

Degradation of Aqueous Poly(acrylic Acid) and Its Sodium Salt Solutions by High-Speed Stirring

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Synopsis

Poly(acrylic acid) and 100% neutralized poly(acrylic acid) in pure water were stirred at 30°C at 30,000 rpm with a T.K. Homomixer at polymer concentrations ranging from 2% w/v to 0.0025% (25 ppm) for 2 hr to investigate the effect of polymer chain conformation on chain scission by high-speed stirring. After 2 hr of stirring at low concentration, intrinsic viscosity measured in 1.00 mole/l. NaCl solution at 30°C for 100% neutralized polymer was lower for the polymer which was stirred after 100% neutralization than for the one before 100% neutralization, showing that expanded polymer chains were more easily ruptured.

INTRODUCTION

The authors have been studying the degradation, by high-speed stirring, of solutions of various polymers¹⁻⁷ and the effects of polymer concentration and some other factors. It was found that the scission rate of polymer chains was affected by polymer concentration^{3,4,5,7} and solvent.^{2,3,5} These results have been discussed in terms of hydrodynamic volumes.⁵ In the preceding paper,⁷ the effect of methyl orange on the chain scission of poly(vinylpyrrolidone) solution by high-speed stirring was investigated because it had been reported^{8,9} that the addition of the dye increased the viscosity of aqueous solutions of the polymer, suggesting the unfolding of the macromolecule chains. The increase in viscosity by addition of the dye was confirmed, but 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).⁷

In this paper, the effect of polymer coil expansion on polymer chain scission in aqueous solution by high-speed stirring was studied using poly(acrylic acid), a typical polyelectrolyte.

It is well known that polyelectrolytes dissociate in polar solvents such as water, forming polyion, and that the degree of expansion of the chain of polyion is remarkably dependent on degree of dissociation, polymer concentration, and ionic strength of the medium. Consequently, we thought that the high dependence of chain scission on chain expansion should be confirmed by use of the system polyelectrolyte and water. The study on the effect of polymer concentration was also developed in the extremely low concentration range.

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EXPERIMENTAL

Materials

Poly(acrylic acid) (PA-H) was obtained by polymerizing 300 ml purified acrylic acid monomer (bp 44°C under 14 mm Hg) in purified methyl ethyl ketone (bp 79°–80°C) without any initiator in a 2-liter round-bottomed flask by standing outdoors for 17 days. Polymer containing methyl ethyl ketone was washed with methanol, filtered off, and dried to constant weight. The intrinsic viscosity of the thus obtained PA-H in dioxane at 30°C was 0.52 dl/g. The molecular weight calculated from the equation¹⁰

$$[\eta] = 8.5 \times 10^{-4} M^{0.5}$$

was 370,000 (degree of polymerization \bar{P} , 5200).

The sodium salt of poly(acrylic acid) (PA-Na) was obtained by neutralization of aqueous solution of PA-H with the required amount of aqueous sodium hydroxide solution. Water was used after purification through ion exchange resin. Sodium hydroxide and sodium chloride were pure grade.

Apparatus for Stirring 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

First, for the sake of decreasing errors between experimental runs a large amount of aqueous concentrated solution of PA-H was prepared for more dilute solutions, neutralized solutions, and neutralized solutions containing sodium chloride. Then, a second solution containing PA-Na was prepared from the first source by neutralization. In the case of solutions containing PA-Na, the polymer concentration was estimated on the basis of the PA-H. Each solution was prepared from the sources by dilution or addition of sodium chloride.

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 $30 \pm 5^\circ\text{C}$ and the mixer safe from harm by superheating, 5 min of stirring and 5–10-min pauses for cooling were alternated. After stirring for a given time, about 10 ml stirred solution was taken out and stirring was continued. Dilute solutions less than 0.2% g/ml were stirred batchwise.

In the case of extremely dilute solutions below 0.01% w/v a large amount of solution such as 1000 ml, whose weight was more than the weight required for measurement of intrinsic viscosity, was prepared, divided into 200-ml portions, and each portion was stirred under the same condition. After stirring, these solutions were gathered and concentrated by a rotary evaporator below 50°C under reduced pressure for $[\eta]$ measurements.

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

Polymer solutions stirred for a given time were subjected to measurement of intrinsic viscosity $[\eta]$ of PA-H. However, the $[\eta]$ of PA-H in water cannot be measured because of the nonlinearity of the relationship between the reduced

viscosity, η_{sp}/C and polymer concentration. The reduced viscosity increased with dilution. Therefore, the intrinsic viscosities of degraded polymers were all measured in 1.00 mole/l. aqueous NaCl at 30°C by means of an Ubbelohde viscometer after 100% neutralization with aqueous sodium hydroxide solution. In the measurements, the normal decrease in reduced viscosities with decreasing polymer concentration was observed. Thus, all results can be compared under the identical measuring condition of intrinsic viscosity.

The relationship between intrinsic viscosity and molecular weight was obtained from the different PA-H samples with different degrees of polymerization which were obtained on degradation by high-speed stirring; $[\eta]$ was $3.7 \times 10^{-4} M^{0.65}$ (dl/g) in 1.00 mole/l. aqueous NaCl at 30°C for 100% neutralized polymer.

RESULTS

Effect of Concentration of Scission of Poly(acrylic Acid)

Aqueous solutions of poly(acrylic acid) (PA-H) of concentration ranging from 2% to 0.0025% (20,000 to 25 ppm) were prepared and stirred at a speed of 30,000 rpm. Decrease in $[\eta]$ in 1.00 mole/l. aqueous NaCl at 30°C of the polymer after 100% neutralization is shown versus stirring time in Figure 1. The value of $[\eta]$ decreased rapidly at first and then slowly, reaching a constant value depending on the polymer concentration. It was found that in the concentration range over 0.02% (200 ppm) the rate of decrease in $[\eta]$ increased, and the final $[\eta]$ decreased with decrease in polymer concentration. The tendency was like that obtained for other polymers^{3,5} in concentrations over 0.02%. However, in the concentrations below 0.02% neither increase in the rate of scission nor decrease in the $[\eta]$ reached could be found with decreasing concentration.

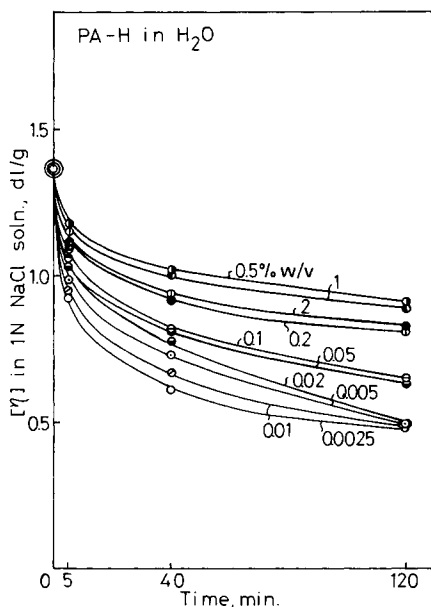


Fig. 1. Degradation of poly(acrylic acid) (PA-H) in water by high-speed stirring for various polymer concentrations (30,000 rpm, 30°C). $[\eta]$ was measured in aq. 1N NaCl solution at 30°C for polymers after neutralization.

Behaviors of Aqueous Solution Containing Poly(acrylic Acid) or Its Sodium Salt

Aqueous solutions containing PA-H at a constant concentration were neutralized (to PA-Na) with aqueous solution of 1.00 mole/l. sodium hydroxide required for just 100% neutralization, and then concentrations were precisely arranged by dilution with pure water. The addition of sodium hydroxide to aqueous PA-H solution was found to strikingly increase viscosity of the solution. The effect of sodium hydroxide on viscosity is shown in Figure 2, where the ordinate indicates the falling time at 30°C of aqueous PA-H, PA-Na, and PA-Na plus NaCl solutions through a capillary, namely, viscosities; and the abscissa indicates residual polymer group concentration. Values of pH of the solutions are, of course, changed by neutralization and dilution. They are shown in Figure 3. A glass electrode-type pH meter (Model PT-1S) made by Toyo Kagaku Sangyo Kaisha., Ltd., was used for the pH measurements.

Effect of Concentration of Scission of Sodium Salt of Poly(acrylic Acid)

The obtained aqueous solutions of sodium salt of poly(acrylic acid) (PA-Na) at various concentrations ranging from 2% to 0.0025% calculated on the basis of residual polymer (PA-H) were stirred under the same conditions as above (30,000 rpm, 30°C). Degradation curves are shown in Figure 4. The same tendency as above is found, showing that chain scission rate is increased with decreasing polymer concentration. In the case of PA-Na, however, no boundary concentration where concentration dependence disappeared, for example, 0.02%, was found. Even below 0.005%, the lower the polymer concentration, the lower was the intrinsic viscosity reached by high-speed stirring.

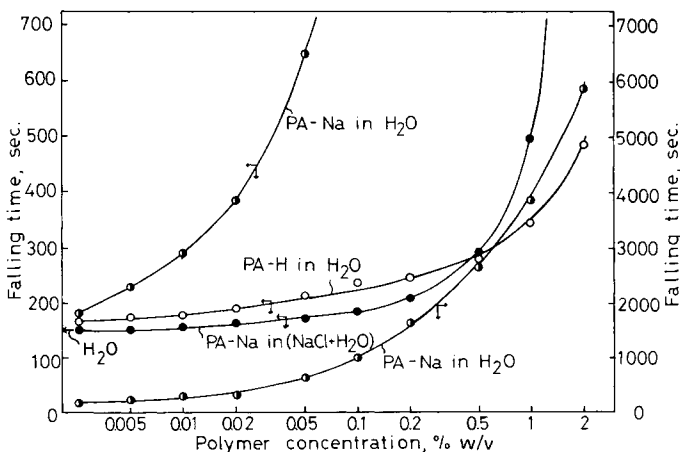


Fig. 2. Viscosities of poly(acrylic acid) (PA-H) in water and of its sodium salt (PA-Na) in water or in aq. NaCl solution for various polymer concentrations at 30°C. Concentrations of aq. NaCl were 1.00 mole/l. for PA-Na concentrations over 0.05% w/v and 0.125, 0.10, and 0.050, and 0.025 mole/l. for 0.020, 0.010, 0.0050, and 0.0025% w/v PA-Na solution, respectively.

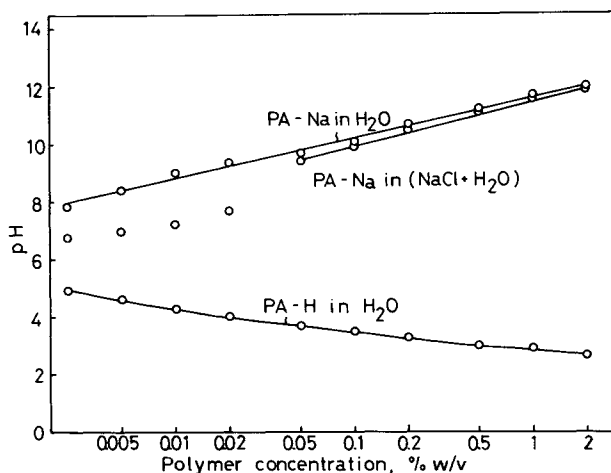


Fig. 3. pH values of poly(acrylic acid) (PA-H) in water and of its sodium salt (PA-Na) in water or in aq. NaCl for various polymer concentrations at 30°C. Refer to Figure 2.

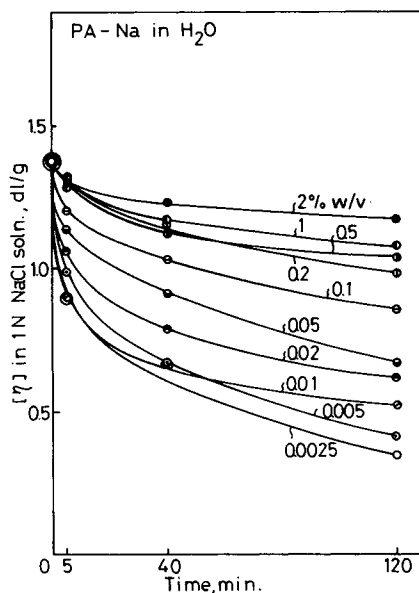


Fig. 4. Degradation of sodium salt of poly(acrylic acid) (PA-Na) in water by high-speed stirring for various polymer concentration (30,000 rpm, 30°C). Refer to Figure 1.

Scission of Sodium Salt of Poly(acrylic Acid) in Aqueous Sodium Chloride Solution

Aqueous solutions of sodium salt of poly(acrylic acid) (PA-Na) and sodium chloride (NaCl) show nearly intermediate behavior between the above two kinds of solution as shown in Figures 2 and 3. These solutions were stirred at various polymer concentrations ranging from 2% to 0.0025% under the same conditions

as above (30,000 rpm, 30°C). The concentrations of NaCl in the solutions were all prepared to be 1.00 mole/l. for polymer solutions above 0.05%. But they varied for solutions of lower polymer concentrations, because the concentrations of NaCl as well as polymer were increased when the dilute solutions after stirring were concentrated by evaporation for measurement of $[\eta]$. The concentrations of NaCl in the stirred solution were diluted so as to be 1.00 mole/l. after evaporation. Thus, the molar ratio of NaCl to residual polymer was made constant to be 10.0 for the solutions of polymer concentration below 0.01%.

The results on the degradation of the solutions by high-speed stirring are shown in Figure 5. Similar curves to the above are found.

DISCUSSION

Effect of Polymer Concentration on Scission

As described above, generally, the intrinsic viscosity reached by stirring decreased with decreasing polymer concentration for the respective system. These features are clearly seen in Figure 6, where intrinsic viscosities of polymers after 40 and 120 min of stirring, measured at 100% neutralization in 1.00 mole/l. NaCl solution at 30°C, are plotted against the logarithm of polymer concentration applied to stirring. The effect of polymer concentration of stirring solution on the rate or limit of chain scission is found to be less for poly(acrylic acid) (PA-H) than for the 100% neutralized one (PA-Na). In other words, the difference between the highest intrinsic viscosity and the lowest is larger for PA-Na.

It has been reported¹¹ that atactic poly(acrylic acid) at 100% neutralization assumes a rigid rod form in salt-free water and that the polymer at NaCl con-

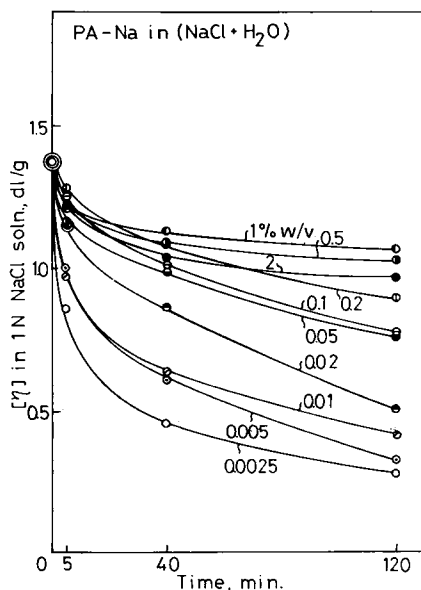


Fig. 5. Degradation of sodium salt of poly(acrylic acid) (PA-Na) in aq. NaCl by high-speed stirring for various polymer concentrations (30,000 rpm, 30°C). Refer to Figures 1 and 2.

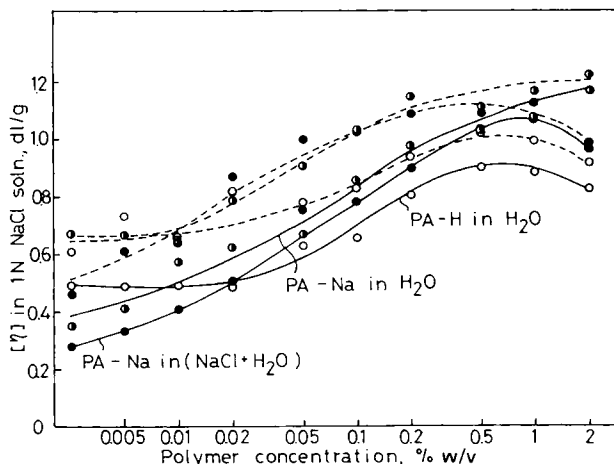


Fig. 6. Intrinsic viscosities of poly(acrylic acid) (PA-H) stirred in water and of its sodium salt (PA-Na) stirred in water or aq. NaCl for 40 or 120 min at various polymer concentrations (30,000 rpm, 30°C: (---) after 40 min stirring; (—) after 120 min stirring. Refer to Figures 1 and 2.

centrations higher than 0.02 mole/l. can be interpreted in terms of a nondraining random coil polymer.

It is clear from Figure 2 that PA-Na solutions without NaCl have always higher viscosities than original PA-H solutions, indicating that the former assume more expanded conformation.

Thus, the above higher dependence of scission on stirring polymer concentration for sodium polyacrylate is considered to be due to the expansion of polymer chain. Similar results had been obtained for poly(methyl methacrylate) in ethyl acetate and chloroform.³

In this study, the boundary concentration described above was discovered only for PA-H in water. Below the boundary concentration, no dependence of chain scission on polymer concentration is found. This indicates that neighboring polymer chains have no effect on a rupturing polymer chain or that the shearing rate in the flow is invariable below the boundary concentration, whereas neighboring polymer chains have suppressing effects on the scission of another polymer chain or they become a disturbing factor of the flow, resulting in decreased shear rate on a rupturing chain over the concentration.⁴ It is not clear how the neighboring polymer chains affect the scission of a polymer chain located in highly shearing flow, whether they are effective in direct ways, such as entanglement, or in indirect ways, for example, affecting the flow so that the resulting shear gradient is responsible for the scission. We suspect that the latter may be reasonable. In any way, the presence of polymer chains of high molecular weight affects the state of flow at very low concentrations, known as "drag reduction effects."

It is reasonable that the boundary concentration was found for PA-H whose chain is less expanded in water. It might be suspected that the boundary concentration shifts to much lower concentration for PA-Na because its chain is much expanded in salt-free water.

Effect of Polymer Conformation on Scission

It is found in Figure 6 that intrinsic viscosities attained after 120-min stirring are lower for PA-H than for PA-Na at high polymer concentrations, but vice versa at low concentrations. These results are considered due to chain expansion. It is doubtful that PA-Na solutions without NaCl were quite salt free and that the polymer chain assumed rigid rod conformation, because the experiments were carried out without special attention to strictly avoid contamination from carbon dioxide in air and the stirring apparatus. Nevertheless, it is clear in Figure 2 that the neutralized polymer chain had more expanded conformation.

Similar results were obtained in a previous study³ for poly(methyl methacrylate). It is considered that the effect of chain conformation on the scission was selectively tested in this study by using only water as solvent, differing from the previous study where different kinds of solvents were used.

According to the recent report,¹² poly(acrylic acid) showed a larger percent drag reduction at higher pH values than at lower values in the polymer concentration range around 25 ppm. Considering the results, the drag reduction phenomenon seems to appear at concentrations around 0.0025% (25 ppm) for the systems in this study, because the degree of polymerization is considerably high. If so, turbulent flow may be less for PA-Na than for PA-H in water, resulting in higher shear rate for the former. Thus, it is considered that a more violent degradation of polymer chain was observed for the former. Because intrinsic viscosities of each polymer in water under stirring could not be obtained, it was impossible to observe the previously suggested relationships⁵ between hydrodynamic volume and chain scission. However, it was confirmed that at a low concentration, more expanded polymer chains are ruptured to lower chain lengths. It is noted that the concentration where the above phenomenon appeared shifted to considerably lower direction. The authors consider that it resulted from extremely expanded polymer chains due to dissociation.

It is noteworthy to review that the addition of methyl orange to aqueous poly(vinylpyrrolidone) solution had no significant effect on the chain scission by high-speed stirring⁷ but that the addition of sodium hydroxide to aqueous poly(acrylic acid) solutions had a significant influence on the scission, both additives increasing the viscosity of each solution. The different results may be caused by different interacting factors, the former being hydrophobic and the latter ionic. It is found that ionic interaction is far stronger than hydrophobic interaction, and remains so even under such high shear rates as rupture polymer chains.

It was reported in the previous paper⁵ that chain scission by a shearing force depended on the rigidity of a polymer chain and that a main chain with higher rigidity was more easily broken at a low polymer concentration. The results for PA-H and PA-Na without NaCl in this study may be interpreted from the same viewpoint, because the latter polymer assumes a rigid rod form and the former, not so rigid a form, as described above.¹¹ However, the results for PA-Na in NaCl solution cannot be interpreted in terms of rigidity of polymer chains, because intrinsic viscosities after 120 min of stirring were always lower than those for that without NaCl, showing that PA-Na chains were more easily ruptured in NaCl solution where they can be regarded as nondraining random coils¹¹ than in pure water where they assume rigid rod forms. The anomalous results are interesting but complicated for the authors to interpret. It might be supposed that the

addition of NaCl increases the drag reduction effectiveness of neutralized poly(acrylic acid) solutions. Therefore, it might be interesting to investigate the effect of addition of salt into neutralized poly(acrylic acid), its kind, and concentration on polymer chain scission by high-speed stirring and on drag reduction effects.

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