The determination of the degree of hydrolysis in poly(acrylamides): simple methods using C^{13} n.m.r., and elementary analysis

Jon A. Zurimendi and Saul J. Guerrero
Departamento de Ciencias de los Materiales, Universidad Simón Bolivar, Apartado 80659, Caracas, Venezuela

and Vladimir Leon
Centro de Fisica, Instituto Venezolano de Investigaciones Cientificas, Altos de Pipe, Caracas, Venezuela

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C^{13} n.m.r. spectroscopy and C, N elementary analysis have been applied to determine the degree of hydrolysis of commercial polyacrilamide samples. The methods proposed do not involve the weighing of the samples, and thus avoid the problems posed by retained water and the presence of inorganic salts. The C^{13} n.m.r. spectrum is sufficiently resolved to allow peak area determinations of the methine carbon in the hydrolysed and non-hydrolysed moieties. Elementary analysis of the solid samples has been applied to obtain the C/N ratio of the polymers, rather than percentage values based on sample weight. A very good correlation is observed between the data obtained via both methods.

(Keywords: polyacrylamides; hydrolysis; C^{13} nuclear magnetic resonance; elementary analysis; carbon/nitrogen molar ratio)

INTRODUCTION

Poly(acrylamides) are water soluble polymers with commercial applications that depend fundamentally on the high viscosity of their solutions. For the same chain length the solution viscosity depends strongly on the degree of hydrolysis of the poly(acrylamide). The hydrolysed polymer is normally obtained through one of the following ways: (i) direct hydrolysis of the homopolymer in the presence of strong bases and high temperature or (ii) by copolymerizing acrylamide with acrylic acid, usually followed by the neutralization of the resulting copolymer.

The two methods most commonly employed to determine the degree of hydrolysis are the potentiometric titration of the polymer in solution[1-3] and by elementary analysis of the solid polymer[4-6]. Both methods rely on an accurate weighing of the sample, and the presence of retained water and of inorganic salts can introduce errors in the calculations. Each method has its own particular drawback. The potentiometric titration is a tedious technique, with the need to achieve equilibrium conditions during the titration. The interpretation of the data from elementary analysis has led to the proposal of chemical structures in the polymers (imides) for which no other evidence exists[7,8].

The present paper deals with two alternate and more absolute methods for determining the degree of hydrolysis in commercial polyacrylamides. One relies on elementary analysis using a different way of interpreting the data; the other is based on the possibility of obtaining adequate C^{13} n.m.r. spectra from solutions of these polymers.

EXPERIMENTAL

Samples

A series of commercial poly(acrylamides) with different degrees of hydrolysis were obtained from two manufacturers. These are samples M, L0, L1, L2 and L3. Two samples in which the hydrolysed poly(acrylamides) are present as the ammonium salt, samples Q1 and Q2, were also analysed.

Preparation of the solutions for C^{13} n.m.r.

Approximately 5% (w/w) solutions of the polymers in 10% NaCl/distilled water were prepared, stirring overnight with a magnetic stirrer to achieve a clear solution of 'fish-eyes' or other inhomogeneities. Once prepared, the solutions were introduced in 12 mm diameter n.m.r. tubes with the reference and internal lock contained in a 2 mm diameter insert.

N.m.r. measurements

The spectra were recorded using a Varian XL-100 (25.2 MHz) interfaced with a pulse generator and data system from Nicolet Technology Corporation. Deuterated benzene was used as a lock and as an internal ppm reference. The spectra incorporated 8190 scans with an acquisition time of 410 ms and a pulse width of 43 μs. Reported integrals were obtained using the corresponding routine.

Carbon-nitrogen elementary analysis

The measurements were carried out on a Perkin–Elmer

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240 Elemental Analyser using Cyclohexanone-2,4-dinitrophenylhydrazone (BDH microanalytical reagents) as standard. The treatment of the instrumental data is described in the text. Polymers which are known to contain NH_4^+ ion were pretreated in order to obtain accurate results. For example, sample Q was treated first with NaOH solution at room temperature; the evolved NH_3 gas was removed under vacuum without heating. The excess base was neutralized (to a final pH between 6 and 7), and the polymer sample dried under vacuum. Polymers were not heated in the presence of strong bases or acids, otherwise further hydrolysis of the polymer would have taken place.

RESULTS

C^{13} n.m.r.

Figure 1 shows a C^{13} n.m.r. spectrum of sample M, with the corresponding assignment of the peaks. The present assignment* generally agrees with results recently published by Inoue *et al.*[9] for unhydrolysed polyacrylamide. *Figure 2* shows the evident dependence of the intensity of peaks A′ and B′ of *Figure 1* on the degree of hydrolysis of the polymer; in *Figure 2* the degree of hydrolysis increases from L0 to L3. The values measured by calculating the ratios of the integrated areas of the peaks at 45 and 47 ppm (B′ and B, respectively, *Figure 1*) give the percentage hydrolysis of the samples, as reported in *Table 1*.

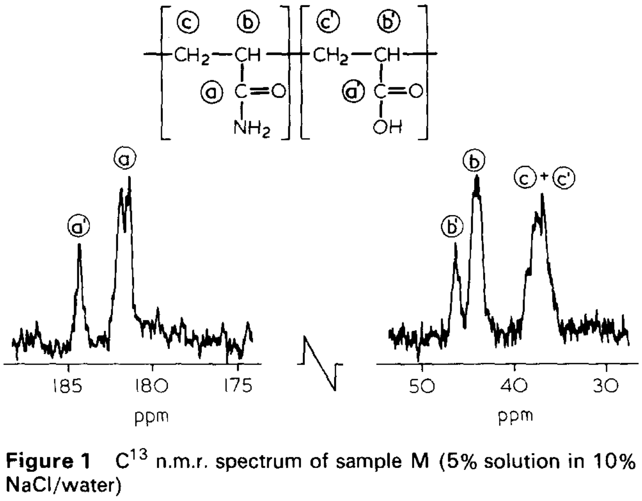

Figure 1 C^{13} n.m.r. spectrum of sample M (5% solution in 10% NaCl/water)

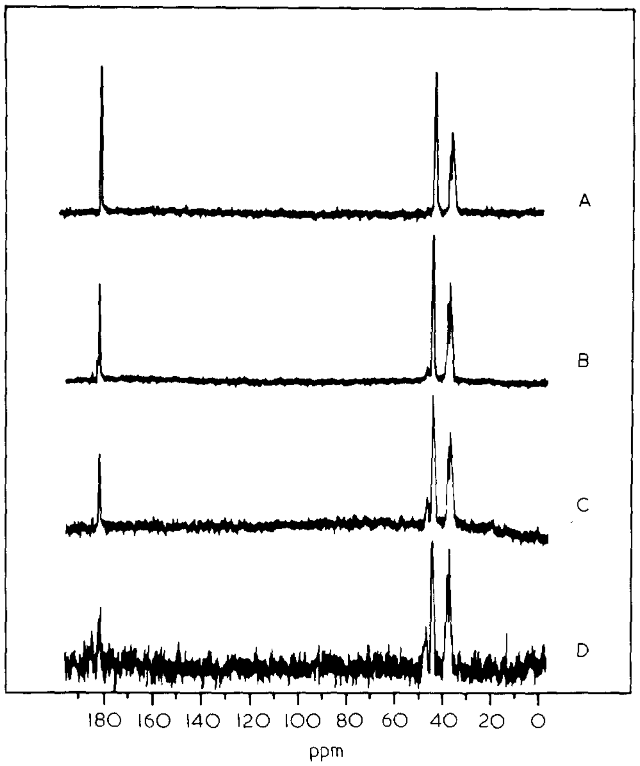

Figure 2 C^{13} n.m.r. spectrum of samples L0 (A), L1 (B), L2 (C) and L3 (D) (5% solution in 10% NaCl/water)

Table 1 Comparison of the degree of hydrolysis measured via C^{13} n.m.r. and elementary analysis

	Degree of hydrolysis (mol.%)	
Sample	C^{13} n.m.r.	Elementary analysis
L0	0	Close to nil
L1	9.9	9.5
L2	18.3	19.9
L3	27.9	28.9

Table 2 Effect of pretreatment on the % hydrolysis values

	Degree of hydrolysis (mol.%)		
	Elementary analysis		
Sample	As received	After pretreatment	C^{13} n.m.r.
L0	Close to nil	2.5	0
Q1	7.8	30.8	32.6
Q2	8.3	29.5	28.1

C,N elementary analysis

In order to confirm the validity of the C^{13} n.m.r. hydrolysis measurements, another absolute and independent method of measuring the degree of hydrolysis was needed.

There is an alternate way of treating C,N elementary analysis data so as to be able to ignore the presence of water and other impurities provided they contain no C or N. This analysis is based on the direct correlation of the molar ratio of C to N in the sample being analysed. First, the Perkin–Elmer analyser was calibrated using the standard referred to in the Experimental section. This compound has a C:N molar ratio of 3:1, as in the polyacrylamide homopolymer. Taking the output voltages given by the instrument for the carbon and nitrogen of the standard as C_{st}, N_{st} and the response for the polymer sample as C_p, N_p. The degree of hydrolysis can be calculated directly from the formula:

$$\%\ \text{hydrolysis} = \left(1 - \frac{C_p/C_{st}}{N_p/N_{st}}\right) \times 100$$

As can be seen from the formula, the weight of the sample (and of the standard) is not needed to calculate the degree of hydrolysis. The main drawback to this method is that the presence of an ammonium ion (NH_4^+) in the sample will give low results. The pretreatment indicated in the

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* The assignment for the methylene and methine carbons was determined using off-resonance irradiation of the protons

Experimental section was applied successfully to samples Q1 and Q2 (see *Table 2*). The effect of the pretreatment on a non-hydrolysed sample (for example, L0) is slight, but obviously needs considering.

DISCUSSION

A comparison of the results set out in *Tables 1* and *2* shows a very good agreement between the two methods employed to determine the degree of hydrolysis. Both methods avoid the exact weighing of the sample, and thus the errors inherent to the presence of water and other impurities. The advantage of the C^{13} n.m.r. analysis over the elementary analysis is that the former needs no previous knowledge of the composition of the sample in order to obtain a reliable result.

A final check on the advisability of using the C^{13} n.m.r. spectra for quantitative analysis was carried out, through the measurement of relaxation times. A gross determination of T_1 shows that the T_1 for the carbonyl group (v500 ms) is at least twice as long as that for the methine carbons. So as to minimize the instrumental time for routine analysis of samples, the two methine carbons were chosen for the corresponding area ratios. The very similar environment for the two methine carbons guarantees similar NOE's for both, so no gate decoupling spectra were necessary to obtain a precise value of the ratio. In a test run no change in the ratio was obtained with or without gate decoupling to obtain the spectrum.

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