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Degradation of Polyacrylamide Molecules in Aqueous Solutions by High-speed Stirring

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Synopsis. The viscosity of polyacrylamide aqueous solutions decreases as a result of high-speed stirring, due possibly to the degradation of the molecules.

It has been observed that the viscosity of the polyacrylamide (PAM) solution decreased with increased high-speed stirring time. This decrease is assumed to be due to a change in the dissolved state and/or the degradation of the PAM molecules. It was experimentally found that the molecular weight decreased, implying that the PAM molecules were degraded.

Experimental

PAM solutions were placed in a type M (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 by 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 α in the equation are given, for PAM in water at 25 °C, as 0.631×10^{-4} and 0.8, respectively.[1]

Results and Discussion

The high-speed stirring effect on the viscosity of PAM solutions is shown in Fig. 1. The figure indicates that the viscosities of the solutions decrease initially, and then saturate as the stirring time is increased. The saturated values depend on the stirring speed.

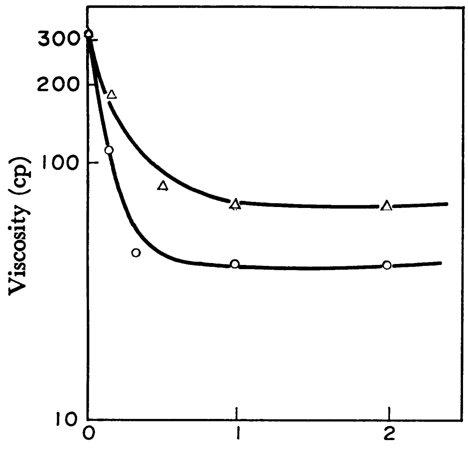

Fig. 1. Viscosity decrease of PAM solutions by high-speed stirring at 25 °C.
(—○—: 7000 rpm, —△—: 4000 rpm)

Two assumptions were made to explain this phenomenon. One is that the dissolved state of PAM solutions changes due to stirring. From various investigations, however, this assumption was found to be invalid.

The other assumption is that the PAM molecules degradate by high-speed stirring. Figure 2 shows the graph of reduced viscosity η_{sp}/C against the concentration C for PAM solutions at various stirring speeds. Here, these solutions are three days after stirring was completed. The figure shows the linear relationship between η_{sp}/C and C as well as the decrease in $[\eta]$ as the stirring speed is increased. The molecular weight cal-

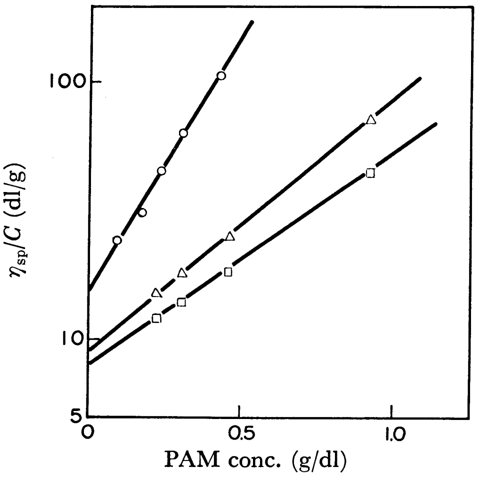

Fig. 2. Reduced viscosity η_{sp}/C of PAM solutions for stirring time at 25 °C.
(—○—: no stirring, —△—: 4000 rpm 1 hr stirring —□—: 7000 rpm 1 hr stirring)

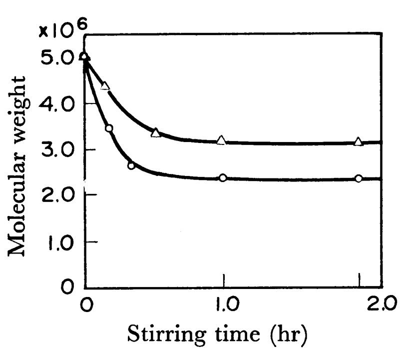

Fig. 3. Molecular weight decrease of PAM by high-speed stirring.
(—○—: 7000 rpm, —△—: 4000 rpm)

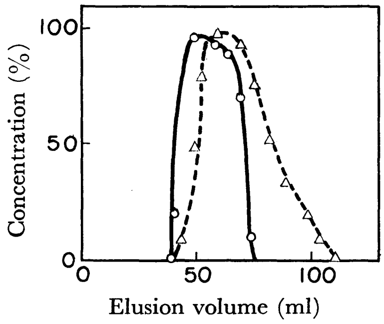

Fig. 4. GPC elusion curve of PAM solution.
(—○—: before stirring, ---△---after stirring)

culated from [η], with respect to the stirring time, is given in Fig, 3. The figure shows that the molecular weight reduced to about a half of the initial value after stirring at 7000 rpm at 25 °C. The distribution of molecular sizes measured by gel permeation chromatography (GPC) is shown in Fig. 4. It is evident from the figure that the molecular size of PAM was reduced after stirring. It can be concluded that the decrease in the viscosity of the PAM solution by high-speed stirring is due to degradation of the PAM molecules.

The degradation mechanism of vinyl polymer has been widely described. Our degradation results for PAM molecules can be explained by employing the formula given by Jellinek,[2]

$$\mathrm{d}B_i/\mathrm{d}t = k(P_i - 1)n_i \quad \text{for } P_i > P_1$$
$$\mathrm{d}B_i/\mathrm{d}t = 0 \quad \text{for } P_i \leqq P_1$$

where B_i is the number of shear degradation, P_i is the degree of polymerization, P_i is the limiting degree of polymerization, n_i is the number of molecules, k is the rate constant, and t is the time. The solution of Jellinek's equation, together with the experimental results, are shown in Fig. 5. The agreement is good, indicating the applicability of Jellinek's theory.

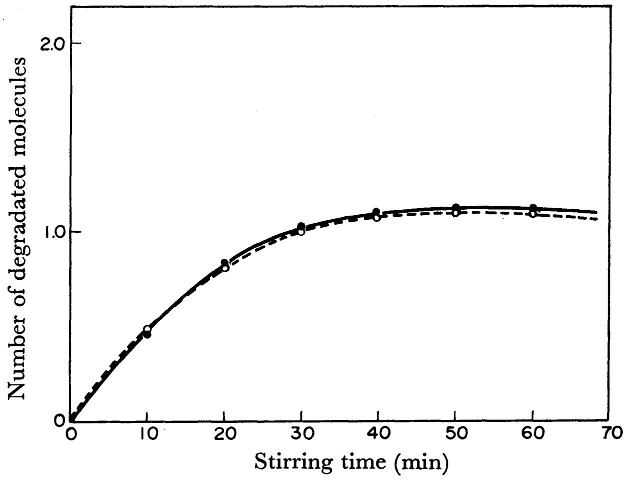

Fig. 5. Relation between the number of degradated molecules and stirring time.
(—●—: Experiment, ---○---: Calculated)

References

1) W. Scholtan, *Makromol. Chem.*, **14**, 168 (1954).
2) H. H. G. Jellinek and G. White, *J. Polym. Sci.*, **6**, 745 (1951).