Degradation of Aqueous Poly(vinylpyrrolidone) Solution by High-Speed Stirring*

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Synopsis

The effect of concentration on scission of poly(vinylpyrrolidone) ($\bar{p}_v = 6,700$) in aqueous solution by high-speed stirring at a speed of 30,000 rpm at 30°C was investigated. Concentration was varied from 0.04 to 2% g/ml. Polymer chains were ruptured to lower molecular weights with decreasing concentration. The rate constant of scission, k, and the limiting degree of polymerization, P_l, in Ovenall's equation calculated for the results were considerably changed in the polymer concentration range from 0.2 to 1% g/ml. The effect of addition of methyl orange on polymer scission was then studied, because the dye had been reported to increase the viscosity of aqueous poly(vinylpyrrolidone) solution because of unfolding of the macromolecule chains. However, no significant effect was found in the concentration range from 0.034 to 0.34 in the molar ratio of methyl orange to poly(vinylpyrrolidone).

INTRODUCTION

The authors have been studying degradation by high-speed stirring of solutions of various polymers such as poly(methyl methacrylate),[1–4] poly(methyl acrylate),[5] poly(α-methylstyrene),[5] polystyrene,[2,3,5] polyisobutylene,[2,5] and poly(ethylene oxide)[1,2,5,6] and the effects of polymer concentration[3,4,5] and solvent.[2,3,5] It was found that the rate of scission of the polymer chains was higher and the final chain length was shorter at lower polymer concentrations for all solvents.[3,5] It was also found that, at a certain low polymer concentrations, the rate of scission was higher and the final chain length was shorter in good solvents than in poor solvents.[3,5] In the previous paper, those results were discussed in terms of hydrodynamic volumes.[5]

In this study, poly(vinylpyrrolidone) (PVP) was chosen as a polymer for degradation because of its interesting property. PVP has a marked ability to bind a variety of small molecules to change its conformation. It is revealed that PVP stands far above any of the other synthetic macromolecules in binding.[7] Killmann and Bittler[8] studied the interaction between PVP and Blancophor dyes and found an expansion of the PVP molecule caused by electrostatic repulsion of the absorbed dye ions by means of viscosity and light scattering

measurements. Nakagaki and Shimabayashi[9] investigated the interaction between PVP and amino acids. Takagishi and Kuroki et al.[7,10] have been researching the interaction of PVP with methyl orange and its homologs in aqueous solution. According to the studies, addition of the dyes into aqueous PVP solution increases the viscosity of the solution, showing unfolding of the random coil of the polymer. They attributed these facts to the hydrophobic interaction between hydrocarbon portions of the dyes and nonpolar parts of the macromolecule.

The effect of polymer concentration of scission of the polymer chain was first investigated. Then, the effect of addition of methyl orange on the scission of PVP in solution by high-speed stirring was also investigated in order to ascertain the previous interpretation,[5] namely, that there is a relation between mechanical scission of polymer chains in solution and their hydrodynamic volumes. The effect of additives on the degradation of polymer solutions has only rarely been investigated.

EXPERIMENTAL

Materials

Poly(vinylpyrrolidone), PVP (K-90), was obtained from Tokyo Kasei Kogyo Corp. The nominal average molecular weight was 360,000. The intrinsic viscosity $[\eta]$ of aqueous solutions of the polymer at 30°C measured by the authors was 1.82 dl/g, and the viscosity-average molecular weight $\overline{M}_v$ was 740,000 according to[11]

$$[\eta] = 14 \times 10^{-5} \, \overline{M}_v{}^{0.70} \tag{1}$$

Water was used as solvent after purification through ion exchange resin. Methanol was used after distillation.

Specially pure-grade methyl orange was supplied by Wako Pure Chemical Industries, Ltd. Polymer and methyl orange were used without purification.

Stirring Apparatus and Method of Stirring

A T.K. Homomixer of HS-M type made by Tokushu-Kika Kogyo Co., Ltd., was used as high-speed stirrer. The stator, turbine, and vessel of the mixer were the same as those used in the previous experiment.[6]

A solution containing a given weight of polymer in 200 ml water was stirred in a 300-ml vessel made of stainless steel. Stirring speed was $30,000 \pm 500$ rpm. For keeping the temperature of the solution at $30° \pm 5°C$ and to keep the mixer safe from harm by superheating, 5 min of stirring and 5- to 10-min pauses for cooling were alternated. After stirring for a given time, about 10 ml stirred solution was removed and stirring was then continued. Dilute solutions of less than 0.2% g/ml were stirred batchwise.

Polymer Separation and Method of Measuring $[\eta]$ and Molecular Weight

Polymer solutions stirred for a given time were dried by a warm-air drier until their weights became constant. Intrinsic viscosities $[\eta]$ of recovered polymers with or without methyl orange were all measured in methanol at $30° \pm 0.02°C$

using an Ubbelohde viscometer. Methyl orange is practically insoluble in methanol, but can be considerably soluble in the presence of PVP. It was ascertained beforehand that, fortunately, methyl orange does not affect $[\eta]$ of PVP in any way. Viscosity-average molecular weight $\overline{M}_v$ was calculated from $[\eta]$ in methanol at 30°C by eq. (2), which was obtained by the authors using PVP's with different $\overline{M}_v$ calculated by eq. (1):

$$[\eta] = 15.6 \times 10^{-5}\, \overline{M}_v{}^{0.70} \tag{2}$$

Since the molecular weight distribution is considered to vary owing to scission of chains during stirring, it is most appropriate to estimate the number-average molecular weight $\overline{M}_n$ for calculation of the number of scissions, but $\overline{M}_v$ was used here according to custom for the sake of convenience.

Rate Constant of Scission, k, and Limiting Degree of Polymerization, P_l

Rate constant of scission, k, and limiting degree of polymerization, P_l, in Ovenall's[12] eq. (3) for obtained results were determined by the method described in the previous paper:[6]

$$\frac{dB_i}{dt} = k(P_i - P_l)n_i \qquad (P_i > P_l)$$
$$\frac{dB_i}{dt} = 0 \qquad (P_i \leq P_l) \tag{3}$$

where dB_i/dt is the rate of scission of molecules of degree of polymerization P_i; n_i is the number of such molecules; k is the rate constant of scission; and P_l is the limiting degree of polymerization below which molecules cannot be degraded.

RESULTS

Effect of Concentration on PVP Scission

Aqueous solutions containing 0.04% to 2% g/ml PVP were prepared and stirred at a speed of 30,000 rpm. Decrease in $[\eta]$ of recovered polymers is shown in Figure 1. The value of $[\eta]$ decreased rapidly at first and then slowly, reaching a constant value depending on the polymer concentration. It is found that the rate of decrease in $[\eta]$ increased and that the final $[\eta]$ decreased with decrease in polymer concentration. The tendency resembles results obtained for polystyrene, and other polymers.[3,5]

The relationship between number of scission per polymer molecule and stirring time is shown in Figure 2. The number of scissions per molecule, B_t/n_0, was calculated by eq. (4):

$$B_t/n_0 = P_0/P_t - 1 \tag{4}$$

where P_0 and P_t are the degrees of polymerization before stirring and after stirring for time t, respectively. The number of scissions increased rapidly at first and then slowly.

The k and P_l values obtained for the above B_t/n_0-versus-time curves are plotted versus polymer concentration in Figure 3. It is found that P_l becomes smaller and k larger with decreasing concentration and that changes in P_l and
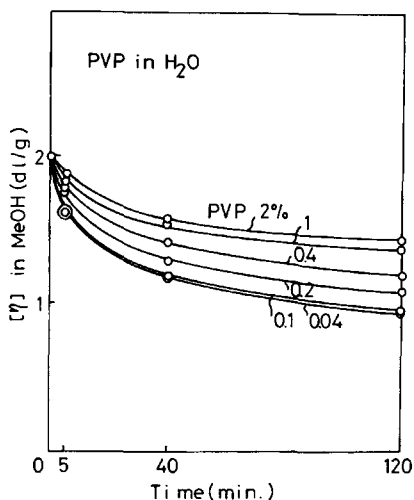
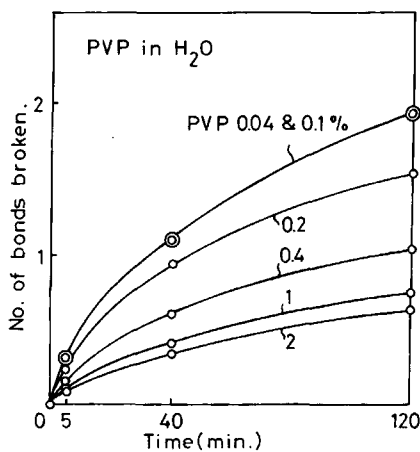Fig. 1. Degradation of PVP by high-speed stirring (30,000 rpm, 30°C).

Fig. 2. Number of bonds broken per polymer molecule during high-speed stirring (30,000 rpm, 30°C).

k values are remarkable in the concentration range of 0.2% to 1% g/ml. The former tendency had been found for other polymers in several solvents.[3,5]

Effect of Addition of Methyl Orange on Viscosity of Aqueous PVP Solution

As described above, addition of methyl orange to aqueous PVP solution was found to increase the viscosity of the solution.[10] The effect of methyl orange on viccosity of aqueous PVP solutions is shown in Figure 4, where the ordinate indicates the falling times of aqueous PVP solutions with or without methyl orange through a capillary (viscosities), and the abscissa shows molar ratios of methyl orange to PVP. Viscosity was scarcely increased with methyl orange at low concentrations, while it increased remarkably at high polymer concentrations.
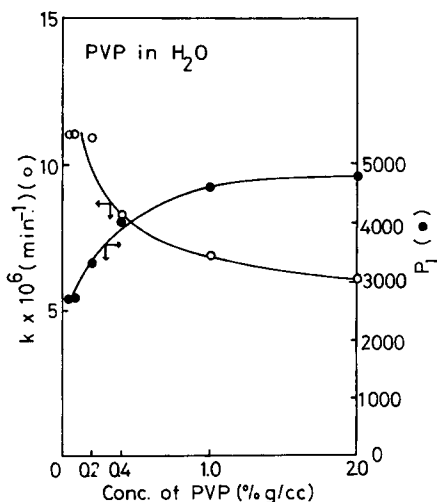
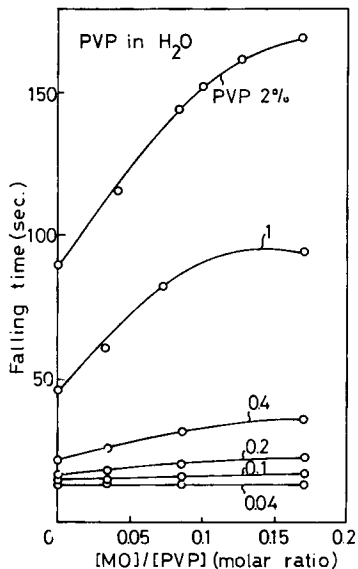Fig. 3. Effect of concentration on PVP on k and P_l (30,000 rpm, 30°C).

Fig. 4. Effect of methyl orange on viscosity of aqueous PVP solution.

It is noted that 0.1%, 0.2%, and 0.4% g/ml PVP solutions containing methyl orange at a molar ratio of 0.17 had nearly the same viscosities as 0.2%, 0.4%, and 1.0% g/ml PVP solutions without methyl orange, respectively. The molar ratio of 0.17 is equal to a weight ratio of 0.5 of methyl orange to PVP.

The effect of methyl orange on the viscosity can be observed from another viewpoint, as shown in Figure 5, where relative viscosities are plotted on the ordinate. The effect was found largest for the solution containing 1% g/ml PVP, while the effect was little for the solution of 0.04% g/ml.

In order to elucidate the effect of addition of methyl orange on $[\eta]$ of aqueous PVP solution, methyl orange and PVP at a certain molar ratio were dissolved
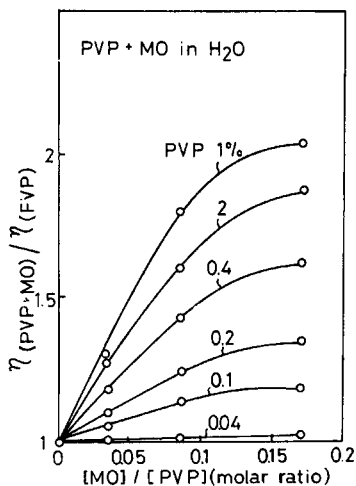
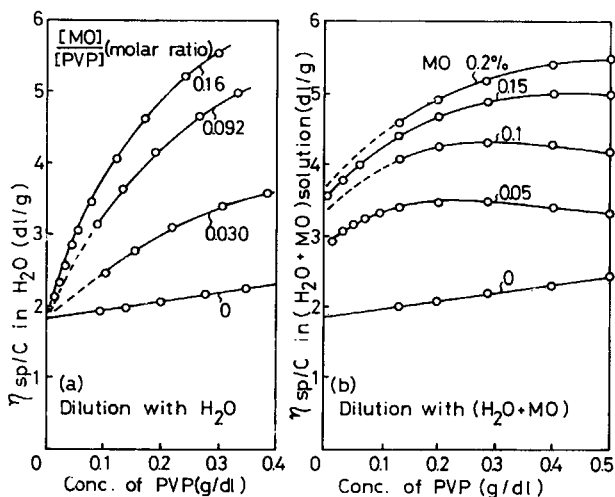Fig. 5. Effect of methyl orange on viscosity of aqueous PVP solution.

Fig. 6. Change in η_{sp}/C of aqueous (PVP plus methyl orange) solution with dilution.

in water, and $[\eta]$ was measured diluting the solution with pure water. The results are shown in Figure 6(a), where η_{sp}/C-versus-C curves (where C is polymer concentration) are not linear except for the solution containing only PVP; but all of the curves seem to converge to a point by extrapolation. When a certain weight of PVP was dissolved in aqueous methyl orange solution with a certain concentration and diluted with the methyl orange solution, the relationship between η_{sp}/C and C showed complicated curves as shown in Figure 6(b). In this case, the molar ratio of methyl orange to PVP increased with dilution, reaching infinity at zero polymer concentration, but it seemed that higher intrinsic viscosities were measured for PVP solutions which were diluted with higher concentrations of methyl orange solution.
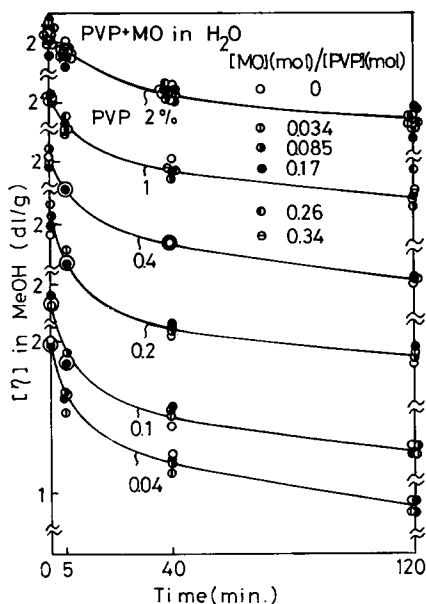
Fig. 7. Degradation of aqueous (PVP plus methyl orange) solution in various molar ratios of methyl orange to PVP by high-speed stirring (30,000 rpm, 30°C).

Effect of Addition of Methyl Orange on PVP Scission by High-Speed Stirring

Degradation of an aqueous PVP solution containing methyl orange by high-speed stirring at a speed of 30,000 rpm at 30°C is shown in Figure 7, where $[\eta]$ of recovered mixtures of PVP and methyl orange in methanol at 30°C is plotted as the ordinate. It was established beforehand that addition of methyl orange does not affect the value of $[\eta]$ of PVP solution in methanol as described above. It was also confirmed by superposition of starting points that any deviations are within experimental error. Not only starting points but also all the degradation curves can be superposed within experimental error, regardless of addition of methyl orange, for each solution with identical PVP concentration. In the case of 1% g/ml PVP solution, an equivalent weight of methyl orange to PVP (that is, 100 parts per 100 parts resin) was indeed added to the solution at highest methyl orange concentration. 100 phr methyl orange corresponds to a molar ratio of 0.34. 2% g/ml PVP solution could dissolve 75 phr methyl orange at highest at 30°C (molar ratio of methyl orange to PVP, 0.26). The other solutions contained 50 phr methyl orange at highest (molar ratio 0.17). Aqueous PVP solutions containing methyl orange at such high concentrations were stirred, and $[\eta]$ of the stirred polymers was measured. The curves were slightly scattered, but no tendency with addition of methyl orange was found. Consequently, it was concluded that the addition of methyl orange does not meaningfully affect scission of PVP chain by high-speed stirring.

In contrast to the above, the effect of concentration of the polymer can be clearly found in Figure 7, that is, the lower the concentration, the faster the degradation.

DISCUSSION

The effect of concentration of the macromolecule PVP on scission of the polymer by high-speed stirring was found as observed above, but no significant effect of addition of the small molecules methyl orange was found. The latter results are reminiscent of the findings that the scission of long-chain poly(methyl methacrylate) was little if at all suppressed by addition of short-chain PMMA.[4] The authors' expectation that there might be a certain effect of methyl orange on the scission of PVP if it unfolded the random chains of the polymer could not be detected.

Reasons for the results can be postulated as follows. (1) The effect of expansion of the polymer chain on scission can more easily be detected for the solution with lower polymer concentration;[3,5] however, the increase in viscosity or the expansion of polymer chain by the addition of methyl orange was not so high for such solution that the effect of the dye could not be detected. (2) Increase in viscosity by adding methyl orange to aqueous PVP solution may result from complicated factors such as intermolecular and intramolecular interactions. If unfolding (expanding) of conformation of polymer chains is not so large as the increase in viscosity, the effect of the expansion on the scission is difficult to detect. (3) Absorption (binding) of methyl orange by PVP is not so strong because of hydrophobic interaction that the binding can no longer hold under enough high shear to rupture polymer chains. In other words, viscosities of PVP solutions containing methyl orange might be shear dependent like poly(acrylic acid) and poly(methacrylic acid).[13,14] It might be expected that the viscosities approach the ones without methyl orange. Unfortunately, probably due to a relatively narrow shear-rate variation range, the authors could not find a shear dependence for 1% g/ml aqueous PVP solutions containing methyl orange in molar ratios from 0 to 0.17 under shear rates from 7.16 to 71.6 sec^{-1}. If so, the effect of methyl orange on unfolding the chains may be decreased. Thus, the effect of the dye on the scission was decreased or eliminated. The authors consider that the third possibility is more probable than the others.

The authors intend to investigate the effect of change in the conformation of polymer chains on scission by another method.

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