Partially Imidized, Water-Soluble Polymeric Amides. I. Partially Imidized Polyacrylamide and Polymethacrylamide

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Synopsis

Five to six million molecular weight polyacrylamide and polymethacrylamides of comparable post-alkaline hydrolysis viscosities were imidized by dissolution and heating in $6N$ HCl. After alkaline hydrolysis, the imidized polymers demonstrated significantly better retention of viscosity to 2% NaCl than did similar partially hydrolyzed polymers. Viscosities in 0.01% NaCl and resistance to shear were not markedly affected by this modification. It is assumed that this improved performance in brine is the result of chain stiffening due to intrachain imide rings.

INTRODUCTION

Sensitivity to brine and hard waters is an undesirable feature of partially hydrolyzed polyacrylamides (HPAM) presently used as mobility control agents in enhanced oil recovery. Under the laboratory conditions described by Kilmer et al.,[1] Martin et al.,[2,3] and Khune et al.,[4] reduced viscosity losses of 85–90% are commonly observed for aqueous solutions of most HPAM when sodium chloride concentration is increased from 0.01% to 2%. Decreases in solution viscosity in the presence of divalent cations are even greater.[2,3,5,6]

One possible approach to this problem is to stiffen the flexible carbon backbone of acrylamide-type polymers. A polymer chain stiffened by steric hindrance or internal rigidity should increase the hydrodynamic size of the randomly coiled molecule. As a consequence, a rigid polyelectrolyte should generate a greater viscosity in brines and hard waters than a similar unstiffened molecule, provided that greatly increased hydrophobicity does not accompany the stiffening.

Partially hydrolyzed polymethacrylamide in 0.01% NaCl demonstrates the large degree of molecular extension (and viscosity) which can arise from steric chain stiffening due to backbone methyl groups.[7] The viscosity retention of these polymers in brine is quite poor, however.

In this investigation, closed rings were introduced into the backbone of acrylamide and methacrylamide polymers in order to induce molecular stiffness through chain rigidity. The fact that the amides imidize under a number of

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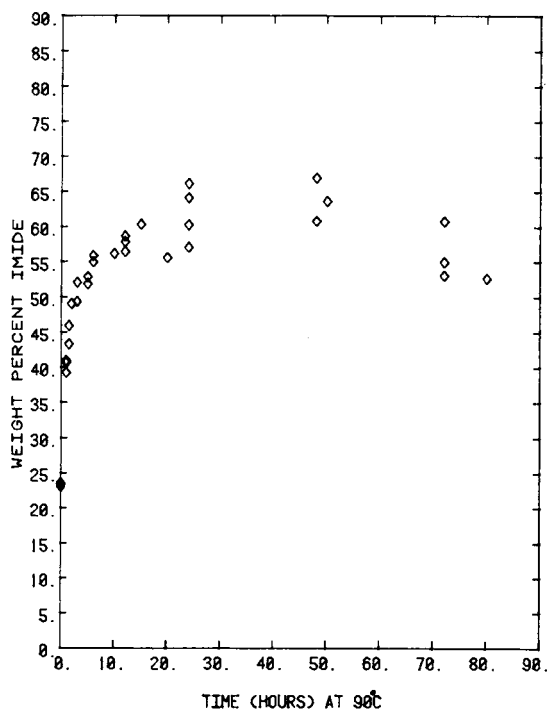‡ Present address: Jet Propulsion Laboratory, Pasadena, CA 91109.

Fig. 1. Formation of imide with time by polyacrylamide at 90°C in 6N HCl.

conditions to form stable intramolecular rings and/or intra- and intermolecular crosslinks provided a way to generate these rigid polymers.[8–13] Due to its convenience and relative ease of control, acid-catalyzed imidization was chosen as the method for affecting this structural modification.

EXPERIMENTAL

Polyacrylamide of 5–6 × 10⁶ (nominal) molecular weight, purchased from Polysciences, Inc., and polymethacrylamide, prepared by persulfate-initiated polymerization in the presence of N,N'-methylenebisacrylamide[7] (to provide branching) were dissolved in 6N reagent grade HCl to form 2–4% (w/v) solutions. Complete dissolution usually required 48–72 h. After dissolution, the polymer solutions were allowed to stir for an additional 48–72 h at room temperature. Although significant amounts of imide were detected at this time, usual practice entailed heating the acid mixtures for periods of 1 h to several days. Both imide types precipitated from the acid during or shortly before this heating phase. Imide formation during this stage of the process was monitored by functional group analyses (Fig. 1) and infrared measurements of carbonyl absorption frequencies.

The imidized polymers were washed with distilled water and isolated as highly hydrated aqueous slurries. The samples were made water-soluble by partial alkaline hydrolysis. The slurries were neutralized and then stirred with stoichiometric amounts of either NaOH or Na₂CO₃ to achieve the desired levels of

hydrolysis. The polymers were then precipitated from the alkaline solutions into 2-propanol, washed, isolated, and air-dried.

Aqueous solutions of these polymers were evaluated for viscosity and sensitivity to brine and shear by the screening procedures described by Kilmer et al.[1] and Martin et al.[2,3] The samples were characterized for degree of hydrolysis by the potentiometric titration methods described by Kilmer et al.[14] Amide and imide contents were measured by an iodometric modification of the colorimetric method of Scoggins and Miller.[15,16] In this procedure, separate portions of the same sample were treated with saturated bromine water at low and high pH's. Under the former conditions, unsubstituted amide nitrogens are brominated, while both amide and imide nitrogens are brominated at pH's greater than 5. Standard iodometric techniques are then applied and weight percent imide is determined by difference.

RESULTS AND DISCUSSION

The Imidization Reaction

Acid-catalyzed hydrolysis appeared to occur simultaneously with ring formation during the initial, low temperature phase of the imidization runs. Both competing reactions were slow at these temperatures, but imide seemed to become the major product 48–72 h after dissolution of the homopolymers. If mixtures were heated before the amount of imide formed became sufficiently greater than the free acid content, further substantial imidization did not take place. Instead, acid-catlayzed hydrolysis (probably aided by a neighboring group effect) proceeded to its theoretical limit. This same behavior was observed with all attempts to imidize polymers already partially hydrolyzed. Prolonged heating of all imidization mixtures eventually resulted in the loss of imide structures, resolubilization of the polymer in the acid medium, and almost complete hydrolysis.

These observations are consistent with the following proposed reaction scenario as shown in Scheme 1.

Polymer Performance

Partially imidized, partially hydrolyzed polyacrylamides and polymethacrylamides with imide contents higher than 8 % displayed significantly greater viscosities in 2% NaCl than HPAM and partially hydrolyzed polymethacrylamides of equivalent carboxyl contents (Tables I and II). The point of diminishing returns was not reached at the maximum levels of imidization achieved in this series of experiments. Viscosities in 0.01% NaCl were comparable to or slightly greater than those of the partially hydrolyzed, nonimidized polymers. No significant increase in sensitivity to shear was observed with the imidized materials. Sensitivities to Ca^{++} and Mg^{++} were increased somewhat, especially for the acrylyl polymers. The performances of all methacrylyl samples, whether or not they were imidized, were quite poor in the presence of divalent cations.

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TABLE I
Comparative Solution Behavior of Partially Imidized, Partially Hydrolyzed Polyacrylamide vs.
Partially Hydrolyzed Polyacrylamide

Carboxyl[a] content (wt %)	Imide content (wt %)	Reduced viscosity[b] (dL/g)		Viscosity retention	
		0.01% NaCl	2.0% NaCl	Shear (%)	Brine (%)
		Imidized polymers			
19.2	18	109.2	29.9	91.5	27.4
30.8	22	154.0	33.1	85.9	21.5
32.5	15	151.2	29.1	88.6	19.2
35.7	12	164.4	30.3	80.5	18.4
37.7	7	145.1	18.6	87.4	12.8
38.2	16	161.8	30.9	85.4	19.1
42.8	20	182.1	36.6	84.5	20.1
58.4	5	80.9	9.2	91.4	11.4
		Nonimidized polymers			
28.6	—	182.0	29.9	56.1	16.4
28.8	—	122.7	12.7	94.1	10.4
31.0	—	95.7	13.3	90.7	13.9
32.0	—	127.9	13.1	95.9	10.3
34.9	—	124.5	17.3	85.8	13.9
38.6	—	118.0	13.0	93.2	11.0
40.5	—	120.7	13.7	95.5	11.4
41.7	—	148.6	18.0	75.2	12.1
43.1	—	121.3	12.7	97.8	10.4
44.1	—	183.4	33.3	79.3	18.1
45.7	—	284.2	31.7	70.5	11.8
52.9	—	165.4	16.7	96.1	10.1

[a] Wt % sodium acrylate.
[b] Viscosities were measured with a Cannon-Ubbelohde Dilution-Type Capillary Viscometer (size 75) at 25°c and pH 9.5.
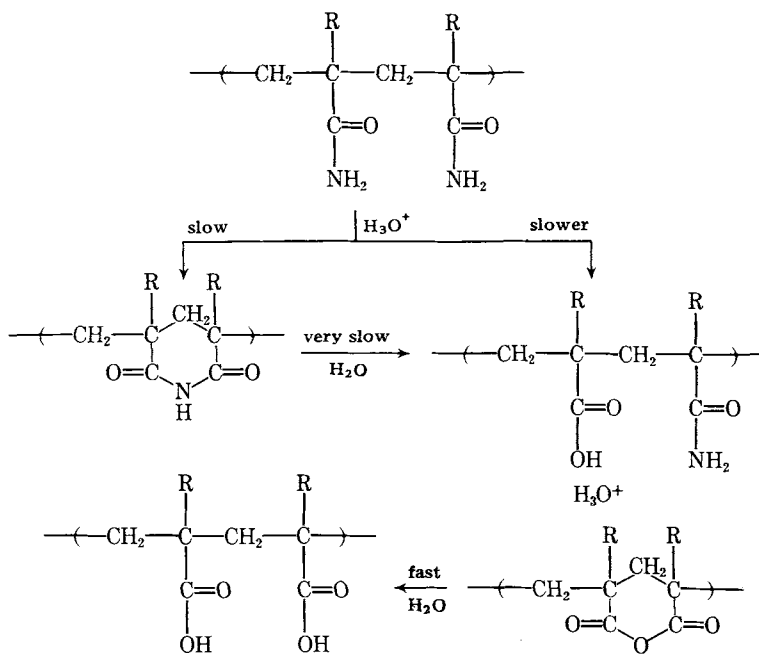

Scheme 1

TABLE II

Comparative Solution Behavior of Partially Imidized, Partially Hydrolyzed Polymethacrylamide vs. Partially Hydrolyzed Polymethacrylamide

Carboxyl[a] content (wt %)	Imide content (wt %)	Reduced viscosity[b] (dL/g)		Viscosity retention	
		0.01% NaCl	2.0% NaCl	Shear (%)	Brine (%)
		Imidized polymers			
29.2	16	159.6	23.8	90.5	14.9
30.3	22	183.9	38.2	75.3	20.7
30.4	24	156.8	36.4	88.4	23.2
31.0	5	116.5	9.5	89.1	8.1
31.2	21	155.9	34.8	85.4	22.3
31.3	15	158.5	23.6	90.5	14.9
31.3	27	140.9	39.8	93.0	28.3
34.2	18	155.2	25.3	89.5	16.3
34.8	25	170.1	41.4	79.5	24.3
37.6	19	150.0	27.5	83.1	18.3
40.2	10	137.5	14.1	84.0	10.3
45.9	15	123.7	16.8	89.0	13.6
		Nonimidized polymers			
25.8	—	81.4	5.4	66.7	6.7
28.3	—	88.7	5.5	71.5	6.2
31.4	—	79.0	6.2	87.5	7.8
37.3	—	103.3	7.9	84.9	7.8
38.0	—	122.1	6.7	71.7	5.5
39.5	—	128.2	9.6	81.7	7.5
40.7	—	95.0	5.3	78.5	5.6

[a] Wt % sodium methacrylate.

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

From this preliminary data, optimum levels of hydrolysis appear to be between 25 and 40 wt % sodium acrylate for the acrylyl samples and between 30 and 45 wt % sodium methacrylate for the methacrylyl polymers.

Imide Stability

Observation of the shelf-life of "dry" polymers and solution stability tests indicate that the methacrylyl imide is substantially less labile than its acrylyl analog. Without carbonate stabilization, "dry" partially imidized, partially hydrolyzed polyacrylamide underwent sufficient imide crosslink formation within 3 weeks to severely limit the polymer's water solubility. The methacrylyl samples remained water-soluble for 10 months under identical conditions. This disparity in performance is also evident in the preliminary solution stability tests (Fig. 2). The study was conducted in 2% NaCl at 93°C with no attempt to exclude oxygen. The solution properties (0.0150 g/dL concentration and 30 dL/g reduced viscosities in 2% NaCl) and compositions (20 wt % imide and 30% degree of hydrolysis) of the two polymers were as nearly identical as possible. Neither polymer was stabilized with Na_2CO_3. The acrylyl sample maintained a reduced viscosity of greater than 20 dL/g for 3 weeks. The imidized polymethacrylamide retained this level of viscosity for a period greater than 12 weeks.
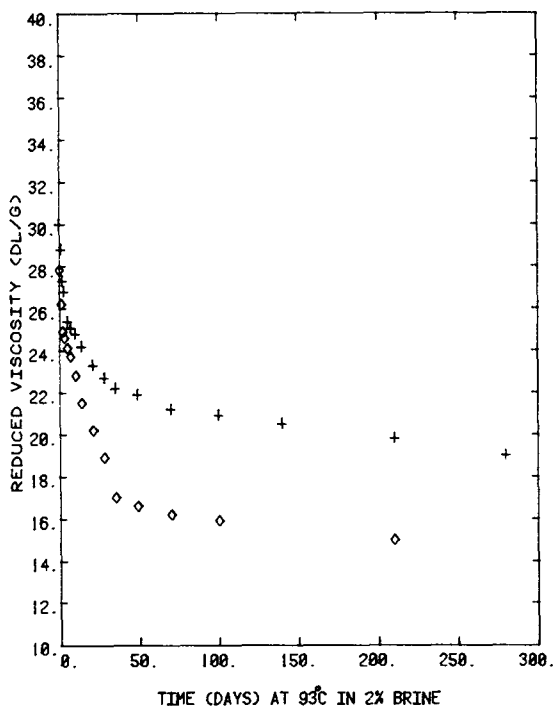
Fig. 2. Loss of solution viscosity at 93°C in 2.0% NaCl by imidized polymethacrylamide (+) and imidized polyacrylamide (◇).

CONCLUSIONS

Although this work with homopolymers is only a preliminary stage in our investigation of imidized polymeric amides, it permits several general conclusions to be made concerning polymers of this type:

1. Chain stiffening by the addition of intramolecular imide rings confers improved viscosity retention in brine on both polyacrylamide and polymethacrylamide after hydrolysis to generate carboxyl groups in the imides.

2. Increased hydrophobicity brought about by acid-catalyzed imidization may increase sensitivity to hard waters, especially for the acrylyl polymers.

3. The methyl-stabilized imides generated in polymethacrylamide are significantly more stable to ring-opening hydrolysis than their acrylyl counterparts.

4. Under the low solids reaction conditions used, the level of imide crosslink formation appears to be insignificant.

5. In agreement with the literature,[8,17,18] infrared imide carbonyl frequencies indicate that six-membered rings greatly predominate over five-membered structures in these materials.

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