

## **Effect of Viscosity in the Radical Polymerization of Acrylic Acid in the Presence of Poly(4-Vinylpyridine) in Methanol**

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### SUMMARY

Acrylic acid (AA) forms a 1:1 hydrogen-bonded complex with the repeating unit of poly(4-vinylpyridine) (P4VP) in dilute solution of methanol. The rate enhancement of the polymerization of AA in the presence of P4VP in methanol coincided with the viscosity change of the same system.

### INTRODUCTION

It is known that the rate of radical polymerization of hydrogen bonding monomers are enhanced by the presence of interacting polymers. The effect of the added interacting polymers has been interpreted as the template effect where the aligned complexed monomer molecules on a template polymer are "zipped-up" in the propagation resulting in an increased rate of polymerization (FERGUSON and SHAH, 1968a, 1968b; BAMFORD, 1968, 1980), and as the matrix effect where the environments created by the domain of the added polymer influences the polymerization (MURAMATSU and SHIMIDZU, 1972). The polymer molecules are dispersed separately in a dilute solution forming individual polymer domains while in a concentrated solution the polymer molecules come to contact each other more closely forming a much larger polymer matrix. Therefore, the definition of the polymer domains created by the added polymer is desired in addition to other information such as the chemical reactivity (NIKOLAYEV and GALPERIN, 1967) and the quantity (the equilibrium constant of the complexation) (ENDO and OKAWARA, 1972) of the complexed monomer in order to consider the effect of added polymer. The initial rate of radical polymerization of acrylic acid (AA) in the presence of poly(4-vinylpyridine) (P4VP) in methanol solution is considered in relation to the viscosity of the system.

### EXPERIMENTAL

Reagent grade AA (Tokyo Kasei) was distilled and fractionally crystallized. 4-Vinylpyridine (4VP) (Fluka) and solvents were fractionally distilled and 2,2'-azobisisobutyronitrile (AIBN) (T.K.) was recrystallized from methanol. P4VP was prepared in  $\text{CHCl}_3$  with AIBN and purified by reprecipitating in diethyl ether. It was further extracted with diethyl ether in a Soxhlet apparatus for 4 days. The average molecular weight of the P4VP was measured to be  $2.90 \times 10^4$  with a Ubbelohde type viscometer in

ethanol/water (92/8 by weight) mixed solvent at 25°C according to the equation  $[\eta] = (M_v)^a$ , where  $K = 1.20 \times 10^{-2} \text{ cm}^3/\text{g}$  and  $a = 0.73$  (BOYES and STRAUS, 1956).

Polymerization of AA was carried out in glass ampules of capacity about 15 cm<sup>3</sup>. The reaction mixture was degassed by the freeze-thaw method and sealed under high vacuum. The conversion was measured by bromometry (LUCAS and PRESSMAN, 1938); the polymerization mixture was quantitatively dropped to 2 M NaOH to precipitate the added P4VP and the filtered solution was brominated and titrated in the dark. Duplicate titrations were performed for each polymerization mixture. For each polymerization system, blank titrations were performed with the same amount of P4VP.

Perkin-Elmer infrared spectrophotometer Type 597 and a refractometer by Bellingham and Stanley (London) were used.

### RESULTS AND DISCUSSION

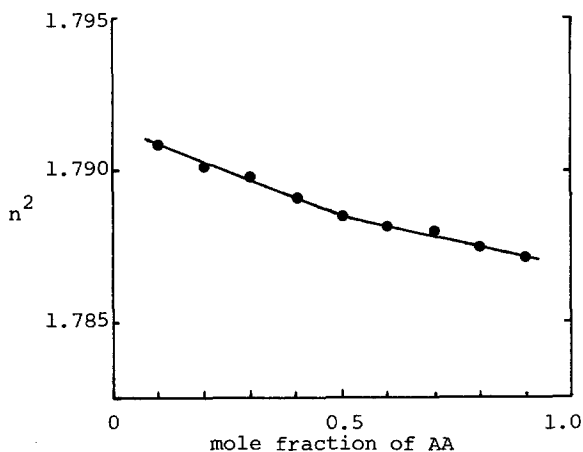
In the infrared, the hydrogen bonded O-H of AA at 2649 and 2575 cm<sup>-1</sup> shifted toward the lower energy side by 169 and 135 cm<sup>-1</sup> respectively, in CHCl<sub>3</sub> in the presence of pyridine when the mole fraction of AA was 0.2 at a constant total concentration of [AA + pyridine] = 3.51 M (TABLE 1).

TABLE 1.  
The IR absorption of bonded O-H of AA in CHCl<sub>3</sub>

Mole fraction of AA	[AA + Pyridine]=3.51 M	
1.0	2649 cm <sup>-1</sup>	2575 cm <sup>-1</sup>
0.8	2560	2490
0.6	2490	2460
0.4	2480	2450
0.2	2480	2440
	$\Delta\nu_{\text{OH}}=169 \text{ cm}^{-1}$	$\Delta\nu_{\text{OH}}=135 \text{ cm}^{-1}$

The stoichiometry of complexation between AA and the 4VP unit of P4VP was found to be 1:1 in methanol at the concentration [AA + P4VP] = 0.200 M by the Job's continuous variation method (JOB, 1928) as shown in Fig. 1. A 1:1 complex between the acidic proton of AA and the nitrogen of the pyridine ring was considered to be formed in methanol. The following polymerization and the viscosity measurements were

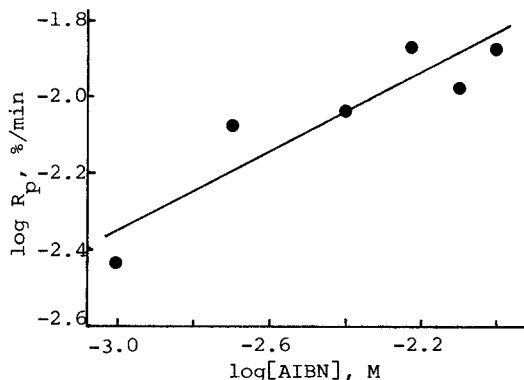
Fig. 1. Continuous variation plot of the square of refractive index,  $n^2$ , versus mole fraction of AA. [AA + P4VP] = 0.200 M in methanol at 25°C.



carried out always in methanol at 60°C at equimolar AA and 4VP unit concentrations.

The initial rate of the polymerization of AA was found to be proportional to 0.51 order of the AIBN concentration in the presence of P4VP at the equimolar concentration of  $[AA] = [P4VP] = 0.0600$  M as shown in Fig. 2. The termination may be regarded to be largely bimolecular reactions of the growing radicals at this

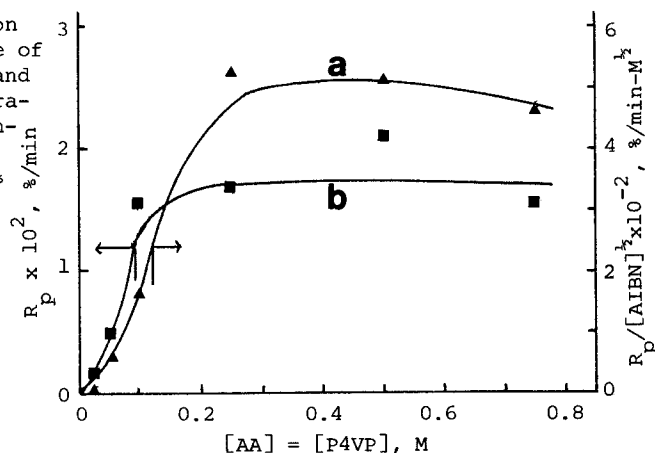
Fig. 2. Dependency of rate,  $R_p$ , on the initiator concentration in the presence of P4VP.  $[AA + P4VP] = 0.0600$  M in methanol at  $60^\circ\text{C}$ .



relatively small concentration of P4VP.

In the Fig. 3, the observed rate was plotted against the con-

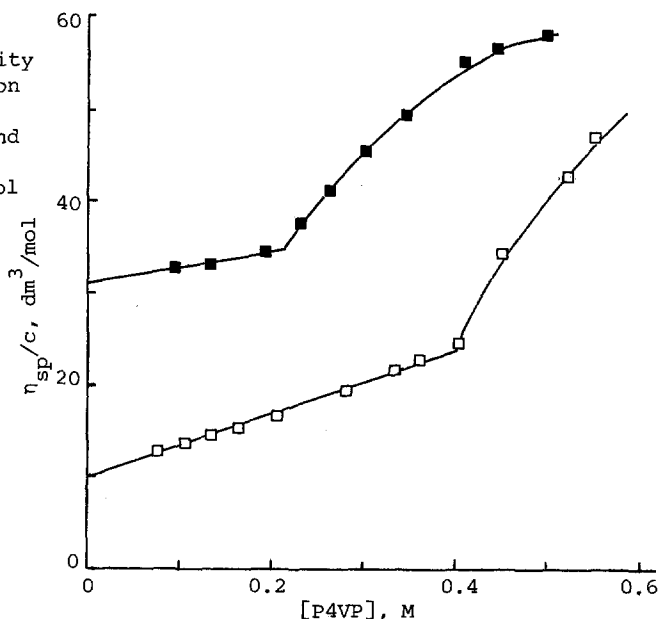
Fig. 3. Relation between the rate of polymerization and monomer concentration. In methanol,  $60^\circ\text{C}$ . (a) with 4.00 mole % of AIBN to AA monomer. (b) with  $[AIBN] = 4.00 \times 10^{-3}$  M.  $\bar{M}_v$  (of P4VP) =  $2.90 \times 10^4$ .



centration of AA in the presence of equimolar P4VP. The effect of the matrix concentration on the rate was examined in two series of experiments. In the plot a, the polymerization was carried out by using 4.00 mole % of AIBN with respect to the amount of AA and in the plot b, the molar concentration of AIBN was kept constant to be  $[AIBN] = 4.00 \times 10^{-3}$  M. In both cases enormous rate enhancement was observed across the matrix concentration of 0.2 M and the rate became approximately pseudo-zero-order with respect to the monomer concentration after this critical concentration region of P4VP.

On the other hand, as shown in Fig. 4, the reduced viscosity of P4VP measured at  $60^\circ\text{C}$  suddenly became large at  $[P4VP] = 0.4$  M in methanol indicating that the polymer molecules commenced forming larger matrix. When equimolar AA monomer to 4VP unit of the P4VP was present, the enhancement of the viscosity was observed in much dilute solution in P4VP at about 0.2 M. It is considered that

Fig. 4. The reduced viscosity of P4VP solution ( $\square$ ) and of equimolar AA and P4VP solution ( $\blacksquare$ ) in methanol at 60°C.  $M_v$  (of P4VP) =  $2.90 \times 10^4$ .



when the concentration of P4VP is sufficiently small, both a growing AA radical complexed to a P4VP molecule and uncomplexed AA monomer molecules can move relatively freely. However, it is possible that the termination reactions become significantly retarded when the continuous polymer matrix begins to prevail because the growing AA chain is complexed on the P4VP matrix and the mobility of the matrix becomes increasingly limited resulting in the rapid increase of the rate. In more concentrated solution of P4VP the system is filled with extensive polymer matrix and the monomer may move much slowly due to the complexation with the matrix, thus retarding the propagation significantly. The balance of retarded termination and propagation reactions that would occur at large matrix concentrations might have resulted in the pseudo-zero-order dependency of the rate on the monomer concentration. This experiment demonstrated that the rate enhancement was closely related to the viscosity of the polymerization system in the presence of interacting polymer.

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