# A Kinetic Study of the Polymerization of Acrylic Acid in the Presence of Polyvinylpyrrolidone

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The polymerization of acrylic acid (AA) in a dilute aqueous solution in the presence of polyvinylpyrrolidone (PVP) has been studied kinetically, with the extent of polymerization followed by a bromometric titration method. The rate of the polymerization changed characteristically with the amount of PVP in the solution and went through a maximum at a certain initial mole ratio of PVP and AA, $[PVP]_0/[AA]_0$, under a constant $[AA]_0$ value. The mole ratio which gave the maximum rate was almost proportional to the reciprocal of $[AA]_0$. In the course of the polymerization, a polymer complex consisting of PVP and polymerized AA was precipitated. Its composition, $(PAA)_c/(PVP)_c$, has been found to be different as the polymerization conditions are varied. Hardly no comparable data between the bromometric method and a turbidimetric method used to measure the rate were obtained. The influence of PVP on the polymerization was assumed to be caused by the local concentration of AA in the vicinity of PVP. A mechanism based on the effect of the local concentration, the "polymer atmosphere binding mechanism," has been found to explain the experimental results well.

Ferguson and Shah have described that the polymerization of acrylic acid (AA) in the presence of polyvinylpyrrolidone (PVP) in a dilute aqueous solution exhibits kinetically the characteristics of a "replica polymerization."[1] In their study, the rate of the polymerization was observed to go through a maximum at an equimolar ratio of PVP and AA under a constant AA concentration. Such a phenomenon has been explained as a "replica polymerization," a "matrix polymerization," or a "template polymerization." Many polymerization systems have been investigated in connection with the matrix polymerization—for example, the polymerizations of 4-vinylpyridine in the presence of polystyrenesulfonic acid or polyacrylic acid by Kabanov *et al.*,[2] that of acrylic acid in the presence of polyethylenimine by Bamford and Shiiki[3] and by Ferguson and Shah,[4] that of methacrylic acid in the presence of polyvinylpyrrolidone by Sakaguchi *et al.*,[5] that of methacrylic acid in the presence of poly-*N*-vinyl-5-methyl-2-oxazolidone by Okawara *et al.*,[6] that of 4-vinylpyridine in the presence of polymaleic anhydride by Kinoshita *et al.*,[7] and that of methacrylic acid or acrylic acid in the presence of polyethylene glycol by Osada.[8]

The interactions between the monomer and the polymer in those polymerization systems are various and multiform in their qualities and strengths. As regards the interaction between a simple electrolyte and a polyelectrolyte, for example, the site binding of simple electrolytes to polyelectrolytes and also the local concentration of simple electrolytes in the vicinity of polyelectrolytes have been considered.[9] These things have also been dealt with in ionic reactions in the presence of polyelectrolytes.[10] Except for the perfect replica polymerization shown in the polymerization of methacrylic acid or acrylic acid using Novolak resins by Kämmerer *et al.*,[11] the replica polymerization could not be declared until the exact duplication of such information on a polymer templates as the molecular weight has been proved, as Kinoshita has reported.[7]

In the present experiment, the polymerization of acrylic acid (AA) in the presence of polyvinylpyrrolidone (PVP) in a dilute aqueous solution, a similar polymerization system which Ferguson and Shah have studied kinetically by a turbidimetric method,[1] has been investigated, with the rate of the polymerization followed by measuring the quantities of an unreacted monomer, AA. In connection with the result concerning the peculiar influence of PVP on the rate of the polymerization of AA, the local concentration of AA in the vicinity of the PVP molecule in the polymerization will be discussed.

## Experimental

*Materials.* Acrylic acid (AA) was purified by sublimation at a pressure below $10^{-1}$ mmHg. Quantities of double bonds more than 97 mol% in the sublimate were detected by bromometric titration analysis. The polyvinylpyrrolidone (PVP) was of a commercial origin and was purified with water and acetone. The PVP of M.W. 24500 was used unless otherwise stated. The polyacrylic acid (PAA) was obtained by the acidification of a commercial sodium polyacrylate with HCl or by the polymerization of AA in an aqueous solution, and was purified by dialysis. The potassium persulfate ($K_2S_2O_8$), used as an initiator, *N*-methylpyrrolidone (MP), and propionic acid (PA) were all of commercial origin, and they were purified in the usual manners.

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[1] J. Ferguson and S. A. O. Shah, *Eur. Polym. J.*, **4**, 343 (1968).

[2] O. V. Kargina, V. A. Kabanov, and V. A. Kargin, *J. Polym. Sci. Part C*, **22**, 339 (1968); V. A. Kabanov, V. A. Petrovskaya, and V. A. Kargin, *Vysokomol. Soedin.*, **A 10**, 925 (1968).

[3] C. H. Bamford and Z. Shiiki, *Polymer*, **9**, 595 (1968).

[4] J. Ferguson and S. A. O. Shah, *Eur. Polym. J.*, **4**, 611 (1968).

[5] Y. Sakaguchi, K. Tamaki, T. Shimizu, and J. Nishino, *Kobunshi Kagaku*, **27**, 284 (1970).

[6] T. Endo, R. Numazawa, and M. Okawara, *ibid.*, **28**, 541 (1970).

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[8] Y. Osada, *Kagaku no Ryoiki*, **25**, 9 (1971).

[9] "Encyclopedia of Polymer Science and Technology," Vol. 10, Interscience Publishers, New York (1968), p. 781.

[10] H. Morawetz, *Accounts Chem. Res.*, **3**, 4152 (1970).

[11] H. Kämmerer and S. Ozaki, *Markomol. Chem.*, **91**, 1 (1966); H. Kämmerer and A. Jung, *ibid.*, **101**, 284 (1966); H. Kämmerer and N. Önder, *ibid.*, **111**, 67 (1968).

*Polymerization Reaction.* The polymerizations of AA were carried out in sealed ampules. Each aqueous solution of AA, PVP, and $K_2S_2O_8$ was charged in an ampule (10 m*l*) and frozen in turn without mixing those portions, and then sealed under nitrogen. The sealed ampules were shaken in a thermostat maintained at 74±0.1°C for a given time.

*Measurement of the Rate of the Polymerization.* The rate of the polymerization of AA was followed by measuring the quantities of the unreacted AA by the Lucass-Pressman method, a bromometric titration method.[12] The additions of bromine were carried out at 40—50°C for 5 min. The effects of $[K_2S_2O_8]$ and [PVP] on the addition of bromine to the unreacted AA were negligible.

*Analysis of the Composition of the Polymer Complex.* A polymer complex which was precipitated in the course of the polymerization of AA in the presence of PVP, the polymer complex (A), was separated by the centrifugation of the reaction solution and then washed with water three times. The composition of the polymer complex (A) was determined by elemental analysis. It was difficult to find any solvent system which could dissociate or dissolve the polymer complex (A) completely. Therefore, the molecular weight of PAA polymerized in the presence of PVP could not be detected. On the other hand, a polymer complex which was formed in mixing PAA and PVP, the polymer complex (B), was purified and analyzed by the same method in order to compare it with the polymer complex (A).

*Examination of a Turbidimetric Method Used in Following the Extent of the Polymerization.* Both the change in the turbidity with the extent of the polymerization of AA in the presence of PVP and the turbidity caused by mixing PAA and PVP were measured in a jacketed turbidity cell (glass; optical path, 2.20 cm; volume, 35 m*l*) or a standard cell (optical path, 1.00 cm), using a hand-made turbidimeter and a Beckman DB-G spectrophotometer.

## Results

Some typical time-conversion curves are shown in Fig. 1. The time-conversion curve of the polymerization of AA in the presence of PVP could be treated as a straight line at the range of 30—60% conversion, as may be seen in Fig. 1, Curve A. As the temperature of this reaction system did not reach a given temperature at the early stage of the polymerization, it is difficult to measure the initial rate accurately. The rate of the polymerization was obtained from the slope of the linear part in the time-conversion curve. The time-conversion curve of the polymerization of AA without PVP is shown as Curve B. In both cases, *N*-methylpyrrolidone (MP), which would be a monomeric analog of PVP, was found to have no effect on the rate of the polymerization, so it is assumed that the pyrrolidone group does not affect the reactivity of AA and the decomposition of $K_2S_2O_8$.

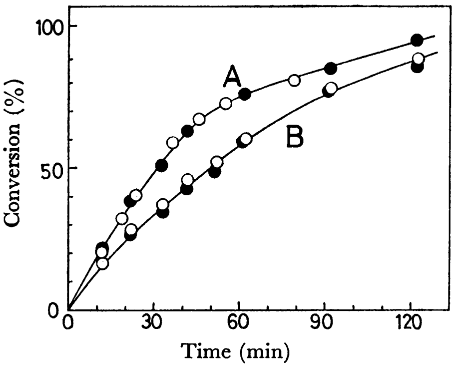

Fig. 1. Typical time-conversion curves of the polymerization of AA.
$[AA]_0=5.0\times10^{-2}$ (mol/*l*); $[K_2S_2O_8]_0=7.4\times10^{-3}$ (mol/*l*); 74±0.1°C.

| Curve | | $[PVP]_0$ (mol/*l*) | $[MP]_0$ (mol/*l*) |
|---|---|---|---|
| A | ○ | $2.5\times10^{-2}$ | 0 |
| | ● | $2.5\times10^{-2}$ | $2.5\times10^{-2}$ |
| B | ○ | 0 | 0 |
| | ● | 0 | $5.0\times10^{-2}$ |

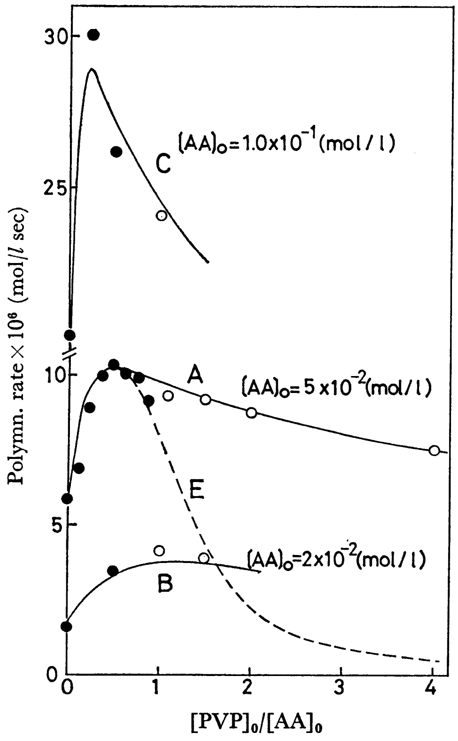

Fig. 2. Influence of $[PVP]_0$ on the rate of the polymerization of AA.
$[K_2S_2O_8]_0=7.4\times10^{-3}$ (mol/*l*);
●, presence of MP ($[MP]_0+[PVP]_0=[AA]_0$);
○, absence of MP; 74±0.1°C.
Curves A, B, C, calcd. by Eq. (B) (Polymer atmosphere binding mechanism).
Curve E, calcd. by Eq. (A-3) (Specific site binding mechanism).

The influence of PVP on the rate of the polymerization is shown in Fig. 2. Under constant initial concentrations of AA, $[AA]_0$, and $K_2S_2O_8$, $[K_2S_2O_8]_0$, the rate of the polymerization went through a maximum at a certain ratio of PVP and AA, $[PVP]_0/[AA]_0$. A similar tendency has been described in, for instance, the studies of the polymerizations of AA in the presence of polyethylenimine,[3,4] of that of methacrylic acid in the presence of poly-*N*-vinyl-5-methyl-2-oxazolidone,[6] and of that of *N*-vinyl-2-oxazolidone in the presence of polymethacrylic acid.[13]

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[12] H. J. Lucass and D. Pressman, *Ind. Eng. Chem. Ana. Ed.*, **10**, 140 (1938).

[13] T. Endo, R. Numazawa, and M. Okawara, *Makromol. Chem.*, **146**, 247 (1971).

The ratios of $[PVP]_0/[AA]_0$ at which the rates were maximum, $\{[PVP]_0/[AA]_0\}_{max}$, were almost proportional to the reciprocal of $[AA]_0$. Moreover, the concentrations of PVP at $\{[PVP]_0/[AA]_0\}_{max}$ were about $2.5\times10^{-2}$ mol/*l*. As for the viscosity of the reaction solution, $\eta_{sp}/[PVP]_0$, it did not change remarkably in the vicinity of the PVP concentration of $2.5\times10^{-2}$ mol/*l*, as is shown in Fig. 3. From those results, the theory that the acceleration of the rate is caused by a conformational change in PVP can be rejected.

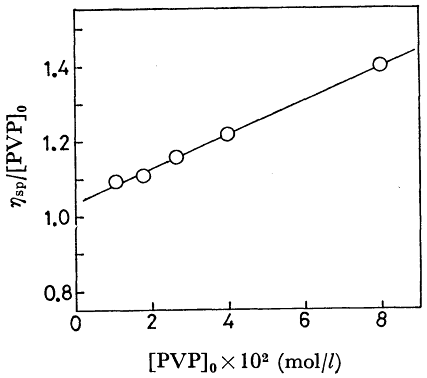

Fig. 3. Viscosity of the reaction solution.
$[PA]_0=2.0\times10^{-2}$ (mol/*l*);
$[K_2S_2O_8]_0=7.4\times10^{-3}$ (mol/*l*); 74±0.1°C.

If this polymerization system were a "replica polymerization system," $\{[PVP]_0/[AA]_0\}_{max}$ would be a constant under different $[AA]_0$ values and would not decrease as $[AA]_0$ becomes higher. It seems rather unlikely, then, that the present polymerization is the "replica polymerization," although there is no direct evidence on this point. Ferguson and Shah have described that the rate of the polymerization went through a maximum rate of $14.7\times10^{-4}$ mol/*l*·sec at almost the same PVP concentration as AA when $[AA]_0$ was $2\times10^{-2}$ mol/*l*.[1] This rate was remarkably different from the $4.2\times10^{-6}$ mol/*l*·sec found in our work. This difference will be discussed later. In Fig. 4, the rate calculated from the AA consumption as measured by the bromometric titration method, and the rate calculated from the yield of the polymer complex (A) formed in the course of the polymerization of AA in the presence of PVP are shown. The rate obtained by the polymer-complex weighing method differs from that obtained by the titration method; this difference will also be discussed later.

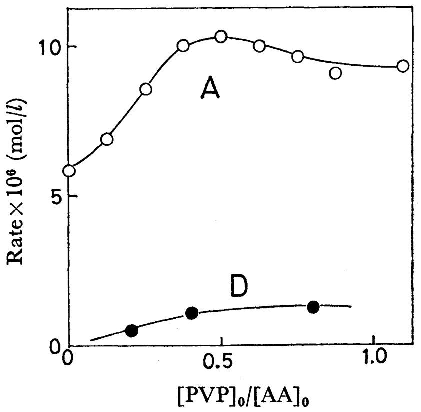

Fig. 4. Comparison of the rates by the titration method and by the polymer complex (A) weighing method.
$[AA]_0=5.0\times10^{-2}$ (mol/*l*); $[K_2S_2O_8]_0=7.4\times10^{-3}$ (mol/*l*); $[PVP]_0+[MP]_0=[AA]_0$; 74±0.1°C.
○: polymerization rate by the bromometric titration
●: precipitation rate of the polymer complex (A)

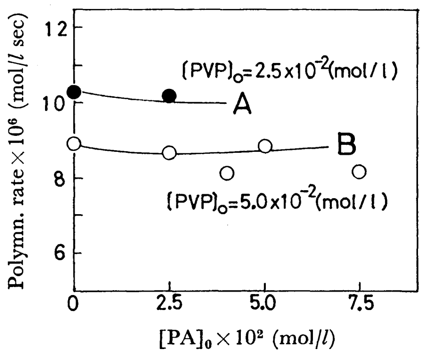

Fig. 5. Influence of PA on the rate of the polymerization of AA.
Conditions as given for Fig. 4.
Curves A, B; calcd. by Eq. (B′), (polymer atmosphere binding mechanism)

The influence of propionic acid (PA), a non-polymerizable analog of the AA monomer, on the rate of the polymerization is shown in Fig. 5. PA had no effect on the rate of polymerization. This result also leads to a negation of hypothesis of the "replica polymerization" for this polymerization system.

Figure 6 shows the dependence of $[AA]_0$ on the rate of the polymerization. Apparently, the rate of the polymerization of AA with PVP was proportional to the 1.9 powers of $[AA]_0$, while the rate without PVP was proportional to the 1.5 powers of $[AA]_0$.

The dependence of the initiator concentration, $[K_2S_2O_8]_0$, on the rate of the polymerization was also studied, as is shown in Fig. 7. The rate was almost proportional to the 0.5 power of $[K_2S_2O_8]_0$

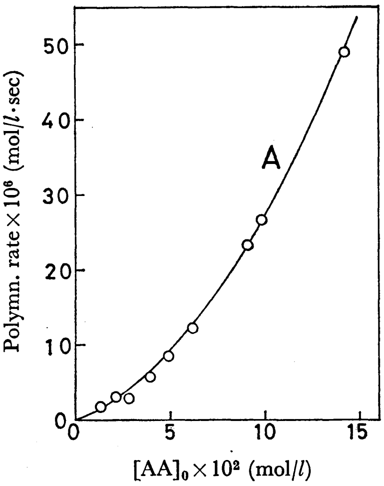

Fig. 6. Influence of $[AA]_0$ on the rate of the polymerization of AA.
$[PVP]_0=5.0\times10^{-2}$ (mol/*l*); $[K_2S_2O_8]_0=7.4\times10^{-3}$ (mol/*l*) 74±0.1°C
Curve A; calcd. by Eq. (B), (Polymer atmosphere binding mechanism)

Table 1. Yield and composition of the polymer complex (A)

| No. | Monomer $[AA]_0$ (mol/$l$) | Polymer $[PVP]_0$ (mol/$l$) | Initiator $[K_2S_2O_8]_0$ (mol/$l$) | Yield $(PAA)_C/[AA]_0$ | Composition $(PAA)_C/(PVP)_C$ | Complexes PVP $(PVP)_C/[PVP]_0$ |
|---|---|---|---|---|---|---|
| 1 | $5\times10^{-2}$ | $2\times10^{-2}$ (No. 1) | $7.4\times10^{-3}$ | 22.6 (%) | 1.183 | 48.0 (%) |
| 3 | $5\times10^{-2}$ | $2\times10^{-2}$ (No. 2) | $7.4\times10^{-3}$ | 24.7 | 1.191 | 51.8 |
| 4 | $5\times10^{-2}$ | $2\times10^{-2}$ (No. 3) | $7.4\times10^{-3}$ | 23.5 | 1.006 | 58.3 |
| 5 | $5\times10^{-2}$ | $4\times10^{-2}$ (No. 1) | $7.4\times10^{-3}$ | 26.1 | 1.004 | 32.4 |
| 6 | $5\times10^{-2}$ | $1\times10^{-2}$ (No. 1) | $7.4\times10^{-3}$ | 9.1 | 1.365 | 33.5 |
| 7 | $5\times10^{-2}$ | $2\times10^{-2}$ (No. 1) | $3.7\times10^{-3}$ | 29.0 | 1.244 | 58.3 |
| 8 | $10\times10^{-2}$ | $2\times10^{-2}$ (No. 1) | $7.4\times10^{-3}$ | 18.2 | 1.800 | 52.3 |
| 9 | $5\times10^{-2}$ | $5\times10^{-2}$ (No. 1) | $7.4\times10^{-3}$ | — | 0.851 | — |
| 10 | $5\times10^{-2}$ | $5\times10^{-2}$ (No. 3) | $7.4\times10^{-3}$ | — | 0.626 | — |

Reaction time, 3 hr; 74±0.1°C.
M.W. of PVP; No. 1, 24500; No. 2, 40000; No. 3, 700000.
$(PAA)_C$ shows the quantity of PAA found in the complex.
$(PVP)_C$ shows the quantity of PVP found in the complex.

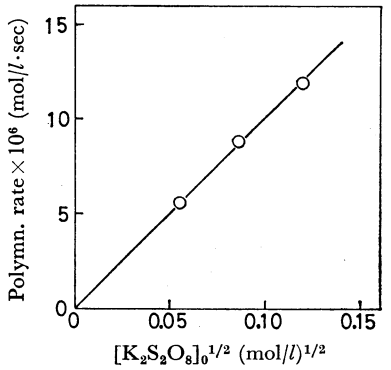

Fig. 7. Influence of $[K_2S_2O_8]_0$ on the rate of the polymerization of AA.
$[AA]_0=[PVP]_0=5.0\times10^{-2}$ (mol/$l$); 74±0.1°C.

at constant AA and PVP concentrations. The rate of the polymerization of AA without PVP has been reported to be proportional to the 0.5 power of the persulfate initiator.[14] These results indicate that the acceleration of the rate of the polymerization of AA in the presence of PVP was not caused by the trapping of radicals in the precipitated phase, the so-called "gel-effect."

Table 1 shows the yield and composition, $(PAA)_c/(PVP)_c$, of the polymer complex (A) precipitated in the course of the polymerization of AA in the presence of PVP. Fig. 8 shows the influence of $[PVP]_0$ on $(PVP)_c/(PAA)_c$ in the polymer complex (A). Even at a constant $[AA]_0$, value where the amounts of PAA formed were similar, the $(PVP)_c/(PAA)_c$ ratios in the polymer complexes (A) were different from one another, and they became smaller as $[PVP]_0$ became smaller. The concentrations of PVP and AA also affected the composition of the polymer complex (A), $(PAA)_c/(PVP)_c$, even though the $[PVP]_0/[AA]_0$ ratios were the same (No. 6, No. 8, in Table 1). Even when the $[AA]_0/[PVP]_0$ ratio was large and the amount of polymerized AA was larger than $[PVP]_0$, not all of the PVP was found in the polymer complex (A) (No. 1—8 in Table 1). These results indicate that not all the polymerized AA formed the polymer complex (A) with an equimolar ratio of PAA and PVP and that the polymer complex (A) formation was not complete. The difference between the rate calculated from the yield of the polymer complex (A) and that calculated from the consumption of AA, as is seen in Fig. 4, can explained as a non-quantification in the formation of the polymer complex (A). The molecular weight of the PVP used also affects the formation of the polymer complex (A) (No. 1, 4, 9, and 10 in Table 1).

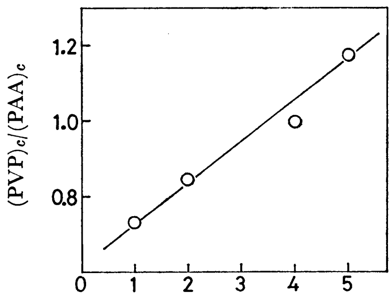

Fig. 8. Composition of the polymer complex (A).
No.'s 1, 5, 6, and 9 in Table 1; M.W. of PVP, 24500

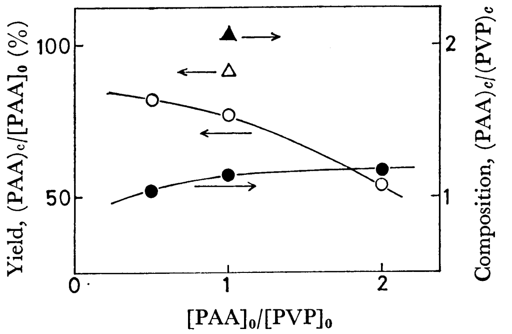

Fig. 9. Yield and composition of the polymer complex (B).
$[PVP]_0=5.0\times10^{-2}$ (mol/$l$); $[K_2S_2O_8]_0=7.4\times10^{-3}$ (mol/$l$); Mixing temperature, 74±1°C.
PAA No. 5; ○, yield; ●, composition
PAA No. 1; △, yield; ▲, composition
M.W. of PAA No. 5, 5300; M.W. of PAA No. 1, fairly higher than that of PAA No. 5.

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[14] H. Ito, S. Shimizu, and S. Suzuki, *Kogyo Kagaku Zasshi*, **58**, 194 (1955).

Figure 9 shows the yield of the polymer complex (B) formed by mixing PAA and PVP, $(\mathrm{PAA})_c/[\mathrm{PAA}]_0$, and the composition of the polymer complex (B), $(\mathrm{PAA})_c/(\mathrm{PVP})_c$. Much as in the discussion of the polymer complex (A), it can be said that the PAA and PVP which did not take part in the formation of the polymer complex (B) still remained in the solution phase. Further, the yield and the composition of the polymer complex (B) depended on the molecular weight of PAA. The ratio in the polymer complex (B), $(\mathrm{PAA})_c/(\mathrm{PVP})_c$, formed with the PAA of a higher molecular weight was larger than that formed with the PAA of a lower molecular weight. The ratio in the polymer complex (A) (No. 9 in Table 1) was smaller than that of the polymer complex (B) formed with the PAA of M.W.=5300. These results suggest that the molecular weight of the polymerized AA in the presence of PVP is probably lower than 5300.

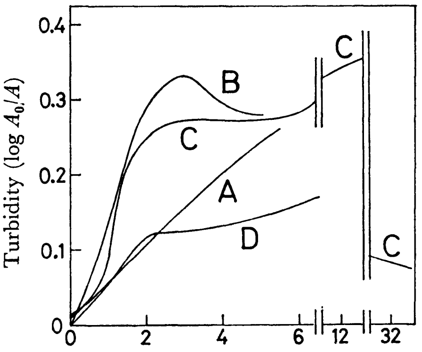

Fig. 10. Variation of turbidity with extent of the polymerization of AA.
$[\mathrm{AA}]_0=[\mathrm{PVP}]_0=2.0\times10^{-2}$ (mol/$l$); $[\mathrm{K_2S_2O_8}]_0=7.4\times10^{-3}$ (mol/$l$); 74±1°C.
Stirring; A, non; B, gentle; C, moderate; D, vigorous.

The turbidimetric method for measuring the extent of the polymerization of AA was examined. After an induction period of 7—13 min the turbidity of the polymerization system increased greatly, went through a maximum, and then decreased, as is shwon in Fig. 10. The variation in the turbidity depended on the stirring of the polymerization system. To compare the bromometric titration method with the turbidimetric method, an aliquot of the reaction mixture, which is shown as Curve C in Fig. 10, was provided for the bromometric titration. From the titration, the conversions in the polymerization of AA were found to increase (conversions of 64% at 12 min and 86% at 32 min, respectively) in spite of the decrease in the turbidity. This shows that the correlation between the turbidity and the conversion was not simple.

The change in the turbidity observed when a concentrated PAA solution was added to a PVP solution in the turbidity cell was also studied (Fig. 11). The turbidity increased greatly within 10 sec after the addition of the PAA solution, went through a maximum, then decreased and reached an equilibrium 2—3 min later. To this solution, a portion of the PAA solution was additionally introduced; the turbidity then changed as before. A linear relationship between the amount of PAA and the equilibrium turbidity was observed; *cf.* the D line in Fig. 11. If the D line is adopted as a calibration curve of the polymerized AA in the polymerization, the rate of the polymerization, shown as Curve C in Fig. 10, should be $5\times10^{-4}$ mol/$l$·sec. This value is similar to that Ferguson and Shah obtained ($14.7\times10^{-4}$ mol/$l$·sec). However, if we adopt the data at the maximum turbidity, the corresponding PAA should be about 200% to the fed-in AA. From these results, it may be considered that it is unreliable to measure the rate of the polymerization by following the turbidity.

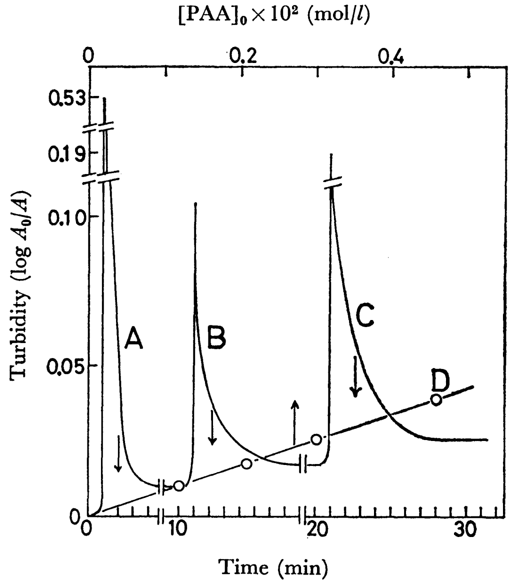

Fig. 11. Variation of turbidity with the amount of $[\mathrm{PAA}]_0$. Reaction solution, 20.0 m$l$; $[\mathrm{PVP}]_0=2.0\times10^{-2}$ (mol/$l$), $[\mathrm{K_2S_2O_8}]_0=7.4\times10^{-3}$ (mol/$l$).

| Curve | Added PAA |
|---|---|
| A | 0.04 m$l$ |
| B | +0.03 m$l$ |
| C | +0.03 m$l$ |

[PAA (M.W.=5300)]$=6.0\times10^{-1}$ (mol/$l$)
Curve D, equilibrium turbidity. 74±1°C.

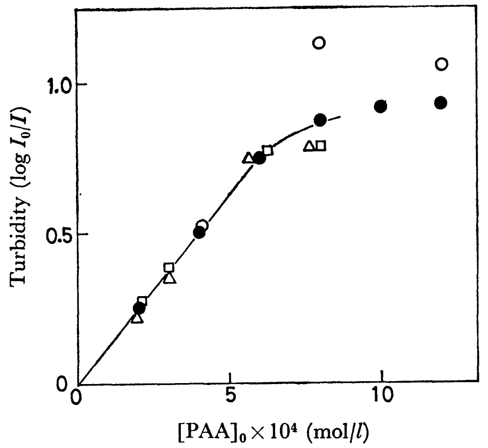

Fig. 12. Variation of turbidity with the amount of $[\mathrm{PAA}]_0$.
$[\mathrm{K_2S_2O_8}]_0=7.4\times10^{-3}$ (mol/$l$);
○, □: $[\mathrm{PVP}]_0=2.0\times10^{-2}$ (mol/$l$);
△: $[\mathrm{PVP}]_0=5.0\times10^{-2}$ (mol/$l$);
●: $[\mathrm{PVP}]_0=[\mathrm{PA}]_0=2.0\times10^{-2}$ (mol/$l$);
M.W. of PAA, 1900; light source, 500 m$\mu$; 74±0.1°C.

Figure 12 shows the turbidity observed when a PAA solution was added to a PVP solution under various conditions. In this case, the turbidity was observed through a photocell (optical path, 1.00 cm) after mixing and shaking the PVP-$K_2S_2O_8$ solution and the PAA solution. As the linear relationship between the turbidity and $[PAA]_0$ was not obtained in the range of over $5\times10^{-4}$ mol/*l* of $[PAA]_0$, this method could not be applied in our study.

## Dscussion

The polymerization in the present study can not be explained as a "replica polymerization," because the mole ratio, $[PVP]_0/[AA]_0$, at which the rate of the polymerization was at its maximum changed with the $[AA]_0$ value (as is shown in Fig. 2), PA did not affect the rate of the polymerization (as is shown in Fig. 5), and the composition of the polymer complex (A) varied with the complex-forming conditions (Table 1).

Here, two simple model mechanisms may be considered:

A) specific-site binding mechanism ("replica polymerization"-AA adsorbed on PVP polymerizes) and B) polymer-atmosphere binding mechanism (AA drawn atmospherically by PVP polymerizes).

A) Mechanisms of Specific-site Binding. *Case A-1*): The adsorption of AA on PVP follows Langmuir's adsorption isotherm, and both adsorbed AA and not-adsorbed AA polymerize. The adsorption may be expressed as follows:

$$[P] + [M_f] \overset{K}{\rightleftarrows} [PM],$$

$$\theta = [PM]/[P]_0 = [M_f]/([M_f]+1/K)$$

where $[M_f]$ and $[PM]$ are not-adsorbed and adsorbed AA respectively and where $[M]_0$ and $[P]_0$ are volume-average concentrations of AA and PVP respectively (they are defined as $[PM]+[M_f]=[M]_0$, $[PM]+[P]=[P]_0$). $K$ is an equilibrium constant of adsorption, and $\theta$ is the fraction of the adsorbed sites.

i) An adsorbed AA can migrate freely on PVP, and the rate of the polymerization of PVP is proportional to the adsorbed AA, ($\theta$); the rate of the polymerization, $V$, can be expressed as:

$$V = [P]_0 k_3\theta + k_4[M_f]^{1.5} = k_3[PM] + k_4[M_f]^{1.5} \qquad \text{(A-1-1)}$$

where $k_3$ and $k_4$ are the rate constants of the polymerization of adsorbed AA on PVP and of not-adsorbed AA respectively.

ii) The rate of the polymerization of the adsorbed AA is proportional to the average length of the continuous sequence of AA molecules adsorbed on PVP, which is expressed as:

$$v = (1-\theta)\sum_{p=1}^{\infty} P\theta^{p-1} = 1/(1-\theta)$$

where $p$ is the length of the continuous sequence of the AA adsorbed on PVP. The rate can, then be expressed as:

$$V = k_3[PM]/(1-\theta) + k_4[M_f]^{1.5} \qquad \text{(A-1-2)}$$

*Case A-2*): An adsorption of AA on PVP follows Freundlich's adsorption isotherm ($n$=2)

$$\theta = [PM]/[P]_0 = a[M_f]^{1/2}$$

similar to i), then,

$$V = k_3[PM] + k_4[M_f]^{1.5} \qquad \text{(A-2-1)}$$

$$V = k_3[PM]/(1-\theta) + k_4[M_f]^{1.5} \qquad \text{(A-2-2)}$$

The calculated rates followed by (A-1-1), (A-1-2), (A-2-1), and (A-2-2) were all monotonous increasing functions with respect to $[PVP]_0$ and did not agree with the characteristics of the experimental results shown in Fig. 2.

*Case A-3*): Bamford *et al.* have presented the following expression for the polymerization on a template.[3]

$$V = C \exp(-\alpha Z^{\beta}/kT)[X]$$

where $\alpha$ and $\beta$ are arbitrary constants, where $C$ is the total radical concentration, where $Z$ is $[P]/[PM]$, and where $[X]$ is $[PM]$. The total rate should be considered to be the sum of the rates of polymerization on and apart from the template. Accordingly, the following equation can be obtained:

$$V = C \exp\{-\alpha([P]/[PM]^{\beta}/kT\}[PM] + k_4[M_f]^{1.5} \qquad \text{(A-3)}$$

The rate curve calculated by Eq. (A-3) using the numerical values of $K$=22.2 (*l*/mol) ($K$ is Langmuir's adsorption constant), $C\exp(-\alpha/kT)/k_4=4.0375$, and $\beta=1.81946$, which were obtained from the initial and the optimum conditions of the experimental data, is shown as Curve *E* in Fig. 2. This curve deviates much from the experimental results obtained at higher concentrations of PVP. In addition, the fact that Eq. (A-3) gave similar values of $\{[PVP]_0/[AA]_0\}_{max}$ at different $[AA]_0$ values differs from the experimental results.

It is difficult to obtain an expression which agrees well with the characteristics of the experimental data in the present study, considering the mechanisms of specific-site binding.

*B*) *A Mechamism of Polymer-Atmosphere Binding.* A local concentration of AA can be expected to be distributed continuously in the reaction system. However, to simplify the discussion, the reaction system is assumed to be divided into two domains. One is a polymer domain where AA is concentrated in the vicinity of PVP (the volume fraction is $f$, the concentrations of PVP and AA in the polymer domain are $[P_p]$ and $[M_p]$ respectively), and the other is a free domain (the volume fraction is $1-f$, and the concentration of AA is $[M_f]$). Because MP did not affect the rate of the polymerization (Fig. 1), and because the dependence of the initiator on the rate of the polymerization of AA differed little in either the presence or absence of PVP (Fig. 7), the fundamental reaction mechanisms in both domains are assumed to be the same as in a homogeneous reaction system. As the PVP is a linear vinyl polymer, the shape of this polymer domain can be considered to be a cylinder along the chain of PVP. The total length of this cylinder is proportional to $[PVP]_0$. The $f/(1-f)$, ratio will increase with $[PVP]_0$ and decrease with $[AA]_0$. The contribution of $[AA]_0$ to the ratio is not simple, since the domain, $f$, will be set through an interdependence of $[M_f]$ and $[M_p]$. Thus, the following expression may be assumed:

$$f/(1-f) = [P]_0/a$$

where $a$ is a function of the monomer and where $[\mathrm{P}]_0$ is the volume average concentration of PVP. Considering the equilibrium and the stoichiometry:

$$[\mathrm{M_f}] + [\mathrm{P_p}] \overset{K}{\rightleftarrows} [\mathrm{M_p}] \quad (K;\ \text{equilibrium constant})$$

$$f[\mathrm{M_p}] + (1-f)[\mathrm{M_f}] = [\mathrm{M}]_0, \qquad f[\mathrm{P_p}] = [\mathrm{P}]_0$$

where $[\mathrm{M}]_0$ is the volume-average concentration of AA. Then, the overall rate of polymerization of AA, $V$ can be expressed as follows:

$$\begin{aligned} V &= fk[\mathrm{M_p}]^{1.5} + (1-f)k[\mathrm{M_f}]^{1.5} \\ &= k[\mathrm{M}]_0^{1.5}\{[\mathrm{P}]_0([\mathrm{P}]_0+a)^2+a([\mathrm{P}]_0+a)^{0.5}(1/K)^{1.5}\}/ \\ &\quad ([\mathrm{P}]_0^2+a[\mathrm{P}]_0+a/K)^{1.5} \end{aligned} \tag{B}$$

As to the influence of PVP on the rate of the polymerization when $[\mathrm{AA}]_0$ is $5\times10^{-2}$ mol/$l$, the rate curve calculated by means of Eq. (B) with $K=64.7$ ($l$/mol) and $a=0.2$ is shown as Curve *A* in Fig. 2. The calculated rate curves with $a=0.38$ ($[\mathrm{AA}]_0=2\times10^{-2}$ mol/$l$) and $a=0.19$ ($[\mathrm{AA}]_0=10\times10^{-2}$ mol/$l$) are also shown as Curves B and C respectively. These curves agree well with the experimental data. Thus, $a$ was found to be a function of $[\mathrm{AA}]_0$, and it increased as $[\mathrm{AA}]_0$ decreased. According to these results, the following empirical formula of $a$ was obtained:

$$a = 1.2[\mathrm{M}]_0 + 0.007/[\mathrm{M}]_0$$

Using this formula, the relation between $[\mathrm{AA}]_0$ and $f$ was found to be as is shown in Fig. 13. At higher concentrations of $[\mathrm{AA}]_0$, $f$ decreased with $[\mathrm{AA}]_0$. Regarding this phenomenon, two tentative considerations will be made. One is a shrinking of PVP by AA; the other is a shielding of PVP by AA according to a Debye-Hückel theory. As to the dependence of $[\mathrm{AA}]_0$ on the rate of the polymerization the rate curve calculated by means of Eq. (B) with $K=64.7$ ($l$/mol) and $a=1.2[\mathrm{M}]_0+0.007/[\mathrm{M}]_0$ is shown as Curve A in Fig. 6. This calculated rate curve was found to agree with the experimental data and to be apparently proportional to the 1.9 powers of $[\mathrm{AA}]_0$. As to the influence of PA on the rate of the polymerization, if the influence of PA to PVP is similar to that of AA to PVP, the rate $V'$, may be expressed as follows:

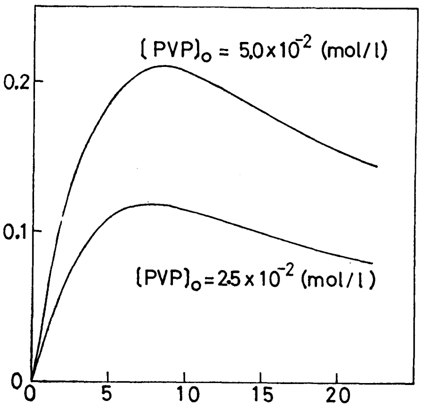

Fig. 13. Relation between $[\mathrm{AA}]_0$ and $f$.

$$V' = ([\mathrm{M_{AA}}]_0/[\mathrm{M}]_0)^{1.5}V \tag{B'}$$

where $[\mathrm{M}]_0$ is $[\mathrm{M_{AA}}]_0+[\mathrm{M_{PA}}]_0$ and where $[\mathrm{M_{AA}}]_0$, and $[\mathrm{M_{PA}}]_0$ are the volume-average concentrations of AA and PA respectively. The calculated rate, $V'$, defined by Eq. (B') with $K=67.4$ ($l$/mol) and $a=1.2[\mathrm{M}]_0+0.007/[\mathrm{M}]_0$ was apparently independent of the $[\mathrm{PA}]_0$ values, which are shown as Curves A and B ($V'_{(\mathrm{B})\mathrm{PA}=0}=9\times10^{-6}$ mol/$l\cdot$sec) in Fig. 5. As has been mentioned above, the polymerization of AA in the presence of PVP in the present study can be explained well by a mechanism considering the locally-concentrated AA in the vicinity of PVP. Moreover, this consideration can also be applied to the other reaction system. Endo, Numazawa, and Okawara[6] have described that the rate of the polymerization of methacrylic acid (MAA) in the presence of poly-*N*-vinyloxazolidone (PNVOx) went through a maximum at [PNVOx]/[MAA] being unity. By applying Eq. (B) to their results without any further consideration, the calculated rate curve was found rather to fit their experimental data with $K=300$ ($l$/mol) and $a=0.07$. The larger $K$ value obtained in their polymerization system can be explained reasonably as arising from a different magnitude of the interactive fource.

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