The Agglomeration of High Molecular Mass Polyacrylamide in Aqueous Solutions

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ABSTRACT: Size distribution information was used to monitor time-dependent agglomeration in aqueous solutions of a high molecular mass polyacrylamide. Although the individual polymer molecules had diameters in the order of 0.4 μm, a high number of agglomerates were seen that may contain four to six polymer chains. As the solution age increased, a significant level of larger microgels (2–15 μm) were also detected. The addition of salts or organic cosolvents modified the solvation properties, altering the extent and rate of agglomeration. The presence of 2%-v/v formamide had a significant effect, substantially reducing agglomeration and increasing solution stability. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2241–2250, 1998

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INTRODUCTION

Studies of the molecular weight distribution of high molecular weight polyacrylamide (PAAm) is complicated by the instability of the polymer in aqueous solutions. As the solid polymer swells and disperses, there are processes of polymer coil entanglement, conformation change, and agglomeration occurring simultaneously. Under acid, alkaline, or warm conditions chemical modification of the functional amide group occurs. An understanding of these processes is a necessary precondition to achieving meaningful molecular weight characterization. The existence of any agglomerated species in a polymer solution may have a detrimental effect on fractionation techniques based on hydrodynamic volume.

PAAm forms a swollen gel in water as the liquid permeates into the polymer, followed by disintegration of the gel as yet more water enters to eventually form a dispersed polymer solution. The solution viscosity may, therefore, be expected to increase with time from that of water to a maximum determined by the polymer concentration and molecular weight. However, early studies[1,2] observed decreasing solution viscosities with time. A closer examination showed that PAAm solutions experienced a rapid increase in viscosity to a maximum after 24 h, before a slower viscosity decrease to a local minimum after 160 to 180 h.[3]

Explanations for viscosity changes have included chain scission due to the action of residual catalyst[2,4,5] or microorganisms,[6] crosslinking,[7,8] hydrolysis,[9] chain disentanglement,[1,3] and conformational changes.[10] Degradation by chain scission has largely been ruled out from static light-

Figure 1 Conformational changes for PAAm in aqueous solution, as proposed by Kulicke,[10] showing highly oriented (A) and random (B) hydrogen bonding.

scattering studies.[10,11] Biocides have been shown to have little effect,[11] while hydrolysis and crosslinking have only been observed at elevated temperatures. As agglomerated polymer will contribute less to the overall solution viscosity than the individual polymer chains, chain disentanglement is also inconsistent with any observed decrease in viscosity over extended time periods. The majority of evidence favors a model for solution instability based on polymer conformational changes derived from intramolecular hydrogen bonds between amide groups, as shown in Figure 1.[11] The presence of highly oriented hydrogen bonding of the type **A** leads to an extended polymer conformation and a maximum in viscosity. With time, the oriented segments are destroyed as the type **A** hydrogen bonds are attacked by water, resulting in a more stable, compact coil with predominantly random hydrogen bonding (type **B**).

Although the above model is quite satisfactory to explain the observed viscosity changes, another possibility is the agglomeration of multiple polymer chains to form a microgel. Such microgel agglomerates may be expected to have a lower viscosity contribution than the individual polymer chains.[12] The presence of microgels in PAAm solution has been previously noted, although rarely studied. Klein and Westerkamp[13] stated that low levels of microgels could result in the plugging of columns during size exclusion chromatography of polyacrylamides. They have been removed from solution by high-speed centrifugation[12] or filtration through a large pore-size filter.[13,14] Boyadjian et al.[15] found that high salt levels were able to disperse the microgel agglom-

erates, and therefore concluded that microgels were not the result of permanent (covalent) crosslinking but of weaker hydrogen bonding or physical entanglement. However, polymer crosslinking as a result of thermally or chemically induced imide bridges may also lead to microgelation.[14]

In this present study, the influence of PAAm microgels on the aging process has been examined through size measurements of the microgels and the bulk polymer in aqueous solutions. The modification of solution properties, by the addition of salts or cosolvents, was also investigated as a means to reduce polymer agglomeration.

EXPERIMENTAL

Reagents

A commercial high molecular weight nonionic PAAm, well known in mineral processing applications, was used in this study. No evidence of acrylate moieties could be detected by FTIR, ^{13}C-NMR, or elemental analysis. The weight-average molecular mass $\bar{M}_w$ of this polymer as measured by multiangle laser light scattering (MALLS) was 20×10^6. All other chemicals used were of analytical reagent grade. Aqueous solutions were made up in high-purity deionized water freshly filtered through a 0.2 μm prefilter (Millipore Opticap™) followed by a 0.1 μm Durapore membrane (Millipore Millipak 40). Solutions containing salts or additives were filtered through a 0.2 μm membrane (Gelman Acrodisc™). PAAm stock solutions were produced by adding small portions of polymer to aqueous solutions pretared in a screwtop glass jar, then shaken overnight on a Chiltern Scientific SS70 orbital shaker at 150 ± 5 rpm. All solutions were prepared in a Gelman HWS laminar flow cabinet.

Flocculation tests were carried out with a standard kaolin substrate (Kaolin RF, Commercial Minerals), with a d_{50} of 3.9 μm as measured by laser diffraction (Malvern Mastersizer™).

Aging Experiments

Polymer stock solutions were aged at ambient temperature for periods of up to 3 months. The polymer solutions were diluted for agglomerate size analysis by adding 5.0 mL of stock, dropwise with swirling, to 100 ± 2 mL of filtered water containing salt or additive at the same level as that in the stock.

An Ubbelohde capillary viscometer (No. 75) was used to measure dilute polymer solution viscosities at 30°C. The procedures for the use of such viscometers and the calculation of viscosities have been described in detail elsewhere.[16,17]

Agglomerate Size

The size distributions of agglomerates in PAAm solutions were measured with a HIAC Royco 9064 Sizing Counter (Pacific Scientific, Silver Spring, MD), fitted with a MicroCount-05 liquid sensor, and controlled by HIAC Royco Particle Distribution Analysis Software (PDAS, Version 2.1). Flow past the detectors (60 mL min^{-1}) was initiated by applying overpressure to the solution with compressed air from a SMC AW3000 filter regulator adjusted to 75 kPa over atmospheric pressure.

The HIAC Royco 9064 Sizing Counter provides the number of counts measured over each of a range of size channels. Light from the 50 mW laser diode interacts with samples passing through the sensor to the collection optics. The sensor's optical system utilizes both forward light-scattering signals to detect particles as small as 0.5 μm in size, and light obscuration to count particles from 1.6 to 350 μm diameter. Each particle passing through the sensor therefore generates an analogue electrical pulse of size-dependant magnitude, which is converted into a "count." For all experiments the flow past the sensor kept constant 60 $\pm$ 1 mL min^{-1} over the 20.0 mL sample volume.

Numerous repeat runs with 0.1 μm filtered water indicated that the signals for the two smallest channels (0.50 and 0.55 μm threshold size) fluctuated considerably. These fluctuations were established as resulting solely from electronic noise. As a consequence, only those channels corresponding to sizes over 0.61 μm were used in size distributions. Although the instrument is typically used for solid particle sizing, light scattering is commonly used to study PAAm solutions,[11] and light obscuration has proved sensitive to the presence of polymer microgels.[18]

Background correction for the Sizing Counter's lower size channels is trivial—for the 0.70 μm channel the background is typically 50 counts, compared with 5000 in the measured solution. Greater care was required for sizes over 1.5 μm, where the low number of counts per channel may be influenced by stray dust from poorly filtered background solutions. The distributions presented were averaged from triplicate determinations of each dilution. Although surface or volume weighting may be applied to the counts distributions to enhance the contribution of the small number of large species, the effect of any contamination will also be enhanced.

Mean Molecular Mass

MALLS measurements were performed on selected flocculant 500 ppm stock solutions using a Dawn-DSP photometer (Wyatt Technology Corporation, Santa Barbara, CA) fitted with a helium-neon laser (wavelength 632.8 nm) and a K5 flow cell. The instrument was calibrated with 0.02 μm filtered toluene and the detectors normalized with a 0.2 μm filtered solution of low molecular weight dextran (T10, Pharmacia). The procedure used to determine the root-mean-square (RMS) radius of gyration and weight-average molecular mass ($\bar{M}_w$) of PAAm by MALLS has been described elsewhere.[19]

Polymer Concentrations

The concentrations of PAAm solutions were determined by Flow-Injection Analysis (FIA), combining N-bromination of the amide functionality and iodometry.[20] The method was modified slightly from that previously described[21] by installing another peristaltic pump after the detector and the addition of a T-piece prior to the detector to prevent bubbles entering the quartz flow cell.

Flocculant Activity

Cylinder tests were conducted using stoppered 100-mL graduated cylinders. Approximately 8 L of a 5 wt % kaolin slurry was stirred at high speed for 90 min prior to use. A peristaltic pump was used to transfer 50 mL of the kaolin slurry from the bulk slurry to a graduated cylinder. Sufficient water was then added to the cylinder so that the final volume of slurry, water, and flocculant was 100 mL. After 10 inversions in a cylinder rotator (30 rpm), the required volume of polymer solution was added by syringe. After a further 10 inversion cycles the cylinder was returned to the vertical position and the rate of fall of the mudline was followed. The hindered settling rate was taken as the initial linear slope of a plot of the mudline height against time.

Figure 2 Overlaid size distributions for a 520 ppm aqueous solution of PAAm before and after 5.0 μm filtration; (a) raw counts distribution, (b) volume-based distribution.

RESULTS

Agglomerate Size

MALLS measurements on aqueous solutions of the high molecular weight polymer indicated that the polymer molecules have RMS diameters in the order of 0.4 μm in deionized water at ambient temperature. On this basis, the Sizing Counter would only be expected to show counts only for the lowest size channels. Figure 2(a) shows the size distribution for an unfiltered solution aged for 6 weeks in the dark, conditions under which the solution exhibited little remaining dynamic instability. A high level of counts were observed at sizes near 1.0 μm, with significant counts up to sizes of 15 μm, well in excess of the expected dimensions for the polymer molecules. The possibility that dilution of stock solution for the agglomerate sizing actually affected the agglomerates was eliminated through dilution of the stock

solution over a range, and observing that only the number of agglomerates above the background varied linearly with dilution and agglomeration is a function solely of stock concentration, as reported below. There may exist a time component, in that allowing the diluted stock to stand increases dispersion of the agglomerates, but this was not an issue as the time from dilution to analysis was kept constant.

Using the MALLS estimate of individual PAAm coil size, polymer agglomerates measured in the 0.7 μm channel of the size distribution may possibly represent four to six associated molecules, while a 15 μm agglomerate would involve over 10^4 individual molecules. Figure 2(a) also provides comparison with the same solution after 5.0 μm filtration, showing the efficiency of the filtration process for the removal or disruption of agglomerates. The spikes observed in the background 0.1 μm filtered water and filtered polymer solution correspond to discrete and irreproducible channel counts, and were attributed to residual dust contamination.

The same data is also presented as a volume-based distribution in Figure 2(b), emphasizing that the relatively low number of microgels have an enormous contribution to a volume-based sizing technique. Difficulties arose in comparing volume distributions because the influence of dust spikes at the larger channel sizes had a disproportionate influence. The following discussion is, therefore, limited to only the raw counts per channel in excess of the background.

Static light scattering at low detector angles is known to be strongly affected by the presence of large particles. For a polydisperse system light scattering returns a z-averaged radius and as such 10–15 μm polymer microgels present in solution should drastically interfere with MALLS size measurements. Considering a sample of monodisperse 0.4 μm diameter polymer coils if there exists 0.1% by number agglomerated to 10 μm, a crude calculation shows that the light scattering should return a mean radius of over 4 μm The diameter of the polymer coil calculated from MALLS was of the expected magnitude for a polymer of this size within light scattering error (±3%), and this suggests that the number of microgels and agglomerated polymer was extremely low compared to the bulk polymer concentration. Using the above model system if the 10 μm agglomerates are in the order 10^{-3}% by number, an overall light-scattering radius of 0.43 μm is obtained, and represents an approximate upper

Table I Effect of Membrane Filtration on the Concentration and Flocculant Activity of Polyacrylamide Solutions Aged for 5 Days

Solution	Measured Concentration (ppm)	Hindered Settling Rate (m h^{-1})[a]
Unfiltered	552 ± 3	22.0 ± 1.0
0.8 μm filtered	538 ± 3	13.3 ± 0.5
5.0 μm filtered	552 ± 3	10.8 ± 0.3

[a] Values interpolated for a dosage of 250 mg kg^{-1}.

limit to the agglomerate concentration. Disruption of any large species by passage through the MALLS flow cell and associated capillary tubing may be discounted, as distributions measured with the Sizing Counter were identical before and after passage through the MALLS system.

Although the Sizing Counter is well suited to the study of agglomerated polymer, its lower size limit precludes measurement of full population size distributions down to individual polymer dimensions. The polymer solution concentration was, therefore, determined before and after membrane filtration. No significant change could be detected after 5.0 μm filtration, while 0.8 μm filtration resulted in a 2.5% reduction in concentration (Table I). Although these results imply that the population of microgels in solution is low, there is also the possibility that any large microgels are quite fragile and that passage through a membrane causes rupture to smaller sized agglomerates or individual polymer coils.

Table I also shows the effect of filtration on the flocculation activity for solutions of PAAm. Although 5.0 μm filtration had no effect on the measured polymer concentration, the activity was found to drop substantially. This was consistent with the observations of Shyluk and Stow,[2] who felt that agglomerates were less likely to take a flattened conformation when adsorbed on a particle, and may enhance polymer bridging. If this is the case, then the consequence of filtration is almost certainly the rupture of any large microgels. Interestingly, the reduction in flocculant activity was not quite as large after 0.8 μm filtration, despite a slight reduction in concentration. It may be that small agglomerates of only a few polymer chains do not contribute greatly to activity.

Aging

Viscometry yields a single, solution-averaged measurement of polymer properties, and as such may not be highly sensitive to minor changes resulting from solution instability. The reduced viscosity (η_{red}) of the solution as a function of time was compared with the counts measured in both the sub- and supramicron range of the size distribution (Fig. 3). The value of η_{red} exhibited only a 13% increase over the 80-day aging period, while counts in the selected size regions varied over a much wider range. The number of counts in the submicron range and the solution η_{red} both increased rapidly after 5–8 days aging [Fig. 3(a)]. This is in good agreement with the viscosity results of Gardner et al.,[3] who believed the changing polymer–solvent interactions favored a chain disentanglement mechanism.

Figure 3(a) also shows that the solution's η_{red} underwent a further increase between 30 and 40 days. However, this behavior was not mirrored by the submicron counts, which displayed a steady downward trend after 20 days. Examination of the supramicron counts [Fig. 3(b)] indicates that the microgel concentration reached a minimum

Figure 3 Comparison of viscometry and HIAC Royco 9064 Sizing Counter data for the aging of PAAm in water. (a) Counts in the range 0.68–0.72 μm; (b) counts > 1 μm.

Figure 4 Submicron counts (0.68–0.72 μm) for the aging of PAAm solutions at different concentrations.

during the first week of aging but then began steadily increasing from that point on. This previously unreported aging behavior for polyacrylamide was observed repeatedly in aqueous solutions of PAAm containing no salts or additives. The increase in supramicron counts following the peak in the number of submicron counts was consistent with the conclusions of Raos and Allegra,[22] who predicted from free energy calculations that substantial coil agglomeration may predate the appearance of larger microgels for solvated polymers under the θ temperature.

Effect of Concentration

The aging of PAAm solutions at lower polymer concentrations was monitored over several months. Figure 4 shows the effect of concentration on the submicron counts. Preparing the stock solution to a lower concentration delays the onset of the peak in the submicron counts, from 8 days at 520 ppm to 16–20 days at 50 and 200 ppm. The magnitude of the measured counts was also substantially lower than expected, even after taking into consideration the reduction in concentration.

Stock solutions containing 100 ppm or less of PAAm had no supramicron counts and showed no sign of gelation whatsoever. A number of polymer–solvent systems are known to exhibit a threshold level for agglomeration, defined as a critical entanglement concentration, $c*$, below which the solution remains well solvated and essentially homogenous.[23,24] For PAAm, this critical concentration has been related to the intrinsic viscosity, $[\eta]$, by the relationship $c* = 2.5 [\eta]^{-1}$.[11] In water this results in a $c*$ of approximately 1250 ppm suggesting that stock polymer solutions

made at or over 0.1% concentration may be highly agglomerated, perhaps exhibiting stable microgelation. The results obtained suggest that significant agglomeration may still be observed at concentrations below $c*$.

Effect of Chemical Additives—Organic Cosolvents

The addition of an alcohol, typically 2-propanol, has been shown to result in enhanced solution stability as measured by viscometry.[5,6] Such additives are thought to prevent microbial or radical attack, although their effect has been questioned.[11] The use of formamide as a solvent for PAAm has also been shown to result in higher stability, as a consequence of improved solvation of the polymer.[11,25] The aging of aqueous solutions of 500 ppm PAAm containing either 2%-v/v 2-propanol or 2%-v/v formamide was examined. The aggregation of the polymer over time was monitored by following the 0.68- to 0.72 μm channel of the size distribution (Fig. 5).

Over an initial period of 2 weeks the presence of 2-propanol does indeed suppress the aging effects, but after this time the alcohol enhanced agglomeration, with the submicron counts steadily increasing to high levels. In contrast, 2%-v/v formamide, known to be a good solvent for PAAm, efficiently suppressed agglomeration over the full aging time scale.

The effect of both additives on supramicron counts is shown in Figure 6. After 1 day of aging a distinct microgel contribution can be seen in the diameter range of 4 to 11 μm for a solution containing 2-propanol [Fig. 6(a)]. By 12 days the concentration of microgels in this solution has

Figure 5 Submicron counts (0.68–0.72 μm) for the aging of PAAm solutions in the presence of 2-propanol or formamide.

Figure 6 Size distributions (overlaid) for a 520 ppm aqueous solution of PAAm containing either 2% 2-propanol or 2% formamide after aging for (a) 1 day, (b) 12 days, and (c) 74 days.

dropped, possibly reflecting optimum dissolution of the polymer [Fig. 6(b)]. However, by 74 days a substantial increase in the supramicron counts was observed, as well as an increase in the microgel size range to include diameters of up to 20 μm. The contradiction with previous aging studies may be a consequence of the relative insensitivity of viscosity measurements to microgel formation, or the fact that many of these studies were not carried out for long enough to show the instability. Again, counts measured in the presence of formamide remained at low levels throughout the same period.

Effect of Chemical Additives—Salts

Solutions of PAAm at 500 ppm were also allowed to age in the presence of varying concentrations of thiocyanate, chloride, and acetate salts chosen to modify hydrogen bonding.[26,27] Aging behavior was found to be influenced by the salt concentration. At high salt concentrations (500 mmol L^{-1}) the formation of submicron agglomerates was suppressed, similar to the effect of 2%-v/v formamide.

In the presence of dilute salts (5 mmol L^{-1}), aging did result in peaks in the submicron counts (Fig. 7), although this effect was reduced and delayed compared to that seen in pure water. In water [Fig. 3(a)] the peak in the 0.68–0.72 μm counts occurred after 6–8 days, while in dilute salt solutions the equivalent peaks were only observed in the range 12–25 days. The extent of agglomeration in the presence of thiocyanate was only slightly reduced compared to that in water, while with acetate the measured peak counts were more than halved. Chloride was the most effective of the dilute salts studied for suppressing agglomeration, with the counts almost reduced to the level seen in formamide solution.

Salts at 500 mmol L^{-1} appeared to limit the formation of submicron agglomerates, but the behavior in the supramicron range was dependent upon the salt type. In the case of potassium thiocyanate solutions, microgel formation remained low over the first weeks of aging [Fig. 8(a)]. However, after 42 days significant levels of microgels could be seen in solution, and subsequently exceeded the levels measured in salt-free solutions. Aging in sodium chloride solutions also initially resulted in low supramicron counts [Fig. 8(b)].

Figure 7 Submicron counts (0.68–0.72 μm) for the aging of PAAm solutions in the presence of 5 mmol L^{-1} salts.

Figure 8 Size distributions (overlaid) after aging 520 ppm aqueous solutions of PAAm containing 500 mmol L^{-1} of (a) thiocyanate, (b) chloride, and (c) acetate.

Like the thiocyanate solutions, an increase in microgel counts did occur in the presence of chloride after 43 days, but this trend was not maintained, with counts returning to lower levels. Sodium acetate produced the strongest suppression of microgelation during initial aging, although a significant increase in counts was observed after 1 month [Fig. 8(c)].

Supramicron counts displayed very similar behavior in either 5 mmol L^{-1} or 500 mmol L^{-1} chloride solutions. Dilute levels of thiocyanate or acetate did not significantly change the extent of microgel formation from that seen in salt-free solutions.

DISCUSSION

The dissolution of PAAm in water is favored due to the high heat of solution of the amide functionality, which compensates for the hydrophobic effects of the nonpolar backbone.[28] Dupuis et al.[29] have stated that collisions between polymer molecules can result in association if the strength of the polymer–polymer and polymer–solvent interactions are similar. At dilute concentrations the formation of large particles was thought unlikely, due to the low probability of multiple collisions. At higher concentrations chain overlap may favor intermolecular interactions, and larger agglomerates may be expected. These conclusions are consistent with the results shown in Figure 4 for the effect of concentration on submicron counts.

Dupuis et al.[29] claim that while large agglomerates may only be favored at higher concentrations, doublets are observed over a wide range of concentrations. A recent study using dynamic light scattering has also detected noncovalent, soluble agglomerates in aqueous solutions of PAAm, which were thought to consist of about four linear chains.[30] This compares favorably with our observation that counts in the size distribution near 0.7 μm may result from the association of four to six molecules. The HIAC Royco 9064 Sizing Counter used in this study, while unable to detect nonassociated PAAm, has proved highly sensitive to the presence of agglomerated polymer.

The size parameter changes with time for PAAm (Fig. 3) show an early peak in the submicron counts, followed by a steady decrease, the latter coinciding with an increase in the supramicron counts. Such behavior is consistent with general predictions for agglomerating polymers,[22] and reflect the balance between polymer–polymer and polymer–solvent interactions. As the conformation of the polymer changes, necessarily the proportion of polar or nonpolar character presented to the solvent varies, and the solvation energies of the polymer changes. Modification of the solvent properties may delay or prevent the formation of large agglomerates that are bound by hydrophobicity.

The observed reduction of submicron counts as the ionic strength was increased suggests that the presence of salt limits PAAm agglomeration. Karlström et al.[31] linked the solubility behavior of model nonionic polymers as a partition of polar and nonpolar segments of the coil, which for polyacrylamide are the amide side units and hydro-

carbon backbone, respectively. Presumably, the salt effect occurs by increasing the water polarity and thereby improving the solvation ability of the amide. A study of lower molecular weight polyacrylamides found that high levels of salt (0.1 mol L^{-1} NaCl) were required to disperse agglomerates in solution.[15] However, results obtained with this study show that ionic strength alone was not effective at preventing the formation of large agglomerates (i.e., microgels of over 2 μm diameter).

Hydrogen bonding bridged by water is of critical importance in determining the conformation of PAAm,[11] and therefore, the modification of hydrogen bonding by salts may be employed to explain their effect on the measured size distributions. Anions may be classified as hydrogen bond makers, which impose a local order by water dipole–ion interaction, and hydrogen bond breakers, which can disrupt existing order.[26,27] This approach was used by Leca[32] to explain how viscosity and coil dimensions of PAAm in 1.0 mol L^{-1} salt solutions increased with hydrogen bond breaking ability. Of the anions studied here, thiocyanate is a strong structure breaker, chloride a weak breaker, and acetate a weak maker. High concentrations of the bond breaking thiocyanate interfere with the water–amide interactions, thereby favoring polymer–polymer interactions and allowing agglomeration processes to continue unabated. Although submicron counts were slightly reduced in the presence of thiocyanate, this may be a consequence of the higher supramicron particles observed.

Chloride does not greatly change polymer interactions, so the microgel levels are largely unchanged, although the increase in ionic strength does allow better dispersal of the submicron agglomerates compared to the salt-free solutions. As a weak hydrogen bond maker, acetate appears to inhibit the formation of supramicron microgels [Fig. 8(c)].

These same effects are more dramatically illustrated in the case of the organic modifiers. The addition of alcohols such as 2-propanol at dilute levels is known to reduce the solvation of polyacrylamide compared with water.[32,33] Polymer–polymer interactions are therefore favored, and as and clearly show, agglomeration and the formation of microgels are much enhanced. In contrast, formamide is known to be a good solvent for polyacrylamide. Ying et al.[30] found that submicron agglomerates readily dissociate in 100% formamide to the constituent linear chains. Even at 2%-v/v formamide, the improved solvency almost totally suppresses sub- and supramicron counts,

with no evidence of aging over an extended period.

CONCLUSIONS

Aqueous solutions of high molecular mass PAAm contained detectable levels of agglomerated polymer, the size distribution of which changed over extended periods of aging. The influence of added salts or solvents on the aging process was dependent upon their ability as hydrogen bond makers or breakers to change the solvation of PAAm. The addition of 2%-v/v 2-propanol reduced the solvent quality, enhancing agglomerate formation. However, the addition of formamide at the same level improved the solvation of PAAm such that agglomeration was at a minimal level and aging effects were eliminated.

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