# Unusual Complexation Behavior of Poly(acrylic acid) Induced by Shear

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ABSTRACT: Poly(acrylic acid) (PAA) in dilute solution undergoes a stable interchain association under high shear flow. This is reflected in a sharp decrease in drag reduction (DR). For this flow-induced deformation to occur the PAA must be of ultrahigh molecular weight ($\geq 5 \times 10^6$), in low concentration ($< 5 \times 10^{-4}$ M), and in a pH range of 6–8. Addition of a minute amount of salt to the shearing PAA solution induced a full recovery of the DR, suggesting a disruption of interchain association. Fluorescence emission of auramine O (AuO) that appears only upon shearing suggests that the shearing has developed a rigidity along the PAA chains. This is probably the direct result of supermolecular chain complexation by interchain H-bonding. The formation and stability of the supermolecular H-bonding is characterized by AuO fluorescence, FTIR, and $^{23}$Na NMR spectra as well as DR.

## Introduction

Macromolecules in dilute solution undergo orientational and extensional chain transitions as a result of fluid motion by mechanical shear. The extent of such chain deformation depends on chain interactions under the influence of solvent, concentration, and shear strain. A significant increase in the viscosity[1] is often observed in flexible macromolecular systems with increasing shear rate, particularly with polymers of ultrahigh molecular weight (UHMW).[2] This is due to a transient deformation resulting from a partial intermolecular association[3] that occurs more readily in concentrations at which molecular overlap becomes appreciable. However, the viscosity decreases as higher orientation and extension are attained in the macromolecules with increasing shear rate. A multiple-site cooperative interaction is expected to take place effectively among the aligned macromolecules, because the overlap concentration decreases with increasing shear so that molecules are more accessible to each other. Certain polymers exhibit shear-induced fiber formation and crystallization[4,5] that commonly require a high concentration and a poor solvent system. However, such oriented and stable interchain association has not been found so far for water-soluble polyelectrolytes, particularly at an extreme dilution, although there is an observation[6] by Katchalsky and his co-workers on the negative thixotropy of an aqueous solution of poly(methacrylic acid) (PMAA) in that a gel state induced by mechanical stirring spontaneously reverts to the sol state upon cessation of the stirring. The gelation occurs only with PMAA (not with PAA) at concentrations about 8–15%.

Drag reduction (DR) has been known for several decades; small amounts (even a few ppm) of certain polymers can alter the turbulent flow property of the solution significantly. This phenomenon is obviously produced by polymer-flow interactions, in that the flow property is modified by chain deformation of polymers induced by hydrodynamic shear. In this sense, DR is molecularly controlled, and the extent depends not only on the polymer structure but also on external conditions. It is generally accepted that conformationally flexible chain molecules with a high molecular weight (MW) are effective for DR.[7,8] However, due to the complexity of turbulent flow configuration, it is difficult to characterize detailed molecular processes in the flow. One of many theories[9-11] assumes that, in high shear flow, polymer molecules undergo a dynamic chain elongation. The macromolecules absorb energy from the turbulent eddies and dissipate it as elastic shear waves, thereby suppressing turbulence, resulting in DR. Since chain elongation (coil–stretch transition) occurs when the shear rate ($\gamma$) in the turbulence is greater than the reciprocal of molecular relaxation time, $1/\tau$, the higher the shear rate applied, the more energy dissipation results. In this regard, both MW and concentration are contributing factors for the relaxation time, as shown in the relationship[12]

$$\tau = \frac{M_v(\eta_{sp}/C)\eta_0}{0.586RT\lambda_1} \quad (1)$$

where $M_v$, $\eta_{sp}$, $\eta_0$, $R$, $T$, and $\lambda_1$ are the viscosity-averaged MW, the specific viscosity, the solvent viscosity, a gas constant, the absolute temperature of the solution, and the first eigenvalue of Zimm theory, respectively. Since $\eta_{sp}$ depends on the polymer concentration to a greater than first power, $\tau$ increases with polymer concentration and the DR is expected to increase with increasing shear rate, MW, and concentration. In a different approach, Brostow assumes[13] that chain solvation leads to domain formation. The domains are largely preserved during flow, resisting to vortex formation and acting as energy sinks for turbulence.

We observed[14] that poly(acrylic acid) (PAA) with UHMW exhibited an unusual DR behavior near neutral pH in a very dilute solution ($1.9 \times 10^{-4}$ M) under a high shear rotating disk flow. With an increase in the shear rate, the DR decreases sharply, accompanied by a decrease in the viscosity but without causing turbidity in the solution. The decreasing DR was, however, instantaneously recovered upon the addition of a minute amount of a salt, e.g., sodium chloride, to the solution under shear. We assumed that this behavior is closely related to a conformational transition resulting from the intermolecular association of the polymer. To our knowledge, this was the first report of stable interchain complexation of PAA in a dilute solution.

We have followed a conformational transition in the sheared PAA molecules using a cationic dye, auramine O,

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bis[4-(dimethylamino)phenyl]methylideneammonium chloride (AuO),[15] as a fluorescence probe. Since AuO fluorescence is a sensitive function of local rigidity,[16] the microenvironmental rigidity change along the PAA chain can be monitored by the fluorescence intensity of the dye which is electrostatically associated with the polyions. We found that AuO fluorescence appeared upon shearing (no fluorescence in unsheared PAA solution), and it increased with shearing time until it reached a plateau. However, the fluorescence of the sheared solution vanished upon the addition of salts.

In this report, we discuss details of conformational transitions of PAA molecules induced by shear, depending on the external conditions such as pH, salt, PAA concentration, shear rate, and PAA molecular weight. We discuss also the mode of interchain interaction and subsequent chain rigidity developed in the PAA through studies[17] by FTIR, $^{23}$Na NMR, and TEM.

## Experimental Section

**Materials and Sample Preparations.** PAA was synthesized by conventional free-radical polymerization using ammonium persulfate as the initiator. A series of PAAs differing in molecular weight were made under varied conditions. The intrinsic viscosity of PAAs used in this study is in the range of 2.6–9.9 dL/g (25 °C in 1.0 M NaCl), corresponding to the average molecular weight range of (1.0–8.0) × $10^6$. AuO was a commercial product and was recrystallized twice from alcohol. An aqueous solution of PAA was neutralized with sodium hydroxide, dialyzed, and subsequently freeze-dried. A stock solution (1.90 × $10^{-3}$ unit mol/L (M)) of PAA Na salt was prepared by dissolution of the salt in deionized water with gentle stirring for 24 h. PAA solutions for flow studies were made by diluting the stock solution with 10 volumes of deionized water under gentle stirring for 1 h. A fresh stock solution was always used within a day. The solution pH was adjusted, if necessary, by adding dilute hydrochloric acid or sodium hydroxide.

**Flow Processing.** The turbulent flow field was generated by a motor-driven stainless steel rotating disk (12.7 cm in diameter by 0.318 cm in thickness) placed in a cylindrical closed Plexiglas container (14 cm in diameter and 1.8 cm in height). Approximately 240 mL of polymer solution was required to fill the container. A dc motor generator coupled with a controller (Cole Parmer Master Servodyne Unit) was used to maintain a preset rotational speed by delivering a variable torque as required by the load on the disk. The polymer solution was sheared in the rotating disk flow at a fixed speed, usually at 2800 rpm (Reynolds number, $Re \approx 1 \times 10^6$) up to 6 min. Since the reduction in torque is proportional to the reduction in frictional drag on the disk surface, the DR is defined by the following:

$$\% \text{ DR} = (1 - \tau_p/\tau_s) \times 100 \quad (2)$$

where $\tau_s$ and $\tau_p$ are the torque in solvent alone and in the presence of polymer, respectively. With the present rotating-disk system, the highest attainable DR is around 40%.

**Fluorescence Measurements.** Sheared samples[18] were removed from the rotating-disk flow container immediately upon the cessation of shearing. Samples for fluorescence measurements were made by adding a 0.2-mL aliquot of a 100 ppm AuO stock solution to a 50-mL sheared (or unsheared) PAA sample solution; this gives a probe concentration of 7.64 × $10^{-7}$ M. Emission spectra of the sheared (or unsheared) solution were recorded with a Spex Fluorolog II fluorimeter in the range of 400–700 nm with an excitation wavelength at 366 nm. The fluorescence intensity change of AuO in the sheared PAA solution is used as a measure of local rigidity along the PAA chain.

**FTIR, $^{23}$Na NMR, and TEM Measurements.** FTIR spectra (100 scans) were recorded on a Perkin-Elmer 1800 spectrophotometer (with 0.2-$cm^{-1}$ resolution) using a KBr dispersion of a freeze-dried sample of sheared (or unsheared) PAA solution. $^{23}$Na NMR spectra of sheared (or unsheared) PAA solutions (1.9 × $10^{-4}$ M) were measured in a Bruker MSL-300 spectrometer at a Larmore frequency of 79.390 MHz and relaxation delay of 250 ms with 216 000 scans. The temperature was maintained at 300 K. A solution of NaCl was used as a standard for chemical shift and line-width comparison. Transmission electron micrographs (TEM) of sheared (or unsheared) PAA solution were made as follows: a drop of the dilute solution was placed on a carbon grid, then a drop of stain (1% uranyl acetate in water) was added, and 15 s thereafter, the solvent was removed by wicking using a piece of filter paper. The samples were viewed on a Zeiss EM 10C instrument.

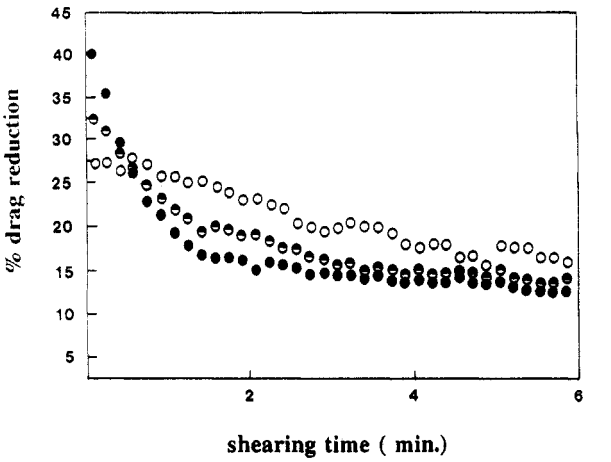


**Figure 1.** Influence of the shear rate on % DR of the PAA solution (1.90 × $10^{-4}$ M) at pH = 8.0. Shear rates of the rotating disk are 27 (○), 33 (⊖), and 47 $s^{-1}$ (●).

## Results and Discussion

**Drag Reduction (DR) and PAA Conformation.** Polymer DR commonly increases with increasing shear rate[8] up to a certain limit (Virk's maximum DR asymptote[19]), after which DR may decrease mainly due to shear degradation. As shown in Figure 1, the initial DR by the PAA increases (25–38%) with increasing shear rate (27–47 $s^{-1}$, corresponding to 1600–2800 rpm), and it decreases disproportionately with continued shearing; the higher the shear rate, the faster the decrease in DR. This behavior is unusual unless there is a chain degradation by shear. The variation in the initial DR (depending on the shear rate) is thought to reflect differences in the initial conformational states (corresponding to the rate of chain extension and relaxation) of the PAA molecules under the shear. Accordingly, the sharp decrease in DR with further shearing must be related to a drastic conformational transition of the PAA, suggesting that extended chains are more susceptible to interchain association. This is evidenced by a decrease in viscosity that occurs in parallel with the DR decrease.[14] It was also found that % DR of PAA (sheared at 47 $cm^{-1}$, 4 min) at 20 °C remained unchanged for 2 weeks after cessation of the shear and that the same experiment at 50 °C gave a similar result.

1. **pH Effect.** Decreases in DR are markedly pH-dependent as shown in Figure 2. Interestingly, the sharpest decrease in the DR occurs at a pH between 6 and 8. The implication is that the time-dependent chain deformation requires the initial conformation of PAA to be in a loosely coiled state. Although the extended coil state (pH >9, for example) could be more susceptible to shear-induced chain deformation in comparison with a tightly coiled state (pH 4, for example), no such deformation occurred, and it appeared that the DR remained unchanged on extended shearing. This suggests the importance of interchain H-bonding for the chain deformation (resulting in the decrease of DR). If this is the case, the DR decrease should be favored by a low pH (4–5). However, it is also difficult to bring about such a drastic

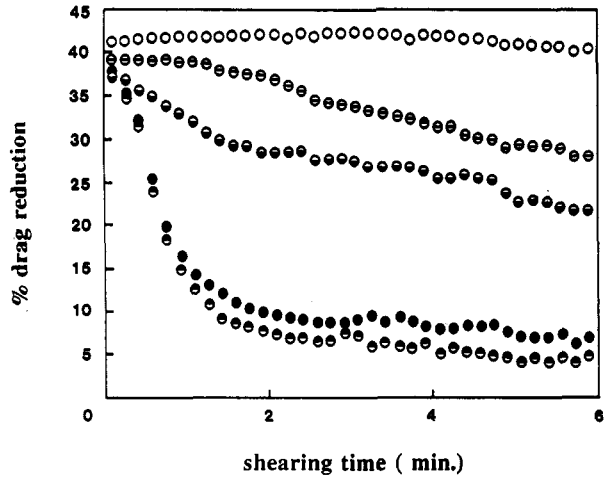


**Figure 2.** Influence of pH on % DR of the PAA solution ($1.90 \times 10^{-4}$ M) at a shear rate of 47 $s^{-1}$. pHs are 4.0 (⊖), 6.0 (⊖), 8.0 (●), 9.0 (⊖), and 9.5 (○).

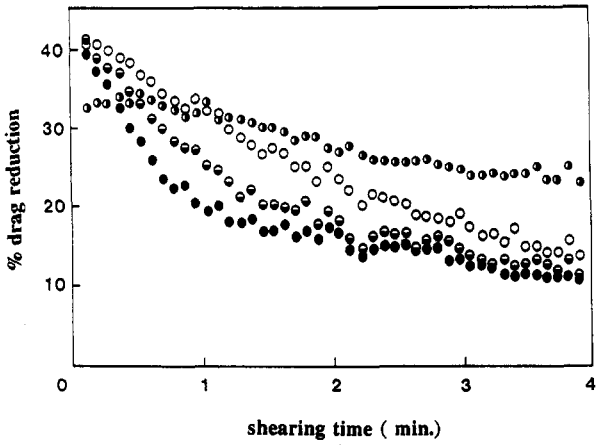


**Figure 3.** Effect of PAA concentration (at pH 8.0) on % DR at a shear rate of 47 $s^{-1}$. Concentrations are $9.50 \times 10^{-5}$ (○), $1.27 \times 10^{-4}$ (⊖), $1.90 \times 10^{-4}$ (●), and $5.70 \times 10^{-4}$ M (◑).

chain transformation, because the conformational state of PAA at the low pH is highly resistant to chain elongation by shear due to intramolecular chain aggregation. Consequently, the pH range, 6–8, must be optimal for the shear-induced chain deformation of PAA. An earlier DR study[20] on PAA in a pipe flow system showed that a maximum DR is attained in the pH range of 6–8, suggesting that, under this condition, PAA molecules are elongated to the greatest extent but unable to undergo chain deformation, because in the pipe-flow system, the residence time of polymer is too short (a few seconds).

**2. Concentration Effect.** Figure 3 shows the concentration dependence of the DR behavior of the PAA solution at pH 8.0 (an optimal condition for chain deformation). At PAA concentrations in the range of $(1.0–3.5) \times 10^{-4}$ M, the initial DR shows the same high level (ca. 40%), while the subsequent decrease in DR with extended shearing depends on concentration. At a concentration (e.g., $5.7 \times 10^{-4}$ M) higher than that range, the DR remains almost unchanged or increases somewhat on prolonged shearing. This seems to indicate that the shear-induced PAA deformation (leading to a decrease in DR) occurs only at concentrations below a certain limit, and beyond that limit, the shear resistance of PAA against chain elongation increases as a result of growing interchain entanglement (Figure 4). Thus, a restriction to chain elongation occurs at a critical concentration, $C_s^*$, defined as the concentration at which a dynamic chain overlap occurs due to shear. Since the dynamic chain overlap is generally attained at a lower concentration than the overlap

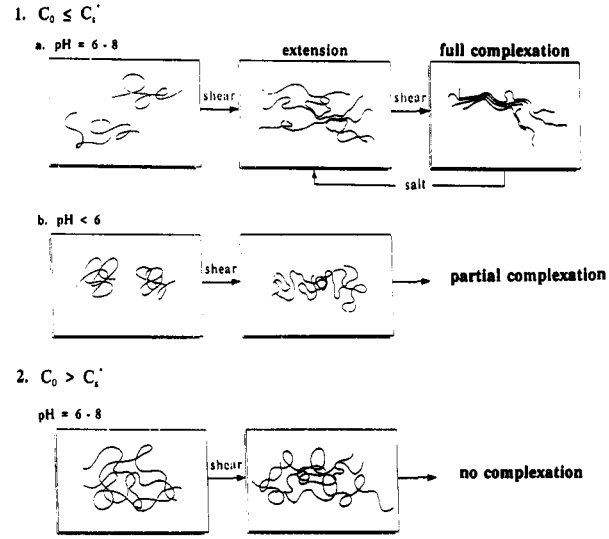


**Figure 4.** Schematic representation of flow-induced chain deformation depending on pH and concentration of PAA.

concentration ($C_0^*$)[21] at rest, the $C_s^*$ is normally smaller than the $C_0^*$. Furthermore, since $C_s^*$ depends on the shear field applied, a polymer concentration ($C_0$) before shearing can become either higher (or lower) than $C_s^*$ or equal to $C_s^*$, depending on the shear condition. The significance of $C_s^*$ relative to $C_0^*$ is given by

$$C_s^* = M/N_A R_s^3 \quad (3)$$

where $M$ is the average MW of the polymer, $N_A$ is Avogadro's number, and $R_s$ is related to the root-mean-square end-to-end distance under shear.

The dependence of the DR change on pH and PAA concentration suggests that the conformational transition of the polymer is dictated by the conformational states before shearing (Figure 4). A sharp DR decrease requires the PAA to be conformationally flexible (intra- and intermolecularly less aggregated) for chain elongation by shear. This can be achieved by an intermediate pH and a shear-manageable dilute solution. Above all, the presence of some free acid residues in the polymer is essential for interchain H-bonding. There is still a critical question how H-bonding with a sparse distribution (at pH 8.0, for example) along the PAA chain can lead to a rigid aggregate in spite of the repulsive force between neighboring polyanions. The interchain charge repulsion may be relieved by counterion condensation. In fact, the H-bonding mediated association of PAA was found to be very stable; no measurable changes in DR and AuO fluorescence were observed with the sheared PAA solution over a period of several weeks, except for a minor fluctuation of the fluorescence intensity during the first couple of days.

**3. Molecular Weight Effect.** Another important factor for the transition of the PAA conformation is MW, which has a major effect on polymer DR. The sensitivity of DR to MW depends on the molecular structure of polymer,[22] but flexible-chain polymers always lead to high efficiency. As shown in Figure 5, the initial DR is higher with high MW PAAs. There is virtually no change in DR observed with PAAs whose MWs are below a million, while the DR change appears when PAA MW becomes 5 million. Furthermore, the decrease in DR is marked with PAA of increasing MW, reminiscent of shear degradation[13,23] of polymers, since high MWs are more vulnerable to shear degradation. However, this is not the case here. As evidenced by the observation[14,24] that the once-decreased DR is instantaneously recovered upon addition

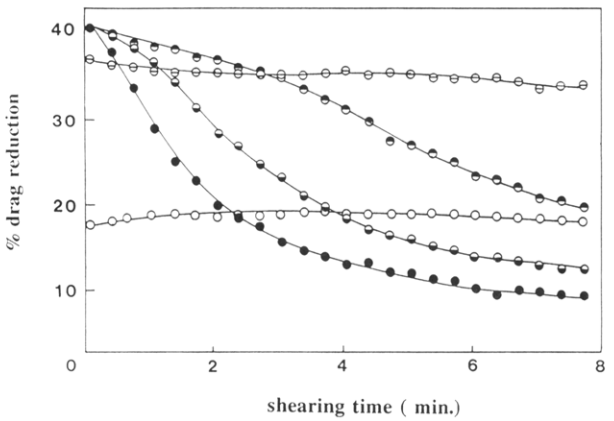


**Figure 5.** Molecular weight (MW) effect of PAA ($1.27 \times 10^{-4}$ M) on % DR at a shear rate of 47 $s^{-1}$. MWs $\times 10^6$ are 1.0 (○), 3.8 (⊖), 5.0 (◓), 6.6 (◒), and 8.0 (●).

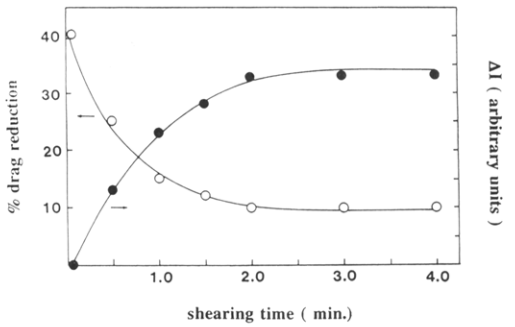


**Figure 6.** Drag reduction and AuO fluorescence intensity ($\Delta I$) of sheared PAA solutions ($1.90 \times 10^{-4}$ M, pH 8.0) as a function of shearing time.

of a minute amount of salt to the PAA solution under shear. The degree of DR recovery depends on the amount of salt added and the length of shearing time:[14] longer shearing (prior to salt addition) produces increasing interchain links, requiring more salt for a full recovery. The MW effect on the DR decrease (during extended shear) seems to suggest that DR is associated with chain relaxation. Under a given shear strain, the relaxation time becomes longer with increasing macromolecular chain length and an increasing number of interchain links, which are in turn dependent on the number of binding sites available per chain. Accordingly, if some change occurs in the relaxation rate of macromolecules during shear, that transition should be reflected in the DR.

**Local Chain Rigidity.** AuO is a unique fluorescence probe for monitoring the rigid local environment.[25] While without shearing, no AuO fluorescence is observable in the PAA solution, with shearing fluorescence appears and its intensity increases with increasing shear rate and shearing time up to 2 min, leveling off thereafter.[15] The increase in AuO fluorescence in the sheared PAA solution is inversely proportional to the DR change during the shear (Figure 6). This clearly indicates that the decrease in DR of the PAA with shearing is associated with a growing rigidity along the polymer chain as a result of a supermolecular complexation through interchain H-bonding. By the same token, AuO fluorescence disappears when the decreasing DR is fully recovered by the addition of salt to the PAA solution under shear, indicating that the local chain rigidity is completely disrupted and returned to an unsheared random-coil state. Clear evidence for the supermolecular rigidity formation in the sheared PAA is demonstrated by the transmission electron micrograph of the sheared sample (Figure 7). The unsheared sample of the PAA solution shows loosely extended coils, while the

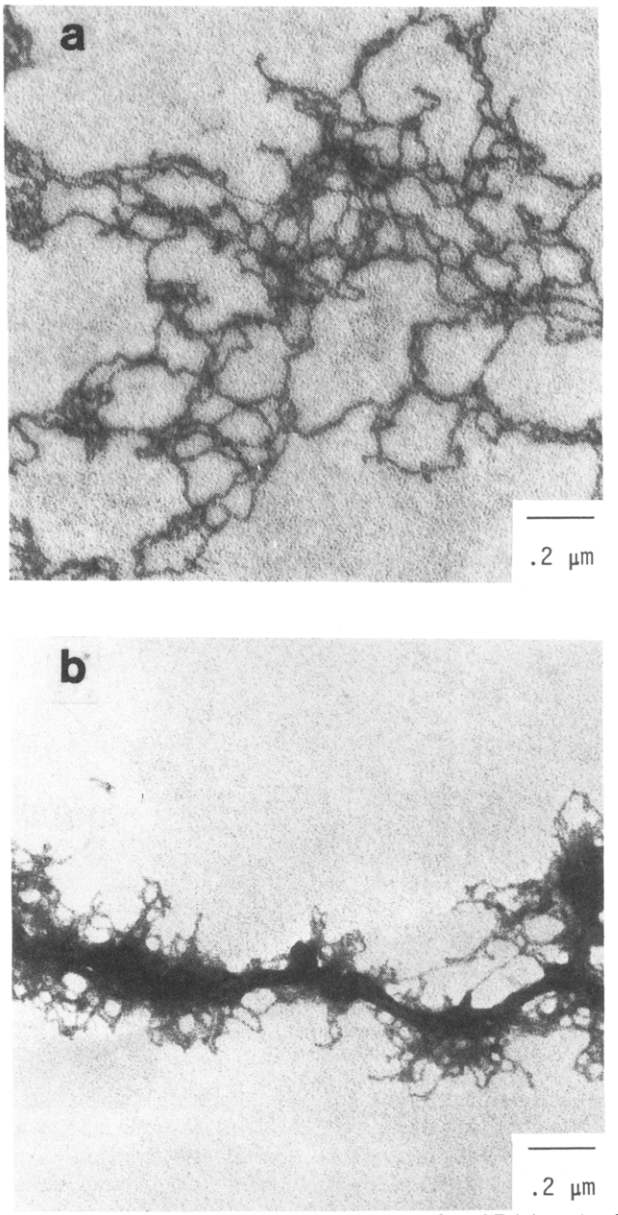


**Figure 7.** Transmission electron micrographs of PAA stained with uranyl acetate: (a) unsheared PAA; (b) sheared PAA.

sheared sample exhibits a bundle of stiff chains. The chain entanglement exhibited in the micrograph of the unsheared sample does not necessarily indicate chain overlap in the solution, since the micrograph specimen was made by removing the solvent so that the molecules which existed as isolated chains in the solution, come to overlap. This micrograph does not, therefore, represent the molecular state in the unsheared solution, but it still is in marked contrast to the specimen from the sheared solution. A similar situation was observed with freeze-dried samples; the unsheared solution produced a fluffy film with a weblike texture in contrast to the solid powder obtained from the sheared solution.

**H-Bonding and Salt Effect.** FTIR spectra (Figure 8) of the sheared and the unsheared PAA samples (at pH 8.0) show a clear difference, although the freeze-dried samples (used for KBr dispersion) may not represent the exact molecular situation in solution. The spectrum of the unsheared sample has a shoulder between 1650 and 1720 $cm^{-1}$, while it splits into two peaks (1674 and 1700 $cm^{-1}$) in the spectrum of the sheared sample. The peak at 1700 $cm^{-1}$ (which is a C=O stretching band associated with dimerization of –COOH)[26] disappears when the

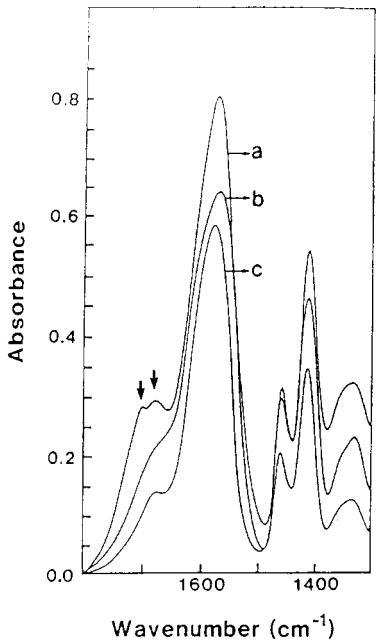


**Figure 8.** FTIR spectra of PAA: (a) sheared (at pH 8.0); (b) unsheared; (c) salt treated (before or during the shear).

sample is made from the salt-treated sheared solution, while the other peak (1674 cm$^{-1}$) is retained, clearly indicating the disruption of the dimeric H-bonding. The same absorption band situation (remaining at 1674 cm$^{-1}$ but not at 1700 cm$^{-1}$) appears when the salt is added to the PAA solution before shearing. As discussed earlier, since the addition of salts ($1.7 \times 10^{-3}$ M NaCl, for example) to the sheared PAA solution ($1.9 \times 10^{-4}$ M) brings about the recovery of DR, disappearance of AuO fluorescence, and restoration of the loose-coil morphology (in TEM), all these phenomena must be rooted in the same origin, namely, the disruption of interchain H-bonding. The peak at 1674 cm$^{-1}$ is assignable to another C=O stretching of free –COOH in association with $-COO^-$ to form H-bonding. Since, under the present pH condition, H-bonding in PAA occurs mainly between –COOH and $-COO^-$ and there also exists a large excess of $-COO^-$ present, some fraction of $-COO^-$ groups are in the H-bonding state (1600 cm$^{-1}$) and the rest in the free state (1575 cm$^{-1}$). The presence of dimeric H-bonding (in addition to the other form of H-bonding) in the sheared sample seems to be particularly important for the stability of the complex. This is probably due to the locally high free carboxyl concentration upon the chain association. Disappearance of the band at 1700 cm$^{-1}$ due to the addition of NaCl is therefore clearly the result of the H-bond breakdown (viscosity return). When the PAA was sheared in the presence of urea, the DR decrease was lessened depending on the amount of urea added (Figure 9), again proving the involvement of H-bonding. The efficiency of urea is far less than that of salts. Kulicke and Kniewske reported[27] that a viscosity decrease (so-called "aging") observed in high molecular weight poly(acrylamide) and a acrylamide–acrylic acid copolymer was not due to chain scission but conformational transition involving H-bonding, because the loss of viscosity was not seen upon the addition of NaCl to the solution. The salt effect[24] in the present system is not limited to alkali-metal salts but is equally effective with amine salts, particularly with $NH_4Cl$. The effect of heavy-metal ions is negligible or negative.

**Counterion Binding.** The key issue is how such a relatively small fraction of free –COOH (ca. 30% estimated from the degree of ionization, $\alpha = 0.7$ at pH 8.0) in PAA can sustain stable H-bonding in a highly repulsive ionic

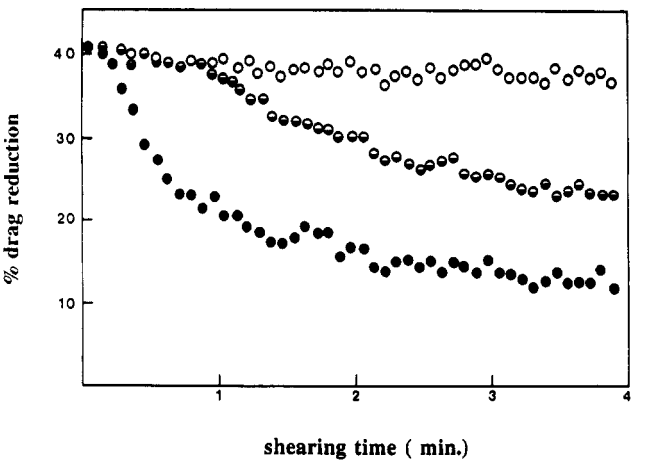


**Figure 9.** DR changes of PAA ($1.90 \times 10^{-4}$ M, pH 8.0) in the presence of urea: 0 (●), 0.7 (⊖), and 2.0 M (○).

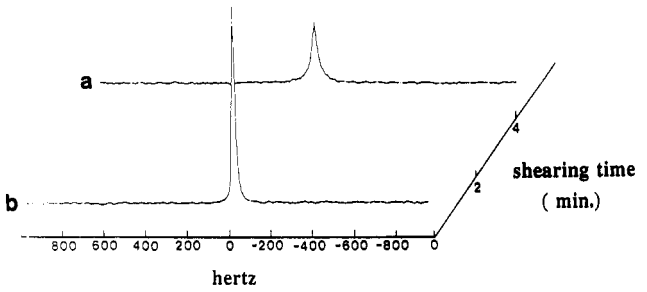


**Figure 10.** $^{23}$NMR spectra of PAA solution ($1.90 \times 10^{-4}$ M, pH = 8.0): (a) unsheared PAA; (b) sheared PAA.

microenvironment. The actual number of effective H-bondings through cooperative interchain interactions will be further decreased due to the restricted movement of the elongated chains. What then is the source of the H-bonding stabilization of the PAA complex? The answer is probably a favorable environmental effect created by counterion ($Na^+$) binding to the polyions, thereby suppressing their repulsive force. Counterion binding increases depending on the degree of ionization in polymers,[28] accompanying dehydration (reflected in counterion binding strength) as a result of mutual perturbation of hydration layers. The resulting volume change and reduced hydration as well as charge neutralization should provide an additional environmental effect for the complex stability. NMR line broadening is associated with quadrupolar relaxation for nuclei with nuclear spin $I > 1$. A broadened line width is observed when $Na^+$ ions are associated with polyions due to the interaction of the nuclear quadrupole moment with the electric field gradient at the nucleus. $^{23}$Na NMR spectra were taken to differentiate the $Na^+$ ion binding (to polyions) between the sheared and unsheared PAA solutions ($1.9 \times 10^{-4}$ M at pH 8.0). As shown in Figure 10, there are marked differences in the line shape and the integrated intensity between the samples; the sheared sample exhibits a broader line shape and a lower integrated intensity. Since the integrated NMR intensity represents the sum of free and binding states of $Na^+$ ions, a 10% lower integrated intensity in the sheared sample may be attributed to a corresponding increment of site-specific binding of $Na^+$ ions, whose extreme quadrupolar line broadening is difficult to observe in the integrated intensity. More noticeably, the broader line shape of the sheared solution is most likely the result of a higher population of binding states relative to free states. These results suggest that PAA polyions in the sheared solution undergo a relatively "tighter" counterion binding. When the cation concentration is increased in the shearing solution by adding salt, a further binding of

counterions may occur to a limit where the interchain H-bonding starts to suffer disruptions. This concentration limit of NaCl, for example, was found to be around $2 \times 10^{-4}$ M, and beyond that the H-bond is broken, resulting in recovery of DR and an increase of viscosity which depends on the amount of added salt. However, the DR is subjected to another transition when the added salt concentration reaches $1 \times 10^{-1}$ M. This is not associated with chain elongation but a chain collapse due to the charge shielding effect by the added salt cations.

In conclusion, poly(acrylic acid) (PAA) in a dilute solution undergoes a conformational transition under shear, resulting in a drastic decrease in drag reduction (DR) with shearing rate and time. Such DR changes are sensitive to pH, molecular weight, and concentration of PAA. The DR decrease is, however, completely recovered with a minute amount of salt added to the solution under shear. Such DR changes are interpreted as a direct result of interchain association through H-bonding. Auramine O fluorescence spectra suggest that shearing of PAA induces a drastic conformational transition that develops rigidity along the PAA chains. It is further concluded that DR is related to polymer chain deformation under shear and that conformational flexibility before shearing and chain relaxation change by shear have an important contribution to PAA complexation. The stability of the supermolecular complexation seems to be sustained by counterion binding.

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