

Emulsion Polymerization of Vinyl Acetate in the Presence of Poly(vinyl alcohol) as Emulsifier

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ABSTRACT: The emulsion polymerization of vinyl acetate(VAc) in the presence and absence of poly(vinyl alcohol)(PVA) as emulsifier was carried out using a dilatometer. Both the potassium persulfate(KPS)—*l*-ascorbic acid(AsA) system and the hydrogen peroxide(HPO)—AsA system were used as initiators. The polymerization initiated by the KPS—AsA system proceeded smoothly even without PVA, and the polymer latex obtained was extremely stable. On the other hand, when the HPO—AsA system was used as the initiator of polymerization, because the polymer particles produced in the absence of PVA settle out as a precipitate, a stable polymer latex was not formed without using PVA. The maximum rate of polymerization initiated at 20°C by the KPS—AsA system was independent of the PVA concentration, but that initiated at 20°C by the HPO—AsA system was proportional to 0.22 power of the PVA concentration. On the basis of these results, the effects of types of various initiators on the emulsion polymerization of VAc were discussed.

KEY WORDS Emulsion Polymerization / Vinyl Acetate / Poly(vinyl alcohol) / Emulsifier / Initiator / Potassium Persulfate—*l*-Ascorbic Acid System / Hydrogen Peroxide—*l*-Ascorbic Acid System / Polymer Particle / Rate of Polymerization /

The theory of the mechanism of emulsion polymerization was quantitatively formulated by Smith and Ewart.¹ This theory was adapted to the emulsion polymerization of styrene,^{2,3} but is unapplicable to the emulsion polymerization of VAc.⁴ According to Okamura, *et al.*, who have studied the effect of emulsifiers on the emulsion polymerization of VAc, the deviation from the Smith—Ewart theory is due both to the relatively high solubility of VAc into water and to the reactivity of radicals toward emulsifiers.⁴ A number of studies have been carried out on the emulsion polymerization of VAc using persulfate as initiator.⁵⁻⁸ The use of persulfate would result in the sulfate end groups in polymer molecules.^{9,10} However, if HPO is used as the initiator of polymerization, the hydroxyl groups must be linked to the ends of the polymer molecules. Although many reports on the emulsion polymerization of VAc have been published, there have been few studies concerning the effect of the end groups of the polymer molecules on the polymerization.¹¹ We

wish to report, in this paper, on the effects of types of various initiators on the kinetics of the emulsion polymerization of VAc in the presence of PVA as emulsifier.

EXPERIMENTAL

Materials

A VAc monomer was purified by distillation under reduced pressure in a stream of nitrogen. The initiators employed were both the KPS—AsA system and the HPO—AsA system. These reagents were the purest chemicals commercially available, and were used without further purification. The PVA (NL-05) was obtained from the Nippon Synthetic Chemical Industry Co., Ltd. Sodium acetate contained in PVA and the low molecules of PVA were removed by dialysis over one week. The degree of polymerization of PVA dialyzed was calculated by measuring the intrinsic viscosity in water at 30°C, using the equation proposed by Nakajima, *et al.*,¹² and was determined to be 720.

Polymerization

The polymerizations were followed by means of a dilatometer without degassing, using a dilatometer having a bulb of about 25 ml and a capillary tube with a diameter of 0.2 cm and a length of 15 cm, as shown in Figure 1. A VAc

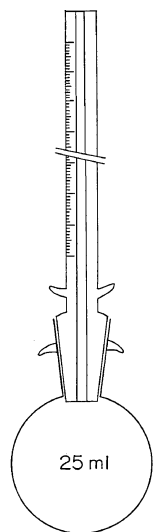


Figure 1. Model of dilatometer used.

aqueous solution was prepared by saturating VAc in water after shaking for 30 min, and the concentration of VAc dissolved in water was determined by alkali saponification. All reagents were mixed in a flask cooled in an ice bath. The bulb of the dilatometer was filled with the reaction mixture, and a capillary tube was then inserted in the bulb. At this time, the level of meniscus of the solution went up to the middle of the capillary tube. The capillary tube and the bulb were fixed by rubber band. The dilatometer was then introduced into a bath thermostatted at a given temperature. The conversions were determined from the volume contraction which was calculated by reading the level of the meniscus in the measuring capillary tube with a travelling microscope.

RESULTS AND DISCUSSION

The Effect of PVA

The polymerization of VAc in aqueous solution

initiated by the KPS—AsA system proceeded smoothly even in the absence of PVA, and gave an extremely stable polymer latex. On the other hand, when the polymerization of VAc in aqueous solution was carried out using the HPO—AsA system without PVA, we could not obtain a stable polymer latex. These facts suggest that the stability of the latex particles is dependent on the hydrophilic end groups of the polymer

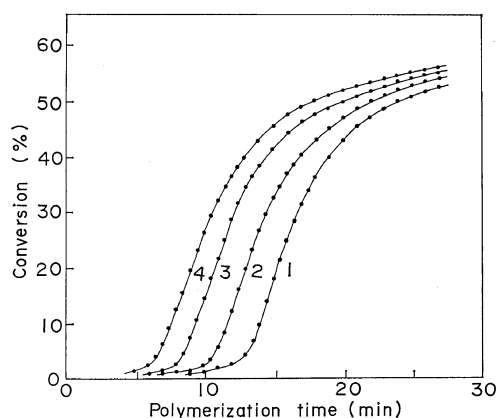


Figure 2. Conversion vs. polymerization time in the emulsion polymerization of VAc by the KPS—AsA system at 20°C: (1) [PVA]=0.74 g/l; (2) [PVA]=1.48 g/l; (3) [PVA]=2.22 g/l; (4) [PVA]=4.44 g/l; [VAc]= 2.29×10^{-1} mol/l; [KPS]= 2.51×10^{-3} mol/l; [AsA]= 2.50×10^{-3} mol/l.

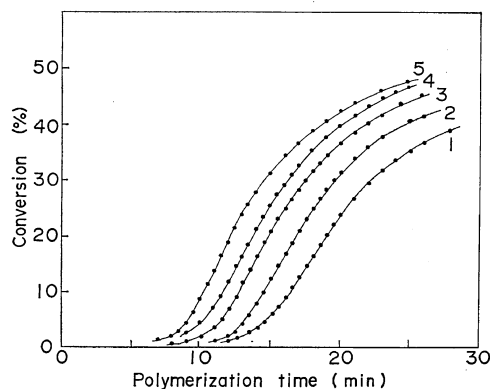


Figure 3. Conversion vs. polymerization time in the emulsion polymerization of VAc by the HPO—AsA system at 20°C: (1) [PVA]=1.48 g/l; (2) [PVA]=2.22 g/l; (3) [PVA]=2.96 g/l; (4) [PVA]=3.70 g/l; (5) [PVA]=4.44 g/l; [VAc]= 2.04×10^{-1} mol/l; [HPO]= 2.47×10^{-3} mol/l; [AsA]= 2.50×10^{-3} mol/l.

molecules coming from the initiators, most of which would be present on the particle surface.

The dilatometer was calibrated gravimetrically by weighing the polymer, and the volume contractions of VAc at the conversion of 100% were found to be 12.2% at 20°C and 13.8% at 40°C, respectively. The time—conversion curves were obtained by use of these contractions.

The results of the emulsion polymerization of VAc in the presence of PVA at 20°C are illustrated in Figures 2 and 3. Figure 2 shows the results obtained by using the KPS—AsA system, while Figure 3 indicates the results which the HPO—AsA system was used as the initiator. The PVA concentrations ranged from 0.74 to 4.44 g/l in water. When PVA was used as the emulsifier, all the latices obtained were stable, regardless of the type of initiator.

The KPS—AsA System

As is well known, the reaction of emulsion polymerization is divided into the following three stages.¹³ The rate of polymerization increases during the formation of the polymer particles (first stage), and then remains constant because the number of the polymer particles is kept constant (second stage), and finally becomes first order with respect to the monomer concentrations (third stage).

From the results in Figure 2, the instantaneous rate of polymerization—conversion curve which refers to the polymerization initiated by the

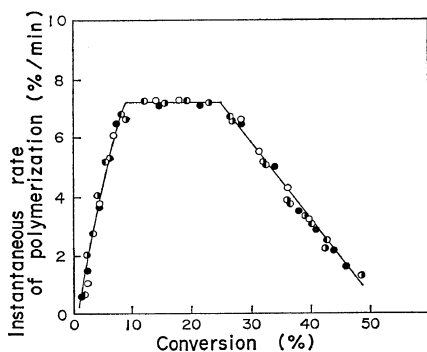


Figure 4. Instantaneous rate of polymerization vs. conversion in the emulsion polymerization of VAc by the KPS—AsA system at 20°C: [PVA]=○, 0.74 g/l; ●, 1.48 g/l; ●, 2.22 g/l; ●, 4.44 g/l; [VAc]= 2.29×10^{-1} mol/l; [KPS]= 2.51×10^{-3} mol/l; [AsA]= 2.50×10^{-3} mol/l.

KPS—AsA system is illustrated in Figure 4. Even if the PVA concentrations in the reaction system were varied, the results obtained fell on the same curve. As can be seen from the shape of the curve, the reaction of the emulsion polymerization of VAc is also divided into three stages. It is obvious from the second stage that the instantaneous rate of polymerization is kept constant at conversions above about 10%. The values of the maximum rate of polymerization obtained from Figure 2 are summarized in Table I, together with the results determined

Table I. The maximum rate of polymerization (R_p) of the emulsion polymerization of VAc initiated by the KPS—AsA system at 20°C

[PVA], g/l	[VAc]× 10, mol/l	[KPS]× 10 ³ , mol/l	[AsA]× 10 ³ , mol/l	R_p , %/min
0.00	2.29	2.51	2.50	7.0
0.74	2.29	2.51	2.50	7.3
1.48	2.29	2.51	2.50	7.3
2.22	2.29	2.51	2.50	7.1
4.44	2.29	2.51	2.50	7.2
0.74	2.29	3.76	2.50	9.2
1.48	2.29	3.76	2.50	9.1
2.22	2.29	3.76	2.50	9.2
2.96	2.29	3.76	2.50	9.2
4.44	2.29	3.76	2.50	9.3
2.22	2.29	1.26	2.50	5.9
2.22	2.29	2.51	2.50	7.1
2.22	2.29	3.76	2.50	9.2
2.22	2.29	5.02	2.50	10.3

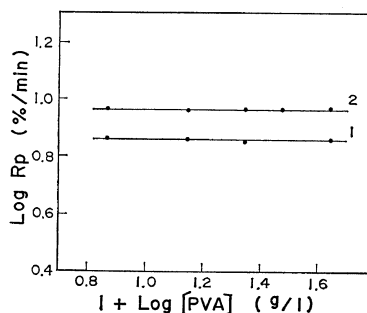


Figure 5. Maximum rate of polymerization (R_p) vs. PVA concentration in the emulsion polymerization of VAc by the KPS—AsA system at 20°C: (1) [KPS]= 2.51×10^{-3} mol/l; (2) [KPS]= 3.76×10^{-3} mol/l; [VAc]= 2.29×10^{-1} mol/l; [AsA]= 2.50×10^{-3} mol/l; [PVA] was varied.

under various conditions. The relationships between the maximum rate of polymerization and the PVA concentration are plotted at the KPS concentrations of 3.76×10^{-3} and 2.51×10^{-3} mol/l in Figure 5. The reaction order with respect to the VPA concentration was found to be zero, independent of the KPS concentration. This result was the same as that found for the emulsion polymerization of VAc by Okamura, *et al.*,⁴ where sodium dodecyl sulfate was used as emulsifier.

The influence of the variation in KPS con-

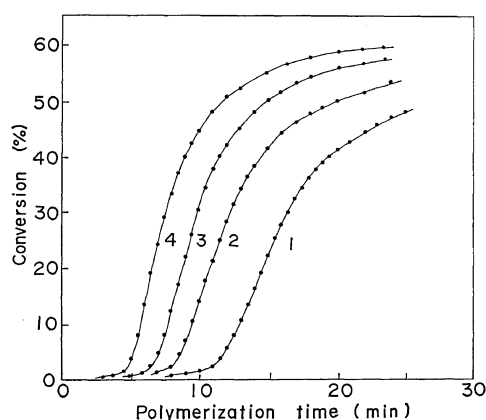


Figure 6. Conversion vs. polymerization time in the emulsion polymerization of VAc by the KPS—AsA system at 20°C: (1) $[KPS]=1.26 \times 10^{-3}$ mol/l; (2) $[KPS]=2.51 \times 10^{-3}$ mol/l; (3) $[KPS]=3.76 \times 10^{-3}$ mol/l; (4) $[KPS]=5.02 \times 10^{-3}$ mol/l; $[PVA]=2.22$ g/l; $[VAc]=2.29 \times 10^{-1}$ mol/l; $[AsA]=2.50 \times 10^{-3}$ mol/l.

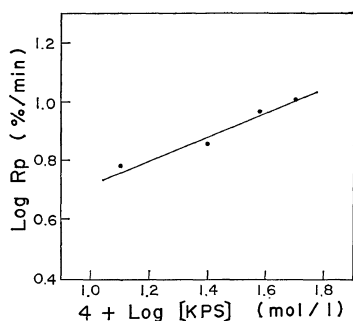
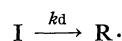


Figure 7. Maximum rate of polymerization (R_p) vs. KPS concentration in the emulsion polymerization of VAc by the KPS—AsA system at 20°C: $[PVA]=2.22$ g/l; $[VAc]=2.29 \times 10^{-1}$ mol/l; $[AsA]=2.50 \times 10^{-3}$ mol/l; $[KPS]$ was varied.

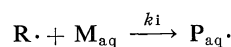
centration on the rate of polymerization has been studied at 20°C. The other conditions of polymerization were at the AsA concentration of 2.50×10^{-3} mol/l, the PVA concentration of 2.22 g/l and the monomer concentration of 2.29×10^{-1} mol/l. Figure 6 shows the time—conversion curves, while in Figure 7 the relation between the maximum rate of polymerization and the KPS concentration obtained from Figure 6 is indicated. It may be seen from the slope of the straight line in Figure 7 that the rate of polymerization varies with the KPS concentration at the power 0.42. The result is in good agreement with the exponent of 0.5 found in the polymerization without emulsifiers by Okamura,¹⁴ where the VAc concentration was below 2% and KPS was used as initiator. Unfortunately, since the micelles of PVA are not observed in water¹⁵ and the rate of polymerization initiated by the KPS—AsA system is independent of the PVA concentration, we would not be able to explain the results obtained in the present work by the Smith—Ewart theory,¹ which is based on the mechanism that the polymerization takes place in the soap micelles.

Therefore, considering the rate equation resulting, the following elementary reactions may be written according to Litt, *et al.*¹⁶

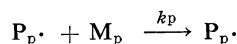
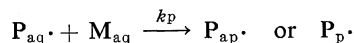
Decomposition of initiator



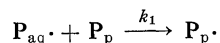
Initiation



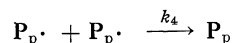
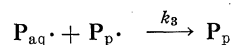
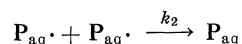
Propagation



Entrance of radical into particle



Termination



where M_{aq} denotes the monomer in aqueous

solution; M_p , the monomer in particle; $P_{ap}\cdot$, the growing radical in water which is soluble in water; $P_p\cdot$, the particle in which radical exists; P_p , the particle in which radical does not exist.

When a steady state is reached, assuming that in the presence of many particles, the formation of new particles and the termination between the growing radicals in water are ignored because the growing radicals in water are easily swept up by particles, eq 1 and 2 result:

$$\frac{d[P_{aq}\cdot]}{dt} = k_d[I] - k_1[P_{aq}\cdot][P_p] - k_3[P_{aq}\cdot][P_p\cdot] = 0 \quad (1)$$

$$\begin{aligned} \frac{d[P_p\cdot]}{dt} &= k_1[P_{aq}\cdot][P_p] - k_3[P_{aq}\cdot][P_p\cdot] - k_4[P_p\cdot]^2 \\ &= 0 \end{aligned} \quad (2)$$

The rate of polymerization is the sum of the consumption rates of monomer in the polymerizations which take place in aqueous solution and in the polymer particles, and is defined as follows:

$$-\frac{d(M)}{dt} = k_p[P_{aq}\cdot][M_{aq}] + k_p[P_p\cdot][M_p] \quad (3)$$

where M represents the monomer.

If the polymer particles are so small that termination takes place very rapidly every time two free radicals are in the same particle, it is considered $k_1 = k_3$. Thus, from eq 1, the following equation is obtained

$$[M_{aq}\cdot] = \frac{k_d[I]}{k([P_p] + [P_p\cdot])} \quad (4)$$

where $k \equiv k_1 = k_3$.

If the fraction of polymer particles having radicals against the total number of particles (N) is taken as f , since $[P_p\cdot] = fN$ and $[P_p] = (1-f)N$, the eq 4 is rewritten by eq 5:

$$[P_{aq}\cdot] = \frac{k_d[I]}{kN} \quad (5)$$

Substituting eq 5 in the eq 2, $[P_p\cdot]$ is expressed as follows

$$[P_p\cdot] = \left\{ \frac{k_d}{k_4} (1-2f) [I] \right\}^{1/2} \quad (6)$$

Thus the rate of polymerization can be obtained from the eq 3 by substituting eq 5 and 6:

$$-\frac{d[M]}{dt} = k_p k_d^{1/2} [I]^{1/2} \left\{ \left(\frac{k_4}{1-2f} \right)^{1/2} \frac{f[M_{aq}]}{k} + \left(\frac{1-2f}{k_4} \right)^{1/2} [M_p] \right\} \quad (7)$$

According to Litt, *et al.*, since f is about 1/1300, $(1-2f)$ can be considered as unity. Equation 7 predicts the square root dependence on the initiator concentration. This theoretical exponent is very close to the experimented result.

The HPO—AsA System

Figure 8 shows the relationships between the conversion and the instantaneous rate of polymerization obtained from the data of Figure 3. The polymerization reactions are also divided

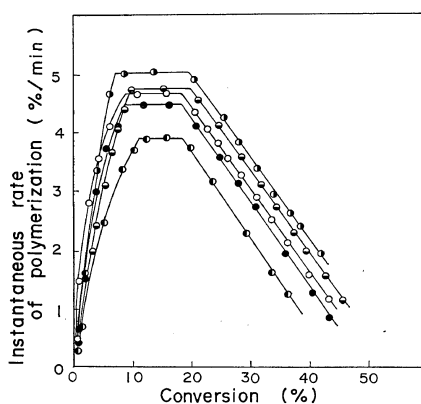


Figure 8. Instantaneous rate of polymerization vs. conversion in the emulsion polymerization of VAc by the HPO—AsA system at 20°C: [PVA]=●, 1.48 g/l; ●, 2.22 g/l; ○, 2.96 g/l; ●, 3.70 g/l; ●, 4.44 g/l; [VAc]= 2.04×10^{-1} mol/l; [HPO]= 2.47×10^{-3} mol/l; [AsA]= 2.50×10^{-3} mol/l.

in three stages. The dependence of the PVA concentration for the rate of polymerization was not observed in Figure 4 where the KPS—AsA system was used, but was obviously found in Figure 8 where the HPO—AsA system was used.

Data of the maximum rate of polymerization initiated by the HPO—AsA system are listed in Table II.

Figure 9 shows the relationship between the maximum rate of polymerization and the PVA concentration. From this result, it can be seen that in the polymerization initiated by the HPO—AsA system at 20°C, the maximum rate of polymerization is proportional to 0.22 power of

Emulsion Polymerization of Vinyl Acetate

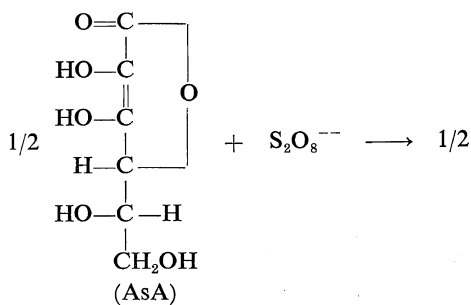
Table II. The maximum rate of polymerization (R_p) of the emulsion polymerization of VAc initiated by the HPO—AsA system

Polymerization temp, °C	[PVA], g/l	[VAc] × 10, mol/l	[HPO] × 10 ³ , mol/l	[AsA] × 10 ³ , mol/l	R_p , %/min
20	1.48	2.04	2.47	2.50	3.9
	2.22	2.04	2.47	2.50	4.5
	2.96	2.04	2.47	2.50	4.6
	3.70	2.04	2.47	2.50	4.6
	4.44	2.04	2.47	2.50	5.0
40	0.74	2.21	0.88	1.14	8.9
	1.48	2.21	0.88	1.14	10.3
	2.22	2.21	0.88	1.14	11.4
	2.96	2.21	0.88	1.14	13.4
20	2.22	2.04	1.24	2.50	3.3
	2.22	2.04	2.47	2.50	4.5
	2.22	2.04	3.71	2.50	5.0
	2.22	2.04	4.94	2.50	6.0
	2.22	2.04	6.18	2.50	6.3

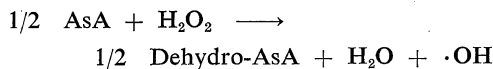
the PVA concentration.

It is believed to form different radicals from both initiator systems used, that is, the sulfate ion radical and the hydroxyl radical, as shown below.

The KPS—AsA system



The HPO—AsA system



These radicals would initiate the VAc radicals which would grow by the further addition of the VAc monomers. Consequently, each polymer molecule should have one or two end groups coming from the initiators by the termination mechanisms.

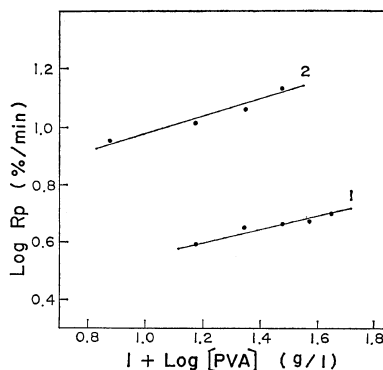


Figure 9. Maximum rate of polymerization (R_p) vs. PVA concentration in the emulsion polymerization of VAc by the HPO—AsA system: (1) at 20°C, [VAc]=2.04 × 10⁻¹ mol/l, [HPO]=2.47 × 10⁻³ mol/l, [AsA]=2.50 × 10⁻³ mol/l, [PVA] was varied; (2) at 40°C, [VAc]=2.21 × 10⁻¹ mol/l, [HPO]=2.47 × 10⁻³ mol/l, [AsA]=2.50 × 10⁻³ mol/l, [PVA] was varied.

Recently, Matsumoto, *et al.*,⁹ investigated the polymer latices of styrene prepared by KPS, and proved by electrophoresis that most of the sulfate end groups of the polymer molecules are present on the surface of the polymer particles. On the other hand, van den Hul *et al.*,¹⁰ have pointed out that the latex particles of polystyrene are stabilized by the sulfate end groups

of the polymer molecules on the surface of particles, the number of which can be determined by means of the conductometric titration method.

Therefore, the fact that the kinetics of the emulsion polymerization of VAc differ by types of initiators shows that the end groups of the polymer molecules coming from initiators must play an important role in the polymerization process.

From this point of view, on the basis of

recent knowledge,^{4,8-10} the emulsion polymerization of VAc in the presence of PVA can be explained as follows.

Since VAc is a hydrophilic monomer, the polymerization of VAc in aqueous solution can be started by initiators which are soluble in water, even in the absence of any emulsifiers. Then, when the polymer particles are formed in water, most of the end groups of the polymer molecules exist on the surface of the resulting particles, and these must contribute to the stabilization of the latex particles both through electrical repulsion and hydration effects, which the end group itself carries naturally. The sulfate end group has both effects, whereas the hydroxyl end group has only one *i.e.*, the hydration effect. Therefore, the degree of stabilization for particles with the sulfate end groups must be more powerful than the hydroxyl end groups. As was previously mentioned, when the KPS—AsA system was used as the initiator of polymerization, a stable polymer latex was formed even in the absence of PVA, but on the other hand, when the HPO—AsA systems was used as initiator, it was impossible to obtain a stable polymer latex without using PVA. These experimental results clearly suggest that the effect on stabilization for particles of the sulfate end groups is superior to that of the hydroxyl end groups.

In the polymerization initiated by the KPS—AsA system in the presence of PVA, the maximum rate of polymerization was independent of the PVA concentration, as shown in Figure 5. It therefore seems possible to conclude that the stabilization of the resulting particles is satisfactorily explained by the sulfate end groups in the polymer molecules, and that the formation of the latex particles would be related, not to the effect of PVA as emulsifier, but more to the effect of the sulfate end groups. On the other hand, in the polymerization initiated by the HPO—AsA system, it was necessary to use PVA as emulsifier in order to obtain the stable latex particles suspended in water. Consequently, the reason why the rate of polymerization is affected by the PVA concentration would come from the following: it is difficult for the resulting particles to be stabilized only by the hydroxyl

end groups of the polymer molecules, so that since the resulting particles come to be protected by the PVA molecules which are present in the reaction system, the number of polymer particles is also affected by the PVA concentration.

Furthermore, the maximum rate of polymerization at 40°C varied with the PVA concentration at power 0.32, unlike the result at 20°C as shown in Figure 9. The difference may be explained by the fact that the effect of the hydroxyl end groups on particle stabilization decreases the as temperature rises.

Figure 10 shows the variation of the time—

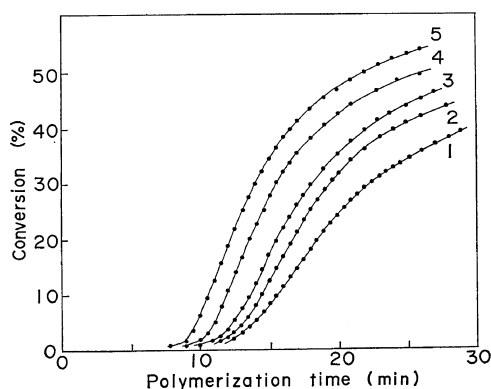


Figure 10. Conversion vs. polymerization time in the emulsion polymerization of VAc by PHO—AsA system at 20°C: (1) $[HPO]=1.24 \times 10^{-3}$ mol/l; (2) $[HPO]=2.47 \times 10^{-3}$ mol/l; (3) $[HPO]=3.71 \times 10^{-3}$ mol/l; (4) $[HPO]=4.94 \times 10^{-3}$ mol/l; (5) $[HPO]=6.18 \times 10^{-3}$ mol/l; $[PVA]=2.04 \times 10^{-1}$ mol/l; $[AsA]=2.50 \times 10^{-3}$ mol/l.

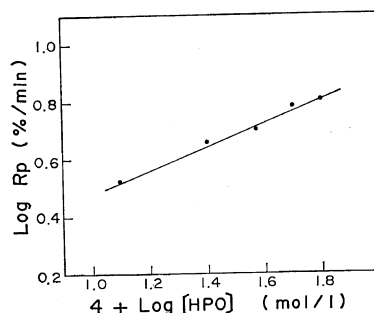


Figure 11. Maximum rate of polymerization (R_p) vs. HPO concentration in the emulsion polymerization of VAc by the HPO—AsA system at 20°C: $[PVA]=2.22$ g/l; $[VAc]=2.04 \times 10^{-1}$ mol/l; $[AsA]=2.50 \times 10^{-3}$ mol/l; $[HPO]$ was varied.

conversion curves at 20°C, changing the HPO concentration in the range 1.24×10^{-3} to 6.18×10^{-3} mol/l, where the AsA, the PVA, and the monomer concentrations are kept constant, respectively. The dependence of the HPO concentration on the maximum rate of polymerization was indicated in Figure 11, where it was seen that the rate of polymerization depends on the HPO concentration at the power 0.40.

Since the rate of polymerization initiated by the HPO—AsA system is dependent on the PVA concentration even without micelles, the theoretical relationship between the rate of polymerization and the initiator concentration in the presence of PVA is not yet clear and is now being studied, together with the number of particles.

In conclusion, the kinetics of the emulsion polymerization on VAc in the presence of PVA vary depending on the type of initiator. The dependence of the PVA concentration on the rate of polymerization is likely to depend on whether or not the resulting particles are stabilized by the end groups of the polymer molecules coming from initiators.

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