

## Degradation of Polyacrylamide Molecules in Aqueous Solutions by High-Speed Stirring

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### Synopsis

It has been observed that the viscosity of polyacrylamide (PAM) solution decreased with an increase in high-speed stirring time. The viscosities of PAM solutions decrease initially and then remain constant as the stirring time is increased. The final values depend on the stirring speed. This decrease was assumed to be due to a change in the dissolved state and/or the degradation of PAM molecules. It was discovered through experimentation that the molecular weight decreased, implying that the PAM molecules were degraded.

### INTRODUCTION

Several papers<sup>1-3</sup> have been published on the degradation of polymer molecules in a solution due to high-speed stirring. Johnson<sup>1</sup> reported that polyisobutylene and polystyrene were degraded by high-speed stirring and that maximal degradation occurs in poor solvents at lower temperatures. Zimm<sup>2</sup> suggested that the degradation of polystyrene or DNA by stirring was high in poor solvents with high viscosity. These authors discussed mainly the extent of degradation under various conditions, but not the quantitative kinetics of the degradation. In this work, it has been observed that the viscosity of polyacrylamide (PAM) solution decreased with stirring time. We studied the cause of the decrease in the viscosity and discuss the kinetics of the degradation of PAM molecules.

### EXPERIMENTAL

PAM solutions were placed in an M-Type (Tokushu Kika) Homo-Mixer and subjected to high-speed stirring for various periods of time. Care was taken that the blades were immersed to the same level in the liquid in each case in order to ensure identical stirring conditions. The viscosities of these solutions were then measured with a Type B viscometer (Tokyo Keiki).

The intrinsic viscosities  $[\eta]$  (reduced viscosity at zero concentration) were obtained by extrapolating the measured values for a 0.1-1.0 g/dl concentration. The molecular weights  $M$  were calculated from the intrinsic viscosities by using the Staudinger equation,  $[\eta] = KM^\alpha$ . The constants  $K$  and  $\alpha$  in the equation are given, for PAM in water at 25°C, as  $0.631 \times 10^{-4}$  and 0.8, respectively.<sup>4</sup>

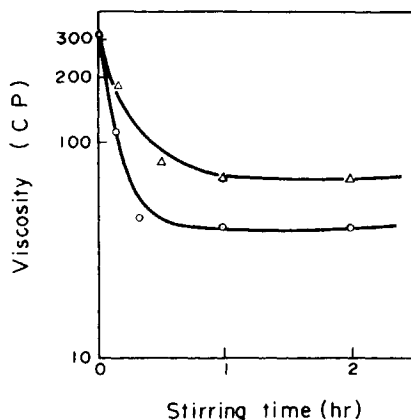


Fig. 1. Viscosity decrease of PAM solutions by high-speed stirring at 25°C: (—○—) 7000 rpm; (—△—) 4000 rpm.

## RESULTS AND DISCUSSION

The effect of high-speed stirring on the viscosity of PAM solutions is shown in Figure 1. The figure indicates that the viscosities of the solutions decrease initially and then remain constant as the stirring time approaches infinity. The final values depend on the stirring speed.

Two assumptions were used in order to explain this phenomenon. First, the dissolved state of PAM solutions changes due to stirring. If this assumption is true, the intrinsic viscosity  $[\eta]$  must change due mainly to the electrostatic repulsion forces by adding salts to the stirred solution. The experimental results before stirring are shown in Table I. The table indicates that the variations in the viscosities are small in both solutions. From these results, the dissolved state of the PAM solution can be considered not to have been changed by stirring. Furthermore, the reversibility of the viscosity by repeated dissolving of the PAM molecules was investigated. After evaporating the solvent of the stirred solutions, the molecules were dissolved again and the viscosity of the solution was measured. The viscosity of the solution was found to be equal to that of the initial stirred solution. This suggests that the decreased viscosities of molecules due to stirring are irreversible. It can be concluded, therefore, that the first assumption is invalid.

TABLE I  
Intrinsic Viscosity of PAM Solution

	1.0 soln. viscosity (cp)	Intrinsic viscosity $[\eta]$ , dl/g	
		No additive	1% Salt added
PAM soln. (no stirring)	312.5	14.5	13.7
PAM soln. (stirring)	42.5	8.0	7.8

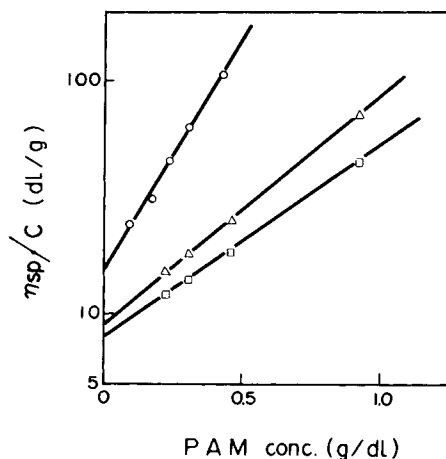


Fig. 2. Reduced viscosity  $\eta_{sp}/C$  of PAM solutions vs. stirring time at 25°C: (—○—) no stirring; (—△—) 4000 rpm 1-hr stirring; (—□—) 7000 rpm, 1-hr stirring.

The second assumption is as follows: The PAM molecules degrade because of high-speed stirring. Figure 2 shows a graph of the reduced viscosity  $\eta_{sp}/C$  against the concentration  $[C]$  for PAM solutions at various stirring speeds. In this case, these solutions were sampled three days after stirring. The figure indicates the linear relationship between  $\eta_{sp}/C$  and  $C$ , as well as the decrease in  $[\eta]$  as the stirring speed is increased. The molecular weight calculated from  $[\eta]$ , with respect to the stirring time, is seen in Figure 3. The figure shows that the molecular weight decreased initially with stirring time and then remained constant. The final values depend on the stirring speed, and the value after 7000 rpm stirring at 25 °C is about half of the initial value.

The distribution of molecular sizes was also measured by gel permeation chromatography (GPC), and the results are shown in Figure 4. It is evident from the figure that the PAM molecular size was reduced after stirring. These experimental results suggest that the decrease in the viscosity of the PAM solution by high-speed stirring with the resulting reduction in molecular weight is due to the degradation of the PAM molecules.

The degradation mechanism of vinyl polymers has been widely described.<sup>5-8</sup> After investigating the applicability of numerous equations to our experimental

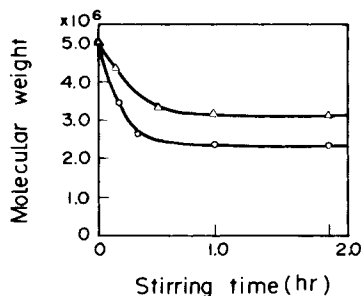


Fig. 3. Molecular weight decrease of PAM vs. high-speed stirring: (—○—) 7000 rpm; (—△—) 4000 rpm.

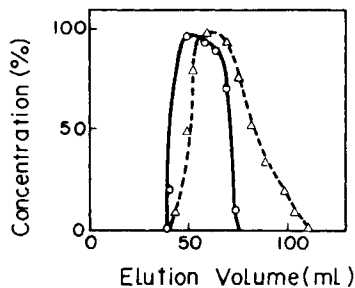


Fig. 4. GPC elution curve of PAM solution: (—○—) before stirring; (---Δ---) after stirring.

results, it was found that the formula given by Jellinek<sup>5</sup> was the most suitable:

$$\begin{aligned} dB_i/dt &= k(P_i - 1)n_i && \text{for } P_i > P_1 \\ dB_i/dt &= 0 && \text{for } P_i \leq P_1 \end{aligned} \quad (1)$$

where  $B_i$  is the number for shear degradation,  $P_i$  is the degree of polymerization,  $P_1$  is the limiting degree of polymerization,  $n_i$  is the number of molecules,  $k$  is the rate constant, and  $t$  is the time. By investigating eq. (1) with boundary conditions, the rate formula of the shear degradation can be obtained as

$$B/n_0 = [(2P_r/P_1) - 1] - [(2P_r/P_1) - 1 + k(P_r - P_1)t]e^{-kP_1t} \quad (2)$$

where  $n_0$  is the initial number of molecules and  $P_r$  is the initial degree of polymerization. The above equation is based on the assumption that all bonds in the polymer are equally likely to break and that the degree of polymerization of molecules, after degrading for a sufficiently long time, are all in the region between 1 and  $P_1$ . The calculated values for shear degradation with Jellinek's treatment of eq. (2), together with the experimental results, are plotted against the stirring time in Figure 5. The agreement is good, indicating the applicability of Jellinek's theory.

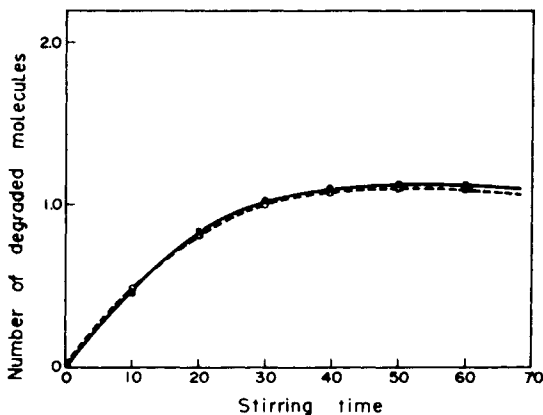


Fig. 5. Relation between number of degraded molecules and stirring time: (—●—) experiment; (---○---) calculated.

## CONCLUSIONS

The decrease in viscosity of PAM molecules in aqueous solutions by high-speed stirring was considered to be due either to the change in the dissolved state or to shear degradation. It has been proven that the dissolved states did not change by investigating both the salt additive effects in solutions and the reversibility of the viscosity by repeatedly dissolving the polymer after the stirring treatment. The shear degradation was studied by calculating the viscosity-average molecular weight of the solutions and by measuring the distribution of molecular sizes with GPC. The molecular weight and size were found to be reduced after stirring: the decrease in the viscosity of the PAM solution by high-speed stirring was due to the degradation of the PAM molecules. It was also found that Jellinek's theory can be applied to the calculation of the degradation rate of PAM molecules.

## References

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Received February 23, 1976