

Crosslinking Aqueous Poly(vinyl pyrrolidone) Solutions by Persulfate

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Synopsis

Aqueous solutions with 1.5 to 6.5 wt-% poly(vinyl pyrrolidone), PVP, are converted to stable gels by reaction with potassium persulfate. Large quantities of persulfate are needed for high-modulus gels, 50% to 150% of the weight of PVP being required typically. The shear modulus G' can be measured during reaction by making the gel the restoring element in a simple torsion pendulum. The increase in modulus to a maximum plateau value of G'_{\max} can be expressed as a first-order process:

$$-\ln[1 - (G'/G'_{\max})] = Kt$$

where t is elapsed time of reaction and K increases with the square root of polymer concentration. G'_{\max} varies with the second power of the polymer concentration. It also increases rapidly with increasing temperature of reaction and with persulfate/PVP ratio.

INTRODUCTION

Poly(vinyl pyrrolidone), PVP, is a water-soluble polymer which exhibits excellent complexing and colloidal properties as well as physiological inertness. Aqueous PVP is permanently gelled when crosslinked by reaction with certain chemical reagents or irradiated with ultraviolet light or gamma rays. Such gels have found biomedical and industrial applications.

It has been shown that the large fraction of water within gel materials is related to their high biocompatibility.¹ Uncrosslinked PVP has had a long history of use in the medical and pharmaceutical fields and has often been found to be nontoxic and nonthrombogenic. The expected low antigenicity of PVP gels makes them suitable for many biomedical applications. The gels have been considered for use as hemodialysis membranes and implantable drug delivery systems.^{1,2} Gels made from a copolymer of vinyl pyrrolidone and hydroxyethyl methacrylate have found applications as soft contact lenses.³ A composite material prepared from a PVP hydrogel and silicone rubber has been investigated for possible applications as an artificial heart component and a blood- and tissue-compatible interface.¹

PVP gels have found industrial applications as well. Gels prepared by treatment of aqueous PVP (K-30) with hydrazine and hydrogen peroxide are useful as thickness, flocculants, protective colloids, and absorbents.⁴ Adding dried, powdered crosslinked PVP (prepared by gamma irradiation) to inorganic acids (such as H_3PO_4 or H_2SO_4) has given gelled compounds useful as sprayable fertilizers and for cleaning surfaces such as concrete or tarnished aluminum.^{5,6}

PVP gel packings are used for the purification of solutions containing acids, aromatic alcohols, and iodine and the chromatography of macromolecules such as ragweed pollen and human serum proteins.^{7,8}

Gels are formed by γ irradiation^{9,10} and by ultraviolet irradiation^{11,12} of aqueous PVP solutions. PVP gels also may be formed from aqueous solution by reaction with strong alkali, inorganic persulfates, or peroxides. Gelation with alkali involves opening of the pyrrolidone ring to form poly(vinyl aminobutyric acid) units.¹³ These gels are of little practical use, however, as they are non-continuous or very weak at best.

In the case of persulfate-crosslinked gels the exact mechanism of linkage is not known. Presumably it involves abstraction of a hydrogen atom from the ring or vinyl group with the subsequent formation of a crosslink at this site. Upon thermal decomposition in aqueous solution persulfate primarily yields two species, the sulfate ion radical and the hydroxyl radical, which are capable of abstracting a hydrogen atom from the polymer molecule. In addition to intermolecular crosslinking, chain scission and other competing reactions may take place.

Two of the most interesting features of gelation of PVP with persulfate are the extremely high concentrations of persulfate (up to 200% based on polymer) required to form gels of reasonable strength and the strong dependence of G'_{\max} on the reaction temperature.¹⁴ Both of these results suggest that other reactions in addition to intermolecular crosslinking are competing for the persulfate.

EXPERIMENTAL PROCEDURE

The simple torsion pendulums used are made from a glass rod which is the inner cylinder and a test tube which is the outer cylinder.¹⁵ The rod is centered by a piece of aluminum screen. The bottom end of the rod is pointed to act as a bearing.

The polymers were all derived from commercial materials and are listed in Table I. Masterbatch solutions of PVP K-30 and K-90 were prepared by dis-

TABLE I
Polymer Samples Studied

Description and Source	Designation	Intrinsic viscosity ^a	$M_v \times 10^{-3}$
1. Fractionally precipitated ²² from PVP:			
K-30	F-1	0.17	25
K-60	F-2	0.36	75
K-60	F-3	0.59	150
K-90	F-4	0.90	275
K-90	F-5	1.20	420
2. Acetone-washed samples:			
K-30	A-1	0.29	55
K-60	A-2	0.61	160
K-90	A-3	1.64	650
3. As received from GAF:			
K-30	G-1	0.23	40
K-90	G-2	1.08	360

^a Intrinsic viscosity measured at 30°C in water, dl/gm; $[\eta] = 1.4 \times 10^{-4} M_v^{0.70}$,²³

solving the polymer as received from GAF Corporation in distilled water. The solutions (10% by weight PVP) were then rocked for 25 hr to assure uniformity. A masterbatch solution of PVP K-60 was prepared by precipitating the polymer from a 45% aqueous solution as received from the manufacturer by addition of acetone. The precipitate was dried in an air oven at 50°C for 24 hr prior to being put into solution. Acetone-washed samples of PVP K-30 and K-90 were prepared from the masterbatch solutions in a similar manner. Various molecular weight samples of PVP were prepared by fractional precipitation of dilute K-30, K-60, and K-90 solutions using acetone as the nonsolvent. Lower-concentration solutions were prepared by dilution of the masterbatches. To minimize bacterial growth, solutions were stored at 4°C.

When crosslinking the polymer with persulfate the required amount of persulfate and 7-g PVP solution were added to a test tube and stirred to assure complete solution (heating to 40°C was required when using high concentrations of persulfate). The pendulum was inserted through a piece of screening (to center the shaft) into the solution. The solution was sparged with nitrogen for 30 min prior to being immersed in the water bath. Timing of the experiment began immediately after immersion.

The gel was tested by gently tapping the moment arm of the pendulum. The frequency of the oscillation was determined by timing a certain number of cycles. Initially, readings were taken every minute, then later every 5 or 10 min depending on the time required to reach an equilibrium modulus.

The storage modulus for the gel was calculated by¹⁶

$$G' = \omega^2 I [(1/r_1)^2 - (1/r_2)^2] / 4L\pi \quad (1)$$

where G' is storage modulus (dynes/cm²); ω is frequency of oscillation (rad/sec); I is moment of inertia, usually 3100 g-cm²; L is height of gel, 7.0 cm; r_2 is radius of test tube, 0.63 cm; and r_1 is radius of bob, 0.25 cm.

RESULTS AND DISCUSSION

Modulus-Time Behavior

For any set of conditions the gelation follows the same general modulus-time behavior. After a brief induction period, incipient gelation occurs. In a monodisperse polymeric solution that is randomly crosslinked, incipient gelation occurs when there is one crosslink for every two molecules.¹⁷ At incipient gelation the gel is pituitous, but with further crosslinking becomes tighter and more rigid as evidenced by the sharp rise in the storage modulus. The modulus reaches a plateau when the network tightens to the extent where macroradicals can no longer easily diffuse to an active crosslinking site. Self-crosslinking, via ring formation, may continue to occur at the free ends. In some cases the gel becomes extremely brittle with increased tightening of the network and develops cracks or pulls away from the pendulum or walls of the test tube (syneresis). It was not possible to obtain a true value of the maximum modulus for such gels.

One can propose a first-order kinetic scheme in which the rate of crosslinking is proportional to the number of crosslink sites available. Since the storage modulus is proportional to the number of crosslinks through rubber elasticity the following expression may be obtained:

$$d(G'/G'_{\max})/dt = K[1 - (G'/G'_{\max})] \quad (2)$$

Then,

$$-\ln [1 - (G'/G'_{\max})] = Kt \quad (3)$$

where G' is storage modulus (dyn/cm^2); G'_{\max} is maximum modulus (dyn/cm^2); K is rate constant (min^{-1}); and t is time (min).

The fractional conversion, G'/G'_{\max} , is a convenient variable for plotting purposes, especially as G'_{\max} typically varied from 1,000 to 100,000 dynes/ cm^2 over the concentration and temperature ranges studied. A plot of $-\ln [1 - (G'/G'_{\max})]$ versus time is well represented as a straight line for most of the data (Fig. 1). The rate constant K is the slope of the line. The effect of polymer concentration and molecular weight, persulfate concentration, temperature, and solution pH on the rate of crosslinking and the maximum modulus is discussed in the sections that follow.

Effect of Polymer Concentration and Molecular Weight

The rate of gelation and the maximum modulus increase with increasing polymer concentration indicating a higher crosslinking efficiency with the more concentrated solutions. At high concentration the polymer molecules associate more readily, therefore increasing the probability of a crosslink being formed. For a given sample, G-2, at 80°C with a persulfate/PVP ratio of 1.0, K depends on PVP concentration (wt-%) in the following manner:

$$K = (0.100 \pm 0.005)(c)^{1/2} \quad (4)$$

The maximum modulus increases with the 1.90 to 2.05 power of the concentration except for the more dilute gels, as seen in Figure 2. The dependence of the maximum modulus on the polymer concentration changes only slightly with persulfate concentration. This may be a real effect, but it is probably due to experimental variability. Gels that form by binary association equilibrium between loci on the polymer chains should show a dependence of modulus on square of concentration if there are no loose end effects.¹⁶ For gelatin gels in water, the maximum modulus has been found to vary with the square of the

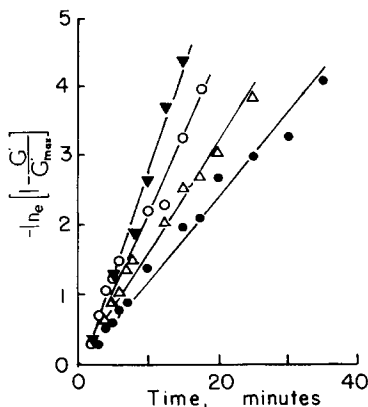


Fig. 1. Effect of PVP concentration on the rate of gelation (sample G-2, persulfate/PVP = 1.0, 80°C). Lines correspond to eq. (4). PVP concentration, in wt-%, is 1.5 (\bullet), 2.5 (Δ), 5.0 (\circ), and 6.5 (\blacktriangledown).

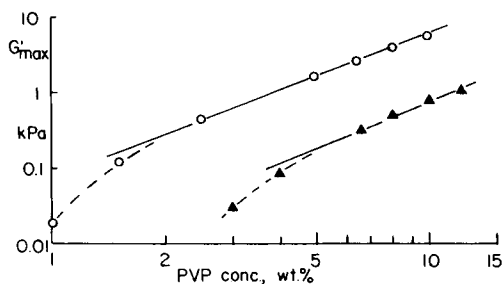


Fig. 2. Dependence of G'_{max} on polymer concentration (sample G-2, 80°C). Persulfate/PVP = 0.5 (▲) and 1.0 (○).

concentration.¹⁶ Van Brederode has found that the maximum modulus of poly(ethylene oxide) gels formed by gamma irradiation varies with concentration to the 2.25 power.¹⁸ As the lower critical concentration is approached, the maximum modulus drops off rapidly as shown by the dotted lines in Figure 2.

Increasing the polymer molecular weight from 25,500 to 150,000 greatly increases both the gelation rate and G'_{max} . The rate and G'_{max} are essentially constant over the molecular weight range of 200,000 to 650,000 (Figs. 3 and 4). The results may be explained by the following analysis. Suppose that sites at or near

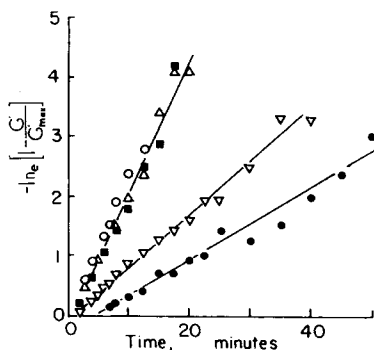


Fig. 3. Effect of polymer molecular weight on rate of gelation for fractionated samples (5% PVP, persulfate/PVP = 1.5, 80°C). Samples F-1 (●), F-2 (▽), F-3 (■), F-4 (Δ), and A-3 (○).

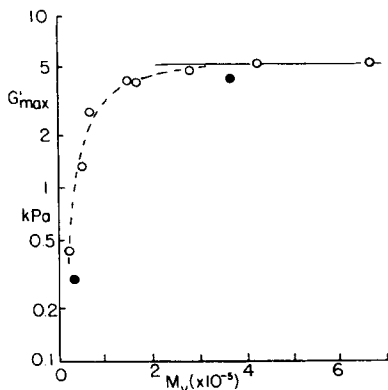


Fig. 4. Dependence of G'_{max} on polymer molecular weight (5% PVP, persulfate/PVP = 1.0, 80°C). Hollow circles represent samples precipitated from aqueous solution by addition of acetone.

the ends of the polymer chain are unreactive. Then at low molecular weight the number of reactive sites is increased with increasing initial molecular weight since the number of chain ends is reduced. At high molecular weight, however, the number of chain ends may be sufficiently low so that further increasing the molecular weight does not significantly increase the reactivity of the molecule.

The various molecular weight samples were prepared by fractionation of the masterbatch solutions using acetone as the nonsolvent. The maximum modulus obtained for solutions in which the polymer had been precipitated from acetone was found to be greater than that found for samples which had not been precipitated. This result was initially thought to be entirely a molecular weight effect since washing with acetone removes low molecular weight fractions (including residual monomer). From Figure 4 it can be seen that the moduli of the nonprecipitated samples fall below the data of the fractionated samples. This indicates that although removal of low molecular weight fractions increases the polymer average molecular weight, this increase alone does not explain the rise in G'_{\max} . It is possible that monomer present in nonprecipitated samples (GAF reports that PVP K-30 and K-90, as received, contain 1% residual monomer) polymerizes, thus competing with polymer for the persulfate.

Effect of Persulfate Concentration and Temperature

The theory of rubber elasticity relates the storage modulus to the absolute temperature and the crosslink density, $N/2$, by¹⁶

$$G' = NRT \quad (5)$$

where N is chain density (moles of chains/cm³); R is gas constant (8.7×10^7 ergs/mol-K); and T is the absolute temperature (K). Assuming that each molecule of persulfate abstracts two hydrogen atoms to produce a single crosslink, one may calculate the theoretical requirement of persulfate for a given value of the storage modulus and temperature. The actual requirement may be estimated by relating the initial persulfate concentration, the time to reach G'_{\max} , and data¹⁹ for the decomposition of $K_2S_2O_8$.

Reacting 7 g of a 5% PVP K-90 solution containing 0.35 g of $K_2S_2O_8$ at 80°C yields a gel with a maximum modulus of 17,000 dynes/cm². The theoretical requirement of $K_2S_2O_8$ for this gel is about 2×10^{-5} g, which is approximately 1/1000 of the amount consumed during the reaction (0.02 g). The requirement of persulfate over and above the amount predicted by rubber elasticity points to the existence of competing reactions. The conclusion is further supported by the strong dependence of G'_{\max} on the reaction temperature as shown in Figure 5. Increasing the reaction temperature from 50 to 95°C increases the maximum modulus by a factor of 20. This indicates an increase in the efficiency of gelation with temperature, perhaps due to crosslinking becoming the more favored reaction at high temperature.

It had to be determined whether or not the measurement temperature was responsible for the above-mentioned effect on G'_{\max} . For a gel which obeys the equation of rubber elasticity, eq. (5), a linear relationship should exist between G' and the measurement temperature. A sample was reacted at 95°C until G' reached a maximum. The modulus of the gel was then measured over the tem-

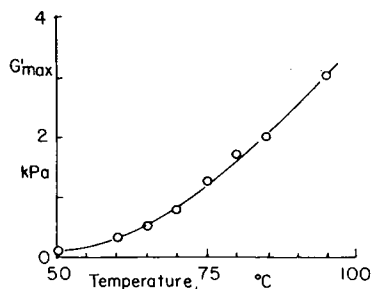


Fig. 5. Dependence of G'_{\max} on reaction temperature (5% G-2, persulfate/PVP = 1.0).

perature range 10 to 95°C. Figure 6 shows that although a linear relationship between G' and temperature does exist over the range investigated, the intercept for $G' = 0$ is not $T = 0$ K as predicted by eq. (5). A similar result was found by Van Brederode¹⁸ for poly(ethylene oxide) gels. He attributed this effect to water becoming a poorer solvent with increased temperature, hydrophobic bonding serving as the source of the additional crosslinks with rise in temperature. However, because G' was found to vary linearly with measurement temperature, the hydrophobic bonding must be a relatively constant factor over the range 10–95°C. Based on the preceding results it is reasonable to conclude that G'_{\max} changes drastically with temperature primarily owing to crosslinking becoming the more favored reaction at high temperature and not simply because the modulus is being measured at a higher temperature.

Crosslinking of PVP with persulfate involves abstraction of a hydrogen atom from the polymer chain by an SO_4^- or OH radical. The macroradical thus formed moves by virtue of molecular or segmental diffusion to another macroradical and forms a stable covalent crosslink. Other reactions in addition to crosslinking are possible.

The macroradical may rearrange to a more stable state by chain scission, via disproportionation, in the neighborhood of the unpaired electron:

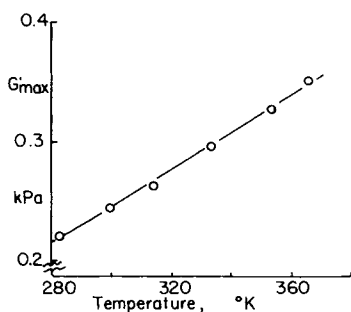
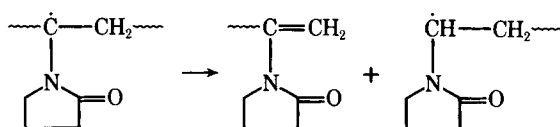
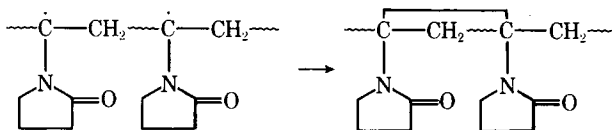


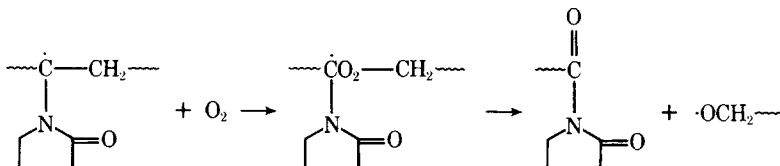
Fig. 6. Dependence of G' on measurement temperature (4% G-2, persulfate/PVP = 1.0). Originally reacted to G'_{\max} at 95°C.

Intramolecular crosslinking may occur giving rise to ring formation:



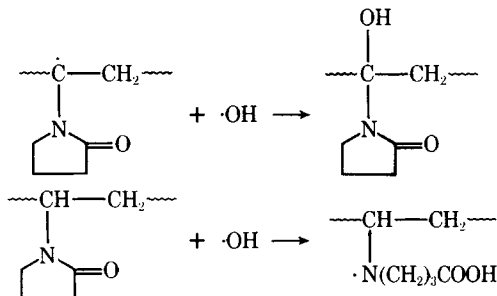
A microgel results when radicals undergo intramolecular crosslinking. Both chain scission and intramolecular crosslinking decrease the hydrodynamic volume of the polymer molecule.¹⁷

In the presence of oxygen, the macroradicals may decay by oxidative degradation:



Oxidative degradation is most likely to occur during the initial stage of the reaction as some dissolved oxygen may still be present in the solution despite sparging of the reaction mixture with nitrogen.

Hydrolysis may occur either by direct addition of $\cdot\text{OH}$ to an active site on a macroradical or by reaction of a hydroxyl radical and a polymer molecule with subsequent opening of the pyrrolidone ring to form amino acid units:



The ring opening has been reported to occur primarily in the presence of strong acid or alkali.¹³ The effect of pH on the extent of amino acid formation is discussed in the next section.

Other competing reactions of possible significance include (i) polymerization of residual monomer, (ii) deactivation of macroradicals by reaction with sulfate in radicals, (iii) deactivated by formation of water and oxygen from two hydroxyl radicals.

The maximum modulus is extremely dependent on persulfate concentration (Fig. 7). The dependence decreases with increasing polymer molecular weight. However, G'_{max} for samples of acetone-washed K-30 and K-90 (A-1, A-2, A-3) was found to depend on persulfate concentration to a higher power than for nonprecipitated K-30 and K-90 (G-1 and G-2). This is true despite the fact that washed samples have a higher molecular weight. This result further supports the conclusion that the effect of acetone washing is not merely an increase in molecular weight. On the other hand, persulfate appears to have almost no effect on the rate of gelation. Runs at 50%, 100%, and 200% all gave the same value for K in eq. (3).

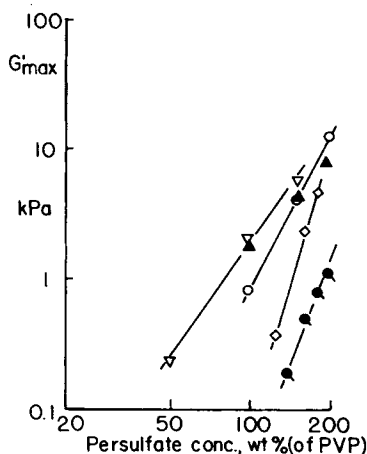


Fig. 7. Dependence of G'_{\max} on persulfate concentration (5% PVP, 80°C). Samples G-1 (●), A-1 (◇), A-2 (○), G-2 (▲), and A-3 (▼).

An Arrhenius plot for the temperature dependence of the rate constant yields an activation energy for gelation of 15.8 kcal/mol. This is based on runs at 70, 80, and 95°C with 5% G-2 (persulfate/PVP = 1.0).

Effect of pH

The effect of pH on the gelation of PVP was investigated over the range of pH 1 to 13 by addition of H_2SO_4 and KOH. For a 5% K-90 solution containing 50% $K_2S_2O_8$ (based on polymer), the maximum modulus is essentially constant between pH 3 and pH 12. At the extremes of pH, G'_{\max} increases markedly, as shown in Figure 8. The latter effect is contrary to that observed by Charlesby for gamma irradiation of PVP.⁹ In the studies involving irradiation of PVP, gelation is inhibited at the extremes of pH due to electrostatic charges being set up on the polymer chains. It was shown by Oster and Immergut²⁰ that at pH 7 PVP is electrically neutral, but at low pH the molecule is positively charged, and at high pH the molecule is negatively charged.

Opening of the pyrrolidone ring to form amino acid units has been observed only at high and low pH. Figure 8 also shows the results obtained by Frank²¹ for the hydrolysis of PVP upon reaction of 2% PVP in NaOH or HCl at 100°C. As can be readily discerned, conversion to polymeric amino acid and the G'_{\max} behave similarly as a function of pH. It is reasonable to assume that for gelation with persulfate the increase of G'_{\max} at extremes of pH is associated with the formation of amino acid units on the polymer chain.

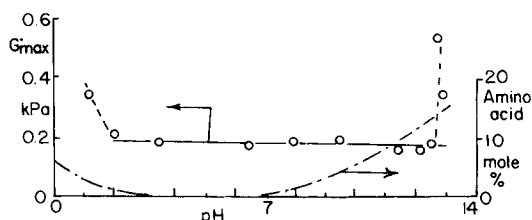


Fig. 8. Dependence of G'_{\max} on pH (5% G-2, persulfate/PVP = 0.5, 80°C). Lower line is the equilibrium conversion of PVP to polymeric amino acid at 100°C.²¹

Gamma irradiation of polymers in aqueous solution involves radiation of high energy and leads to formation of hydroxyl radicals upon radiolysis of the water. The existence of radicals should induce amino acid formation at high and low pH. If conversion to polymeric amino acid is indeed related to the G'_{\max} -versus-pH behavior found for gelation with persulfate, one might expect the dose to gel in Charlesby's work to decrease, rather than increase, at extremes of pH. However, dose-to-gel behavior may not be indicative of equilibrium modulus behavior. Also, radicals or polymer molecules may not behave similarly with and without the presence of ionizing radiation.

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