape of radicals from polymer particles to the aqueous phase in the case of the emulsion polymerization of styrene, the following equation for $\bar{n}$ derived by O’Toole\(^6\), can be applied:

$$\bar{n} = \frac{a}{4} \frac{I_0(a)}{I_{-1}(a)} \quad (6)$$

Where $a = (8\pi N_d/k_T)^{1/4}$, and $I_0$, $I_{-1}$ are first kind of modified Bessel functions of zeroth- and minus first-order, respectively. $\tau$ means the average interval of successive radical entry in a polymer particle, and its reciprocal is obtained from the slope of $2\pi N_d / M_p \bar{n}$.
The reaction time plot shown in Fig. 12. The meaning of this plot is shown in Appendix. The following relation is obtained from Fig. 12.

\[
\frac{1}{\tau} = 7.92 \times 10^{19} \text{ (hr}^{-1})
\]

Volume of single polymer particle swollen with unreacted monomer \( v \) will be expressed by

\[
v = \frac{V_p M_p x}{N} (1 - V_M [M_p])^{-1} \quad x \leq x_{cr}
\]

\[
v \equiv v_{cr} \quad x \geq x_{cr}
\]

In zeroth-order reaction region \( x \leq x_{cr} \) \( v \) is directly proportional to monomer conversion, but \( v \) can be regarded as approximately constant after monomer droplets are consumed \( (x \geq x_{cr}) \), since only monomer inside the particle is converted to polymer.

The values of \( k_t \) can be calculated from Eq.(6) by using observed values of \( n \).

Relation between \( k_t \) and the viscosity inside polymer particles: It has been accepted that in the case of radical polymerization the termination rate constant \( k_t \) decreases gradually with increasing monomer conversion, because the diffusion of polymeric radicals is markedly hindered due to the increasing viscosity of reaction medium. Here the decrease in \( k_t \) in the region of \( x \geq x_{cr} \) will be correlated with increasing viscosity inside polymer particles. The following empirical equation reported by Duerksen and Hamielec\( ^2 \) in the case of styrene polymerization in benzene solution is used for the viscosity inside polymer particles:

\[
\log \eta = -1.06 - 0.522 \log (s + 1)
\]

\[\] - 8.34 \log (1 - w_n) + 0.565 \tilde{P}_w \quad (10)

Since the reaction inside polymer particles will proceed similarly to that of bulk polymerization which has no essential difference from solution system, Eq.(10) can be used to estimate its viscosity by replacing \( s = 0 \). \( k_t/k_{to} \) vs. \( 1 + \mu \) are plotted in Fig. 13, where \( k_{to} \) is the termination rate constant reported by Bamford \textit{et al.} \( ^3 \) and represents that in the region of \( x \leq x_{cr} \).

An empirical equation is obtained between \( k_t/k_{to} \) and \( 1 + \mu \), and it can be written as

\[
\log \left( \frac{k_t}{k_{to}} \right) = -0.0528 \log (1 + \mu) - 0.0373 \left\{ \log (1 + \mu) \right\} ^2
\]

Eq.(11) is shown in Fig. 13 as a solid curve. As for the region of lower viscosities, Duerksen and Hamielec\( ^3 \) have proposed the following empirical correlation in the styrene-benzene solution polymerization system for a limited range of viscosity:

\[
\log \left( \frac{k_t}{k_{to}} \right) = 0.06 \log (1 + \mu) - 0.0934 \left\{ \log (1 + \mu) \right\} ^2
\]

\[3.4 < \mu < 1.8 \times 10^9\]

Eq.(12) is also shown in Fig. 13 as abroken curve for comparison’s sake.

Appendix

Up to time \( \theta \), \( w N_A / M_o P_n \) molecules of styrene monomer are converted into polymers, and the average number of polymer chains formed is \( w N_A / M_o P_n \). Since two initiator radicals are involved to form one polymer chain, \( 2w N_A / M_o P_n \) initiator radicals are consumed. This is related to the constant rate of radical entry \( \rho \) by the equation

\[
2w N_A / M_o P_n = N_A \rho \theta
\]

\[A(1)\]

\[\text{and} \quad \tau = N/\rho N_A \quad (A-2)\]

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{d}_p )</td>
<td>average diameter of polymer particles [cm]</td>
</tr>
<tr>
<td>( I_0 )</td>
<td>initial initiator concentration [mol/l]</td>
</tr>
<tr>
<td>( k_p )</td>
<td>propagation rate constant [l-polymer particle/mol-hr]</td>
</tr>
<tr>
<td>( k_t )</td>
<td>termination rate constant [l-polymer particle/mol-hr]</td>
</tr>
<tr>
<td>( k_{to} )</td>
<td>termination rate constant with no gel-effect [l-polymer particle/mol-hr]</td>
</tr>
<tr>
<td>( M_0 )</td>
<td>initial monomer concentration [mol/l]</td>
</tr>
<tr>
<td>( [M_p] )</td>
<td>monomer concentration in polymer particles [mol/l-polymer particle]</td>
</tr>
<tr>
<td>( M_w )</td>
<td>molecular weight of monomer [g/mol]</td>
</tr>
<tr>
<td>( N )</td>
<td>number of polymer particles [1/l]</td>
</tr>
<tr>
<td>( N_A )</td>
<td>Avogadro number [1/mol]</td>
</tr>
</tbody>
</table>
Strict dimensional form of [molecules/mol] is replaced by modified [1/mol] so that

\[ N/N_A \text{ is expressed as [mol/l]} \]

- \( n \) = average number of radicals per polymer particle
- \( P_n \) = number average degree of polymerization
- \( P_w \) = weight average degree of polymerization
- \( t_p \) = rate of polymerization
- \( t_{po} \) = zeroth-order polymerization rate
- \( S_0 \) = initial soap concentration with respect to the total reaction mixture
- \( S_{0e} \) = critical micelle concentration based on the unit volume of the total reaction mixture
- \( S_w \) = initial soap concentration with respect to the aqueous phase
- \( x \) = solvent concentration
- \( M_w \) = critical micelle concentration based on the unit volume of the aqueous phase
- \( V_M \) = \( M_w/10^4 \rho_M \) [l-monomer/mol]
- \( V_P \) = \( M_w/10^4 \rho_P \) [l-polymer/mol]
- \( v \) = volume of a polymer particle
- \( v_{er} \) = volume of a polymer particle at which monomer droplets disappear
- \( w \) = polymer yields
- \( w_P \) = weight fraction of polymer
- \( x \) = monomer conversion
- \( x_{er} \) = monomer conversion at which monomer droplets disappear

\( \mu \) = viscosity inside polymer particles [c.p.]
\( \rho_M, \rho_P \) = density of polymer and monomer, respectively [g/cc]
\( \rho \) = rate of entry of initiator radicals to polymer particles [mol/hr]
\( \tau \) = average interval of entry of initiator radicals to polymer particles [hr]
\( \nu \) = agitation rate [r.p.m.]
\( \phi_w \) = volume fraction of the aqueous phase to the total reaction mixture

**Literature Cited**