Water-soluble copolymers: 51. Copolymer compositions of high-molecular-weight functional acrylamido water-soluble polymers using direct-polarization magic-angle spinning ^{13}C nuclear magnetic resonance

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(Received 9 June 1993)

Compositions of several high-molecular-weight ($>10^6\,g\,mol^{-1}$) water-soluble copolymers have been determined using direct-polarization magic-angle spinning (d.p.m.a.s.) ^{13}C nuclear magnetic resonance (n.m.r.). Comonomers were studied that comprised acrylamide and sodium 3-acrylamido-3-methylbutanoate, sodium 2-acrylamido-2-methylpropanesulfonate, diacetone acrylamide or isopropylacrylamide. A copolymer of sodium 2-acrylamido-2-methylpropanesulfonate and 2-acrylamido-2-methylpropanetrimethylammonium chloride was also included. The technique is rapid and provides copolymer compositional analysis with accuracies close to those obtained by conventional elemental analysis and solution n.m.r. techniques. Spectral resolution is excellent and d.p.m.a.s. n.m.r. allows shorter acquisition times and smaller sample size. The technique is applied to a variety of acrylamide copolymers including polyelectrolytes, polyampholytes and hydrophobically associating polymers. The results are compared to copolymer compositions obtained from elemental analysis and solution ^{13}C n.m.r. spectroscopy.

(Keywords: copolymer composition; solid-state ^{13}C n.m.r.; water-soluble polymers)

INTRODUCTION

Copolymer characterization of polymer systems is a necessary requirement for the determination of reactivity ratios and interpretation of observed solution properties. For high-molecular-weight (*HMW*) acrylamide-based polymers, techniques such as elemental analysis require careful drying to remove adsorbed water; samples are usually submitted to outside laboratories for analysis. Additionally, analysis by ^1H nuclear magnetic resonance (n.m.r.) spectroscopy may not be possible owing to broad, overlapping spectral lines resulting from high molecular weights.

Solution ^{13}C n.m.r. has been employed extensively in the characterization of *HMW* acrylamide-based polymers that are routinely synthesized in our laboratories and has been shown to yield copolymer compositions consistent with those obtained by elemental analysis[1,2]. However, the technique is time-consuming, often requiring 12–15 h of scanning time to yield a proper signal-to-noise ratio for accurate determination of copolymer ratios. In addition, the solution technique necessitates concentrations of 5–20% w/w in H_2O/D_2O, requiring several days for complete dissolution of high-molecular-weight polymers ($>10^6\,g\,mol^{-1}$) to obtain quality solution spectra.

Recently, solid-state ^{13}C direct-polarization magic-angle spinning (d.p.m.a.s.) n.m.r. studies have been performed on hydrated polymer samples[3] and solvent-swollen gels[4,5]. The high solids content ($<75\%$ w/w solvent) along with considerable segmental mobility of the solvent-swollen polymer chains can yield ^{13}C m.a.s. n.m.r. spectra rivalling those obtained at the lower concentrations employed in solution n.m.r. The gel-state regime that lies between that of an uncrosslinked solid and a dilute solution involves considerable chain entanglement that restricts overall tumbling of the polymer. The averaging of the molecular motions necessary for narrow lines in n.m.r. spectra is often not achieved in conventional solution spectroscopy. However, magic-angle spinning at moderate rates combined with high-power decoupling can impart a considerable decrease in linewidths[3–7].

D.p.m.a.s. spectra of a superabsorbing hydrolysed starch-*g*-acrylonitrile with minimal hydration of the polymer have been reported[3]. The dynamic behaviour of the polymer chain as a function of hydration was studied by monitoring changes in longitudinal relaxation times and nuclear Overhauser enhancements (NOE). Clearly resolved spectra were obtained at polymer concentrations in water exceeding 50% w/w. Similar behaviour has previously been observed in synthetic polymers[6] and biopolymers[7].

The quantitative analysis of polymers by conventional

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0032-3861/94/05/0935-04

^{13}C n.m.r. has been well documented[8,9] and continues to be a routine technique for copolymer characterization[2,10]. Certain requirements must be met in order to obtain quantitative information from ^{13}C n.m.r. A delay of at least $5T_1$ after the excitation pulse is needed for more than 90% of the nuclei to return to the ground state. Additionally, the effect of the NOE must be reduced if the system is not outside the extreme narrowing regime where the NOE values may reach their maximum of 1.998[11]. For almost all of the systems of this study, the extreme narrowing condition is violated, resulting in varying NOE values depending on the backbone segmental motion and the motions of the pendent side chains[1]. This problem can be circumvented by employing gated decoupling. Since the ^{13}C–^{1}H decoupling is essentially instantaneous compared to the build-up of NOE[11], the benefits of decoupled spectra are realized without NOE.

Previous ^{13}C n.m.r. studies in our laboratories on sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and diacetone acrylamide (DAAM) polymers have demonstrated short relaxation times (< 1.25 s) and near-equivalence of the T_1 and NOE values for the respective carbonyl moieties[2]. Thus, integration of the carbonyl peaks yielded copolymer compositions in agreement with those obtained from elemental analysis. Subsequent studies of the recycle times demonstrated that relaxation delays of as low as 2 s could be employed without introducing significant error in the integration of the carbonyl peaks.

In this work, we describe a d.p.m.a.s. technique appropriate for compositional analysis of highly concentrated copolymer samples that allows much shorter acquisition times by employing highly concentrated samples. The copolymer compositions determined in this manner are compared with those obtained from elemental analysis to establish the validity of the technique. Gated decoupling and short relaxation delays of less than $5T_1$ were utilized to minimize instrument time. N.m.r. spectra were obtained by employing a 90° pulse angle, gated decoupling and relaxation delays of 2 and 10 s. The technique is much faster than solution techniques owing to the highly concentrated samples, and generally requires less sample. Several random copolymers of acrylamide with ionic, hydrophobic and ampholytic moieties are reported.

EXPERIMENTAL

The syntheses of the polymers characterized in this work have been previously reported[12–15]; however, a brief description will be provided here. The appropriate amount of comonomer — sodium 3-acrylamido-3-methylbutanoate (NaAMB), sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), diacetone acrylamide (DAAM), or isopropylacrylamide (IPAM) — with acrylamide (AM) is dissolved in water at 30°C and $K_2S_2O_8$ added as an initiator under nitrogen. NaAMB-25 refers to the polymer obtained from a 25/75 NaAMB/AM mixture in the feed. The ATAS polyampholyte is a copolymer of NaAMPS and 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC). ATAS-50 refers to a 50/50 copolymer. The polymers were precipitated into acetone, redissolved in water, dialysed and freeze-dried. All polymers were vacuum dried at 40°C overnight before use. Samples were prepared by placing approximately 0.1 g of polymer in 0.6 ml centrifuge tubes and adding an equivalent amount of water (50% w/w). The samples were placed in a desktop centrifuge and allowed to spin overnight. Complete dissolution of the samples proved unnecessary as excellent spectra were obtained on samples that were clearly not completely dissolved. Most samples were essentially hydrogels that could be easily handled although some of the samples were highly viscous and would flow given sufficient time.

Copolymer compositions were determined by solid-state ^{13}C n.m.r. spectroscopy on a Bruker MSL-400 operating at 100.6 MHz ^{13}C frequency. Direct-polarization magic-angle spinning spectroscopy employed for solid samples yielded high-resolution spectra with low signal-to-noise ratios. The sample was placed in a 7 mm ZrO rotor and spun at 2 kHz. Spinning of the samples was relatively easy since the samples quickly conform to the rotor and are essentially self-balancing. A recycle time of 2 s was employed with a flip angle of 90°. Generally, only 2000 scans were necessary to yield excellent signal-to-noise ratio. The spectra were resolution-enhanced by the Lorentzian method using a line-broadening factor of 6 Hz and integrated to yield the copolymer ratio. The approximate error of the d.p.m.a.s. technique based on repetitive measurements is ±2%.

RESULTS AND DISCUSSION

Table 1 lists feed compositions as well as copolymer compositions obtained from elemental analysis and d.p.m.a.s. n.m.r. for copolymers described in the 'Experimental' section. The structures of the polymers are given in *Figures 1–5* with representative spectra from each polymer group. The peak assignments are also provided for each polymer in the figures. In general, the agreement between the elemental analysis and n.m.r. data is excellent. The types of polymers investigated were selected to provide a cross-section of the acrylamide-

Table 1 Feed ratios and copolymer ratios obtained from elemental analysis and ^{13}C n.m.r.

Copolymer	Comonomer in feed (mol%)	Copolymer composition[a] (mol% comonomer) Elemental analysis	^{13}C n.m.r.
NaAMB-5[b]	5	5.3	4.9
NaAMB-25[b]	25	22	21
NaAMB-40[b]	30	34	32
NaAMB-75[c]	75	64	62
NaAMPS-5[b]	5	4.7	3
NaAMPS-10[b]	10	9.2	8
NaAMPS-15[b]	15	13	14
NaAMPS-20[b]	20	18	17
DAAM-20[b]	20	20	20
DAAM-25[b]	25	26	26
DAAM-35[b]	35	35	35
IPAM-40[d]	40	41	41
IPAM-55[d]	55	56	53
IPAM-70[d]	70	72	68
IPAM-85[d]	86	85	82
ATAS-50[e]	50	50	48

[a] Two second recycle time, approximate error ±4%
[b] Ref. 13
[c] Ref. 14
[d] Ref. 15
[e] Ref. 16

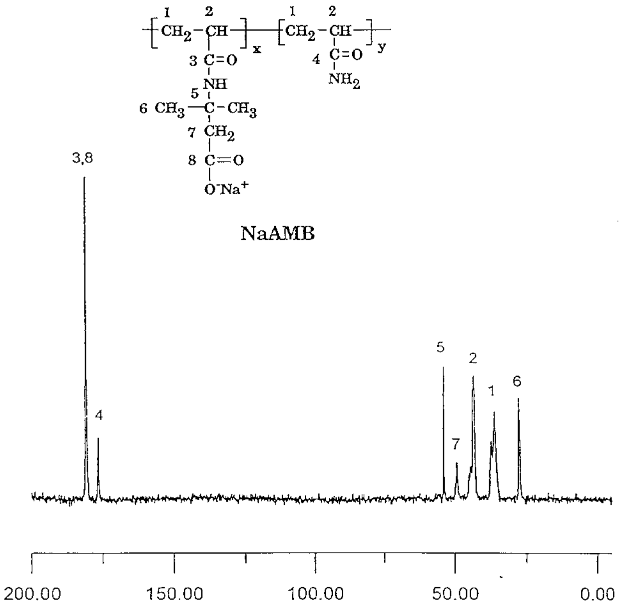

Figure 1 D.p.m.a.s. spectrum of NaAMB-25. Assignment of the spectrum is shown along with the structure of the polymer

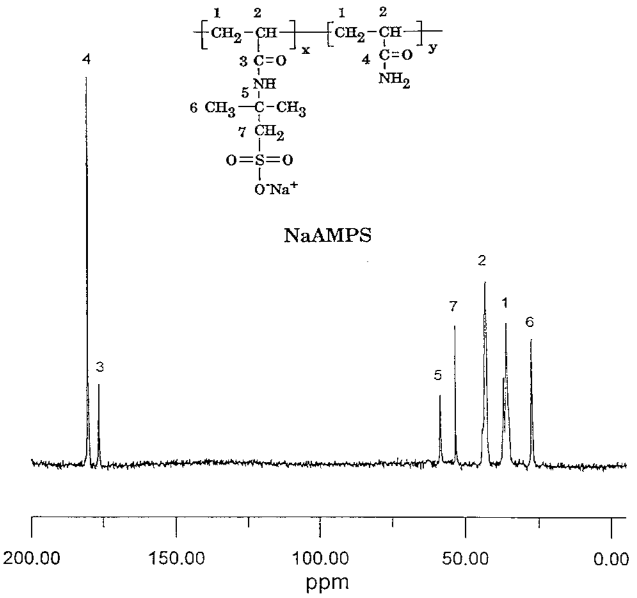

Figure 2 D.p.m.a.s. spectrum of NaAMPS-20. Assignment of the spectrum is shown along with the structure of the polymer

based water-soluble copolymers routinely synthesized in our laboratory. NaAMPS and NaAMB are sulfonate- and carboxylate-containing polyelectrolytes, respectively. The DAAM and IPAM series represent a class of hydrophobically associating copolymers, and ATAS is a polyampholyte.

In *Figure 1*, the d.p.m.a.s. spectrum is shown for NaAMB-25. The feed ratio in the polymerization was 25 mol% of the NaAMB monomer. The peak labelled 3, 8 is due to the acrylamido and carboxylate functionalities in NaAMB and peak 4 is due to the acrylamide carbonyl moiety. The backbone methine (2) and methylene (1) peaks are broadened due to their hindered motion. The side-chain peaks (5, 6 and 7) are considerably sharper due to less restricted motion. The copolymer characterization is obtained by integration of the peaks at 176 ppm (acrylamide) and 180 ppm (NaAMB). However, the acrylamido peak and the carboxylate peak from the NaAMB moiety overlap. This problem is circumvented by integration of the peak area at 53 ppm (the quaternary carbon) and subtraction from the peak area at 180 ppm. The copolymer ratio is therefore the ratio of the peak area at 176 ppm to the corrected area at 180 ppm. The technique yields a value of 21 mol% NaAMB in the polymer compared with 22 mol% from the elemental analysis data. In *Table 1*, d.p.m.a.s. and elemental analysis data are presented for NaAMB copolymers with 5 to 75 mol% compositions.

In *Figure 2*, a representative spectrum of a copolymer from the NaAMPS copolymer series is shown. The feed ratio employed in this polymerization was 20 mol% NaAMPS. Assignment of the spectrum is similar to that

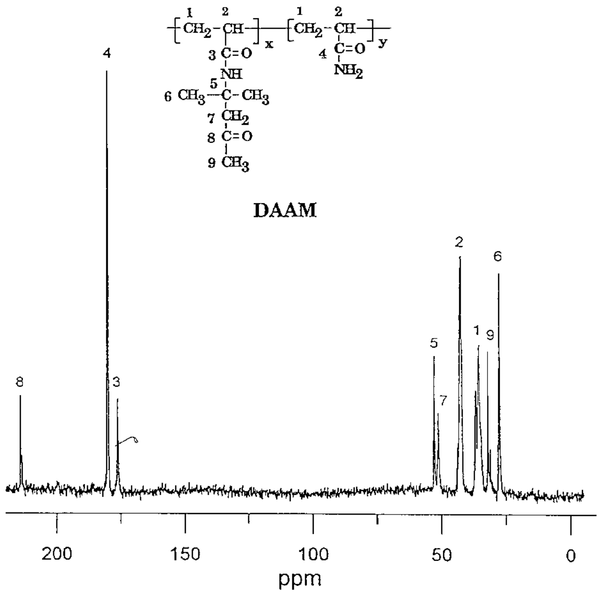

Figure 3 D.p.m.a.s. spectrum of DAAM-20. Assignment of the spectrum is shown along with the structure of the polymer

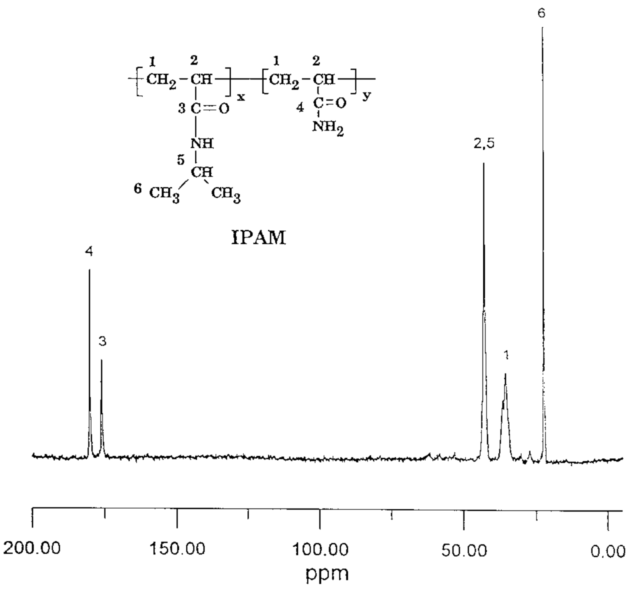

Figure 4 D.p.m.a.s. spectrum of IPAM-40. Assignment of the spectrum is shown along with the structure of the polymer

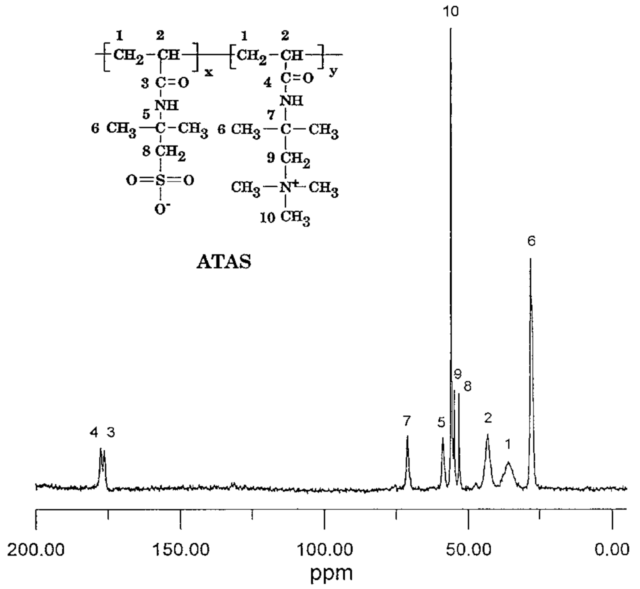

Figure 5 D.p.m.a.s. spectrum of ATAS-50. Assignment of the spectrum is shown along with the structure of the polymer

for NaAMB with the exception of the carboxylate peak. The composition is the ratio of the peak area at 176 ppm to the combined areas of the peaks at 176 and 180 ppm. The agreement between the elemental analysis data and n.m.r. is good (see *Table 1*).

Similar methods for determination of the copolymer composition by ^{13}C n.m.r. are employed for the DAAM series of copolymers (DAAM-20 is shown in *Figure 3*). The DAAM copolymers range from 20 to 35 mol% DAAM comonomer in the feed. The composition of the DAAM comonomer in the final copolymer may be found by utilizing the carbonyl peaks at either 220 or 176 ppm. Similar results are found for the IPAM copolymer series (IPAM-40 is shown in *Figure 4*), and the ATAS (*Figure 5*) copolymer. For ATAS-50, although the carbonyl peaks are not completely resolved, the integration yields excellent results. Data presented in *Table 1* illustrate the excellent agreement in compositions from elemental analysis and d.p.m.a.s. n.m.r. measurements.

CONCLUSIONS

The data presented and the comparisons made in this study demonstrate the utility of the d.p.m.a.s. ^{13}C n.m.r. technique for the purpose of determining copolymer compositions of solvent-swollen, high-molecular-weight acrylamide copolymers. The samples can generally be prepared in 24–48 h and require considerably less sample than do solution methods. The technique is faster than the solution method and often yields spectra with resolution similar to that obtained from solution ^{13}C n.m.r. techniques. The method is shown to be useful for several high-molecular-weight acrylamide-based copolymers and should be applicable to a wide variety of polymers.

ACKNOWLEDGEMENTS

Research support from the Office of Naval Research, DARPA and the Department of Energy is gratefully acknowledged.

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