Characterization of Polyacrylamides Used in Enhanced Oil Recovery

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Synopsis

Polyacrylamides can be readily characterized using techniques such as IR spectroscopy, ^{13}C-NMR, elementary analysis, TGA, and x-ray diffraction. The first three techniques can also be used quantitatively to measure the degree of hydrolysis of the polymers, without the need to know accurately the weight of the sample. The presence of inorganic salts, such as Na_2SO_4, $Na_4(CO_3)SO_4$, and Na_2CO_3, is readily detected via IR or wide-angle x-ray diffraction. No evidence of crystallinity is found in the samples studied.

INTRODUCTION

The application of certain classes of water-soluble polymers in enhanced oil recovery techniques (i.e.. polyacrylamides) has prompted the publication of papers dealing with solution properties and tabulations of viscosity data (for example, Refs. 1–4). Data on the structure of these polymers has also been reported,[5–15] with perhaps a greater emphasis on those techniques which study the polymer in solution.

The present paper presents the application of standard characterization techniques (infrared spectroscopy, wide angle x-ray diffraction, and thermal gravimetric analysis) to the study of these polymers. Together with the results obtained from ^{13}C-NMR spectroscopy and C/N elementary analysis of polyacrylamides,[16] a self-consistent set of data from the analysis of commercial samples is now proposed.

EXPERIMENTAL METHODS

Infrared Spectroscopy. Samples were prepared by casting films on AgBr plates from concentrated solutions. To prepare the salt form of the hydrolyzed polymer, buffer solutions (pH 10) of borax/sodium hydroxide were used instead of distilled water. The use of a buffer will guarantee a constant, not too alkaline pH during the drying of the film on the AgBr plate. Spectra were recorded on a Perkin-Elmer 1320 IR Spectrophotometer.

^{13}C-NMR. Details have been given elsewhere.[16]

Thermal Gravimetric Analysis (TGA). The TGA curves were recorded on a Dupont 990 Thermal Analysis instrument, at rates of 10°C, 20°C, and 50°C/min, using an air or helium atmosphere. Samples must be in the form of fine powders; otherwise, problems will arise due to a popcorn effect, which expels large particles from the TGA pan.

Dialysis. In order to eliminate the inorganic salts present in some samples, concentrated solutions of the polymers were dialyzed through a "Pa-

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trician" preservative (a product of Youngs Corp. DBA, San Francisco) previously washed with acetone and distilled water.

X-Ray Diffraction. A Philips 1730 x-ray Generator equipped with a vacuum vertical diffractometer was used to register the diffraction profiles of powdered specimens, using CuKα radiation (Ni filter), with a 0.1° (2θ) step scan, 100-s counting time; 1° scatter and receiving slits were used. Diffraction patterns were recorded on photographic film in a Warhus vacuum flat plate camera, equipped with a heating stage.

Samples. The samples under study comprise a representative sampling of commercial polyacrylamides currently available, both in powder or emul-
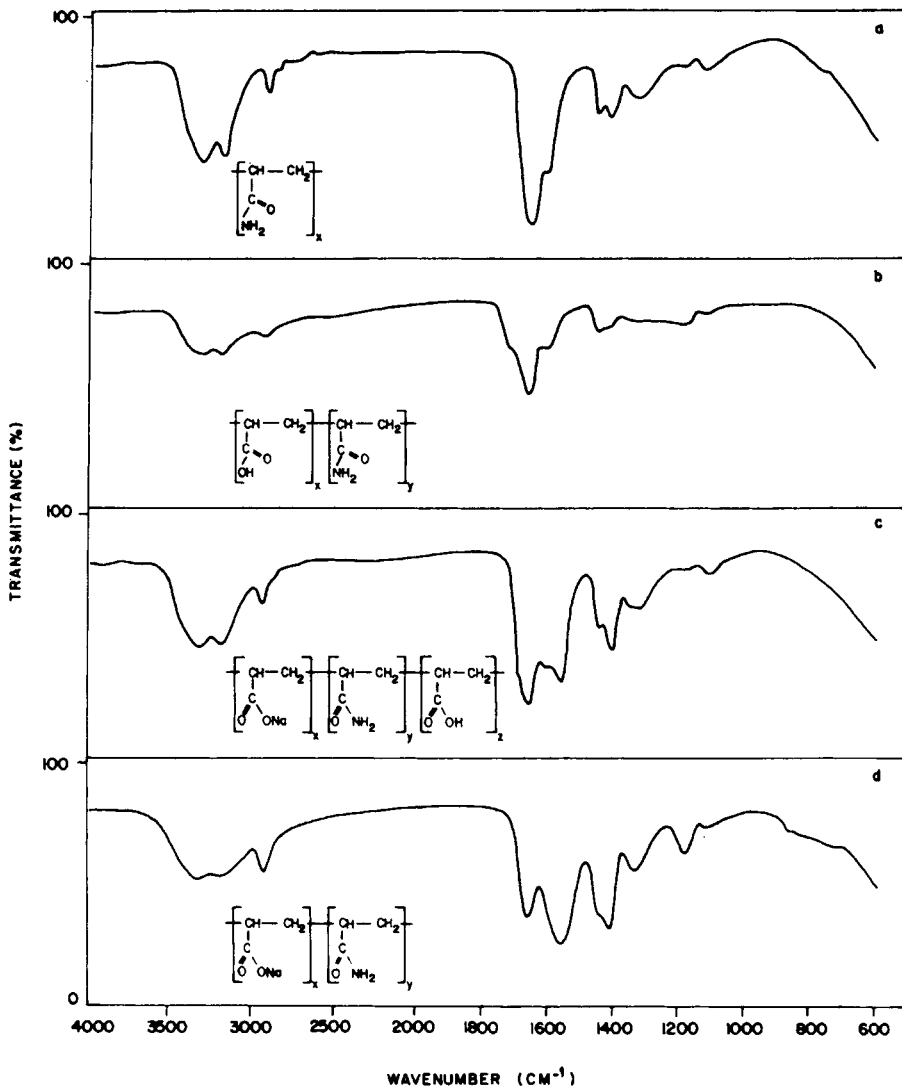

Fig. 1. Infrared spectra of polyacrylamide homopolymer (a) and of the hydrolyzed polyacrylamide as obtained when casting from solutions at pH 2.3 (b), pH 7.3 (c), and pH 12.4 (d).

sified form. The latter have been precipitated in methanol in order to study them. L0–L5, M1–M3, and O1 and O2 are solid samples from three different manufacturers. Samples M0 and N0–N4 are emulsions from two different manufacturers. A homopolymer from Aldrich Chemical Co. (Ref. 17,127-7) was also studied, and will be refered to as sample PAA.

RESULTS AND DISCUSSION

Information on the Type of Polyacrylamide Present in a Commercial Sample

The choice technique for overall information is definitely infrared (IR) spectroscopy. The basic IR spectrum for a polyacrylamide homopolymer is shown in Figure 1(a), which agrees with published results. Hydrolysis of this structure introduces bands corresponding to the acidic group newly formed in the polymer. The resulting spectra will depend both on the degree of hydrolysis and on the pH at which the sample is prepared. The latter fact is evident on comparing Figures 1(b), 1(c), and 1(d), all corresponding to the same sample. The appearance of new bands, of changing intensity, is consistent with the assignments given in Table I. Deductions based on IR spectra of hydrolyzed polyacrylamides are only valid if the pH of the sample is known. Changes in the original degree of hydrolysis can be induced at very low or very high pH values, during the drying of the film. For example, Figure 1(d) shows weaker bands in the 3000–3500 cm^{-1} region (corresponding to the—NH$_2$ group) than the previous spectra. Since the same sample was used for spectra 1b–1d, this confirms the drawback of using solutions which are not buffered.

The evident changes in the spectra as a result of the hydrolysis of the structure makes possible an IR quantitative determination of the degree of hydrolysis. Figure 2 effectively demonstrates the feasibility of the method, showing a good correlation between the absorbance ratio of the bands at 1560 cm^{-1} and 1660 cm^{-1}, and the quantity % hydrolysis/(100 − % hydrolysis).

TABLE I
Assigment of Main IR Bands Observed in Polyacrylamide Polymers (Homopolymers and Hydrolized Samples)

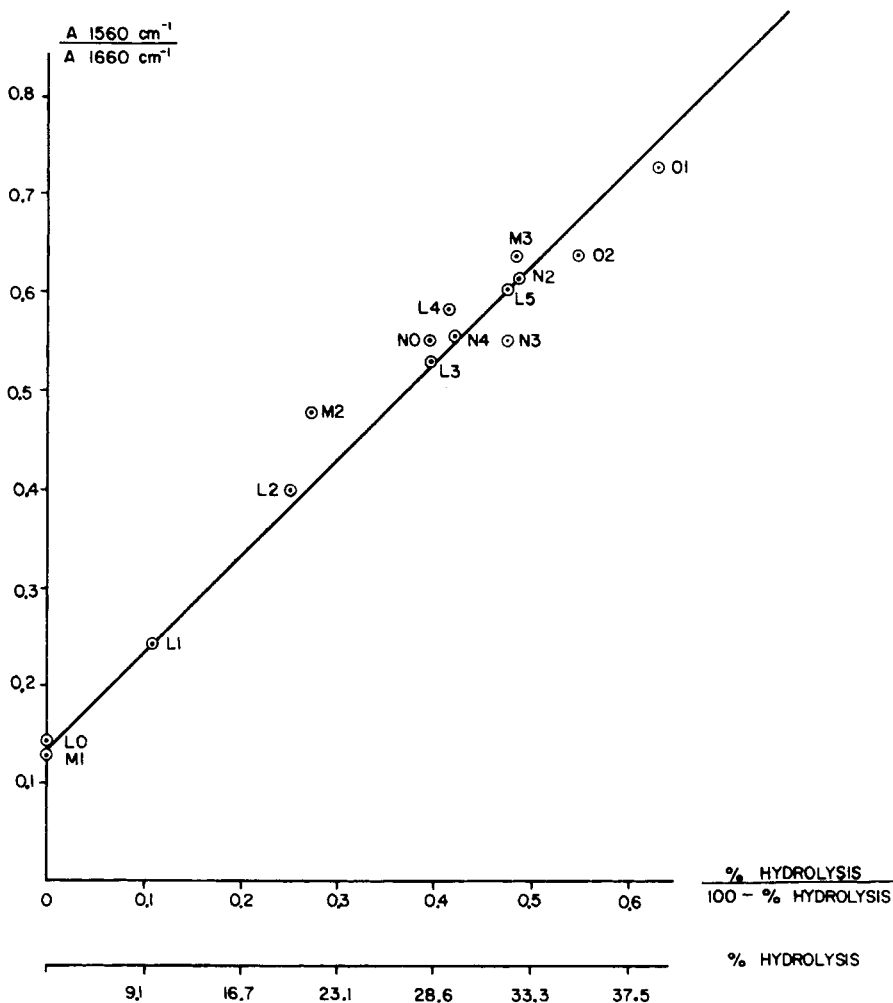| Functional group	Wavenumber (cm^{-1})
—CH$_2$—	2926 (w)
	1450 (m)
—CONH$_2$	3330 and 3190 (s)
	1655 (vs)
	1620 (s)
	1420 (m)
—CH—	1350 w)
H$_2$O	>3320 (sh)
—COOH	1660 (vs)
—COO$^\theta$	1560 (m)
	1410 (m)

Fig. 2. Plot of the absorbance ratio $A_{1560 \text{ cm}^{-1}}/A_{1660 \text{ cm}^{-1}}$ measured from IR spectra of film samples cast from basic (pH 10) solutions vs. % hydrolysis values obtained from ^{13}C-NMR and C/N elementary analysis.[16]
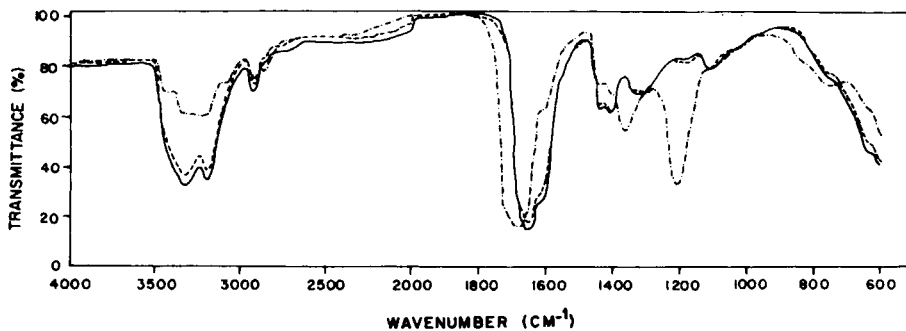

Fig. 3. IR spectra of sample M1 (_____), after heating 1 h at 150°C (– – – –) and after heating 0.5 h at 200°C (– · – · – –).
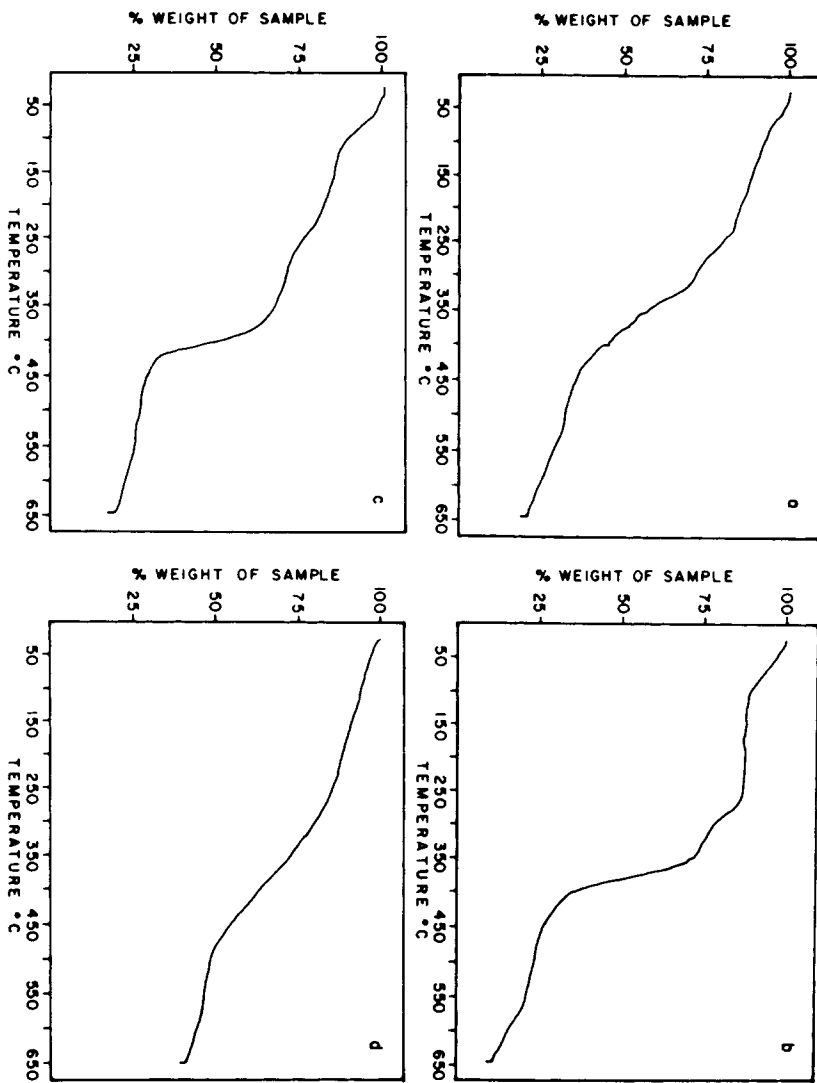
Fig. 4.   TGA curves of samples (a) L1, (b) M1, (c) NO, and (d) O1. Heating rate 20°C/min in helium atmosphere.

To obtain this calibration curve, hydrolysis values obtained via C-13 NMR and elementary analysis were used.[16] The IR determination of hydrolysis values shares the same advantage as the ^{13}C-NMR and elementary analysis methods: there is no need to weigh the samples.

Much has been published in the literature regarding the presence or absence of imide structures in these polymers.[7-9] The IR spectra of thermally degraded samples (see Fig. 3) indeed show among other changes the emergence of bands at 1370 cm^{-1}, 1210 cm^{-1}, and 1660 cm^{-1}, the last certainly corresponding to the formation of imide groups.[7,9] However, their absence in nondegraded samples (see, for example, Fig. 1) argues against there being an important imide fraction in all the samples studied. Furthermore, C/N molar ratios measured on unhydrolyzed polyacrylamide samples[16] correspond to the values expected of the homopolymer, that is, 3 to 1. Finally, no ^{13}C-NMR spectrum has shown any peak that could correspond to an important imide fraction.[16]

All the cited evidence seems to confirm the fact that low nitrogen values in elementary analysis of polyacrylamide homopolymers is a result not of imide structures but of retained water, which cannot be eliminated under normal conditions or without risking the degradation of the polymer. This agrees with other published results.[9,13] The tenacity with which this water is retained is shown via TGA thermograms. TGA curves of four different types of polyacrylamide samples have one thing in common (see Fig. 4): the loss of water up to a temperature of approximately 250°C. Thereafter, the loss of weight is due to the formation of NH$_3$ gas and resulting inter- and
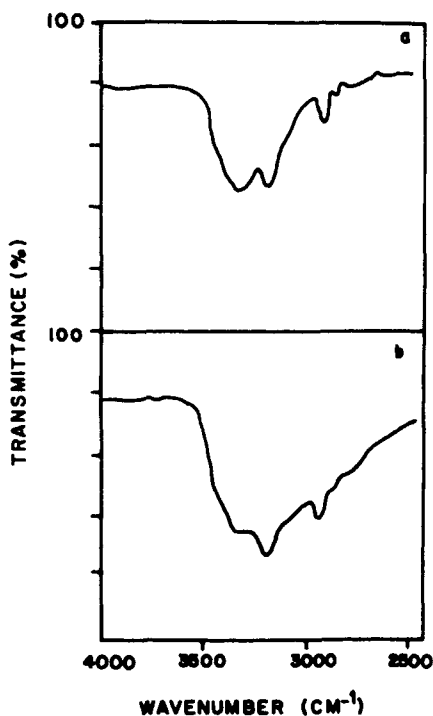

Fig. 5. Changes in the 3500 cm^{-1} to 3000 cm^{-1} region of the IR according to the nature of the salt of the hydrolyzed polyacrilamide: (a) Na$^+$ salt, (b) NH$_4^+$ salt.
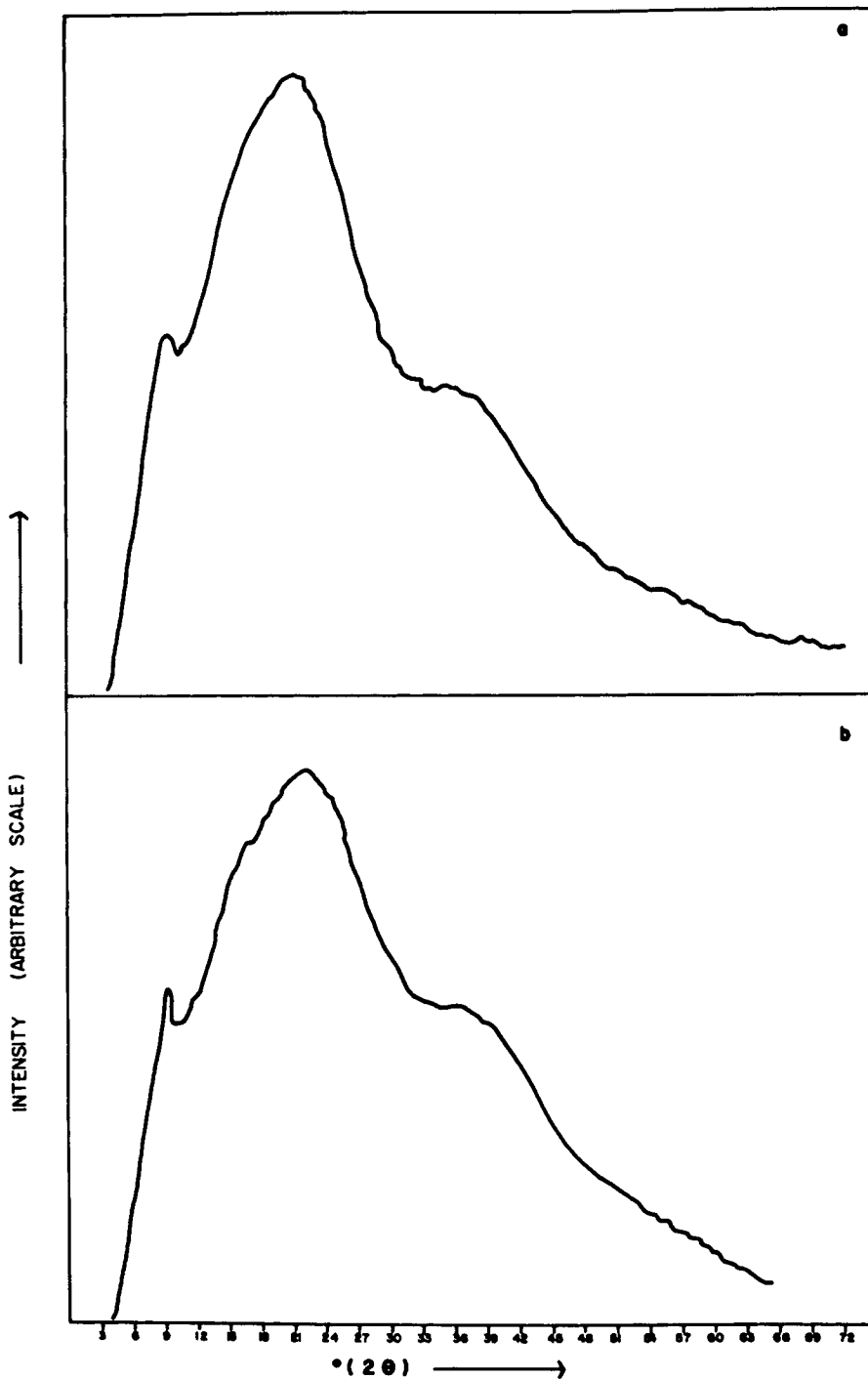
Fig. 6.   Wide angle x-ray diffractometer curves of samples (a) M1 and (b) L4. Peak observed at $2\theta \simeq 9°$ corresponds to sample holder.

intramolecular imidization of the pendant groups (for example, see Ref. 13). The weight loss in the NH_3 elimination stage on the TGA curve can be indicative of the degree of hydrolysis of the sample being studied [compare Figs. 4(b) and 4(d)]. The more pronounced loss corresponds to the less hydrolyzed polymer. The exception are those hydrolyzed polymers sold as the ammonium salt of the polyacid. In this case [Fig. 4(c)] the total evolved NH_3 comes both from the polyacrylamide fraction of the polymer, and from the NH_4^+ cation present in the sample. The presence of the NH_4^+ can be determined from the IR spectrum of the sample, as shown in Figure 5.

One last point that needs considering is the uncertainty as to the crystallinity of these samples, since opposing views have been published in the literature.[11,14] It would be expected that the presence of crystallinity would make these polymers harder to dissolve in water at ordinary temperatures. x-ray diffraction patterns of the hydrolyzed and nonhydrolyzed polymers show at room temperature just the presence of two broad maxima, centered at $2\theta \simeq 25°$ $(d \simeq 4.2 \text{ Å})$ and $2\theta \simeq 36°$ $(d \simeq 2.5 \text{ Å})$, as shown in Figure 6. Heating the polymer and recording on photograph the wide angle x-ray patterns fails to reveal any appreciable crystallinity up to 100°C (see Fig. 7). Other diffraction patterns recorded up to 220°C failed to reveal crystallinity. This would seem to imply that it is not the presence of retained water that hinders the development of crystallinity, but that other reasons (for example, tacticity) must be sought.

Detection of Impurities in the Samples

The majority of the samples studied either contained nothing other than the polymer, or else the presence of impurities was so obvious that steps could be taken to eliminate them (for example, the oil and water in the emulsified samples). However, there are instances where a sample does have an appreciable amount of inorganic salts present. Compare for example the infrared spectra of Figure 8 with those of Figure 1. Bands have
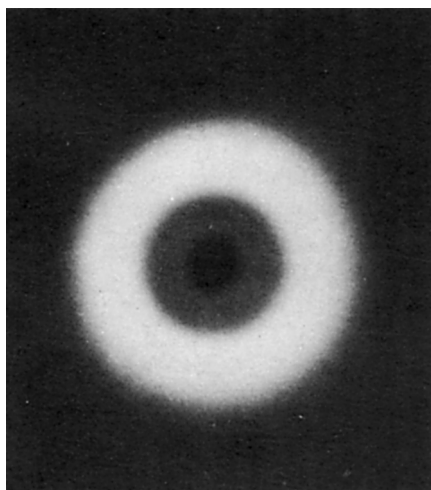

Fig. 7.   Wide angle x-ray diffraction photograph of sample M1 obtained at 100°C. Sample to film distance: 5 cm.
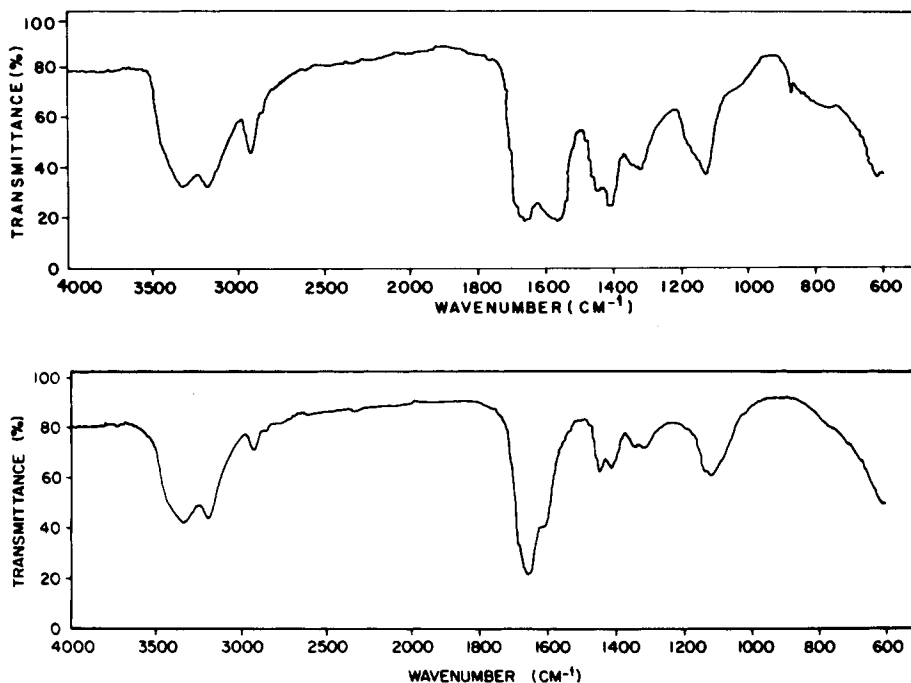
Fig. 8. IR Spectra of (a) sample 01 and (b) sample PAA.

appeared which were not present in what can now be called "pure" samples. Figure 8(a) corresponds to a commercial powder samples (01), and Figure 8(b) is that of a polyacrylamide bought from Aldrich Chemical Co. Basically two new bands appear: (i) a broad band at around 1125 cm^{-1}, which varies in shape in Figures 8(a) and 8(b), and (ii) a sharp peak in Figure 8(a) at 880 cm^{-1}.

The latter can be assigned straightforwardly to Na_2CO_3. The former, assignable to a sulfate group, needs further study, since the sulfate containing group may or not be covalently bonded to the polymer chain.

Dialysis of the Aldrich Chemical polymer reduces the intensity of the 1125 cm^{-1} (see Table II) without altering the rest of the spectrum. An x-ray diffraction pattern of the Aldrich Chemical sample reveals the presence of a highly crystalline fraction, identifiable from its d-spacings as sodium sulfate (see Table III). Figures 9(a) and 9(b) illustrates the disappearance of the x-ray crystalline reflections as the 1125 cm^{-1} band decreases in the IR proportional to the duration of the dialysis treatment (refer to Table II).

In the case of sample 01, a similar x-ray analysis reveals the presence of

TABLE II
Variations in Intensity of 1125 cm^{-1} Band during Dialysis of PAA Polymer Solution

Duration of dialysis (days)	Absorbance ratio 1125 cm^{-1}/1660 cm^{-1}
0	0.28
7	0.13
12	0.09

TABLE III
Correlation between Observed *d*-Spacings of Crystalline Reflections of Sample PAA and
Reported Values for Na₂SO₄

PAA (Observed)		Na₂SO₄ (file-24 1132, ref 17)	
d (Å)	I Relative	d (Å)	I Relative
2.80	100	2.78	100
2.67	70	2.65	48
4.72	40[a]	4.66	73
3.95	25[a]	—	—
3.20	25	3.18	51
3.10	25	3.10	47
1.87	20	1.86	31
3.80	15	3.84	18
2.40	15[a]	—	—
2.35	15	2.33	21
3.47	10[a]	—	—
1.68	10	1.68	12
1.60	10	1.61	5
1.57	10	1.55	10
1.96	5[a]	—	—
1.74	5[a]	—	—
1.44	5[a]	—	—
1.81	2[a]	—	—
1.50	2[a]	—	—

[a] Can be assigned to the Na₂SO₄ crystalline form of file 5-0631 (Ref. 18).

Na₄(CO₃)SO₄ (see Table IV), thus explaining the difference in the 1125 cm⁻¹ bands of both samples (Fig. 8).

It is interesting to note that some of the published spectra of polyacrylamides[18] also show a very prominent 1125 cm⁻¹ band. It now seems likely that such samples must contain a certain fraction of inorganic sulfates, introduced at some point in the polymerization or precipitation of the polymers. A residual band at 1125 cm⁻¹, of weak intensity, has, however, been observed in all the polymers studied, and it has not been established whether it corresponds to the polymer structure or to residual traces of inorganic salts.

Finally, it should be emphasized that the detection of Na₂CO₃ in the combustion ashes of these polymers does not imply that it was present in the sample. The sodium cation of the salt of the acid group present in the hydrolyzed polymer can react with the combustion gases to give Na₂CO₃. Thus, high residual weights measured by TGA in air do not imply contaminated samples, but rather samples of high hydrolysis. Wide angle x-ray diffraction is necessary to confirm the presence of such salts, and offers a better guarantee of detection than IR in the case of salts such as NaCl.

CONCLUSIONS

Though the basic aspects of the IR spectra of polyacrylamides have been published before,[9,10] both the effect of pH on the spectrum and the nature of the 1125 cm⁻¹ band had not been analyzed up to now. Infrared spec-
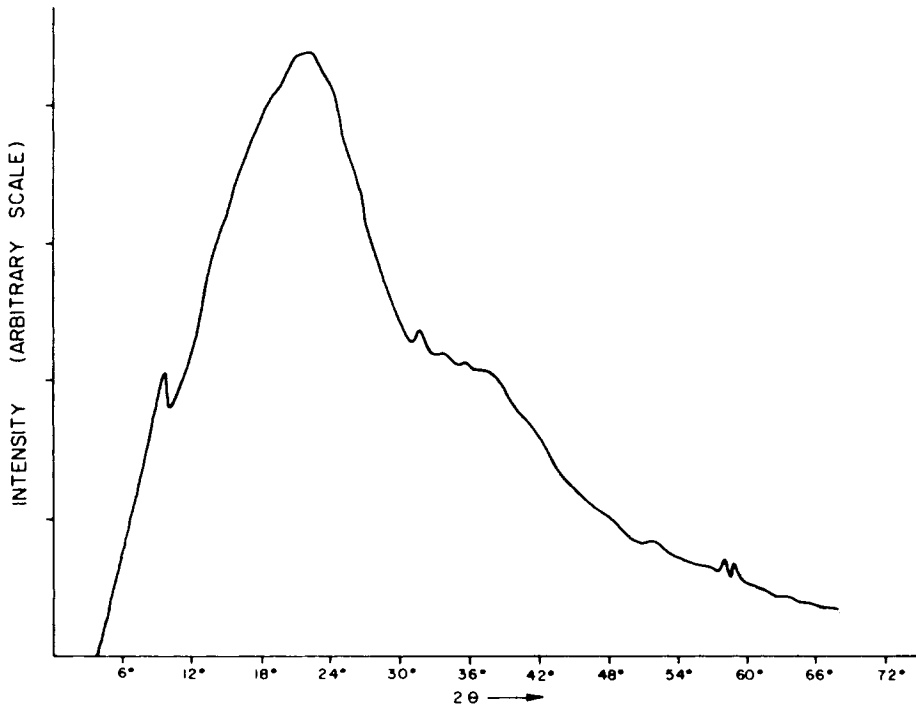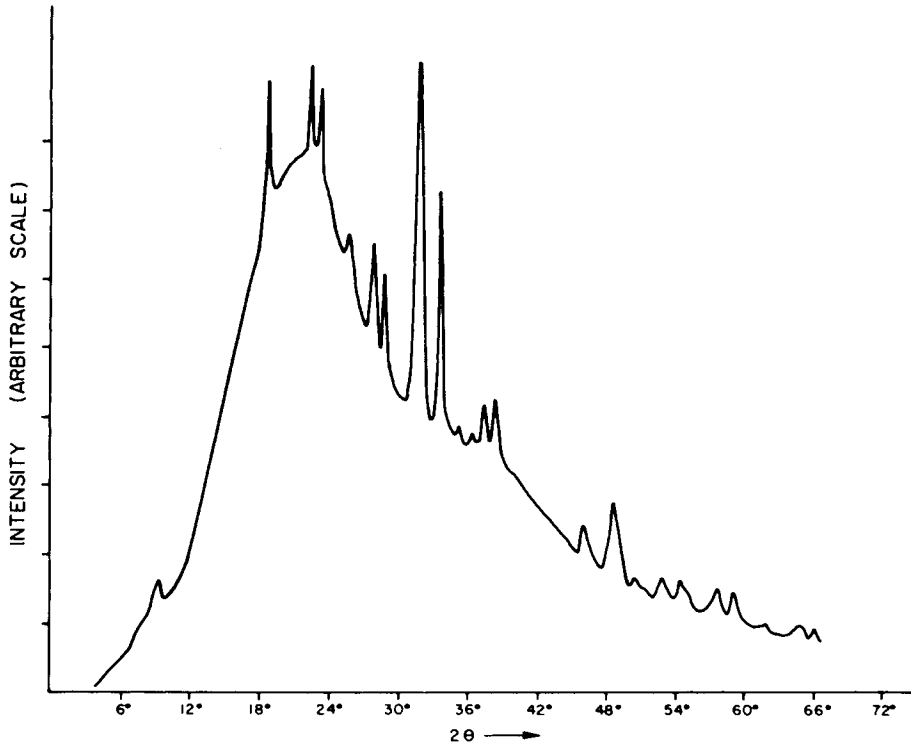
Fig. 9.   Wide angle x-ray diffractometer curves of sample PAA (a) before the dialysis and (b) after 7 days of dialysis.

TABLE IV
Correlation between Observed d-Spacings of Crystalline Reflections of Sample 01 and
Reported Values for $Na_4(CO_3)SO_4$

01 (Observed)		$Na_4CO_3SO_4$[a]	
d (Å)	I Relative	d (Å)	I Relative
2.76	100	2.74	100
3.75	85	3.78	60
2.62	70	2.61	70
3.45	40	3.44	45
1.89	35	1.89	35
1.74	15	1.72	8
1.46	10	1.44	8
1.53	10	1.53	9
4.77	10	—	—
2.29	10	2.26	2
2.13	10	2.15	14
4.19	5	—	—
2.35	5	—	—
1.63	5	—	—
1.61	5	1.61	1
1.50	5	1.51	6

[a] File-24 1138, Ref. 17.

troscopy reveals itself as a most versatile tool for the routine analyses of these polymers, offering information on the nature of the cation of the salt of the polyacid, detecting the presence of inorganic salts and confirming the absence of imide structures. Additionally, it provides a method for determining the degree of hydrolysis with good accuracy using an adequate calibration curve. The main advantage to this determination is that, similar to ^{13}C-NMR and C/N elementary analysis, no accurate weighing of the sample is needed. Only the pH of the solution used to cast the films must be carefully controlled.

It now seems evident that the presence of imide structures in these polymers has been overestimated. None of the techniques used either in this paper or related papers[8,16] can detect an appreciable fraction of these structures in unheated samples.

The lack of crystallinity to any observable degree points to an heterotactic nature of the polymers studied, as suggested recently by Inoue et al.[15] This would contradict previous statements to the contrary,[14] though in the cited work only low molecular weight polyacrylamide was studied.

The tenacity with which these polymers retain water cannot be understated. Any method where the accuracy of the result relies on an exact weighing of the sample will incur in a systematic error, anywhere between 7% and 15% in the best of cases. This unavoidable fact underscores the importance of methods for determining the degree of hydrolysis of these polymers, which are independent of any accurate weighing of the sample.

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