Water-soluble copolymers: 15. Studies of random copolymers of acrylamide with *N*-substituted acrylamides by ^{13}C n.m.r.

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Quantitative ^{13}C n.m.r. analysis has been used to determine composition of copolymers of acrylamide and sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS) copolymers of acrylamide with *N*-(1,1-dimethyl-3-oxobutylacrylamide (DAAM), and terpolymers of acrylamide, NaAMPS and DAAM. The n.m.r. analyses are unaffected by bound water, are relatively fast, require little sample preparation, and are non-destructive. The method involves the accumulation of spectra using pulse repetition which allows for retention times greater than $5T_2$ (spin–lattice relaxation time), as well as the use of gated decoupling to remove nuclear Overhauser enhancement (NOE) effects. NOE and T_1 data are reported for the polymer systems studied; a justification of the parameters utilized is given. Compositional data obtained by ^{13}C n.m.r. are in agreement with those determined by elemental analysis.

(Keywords: acrylamide copolymers; ^{13}C n.m.r. spectroscopy; spin–lattice relaxation; quantitative analysis; elemental analysis)

INTRODUCTION

In recent years the use of acrylamide-based copolymers in applications including mobility control, viscosity modification and flocculation has increased. Since the ultimate performance of these polymers is based on composition, analytical techniques for accurate rapid analysis have been sought.

Compositional analyses of acrylamide copolymers have traditionally been based on elemental nitrogen analysis[1–5], potentiometric titration[6–8], and more recently on thermogravimetric analysis[9]. However, the hygroscopic nature of these polymers can result in errors in weight determination; additionally, extensive drying can result in covalent or associative crosslinking preventing subsequent dissolution[10].

Only recently has the tacticity of polyacrylamide been elucidated[11,12]. McCormick, Chen and Hutchinson have demonstrated the utility of ^{13}C n.m.r. quantitative determination of copolymer compositions by comparing the results with i.r. spectroscopy and elemental analysis techniques[13]. The determination of copolymer composition by proton n.m.r. has been well documented[14–16]; however, acrylamide-based copolymers are soluble in few solvents suitable for proton analysis. These copolymers are, fortunately, very soluble in water, an ideal solvent for ^{13}C n.m.r. due to the absence of interfering resonances.

Quantitative analysis of polymers by ^{13}C n.m.r. has been addressed in a number of reviews[17–19]. In general two major conditions must be met when attempting to extract quantitative information. When using 90° pulse angles, pulse repetitions of greater than five times the spin-lattice relaxation time, T_1, should be employed. This time period allows for the re-establishment of the Boltzmann distribution of nuclei. Some allowance must also be made for the possible inequality of the nuclear Overhauser enhancement (NOE)[20] of the observed resonances. The equalization of the NOE's can be accomplished by the addition of a paramagnetic impurity[21]; however, this practice often results in excessive broadening of the carbon peaks. Freeman, Hill and Kaptein[22] suggested using a gated decoupling technique in which the NOE's were eliminated by cycling the decoupler on only during signal acquisition. This process results in completely decoupled spectra with no NOE.

The intention of this study is to demonstrate the utility of quantitative ^{13}C n.m.r. for determining the copolymer composition of a series of water-soluble, acrylamide-based copolymers. Random copolymers of acrylamide (AM) with sodium 2-acrylamido-2-methyl-propanesulphonate (NaAMPS) and *N*-(1,1-dimethyl-3-oxobutyl) acrylamide (DAAM) have been studied as well as a terpolymer series of the three monomers. Consideration has been given to the molecular motion of the copolymers in solution as it pertains to the quantitative procedure.

EXPERIMENTAL

The syntheses of the random copolymers have been described previously[23]. Before use the polymers were dried at 40°C under vacuum. Polymer solutions were prepared by weighing a known amount of dried polymer and adding it to 2 ml of D_2O in a 10 mm o.d. n.m.r. tube. The polymer concentration used for this study was kept at 5% w/v to alleviate viscosity problems. Dissolution was usually accomplished in a 2-day period.

All n.m.r. spectra were obtained on a JEOL FX 90Q spectrometer operating at a ^{13}C n.m.r. frequency of 22.5 MHz. A 5000 Hz window was employed with exponential weighting. The spectra were referenced to either an external or an internal DSS standard. The probe temperature was maintained at 32°C ± 2°C.

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The spin-lattice relaxation times were determined through either an inversion recovery method[24] or a fast inversion recovery method[25]. Peak intensity/pulse interval data were analysed by utilizing a three-parameter fit proposed by Sass and Zeissow[26]. The procedure involves a Newton iteration of the error-analysed equation utilizing a computer program written for this purpose. These methods have been reported to yield accurate T_1 values in the least amount of time[27]. The relaxation times are reported within ±15% due largely to low signal/noise ratios of these high molecular weight and highly viscous sample solutions.

Determinations of NOE values were performed for a number of polymer samples in order to justify the use of gated decoupling. Alternate n.m.r. studies were conducted with and without gated decoupling. A pulse interval of ten times the longest observed T_1 values was used to eliminate the error as outlined by Canet[28]. The peaks for each spectrum were integrated under identical conditions and the NOE values determined. A maximum error of ±0.2 NOE units is reported.

Evaluations of copolymer composition were performed utilizing a 90° pulse angle, gated decoupling, and pulse repetitions $>5T_1$ values. Well-resolved representative peaks were chosen from each monomer and multiple integrations were carried out. The maximum estimated error for the determinations is ±10%. Typically 5000–10 000 transients were accumulated.

RESULTS AND DISCUSSION

Monomers used in synthesis of copolymers analysed in this study are illustrated below. In this section assignments of ^{13}C resonances are made and relaxation times given. Additional comparisons of copolymer compositions are discussed in relation to those determined by other methods.

Figure 1 illustrates the completely decoupled ^{13}C n.m.r. spectrum of NaAMPS-3, a copolymer of acrylamide (AM) with sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS). With the aid of off-resonance decoupling and comparison with model compounds, all of the peaks were assigned as shown in *Figure 1*. The relative chemical shifts change very little throughout the series of copolymers. Therefore, all of the peaks except those of the backbone carbons, which are broad and overlapping, have the potential to be used for determination of the copolymer composition.

The use of gated decoupling to equalize NOE values is necessary when the observed NOE values are different for different carbons. Evaluation of these NOE values is then justified. Rapidly reorienting carbons, which relax through a dipole–dipole mechanism, often exhibit a maximum NOE value of 2.9. However, some large biomolecules and synthetic polymers exhibit reduced NOE values due to an apparent violation of the extreme narrowing condition[29]. *Table 1* shows the measured NOE values for the NaAMPS series. It is obvious that these polymers are, in fact, violating the extreme narrowing condition since most of the carbons are relaxed predominantly through dipole–dipole relaxation.

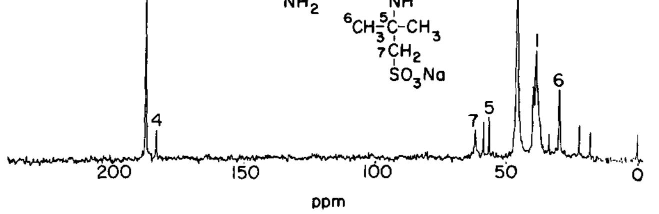

Figure 1 Gated decoupled FT ^{13}C n.m.r. spectrum of a 5% w/v solution of AMPS-35 in D_2O with an 8 s pulse repetition, a 90° pulse angle, 7500 transients, at 32°C

Table 1 Nuclear Overhauser enhancements[a] for the NaAMPS series

Sample	3[b]	4	5	6	7
AMPS[c]	–	1.7	–	2.3	1.6
1	2.3	1.8	2.5	1.9	2.5
2	1.8	2.1	2.4	1.9	2.5
3	1.2	1.2	1.3	1.8	1.8
7	1.2	1.2	1.4	1.8	1.4

[a] ±0.2 units
[b] From *Figure 1*
[c] Homopolymer

Table 2 Spin-lattice relaxation times[a] for the NaAMPS series

	Carbon no.[b]						
Sample	1	2	3	4	5	6	7
AMPS[c]	0.03	0.06	–	0.83	0.80	0.15	0.04
1	0.05	0.09	1.23	1.09	0.95	0.22	0.04
2	0.04	0.08	1.12	1.03	1.07	0.16	0.06
3	–	0.08	1.03	0.97	0.90	0.17	0.05
7	–	–	0.70	0.80	0.76	0.16	0.05

[a] Estimated accuracy ±15% (seconds)
[b] From *Figure 1*
[c] Homopolymer

The data are also indicative of the presence of copolymers rather than a mixture of two homopolymers. In general the NOE values decrease with the amount of NaAMPS in the copolymer. The successive introduction of AMPS into the copolymer has the effect of stiffening the polymer chain, possibly through bulky side group interactions. This results in changes in the effective correlation time and further decreases the polymer motion. Consequently these data indicate the need for gated decoupling to eliminate the NOE for quantitative analysis.

Table 2 lists the measured spin-lattice relaxation times for the NaAMPS series. The longest T_1's are those of the carboxyl and the quarternary carbons, which are a result of the absence of bonded hydrogens. Since the quantitative process requires the use of the AM carboxyl, pulse repetition times are long. The values for the backbone carbons are only apparent values since resonances from each monomer overlap. However, the bulk measured T_1 is a good approximation due to the similarity in the individual carbon T_1's[30]. For the backbone carbons, a factor of two difference is noted in measured T_1. This is due to the bonded proton dependence of the two carbons (2 protons on one to only one proton on the other). This dependence on bonded protons is evidence that they are undergoing isotropic motion only. Increased segmental motion in the side chain is observed through the methylene resonances. Additionally the mechanism of spin-rotation relaxation is observed for the side chain methylene groups resulting in T_1 values on the order of 0.2 s.

Copolymer compositions were calculated using the acrylamide carbonyl and carbonyl and methyl resonances of the NaAMPS monomer. Equation (1) was utilized for the calculations. I_{AMPS} represents the NaAMPS monomer peak integral and I_{AM} the acrylamide carbonyl integral.

$$\frac{I_{\mathrm{AMPS}}}{I_{\mathrm{AMPS}}+I_{\mathrm{AM}}}\times 100=\mathrm{mole\%\ AMPS} \qquad (1)$$

Comparisons of these values with those from elemental analyses are shown in *Table 3*.

Figure 2 represents the completely proton-decoupled ^{13}C n.m.r. spectrum of DAAM-41, a copolymer of acrylamide with *N*-(1,1-dimethyl-3-oxobutyl) acrylamide (DAAM). Distinct peaks can be seen for individual carbons in the polymer with the exception of the backbone carbons. Copolymer compositions were determined as previously discussed utilizing the individual amide carbonyl peaks as well as the quaternary, methylene and methyl resonances of the DAAM side chain (equation (1)).

Table 4 contains the measured spin-lattice relaxation times of the DAAM series. Once again a general tendency is noted for the T_1 values to decrease with the successive introduction of the bulky monomer into the chain. The NOE data in *Table 5* show the same trend, indicative of the slow rotation of these polymers in solution again resulting in extreme narrowing condition violations.

By using pulse repetitions greater than 6 s, analysis of copolymer from this series agreed well with elemental analysis data as shown in *Table 6*. No effort was made to include the keto carbonyl resonance owing to its relatively long T_1 value (> 2 s) and its proximity to the outer edge of the 5000 Hz window which is used in these spectral determinations. Additionally, the peak integrated poorly owing to uneven excitation in this area.

Table 3 Material specifications for the NaAMPS series

Sample	%N[a]	%S[a]	Mole % AMPS Elemental analysis[a]	 ^{13}C n.m.r.
1	14.03	3.05	9.51	10.7
2	12.15	5.28	19.01	17.3
3	10.65	6.78	27.85	27.2
7	6.94	10.43	65.75	69.5

[a] Ref. 33

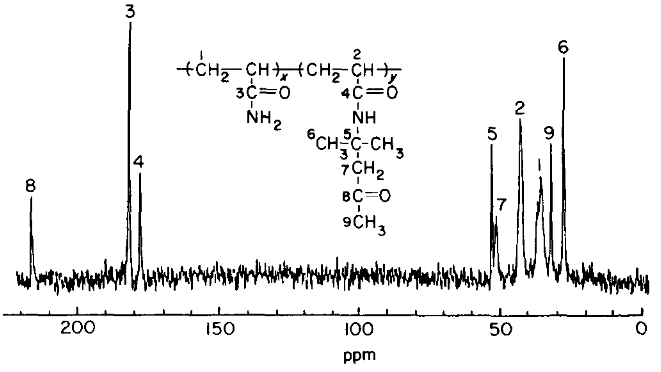

Figure 2 Gated decoupled FT ^{13}C n.m.r. spectrum of a 5% w/v solution of DAAM-31 in D_2O with a 6 s pulse repetition, a 90° pulse angle, 7500 transients, at 32°C

Table 4 Spin-lattice relaxation times[a] for copolymers of acrylamide with *N*-(1,1-dimethyl-3-oxobutyl) acrylamide (DAAM)

Sample	Carbon no.[b] 1	 2	 3	 4	 5	 6	 7	 8	 9
11	0.04	0.08	1.22	1.10	1.04	0.22	0.06	2.22	0.9
21	0.03	0.08	1.02	0.96	1.16	0.21	0.07	2.20	0.9
31	0.03	0.06	0.93	0.84	0.91	0.19	0.06	1.75	0.8
41	0.03	0.06	1.01	0.94	0.82	0.19	0.06	1.55	0.9

[a] (s), ±10% estimated accuracy
[b] From *Figure 2*

Table 5 NOE values[a] for DAAM copolymers

Sample	Carbon no.[b] 1	 2	 3	 4	 5	 6	 7	 8	 9
11	1.8	2.1	1.8	1.9	–	2.6	2.0	–	1.9
41	–	1.7	1.5	1.6	–	2.1	1.7	–	1.9

[a] ±0.2 units
[b] From *Figure 2*

Table 6 Material specifications for the DAAM series

Sample	%C[a]	%N[a]	% DAAM Elemental analysis[a]	 ^{13}C n.m.r.[b]
11	53.10	16.90	11.1	10.5
21	56.60	14.85	22.8	21.7
31	57.09	13.64	31.4	31.3
41	58.57	12.49	41.2	38.8
BH-DA-31	53.20	12.76	31.1	31.4
BH-DA-21	–	–	–	22.7

[a] Ref. 33
[c] ±10% estimated accuracy

^{13}C n.m.r. quantitative analysis techniques can also be applied to terpolymers with relative ease. By comparison, elemental analysis equations for determining compositions are often quite complicated. *Figure 3* is the completely decoupled n.m.r. spectrum of T-12, which consists of AM, NaAMPS and DAAM. Individual peaks indicative of each monomer are readily discernable. The peak at 177 ppm contains the overlapped carbonyl resonances for the DAAM and NaAMPS monomers. Relaxation time data for these polymer indicate that the longest T_1 of a usable peak is about 1.5 s necessitating an 8 s pulse repetition. Typically 10000 transients were accumulated. The terpolymer compositions were determined utilizing the two carbonyl resonances at 182 and 177 ppm and the NaAMPS methylene side chain carbon peak at 61 ppm according to equations (2), (3) and (4).

$$X_{\mathrm{AMPS}}=\frac{I_{61}}{I_{182}+I_{178}}\times 100 \qquad (2)$$

$$X_{\mathrm{DAAM}}=\frac{I_{178}-I_{61}}{I_{182}+I_{178}}\times 100 \qquad (3)$$

$$X_{\mathrm{AM}}=\frac{I_{182}}{I_{182}+I_{178}}\times 100 \qquad (4)$$

Table 7 Material specifications for the terpolymer series of AM–DAAM–NaAMPS

				Mole %					
				AM		DAAM		NaAMPS	
Sample	%C[a]	%N[a]	%S[a]	EA[b]	^{13}C	EA[b]	^{13}C	EA[b]	^{13}C
11	46.89	13.55	2.99	79.5	82.2	10.6	6.9	9.6	10.8
12	45.69	12.34	4.44	72.7	74.9	11.3	12.4	15.7	12.5
13	43.11	9.83	6.88	54.5	56.2	14.7	12.3	30.5	31.8
14	39.67	7.13	9.45	22.5	26.8	19.4	17.5	57.8	55.7

[a] Ref. 33

[b] EA, elemental analysis

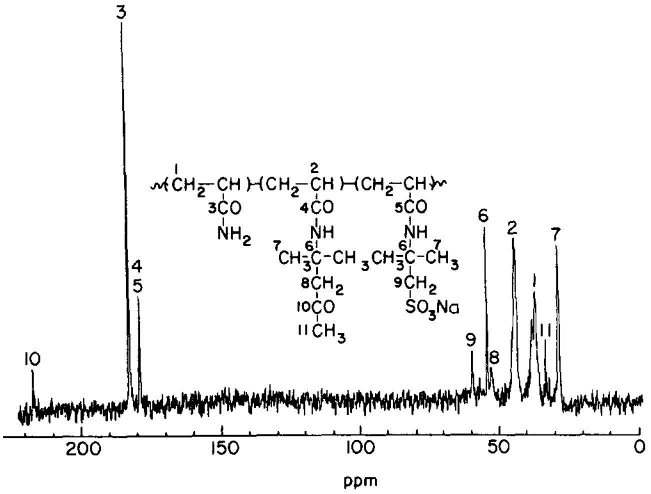

Figure 3 Gated decoupled FT ^{13}C n.m.r. spectrum of a 5% w/v solution of a terpolymer of AM, DAAM and AMPS in D_2O with an 8 s pulse repetition, a 90° pulse angle, 7500 transients, at 32°C

The calculated data are given in *Table 7*. The values are generally in excellent agreement with those predicted by elemental analysis.

CONCLUSIONS

Quantitative ^{13}C n.m.r. has been used little previously in determining copolymer compositions, especially for water-soluble polymers. It represents, however, a relatively simple and facile means of obtaining compositional data. The analyses are not affected by bound water, or other impurities such as residual precipitating solvent. Little sample preparation is required, and the analyses are non-destructive. Additionally, information on microviscosity effects can be obtained from T_1 values to correct for NOE effects and relaxation differences. Spectra have been obtained and analysed for copolymers of acrylamide and NaAMPS, copolymers of acrylamide and DAAM, and terpolymers of acrylamide, NaAMPS, and DAAM. The quantitative analysis data from n.m.r. were in excellent agreement with elemental analysis data.

Further efforts are underway presently to decrease the required analysis times and to improve the signal-to-noise ratios of the spectra by incorporation of the Ernst equation[31] as suggested by Visintainer[32]. These efforts to further shorten the n.m.r. analysis times have also been applied to other random and graft copolymer systems[33].

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