

Aging and Loss of Flocculation Activity of Aqueous Polyacrylamide Solutions

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Synopsis

There is a rapid and a slow stage in the decrease of reduced specific viscosity versus time (aging) for a solution of a high intrinsic viscosity polyacrylamide in water. The rapid stage is irreversible and has a fairly high temperature coefficient. Results of the latter type are usually associated with a weak-link scission mechanism, but they can also be reconciled with a disaggregation mechanism. A disaggregation mechanism is also indicated for the rapid stage by an increase in the first-order rate constant with a decrease in the polymer concentration or an increase in the shear rate and by the absence of the rapid stage during the aging of the same sample in formamide. Chemical changes in the polymer are suspected as being responsible for the RSV change during the slow stage in the aging of the high intrinsic viscosity polyacrylamide and also in the aging of a polyacrylamide of low intrinsic viscosity. The aging of the polyacrylamide of high intrinsic viscosity is paralleled by a decrease in the ability of the polymer to increase the subsidence of kaolin suspensions. This decrease in the flocculation activity is attributed to a weakening of the interparticle bridging by a change from a strong adsorption of the bridging polymer to two particles to a strong adsorption of the bridging polymer to one particle but weak adsorption of the bridging polymer to the other particle.

INTRODUCTION

Polyacrylamide of high intrinsic viscosity dissolved in water undergoes a slow aging (loss of viscosity) during storage at room temperature. Narkis and Rebhun¹ have proposed that the disaggregation of entangled polyacrylamide molecules is being completed during aging. They suggest that the entanglement originates because of the random growth of polymer chains during the polymerization.

Fibrillar aggregates appear to be present in aqueous solutions of a high intrinsic viscosity polyacrylamide. They can be observed by electron microscopy when a solution is dilute enough to deposit individual molecules during the preparation of specimens by evaporation.^{2,3} Electron microscopic studies on aqueous solutions of other water-soluble polymers also suggest fibrillar aggregates.^{4,5} A recent electron microscopic study on aqueous solutions of poly(sodium ethylene sulfonate) showed that the aggregation was changing during aging.⁶

Solutions of other water-soluble polymers undergo similar aging, but quantitative studies have not been made. We have found that high in-

intrinsic viscosity poly(ethylene oxide) loses viscosity rapidly at 0.10% concentration in water at 5°C. Aqueous solutions of polyvinylpyrrolidone and poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) were aged to complete the suspected disaggregation of the polymer molecules before these polymers were used in adsorption measurements.^{7,8}

Our interest in the aging of aqueous polyacrylamide solutions is related to our efforts to define the optimum characteristics of a water-soluble polymer for the flocculation of particulate suspensions. As was pointed out by Narkis and Rebhun, there is the question of whether aggregates or molecules exist in unaged solutions. Molecular weight measurements are meaningless without a knowledge of the state of solution of the polymer molecules. Also, the state of solution of the polymer molecules must be known before the adsorption characteristics can be related to their effectiveness in flocculation. This paper presents some of our work which relates the aging to the loss of flocculation activity and gives some additional insight into what is happening during the aging process.

RESULTS AND DISCUSSION

Reduced specific viscosities (RSV) were used to follow the aging of a high molecular weight sample of polyacrylamide. The RSV is related as follows to the intrinsic viscosity by Martin's equation:⁹

$$\log(\eta_{sp}/c) = \log(\eta_{sp}/c)_{c=0} + kc(n_{sp}/c)_{c=0} \quad (1)$$

When intrinsic viscosity is high and the polymer concentration is low, the last term in eq. (1) becomes negligible ($k = 0.15$), and the RSV is very

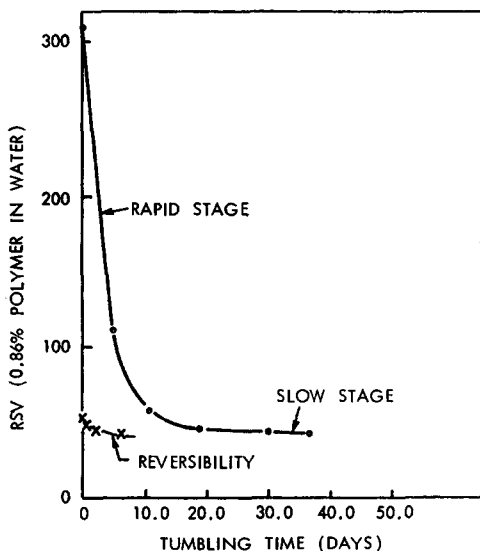


Fig. 1. Aging of polyacrylamide of high intrinsic viscosity in water; 0.86% sample A; room temperature.

close in magnitude to the intrinsic viscosity. An intrinsic viscosity is usually considered to be proportional to the ratio of the effective volume of the polymer molecule to its molecular weight,¹⁰ so that an RSV would be expected to be affected by a change in the extension of the molecule and/or the molecular weight.

Two processes appear to be occurring simultaneously to give a rapid stage and a slow stage in the aging of a polyacrylamide of high intrinsic vis-

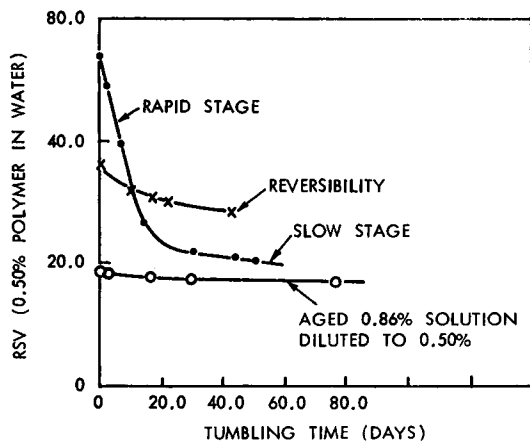


Fig. 2. Aging of polyacrylamide of high intrinsic viscosity in water; 0.50% sample A; room temperature.

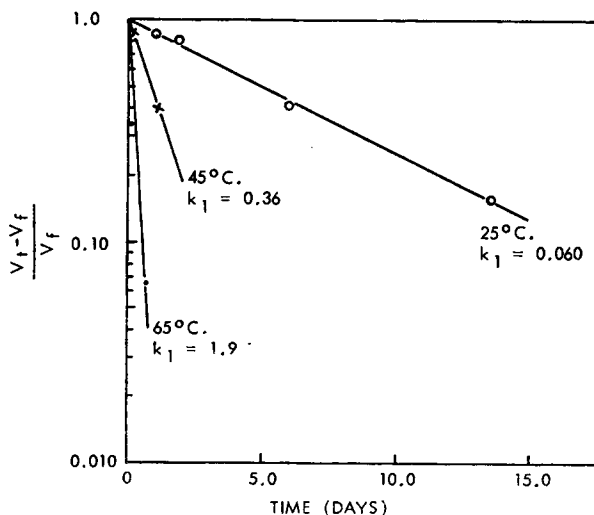


Fig. 3. Effect of temperature on aging of polyacrylamide of high intrinsic viscosity in water; 0.50% sample A. V_t = RSV at time t ; V_f = average RSV for the slow stage. No agitation was used.

cosity in water. Typical data for the RSV changes that occur during aging are given in Figures 1 and 2. In addition to the big decrease in RSV, the polymer solutions lose their spinnability during the rapid stage. As defined by Inagaski,¹¹ a decrease in spinnability results in a decrease in the length of solution that can be spun below a glass rod as it is withdrawn from the solution. However, no quantitative data were obtained in these experiments. The polymer solution also loses its tendency to crawl up the stirrer during the rapid stage of aging.

First-order plots for the rapid stage of aging are shown in Figure 3. A 6-fold increase in k_1 , the first-order rate constant, with a 20°C increase in

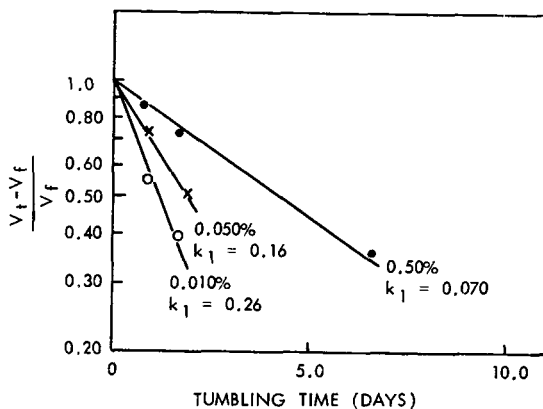


Fig. 4. Effect of polymer concentration on aging of polyacrylamide of high intrinsic viscosity in water; sample A; room temperature. V_t = RSV at time t ; V_f = average RSV for the slow stage.

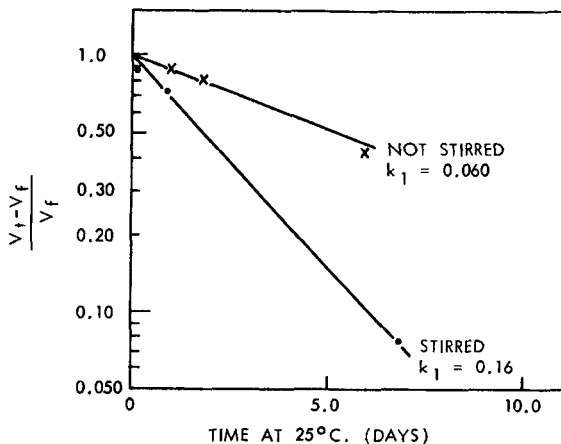


Fig. 5. Effect of stirring on the aging of polyacrylamide of high intrinsic viscosity in water; 0.50% sample A. V_t = RSV at time t ; V_f = average RSV for the slow stage.

temperature indicates a fairly high temperature coefficient. The rate constant also increases when the polymer concentration is decreased (Fig. 4) or when the solution is stirred (Fig. 5). The same rates are observed whether the aging is done under oxygen or under nitrogen.

The changes that occur during the rapid stage of aging are essentially completed when the slow stage is reached. Thus, the rapid stage is no longer evident when the aged 0.86% solution from the experiment in Figure 1 is diluted to 0.50% (Fig. 2).

The changes that occur during the rapid stage of aging cannot be reversed by concentrating an aged polymer solution to the high polymer concentration of the polymerization. Figure 1 shows a reversibility experiment which involved aging at a 0.010% polymer concentration to the slow stage, concentrating to dryness at room temperature with a very slow stream of nitrogen, equilibrating at a 10% concentration in water at room temperature for 15 days, and immediately measuring the RSV-time change after diluting to a 0.86% concentration. The reversibility experiment in Figure 2 involved aging at a 0.010% polymer concentration to the slow stage, concentrating in a rotary evaporator at 45°C to a 10% concentration, equilibrating at the 10% concentration at room temperature for 25 days, and measuring the RSV-time change after diluting to 0.50%.

As calculated from Sholtan's relationship¹² between intrinsic viscosity and molecular weight, the apparent molecular weight M_{app} decreased from 5.6×10^6 to 1.6×10^6 during aging at room temperature (Fig. 6). An equilibrium ultracentrifuge run (Fig. 7) on the unaged polymer did not permit a reliable extrapolation of $1/M_{app}$ to zero concentration. However, if the extrapolation is made using only the points for the two lower concentrations, a very high molecular weight is indicated because $1/M_{app}$ is close to zero. Thus, the above molecular weights from the intrinsic viscosity relationship are of the right order of magnitude.

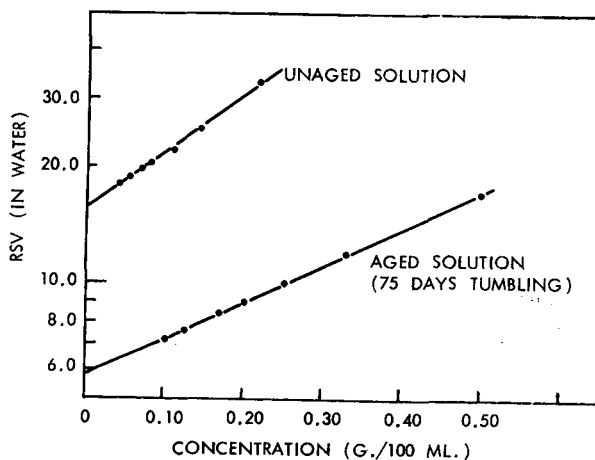


Fig. 6. Intrinsic viscosities of the polyacrylamide of high molecular weight before and after aging in water; sample A.

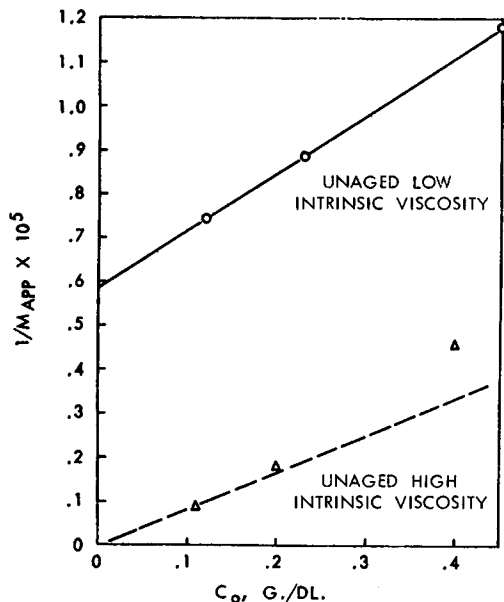


Fig. 7. Estimation of the molecular weights of the polyacrylamides of high and low intrinsic viscosity by the equilibrium method of ultracentrifugation; sample A.

Ultracentrifuge measurements suggest that the unaged and aged polymer aggregates and/or molecules are crowded at concentrations above 0.10%. Thus, independent sedimentation is not possible at a concentration of 0.4% and no fractionation is evident in the schlieren patterns in Figures 8B and 8D. The crowding is somewhat relieved at a 0.1% concentration with the aged polymer and some fractionation occurring (Figure 8C). Such an effect of concentration on the sedimentation is shown by another highly extended polymer molecule, DNA.¹³

A sample of polyacrylamide of low intrinsic viscosity showed a normal behavior during ultracentrifugation. A normal fractionation is indicated by the schlieren pattern at 0.45% which is the concentration that did not permit fractionation with the higher molecular weight sample (compare Figs. 8A and 8B). Equilibrium data in Figure 7 give a molecular weight of 170,000, as compared to 180,000 from Sholtan's equation and the intrinsic viscosity in Figure 9.

This lower molecular weight polyacrylamide did not show the rapid stage in aging that the higher molecular weight sample showed (compare Figs. 1 and 10). It did, however, show the slow stage of aging.

On the basis of the irreversibility and the fairly high temperature coefficient, it would appear that the decrease in RSV in the rapid stage is due to a scission of weak chemical links. Weak links of the peroxy type were

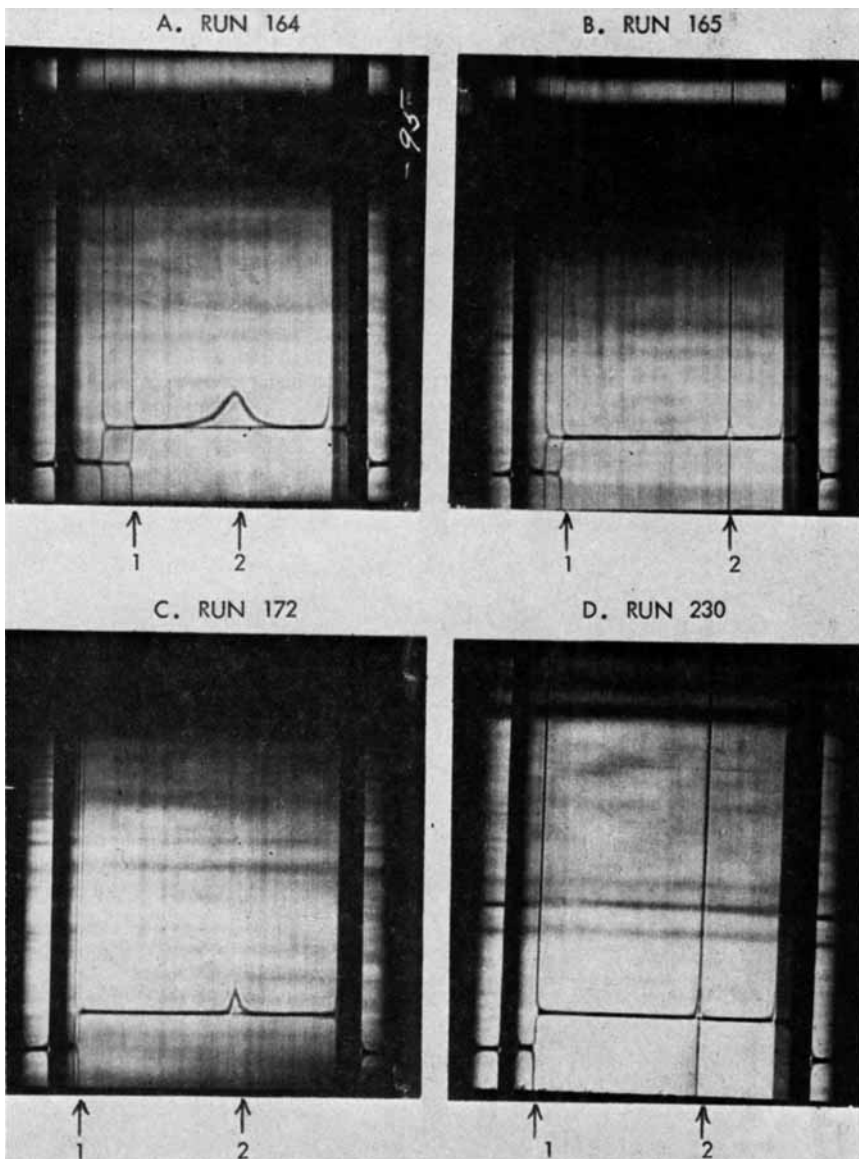


Fig. 8. Schlieren patterns for ultracentrifugation runs on the polyacrylamides of high and low intrinsic viscosity in water: (1) solution meniscus; (2) polymer boundary (direction of sedimentation is to right at 59,780 rpm); (A) run 164, unaged low intrinsic viscosity sample at a 0.45% concentration after 8,276 sec; (B) run 165, unaged high intrinsic viscosity sample A at a 0.43% concentration after 10,600 sec; (C) run 172, high intrinsic viscosity sample A aged by tumbling at a 0.10% concentration for 5 days after 4,360 sec; (D) run 230, high intrinsic viscosity sample A aged by tumbling for 37 days at a 0.86% concentration and then diluting to 0.43% for the ultracentrifugation after 10,994 sec.

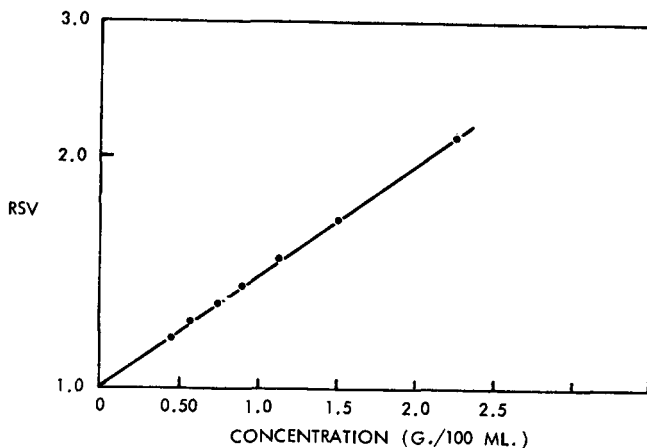


Fig. 9. Intrinsic viscosity of the unaged low molecular weight polyacrylamide.

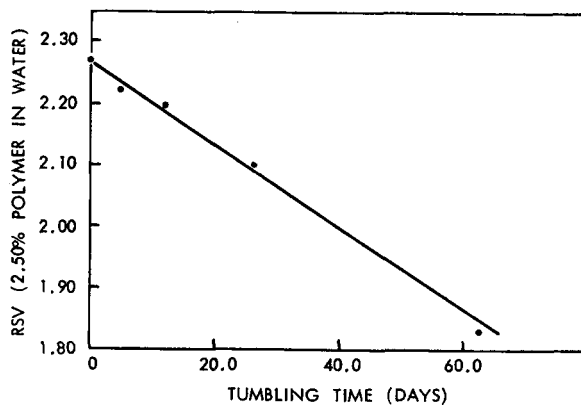
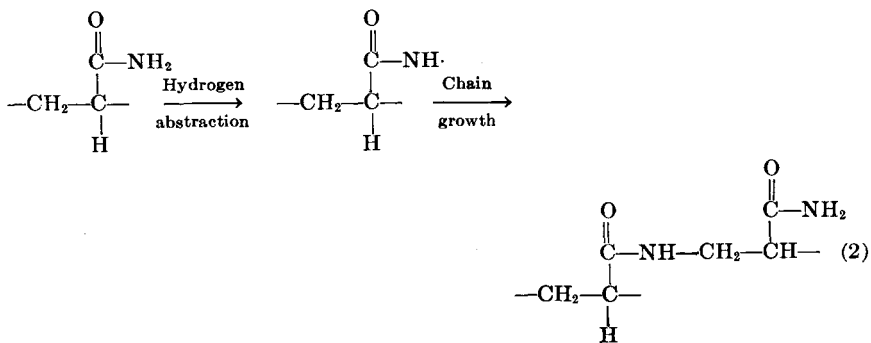


Fig. 10. Viscosity loss of a 2.50% aqueous solution of the low molecular weight polyacrylamide.

recently considered in the interpretation of the loss of viscosity in solutions of other vinyl-type polymers.¹⁴ Such weak links can be formed in the chain by copolymerization with oxygen.¹⁵ A hydrolyzable branch point in the chain can be formed by a reaction with persulfate [eq. (2)]:



Potassium persulfate, the initiator that was used in the preparation of the polymers for these studies, does crosslink polyacrylamide, but the mechanism has not been defined.¹⁶ It should be mentioned that current work is indicating that a polyacrylamide of high intrinsic viscosity can be prepared which does not undergo the rapid stage of aging. It therefore appears that the viscosity instability of the polyacrylamides of high intrinsic viscosity that were used in this study is due to the use of potassium persulfate.

An alternate mechanism for the rapid stage of aging is that a disaggregation of polymer molecules is occurring. As suggested by Narkis and Rebhun,¹ an abnormal degree of entanglement can result during the rapid, random growth of polymer molecules. Some of this entanglement can then persist in the form of aggregates of entangled polymer molecules in solutions of polyacrylamide.

One of the arguments in favor of the disaggregation mechanism is that the rate constant increases when the polymer concentration is decreased (Fig. 5). Less crowding at the lower polymer concentration facilitates the disentanglement of the molecules from the aggregate. Stirring also facilitates the disentanglement by causing a tighter coiling of the molecules and thus decreasing the crowding. Therefore, the increase in the rate constant when the solution is stirred (Fig. 6) is also consistent with the disaggregation mechanism. If one accepts the proposal that a high degree of entanglement can only be established during the polymerization, then the irreversibility of the rapid stage is consistent with the disaggregation mechanism. Finally, to reconcile the fairly high temperature coefficient with the disaggregation mechanism, it is necessary to postulate that there are several barriers to disaggregation. Physical entanglement, intermolecular hydrogen bonding, and solution crowding are possible barriers. According to the work of Ueberreiter and Asmussen,¹⁷ the activation energy for the dissolution of polystyrene is 2.13 kcal/mole. This value is the best available estimate of the activation energy for the diffusion of polymer molecules away from a swollen gel (physical disentanglement into an uncrowded solution). Considering the work of Silberberg et al.,^{18,19} intermolecular hydrogen bonding would be expected to provide a barrier against disaggregation. Their study of the temperature dependence of the light scattering and viscosity of dilute polyacrylamide solutions suggests that the hydrogen bonding decreases with an increase in temperature. There would be a significant contribution to the energy barrier for disaggregation if several hydrogen bonds have to be broken simultaneously. In a similar study, Beevers²⁰ concluded that two dipole-dipole bonds have to be broken to explain the temperature coefficient for the disaggregation of polyacrylonitrile. It is likely that the interaction of amide groups is enhanced by stereoregularity. There is no published information about the stereoregularity of polyacrylamide. However, stereoregular polymers are formed by the free radical mechanism of other polar vinyl monomers, e.g., acrylonitrile²¹ and glycidyl methacrylate.²² The effect of stereoregularity on the dilute solution properties of polymers is now receiving some attention.²³⁻²⁵

Aging studies in formamide are also easier to interpret in terms of the disaggregation mechanism. Thus, the absence of the rapid stage during the aging of another sample of a polyacrylamide of high intrinsic viscosity in formamide (Fig. 11) can be attributed to a completion of the disaggregation during the dissolution of the polymer. In these experiments, two aliquots of the same stock solution in water were freeze-dried, the freeze-dried polymers were dissolved by a similar technique in water and formamide, and the RSV-time measurements were made. The following experiments showed that the lower RSV that resulted when the freeze-dried polymer was redissolved in formamide (compare the two zero-time RSV's in Fig. 11) was not due to a solvent effect on the RSV. Two aliquots of the same stock solution were freeze-dried, the freeze-dried polymers were redissolved in water and formamide, both polymers were precipitated with acetone, and finally both polymers were redissolved in water. Only the polymer that was initially in water had an RSV that was close to the zero-time RSV of 44 (Fig. 12). The RSV of the polymer that was initially in formamide remained close to the zero-time value of 15 for the formamide solution in Figure 12.

In terms of the alternate weak-link interpretation of the rapid stage, formamide would have to accelerate the scission of the weak links during the dissolution of the polymer in formamide. There does not appear to be a basis for this if it is assumed that the weak links are of an amide type.

If one accepts that there is disaggregation in the rapid stage for the aging in water and that the disaggregation is complete in an unaged solution of the polymer in formamide, the following experiments show that it is

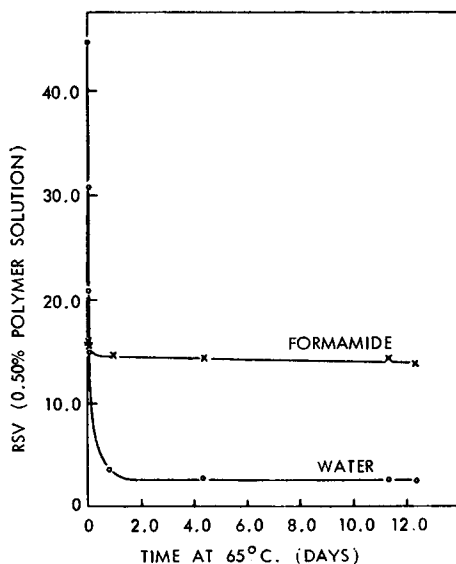


Fig. 11. Aging of polyacrylamide of high intrinsic viscosity in water and formamide; 0.50% sample B.

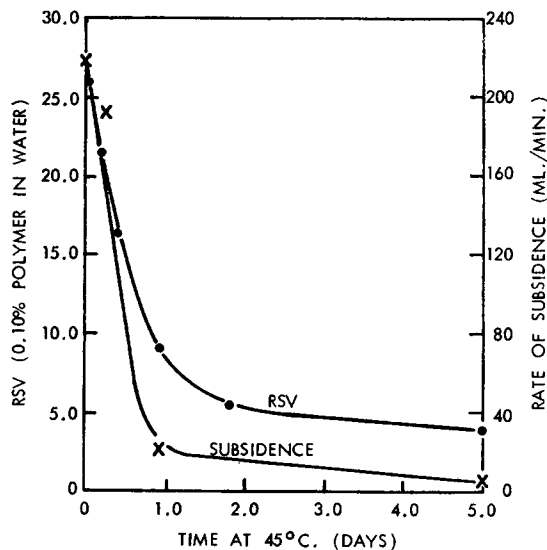


Fig. 12. Effect of aging on the ability of the polyacrylamide of high intrinsic viscosity to promote the subsidence of a 5.0% kaolin suspension in water; sample C. No agitation was used during aging.

necessary to consider that there is an additional change in the polymer during the rapid stage for the aging in water. Two freeze-dried samples were dissolved in formamide and water and aged for one day as in the experiments of Figure 11. When these two aged polymer samples were recovered by precipitation, the RSV's remained unchanged when the solvents were reversed. Thus, the sample that was aged in formamide had an RSV close to 15 (as in Fig. 11) when it was recovered and redissolved in water. The sample that was aged in water had an RSV close to 3 when it was recovered and redissolved in formamide. Current work in our laboratory by Waldman²⁶ indicates that carboxyl groups are being formed during the aging in water and that these might be responsible for the additional decrease in RSV for the aging in water (e.g., by hydrolysis of amide-type of weak links), as compared to the aging in formamide.

As mentioned above, there is no rapid stage in the aging of the polyacrylamide of low molecular weight (Fig. 10). It is very probable that the changes occurring are the same as those for the slow stage with the high molecular weight sample (Figure 1). Light-scattering studies are being carried out in our laboratory to establish whether conformational or molecular weight changes are responsible for the aging of the low molecular weight polyacrylamide. We are also checking for chemical changes that might be expected to occur. For example, the intramolecular and intermolecular interaction would be affected by the hydrolysis of the amide groups.

The decrease in RSV that occurs during aging is paralleled by a decrease in the effectiveness of polyacrylamide in promoting the subsidence of a kaolin suspension (Fig. 12). On the basis of the above discussion, the de-

creased effectiveness of the polymer as a flocculant would be due to a scission of weak links and/or to a disappearance of aggregates during aging. It was suggested in our earlier publication²⁷ that the decreased effectiveness of the polymer as a flocculant is due to a decrease in the strength of the bridge that the adsorbed polymer forms between two particles. A decrease in the extension of the bridging polymer as a result of aging decreases the chance of adsorption with the high degree of interparticle bonding that is necessary for a strong bridge. Once a high degree of bonding to a single particle is established, there can only be weak bridging to a second particle. The importance of polymer extension has been thoroughly demonstrated in the work of Sakaguchi and Nagase,²⁸ in which they found a good correlation between intrinsic viscosities or root-mean-square end-to-end distances of various samples of polyacrylamide and the subsidence rates of the flocculated kaolin suspensions. An aggregate would also be expected to have a smaller tendency to collapse to a flattened conformation, so this would also increase the chances of adsorption with a high degree of interparticle bonding.

EXPERIMENTAL

Polyacrylamide of High Intrinsic Viscosity

A solution of 30.0 g of recrystallized acrylamide and 0.073 g. of potassium persulfate in 270 g of water was polymerized under nitrogen in a 35°C bath. When the reaction mixture became almost nonflowing, it was diluted with 1226 g of water, and the mixture was stirred for 30 min. At this stage, the mixture had a tendency to climb up the stirrer. The mixture was dialyzed three times against 3 l. of water with at least overnight tumbling (end-over-end rotation of bottle at 6 rpm). The resulting smooth and stringy solution had a 0.864% polymer concentration as determined by the weight of residue after overnight drying of an aliquot at 105°C. On this basis, it is estimated that the conversion to polymer for sample A was 36%. This sample was used in all of the experiments given in Figures 1-8. Sample B was prepared by a similar procedure, except that the potassium persulfate concentration was 10 times higher and the conversion to polymer was 23%. The latter sample was used for the experiments that compared the aging in water and in formamide (e.g., Fig. 11). Sample C was prepared by the same procedure to that used in the preparation of sample A, but the conversion to polymer was 17%. Sample C was used in the experiments in Figure 12.

Polyacrylamide of Low Intrinsic Viscosity

The procedure was similar to that used for the high intrinsic viscosity polymer except that 0.365 g. of potassium persulfate and 0.135 g. of sodium bisulfate were used to get a much higher initiation rate. After a 5 min. polymerization interval, the conversion to nondialyzable polymer was

45%. Less water was used to dilute the polymerization mixture so that the stock solution had 4.52% polymer.

Aging

In the room temperature aging, the polymer solutions were tumbled under air in polypropylene centrifuge tubes at 30 rpm. When no agitation was required, the aging was done in a No. 1 Ubbelohde viscometer at the required temperature. No weight loss was detected at the higher temperatures when the viscometer was sealed with rubber stopples.

Viscosities

The polymer solution was centrifuged or filtered through a 100-mesh screen to remove large, extraneous particles. Flow times were all measured at 25.0°C in a No. 1 Ubbelohde viscometer. A dilution-type viscometer was used in the determination of the intrinsic viscosities.

Ultracentrifugation

The partial specific volumes were obtained²⁹ from density measurements in 25 ml pycnometers by using the relationship:

$$\bar{V} = (1/\rho_0) - (1/X) (\rho - \rho_0)/\rho \quad (3)$$

where \bar{V} is partial specific volume, ρ_0 is solvent density, and ρ = solution density. Values of 0.346 and 0.333 were obtained for $(1 - \bar{V}\rho)$ for the high and low intrinsic viscosity polyacrylamide, respectively. For the conversion of schlieren patterns to concentration, F values (concentration/area) were 2.770 and 2.851 for the high and low molecular weight samples, respectively. In the equilibrium runs, the apparent molecular weight (M_{app}) was calculated as follows:

$$M_{app} = \frac{(C_b - C_a)}{C_0} \frac{1}{AE(b^2 - a^2) (1 - \bar{V}\rho)} \quad (4)$$

where $C_b - C_a$ is the difference in concentration at the bottom and meniscus of the cell; C_0 is the initial concentration. The values of $1/M_{app}$ at $\omega^2 = 0$ were first obtained from a plot of $1/M_{app}$ against ω^2 . The plots of $1/M_{app}$ against C_0 in Figure 7 give the reciprocal of the molecular weights after extrapolation to $C_0 = 0$.

Aging and Loss of Flocculation Activity

The stock solution of the high molecular weight polyacrylamide was diluted with water to give a 0.10% solution. This solution was kept in a pressure bottle at 45°C for the required time. After cooling the solution to 25°C, a portion of the solution was filtered through a 100-mesh screen, and the RSV was measured. Another 2.5-g portion of the solution was diluted to 50.0 g with water. The diluted solution was added to 50.0 ml of an aged 10.0% suspension of kaolin (Hydrite 121, Georgia Kaolin Co.)

in a 100-ml graduated cylinder. After rocking the graduated cylinder 20 times through 180°, the volume of kaolin versus time was recorded. The subsidence rate³⁰ is equal to the initial slope of a plot of the kaolin volume versus time.

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