

Polyacrylamide Solution Aging

The use of high molecular weight polyacrylamide solutions in drag reduction studies has been investigated by a number of workers. Although the mechanism of drag reduction is not fully established, many theories and explanatory mechanisms do not appear to take into consideration the peculiar solution properties of polyacrylamide.^{1,2} It is perhaps salient, with respect to these unusual solution properties, to mention the findings of Narkis and Rebhun.³ These workers concluded that polyacrylamide solutions undergo an aging effect which they explained as being primarily due to chain disentanglement, the disentanglement process proceeding to an equilibrium stage which was concomitant with the observed decreasing viscosity to a limiting value. Shyluk and Stow reinforced this finding by the observation that there was a two-stage aging process—a rapid initial viscosity decrease, followed by a slower gradual decrease.⁴

Subsequent to this work, Haas and MacDonald investigated this decrease in aqueous solution viscosity and, contrary to the previous conclusions, explained the effect as due to the presence of residual persulfate.⁵ The later work of Peyser and Little has apparently dismissed the possibility of adsorption.⁶ Shin has also indicated that the effect could be explained by chain degradation.⁷

In this note, we would like to report the following findings. Four high molecular weight polyacrylamide samples were prepared, three by a photopolymerization technique sensitized by riboflavin (P_1 , P_2 , and P_3), and one by persulfate initiation (P_4). Aqueous solutions of these polymers were allowed to stand in closed Pyrex flasks at 30°C and the relatively short period aging investigated 24 hr after the solutions were prepared.

From Figure 1, it can be seen that for both types of polymer solution there was an apparent rapid increase in reduced viscosity $[\eta]$, with a maximum value between 5 and 24 hr. Again for both types of solutions, $[\eta]$ proceeded to decrease with a minimum position after approximately 160–180 hr, and this was followed in almost all cases by a further increase. A surprising result was observed in the individual plots of η_{sp}/c versus c for the individual aging points. Table I shows how the slope of the plotted points dramatically changes upon aging. This latter effect does not appear to have been previously reported, even though it strongly suggests the changing polymer-solvent interactions and gives support to the chain disentanglement theory. It is also interesting to note that, in contrast

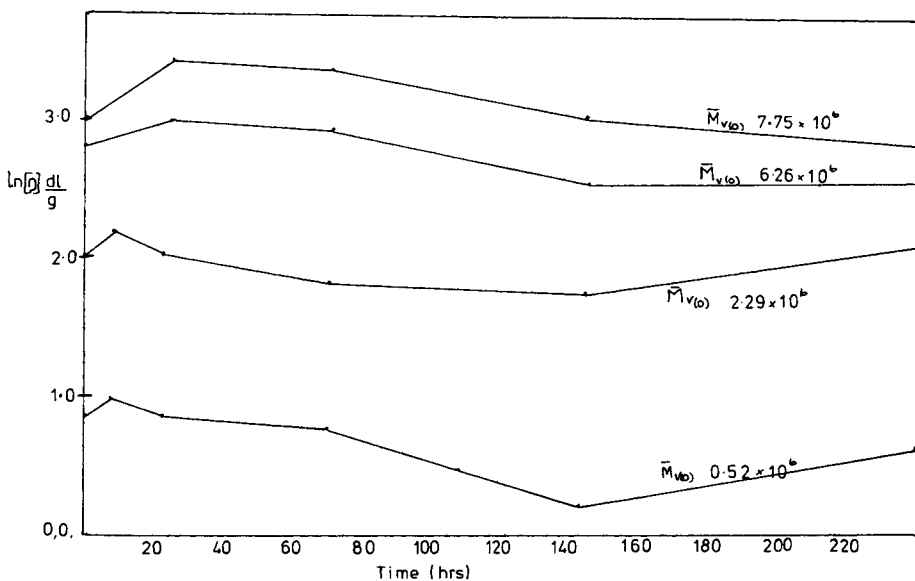


Fig. 1. Change in reduced viscosity of polyacrylamide solutions with aging time at 30°C.

TABLE I
Change of η_{sp}/c - c Slopes with Aging Time

Aging time, hr	Slope P ₁	Slope P ₄
0	34.50	-24.70
5	2.52	-32.20
24	97.80	-34.20
72	83.90	-23.80
144	97.80	27.30
240	-6.44	1.19

to the work of Haas and MacDonald, when a polyacrylamide solution lacked persulfate, as was the case with the photopolymerized samples, aging still occurred.

The presence of negative slopes of η_{sp}/c versus c plots has, however, been previously noted before by Raju and Merrill.⁹ They suggested that reduced viscosity rises with decreasing polyacrylamide concentration because dilution allows mobile ions to leave the regions of the chains and these subsequently develop net charges and expand. What is not clear, however, is how polyacrylamide with only amide side chains is able to act as a polyelectrolyte. It seems unlikely that under the normal experimental conditions the amide would become protonated. Also, the extent of hydrolysis of the amide group over the aging period was found to be small, 3.9% and insufficient to explain the observed behavior. The effect of a microgel formation could not be discounted.¹⁰

In conclusion, therefore, the chain entanglement and molecular aggregation of polyacrylamide in aqueous solution is apparently important in influencing the viscosity-time relationship. Observations from drag reduction studies of such solutions must therefore also take into account this time-dependent aging effect.

References

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K. L. GARDNER
W. R. MURPHY
T. G. GEEHAN

Department of Industrial Chemistry
The Queen's University of Belfast
Belfast 9, Northern Ireland

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