

The Preparation of High-Viscosity, Partially Hydrolyzed Polymethacrylamides

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Synopsis

Due to the high chain transfer to monomer, the homopolymerization of methacrylamide yields polymers of extremely low molecular weight. On partial alkaline hydrolysis, the viscosities of these polymers in aqueous solution are much inferior to those of partially hydrolyzed polyacrylamide (HPAM). However, polymethacrylamides prepared by room temperature, persulfate-initiated polymerization in the presence of small amounts of *N,N'*-methylenebisacrylamide demonstrate posthydrolysis reduced viscosities in 0.01% NaCl comparable to typical commercial HPAM materials.

INTRODUCTION

Numerous synthetic methods exist for the homopolymerization of methacrylamide.¹⁻⁵ These methods yield products of very low molecular weight however, probably as a result of high chain transfer to monomer.⁶ On partial alkaline hydrolysis, even the best of these polymers compare very unfavorably as aqueous solution viscosity builders with partially hydrolyzed polyacrylamides (HPAM). Low molecular weight is a major factor in limiting the ability of polymethacrylamide to compete with polyacrylamide in many water-soluble resin applications.

This communication describes the preparation of methacrylamide polymers which, on partial alkaline hydrolysis, produce solution viscosities in 0.01% NaCl comparable to those of most commercial HPAM polymers of similar degrees of hydrolysis. These materials were prepared by persulfate-initiated aqueous polymerization in the presence of small amounts of the crosslinking agent *N,N'*-methylenebisacrylamide (NNMA).

EXPERIMENTAL

Methacrylamide was purchased from Polysciences, Inc., Warrington, Pa. Potassium persulfate (reagent grade) was obtained from J. T. Baker Chemical

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TABLE I
Preparation of Methacrylamide Polymers: Increasing *N,N'*-Methylenebisacrylamide at
Constant Initiator Concentration^a

| Sample no. | Methacrylamide (g) | <i>N,N'</i> -methylene-bisacrylamide (g) | Potassium persulfate (g) | Intrinsic ^b viscosity (dL/g) |
|------------|--------------------|--|--------------------------|---|
| M4 | 29.93 | 0 | 0.1077 | 0.13 |
| M5 | 30.22 | 0.0003 | 0.1076 | 0.88 |
| M6 | 30.05 | 0.0004 | 0.1072 | 1.21 |
| M7 | 30.01 | 0.0006 | 0.1072 | 1.21 |
| M8 | 30.00 | 0.0009 | 0.1072 | 1.43 |
| M9 | 30.08 | 0.0018 | 0.1071 | 1.98 |
| M10 | 29.98 | 0.0027 | 0.1071 | c |
| M11 | 30.10 | 0.0045 | 0.1071 | c |

^a All polymerizations were run in 600 mL deaerated, distilled water at an ambient temperature for 168 h.

^b In ethylene glycol.

^c Insoluble.

Co., Phillipsburg, N.J., and *N,N'*-methylenebisacrylamide (electrophoresis grade) from the Aldrich Chemical Co., Milwaukee, Wisc.

Methacrylamide was dissolved in deaerated, distilled water to form 5.0% (w/v) solutions. Initiation was accomplished with 0.35 wt% (of monomer) of potassium persulfate. *N,N'*-methylenebisacrylamide in 0.001–0.015 wt% (of monomer amounts) was added and the reaction vessels sealed under dry nitrogen. Polymerizations were allowed to proceed at room temperature (21–24°C) for 168 h. Polymerization appeared to be essentially complete within 24 h, but the mixtures were allowed to stand in order to take advantage of any possible Trommsdorff effect. The resulting opaque gels were hardened and washed with 2-propanol, isolated, and air-dried. Conversions were from 70% to 82%. Details of these polymerizations are contained in Table I.

Once an optimum degree of NNMA inclusion had been established, the initiator concentration was systematically decreased until the results of individual polymerizations were no longer reproducible. Conditions for this series of experiments are contained in Table II.

The homopolymers were partially hydrolyzed in aqueous slurry with sufficient NaOH to give the desired carboxyl contents. The hydrolyses were conducted

TABLE II
Preparation of Methacrylamide Polymers: Decreasing Initiator Concentration with Constant
N,N'-Methylenebisacrylamide^a

| Sample no. | Methacrylamide (g) | <i>N,N'</i> -methylene-bisacrylamide (g) | Potassium persulfate (g) | Intrinsic ^b viscosity (dL/g) |
|------------|--------------------|--|--------------------------|---|
| M9A | 30.04 | 0.0018 | 0.1070 | 2.00 |
| M9B | 30.00 | 0.0018 | 0.0603 | 2.56 |
| M9C | 29.98 | 0.0018 | 0.0300 | 2.67 |
| M9D | 30.01 | 0.0018 | 0.0151 | 2.70 |

^a All polymerizations were run in 600 mL deaerated, distilled water at an ambient temperature for 168 h.

^b In ethylene glycol.

TABLE III
Viscosities and Brine and Shear Sensitivities of Partially Hydrolyzed Polymethacrylamides Compared with Those of Partially Hydrolyzed $5-6 \times 10^6$ MW Polyacrylamide

| Sample no. | Carboxyl ^a content (wt%) | Reduced viscosity ^b (dL/g) | | Viscosity Retention | |
|-----------------|-------------------------------------|---------------------------------------|-----------|---------------------|-----------|
| | | 0.01% NaCl | 2.0% NaCl | Shear (%) | Brine (%) |
| Methacrylamides | | | | | |
| M4 | 20.4 | 22.3 | 2.3 | 92.8 | 10.3 |
| M5 | 23.0 | 28.5 | 2.1 | 93.3 | 7.3 |
| M6 | 27.3 | 27.4 | 2.1 | 99.9 | 7.6 |
| M7 | 31.0 | 29.3 | 2.4 | 99.9 | 8.0 |
| M8 | 27.9 | 60.3 | 5.7 | 97.3 | 9.4 |
| M9 | 38.0 | 122.1 | 6.7 | 71.7 | 5.5 |
| M10 | 40.7 | 95.0 | 5.3 | 78.5 | 5.6 |
| M11 | 31.4 | 78.9 | 6.2 | 73.5 | 6.2 |
| M9A | 28.1 | 114.1 | 7.1 | 73.5 | 6.2 |
| M9B | 38.3 | 138.1 | 8.1 | 70.2 | 5.9 |
| M9C | 40.1 | 140.2 | 8.2 | 69.8 | 5.9 |
| M9D | 40.3 | 140.1 | 8.2 | 70.4 | 5.9 |
| Acrylamides | | | | | |
| HPAM 1 | 16.1 | 106.2 | 14.8 | 91.4 | 13.9 |
| HPAM 2 | 20.8 | 112.5 | 15.1 | 90.9 | 13.4 |
| HPAM 3 | 25.4 | 117.8 | 13.6 | 92.8 | 11.6 |
| HPAM 4 | 28.8 | 122.7 | 12.7 | 94.1 | 10.4 |
| HPAM 5 | 38.6 | 118.0 | 13.0 | 93.2 | 11.0 |
| HPAM 6 | 40.4 | 120.7 | 13.7 | 95.5 | 11.4 |

^a Wt% sodium methacrylate for methacrylyl samples and wt % sodium acrylate for HPAM.

^b Viscosities were measured with a Cannon-Ubbelohde Dilution-Type Capillary Viscometer (size 75) at 25°C and pH 9.5.

at room temperature for 120 h. The solubilized, partially hydrolyzed polymers were isolated by precipitation into 2-propanol.

The results of these polymerizations were evaluated in two ways. First, the viscosities of the homopolymers were compared directly with that of $5-6 \times 10^6$ molecular weight (nominal) polyacrylamide (Polysciences, Inc., Warrington, Pa.—lot 3-1590) in ethylene glycol. Viscosities were measured on a Contraves LS-30 Rheometer, and intrinsic viscosities were calculated using a computer program written by one of the authors (Ward). Barring radically different solvation of the two polymer types by ethylene glycol, these data give some indication of relative molecular weights.

Secondly, the viscosities of partially hydrolyzed samples were compared with those of HPAM of similar carboxyl contents by the method described by Kilmer et al.⁷ and Martin et al.^{8,9} These results are shown in Table III. HPAM was prepared from $5-6 \times 10^6$ MW polyacrylamide (Polysciences, lot 3-1590) after the method of Meister et al.¹⁰

DISCUSSION OF RESULTS

At an initiator concentration of 0.35 wt% of monomer, the charge of *N,N'*-methylenebisacrylamide-producing polymers exhibiting maximum intrinsic viscosity in ethylene glycol and maximum reduced viscosity in 0.01% NaCl when partially hydrolyzed was found to be between 0.006 and 0.009 wt% of monomer.

Samples M10 and M11 (0.009 and 0.015 wt% crosslinked, respectively) were not soluble in ethylene glycol. It is assumed that this was due to crosslinking.

Increases in polymer viscosity were observed with decreasing potassium persulfate concentrations down to 0.05 wt% of monomer. Below this level, polymerizations did not yield reproducible results, and the viscosities of individual samples varied widely.

From the direct comparisons in ethylene glycol of these polymethacrylamides with $5-6 \times 10^6$ molecular weight polyacrylamide, it appears that the molecular weights of these materials still fall far below that of the acrylamide polymer. After partial alkaline hydrolysis, the best of these samples exhibit viscosities in 0.01% NaCl which are equal to or better than HPAM of similar degrees of hydrolysis prepared from the $5-6 \times 10^6$ molecular weight polyacrylamide as well as commercial HPAM. This difference in behavior may illustrate the enormous contribution of backbone methyl group stiffening to hydrolyzed polymethacrylamide.

As expected, the more hydrophobic methacrylamide polymers are more sensitive to brine than their acrylyl analogs. Average viscosity retained in brine falls from 10–15% for HPAM to 5–7% for partially hydrolyzed polymethacrylamide.

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