NOTES

Residual Unsaturation in Polyacrylamide

In an effort to obtain a monomer-free polyacrylamide, a number of physical and chemical treatments were performed on the polymer in order to either remove the residual monomer or convert it into polymer or other harmless products. Invariably it was found impossible to eliminate the last traces of unsaturation. The nature of this final residual unsaturation was therefore investigated.

Polyacrylamide used in this study was prepared by polymerizing acrylamide (from American Cyanamid Co.) in aqueous solutions at about 10% concentration with ammonium persulfate as the initiator at 80°C. to 98–99% conversion. The unsaturation, numerically expressed as per cent monomer in polymer, was determined by either of two methods: (*1*) the bromate-bromide iodine number determination and (*2*) a coulometric method, developed by E. W. Hobart, Jr., formerly of these laboratories, in which the sample is oxidized by permanganate, followed by coulometric titration of the excess permanganate, with a sensitivity of about 0.002% (20 ppm).

Polyacrylamide is soluble in water but insoluble in organic solvents such as acetone, dioxane, or methanol. Acrylamide monomer is soluble in both types. By repeated precipitation of the monomer-containing polymer from an aqueous solution with an organic solvent, conceivably a monomer-free polymer can be obtained. A set of results is shown in Table I. In this case the polymer was precipitated from the aqueous solution with acetone, filtered, the precipitate redissolved in water, and the precipitation repeated. A sample was taken after each precipitation and the residual unsaturation determined by the iodine number method.

TABLE I
Residual Unsaturation of Precipitated Polyacrylamide

No. of precipitation	Residual unsaturation, %
0	1.62
1	0.090
2	0.039
3	0.031
4	0.087(?)
5	0.036
6	0.025

It is clear from Table I that the unsaturation remains practically constant after one or two precipitations. (The value after the fourth precipitation is erratic, most probably due to experimental error.) Similar results were obtained in repeated precipitation runs using methanol or dioxane. The ultimate unsaturation value fell in the range of 0 005–0.05%. Evidently, the material which is responsible for the unsaturation cannot be physically extracted from the polymer.

If we assume that the termination step of the polymerization reaction is through disproportionation, the polymer molecules would contain terminal double bonds. If this is the case, the unsaturation would be dependent on the molecular weight. Quantitatively, we can calculate the residual unsaturation from the number-average molecular weight or vice versa. As every two polymer molecules possess one double bond, and the unsaturation is expressed as per cent monomer based on the total quantity of polymer, then

$$\% \text{ unsaturation} = [1/2\,(\mathrm{DP})_n] \times 100$$

$$= 100/[2 \times (\bar{M}_n/71)] = 3550/\bar{M}_n$$

Two samples of polyacrylamide of known weight-average molecular weight were precipitated with methanol and the precipitated polymers analyzed for unsaturation by the coulometric method. The number-average molecular weights of these samples, and in turn the $\bar{M}_w/\bar{M}_N$ ratios, were calculated. From the known equations relating intrinsic viscosity to molecular weight for unfractionated polyacrylamide,[1,2]

$$[\eta] = 3.73 \times 10^{-4}\,\bar{M}_w^{0.66}$$

$$[\eta] = 6.8 \times 10^{-4}\,\bar{M}_n^{0.66}$$

$\bar{M}_w/\bar{M}_n = 2.5$. This value may be used as a reference point for comparison. The experimental results are shown in Table II. They demonstrate that the unsaturation is indeed affected by the molecular weight. The calculated $\bar{M}_w/\bar{M}_n$ ratios are of the right order of magnitude. It may be concluded that (*1*) the ultimate residual unsaturation in polyacrylamide is due to terminal double bonds, and (*2*) the termination step of polymerization of acrylamide at 80°C. is to a large extent through disproportionation.

TABLE II
Calculated Molecular Weight Values

$\bar{M}_n$	% unsat., found	$\bar{M}_n$, calc.	$\bar{M}_w/\bar{M}_n$
2.0×10^5	0.023–0.038	1.6 to 0.93×10^5	1.3–2.1
1.4×10^6	0.005–0.01	0.71 to 0.36×10^6	2.0–3.9

References

1. American Cyanamid Co., *Polyacrylamide*, New Product Bulletin No. 34, 1955, p. 2.
2. Collinson, E., F. S. Dainton, and G. S. McNaughton, *Trans. Faraday Soc.*, **53**, 489 (1957).

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