Effect of crosslinking on the ^{13}C nuclear magnetic resonance spectra of superabsorbent poly(sodium acrylates)

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The application of ^{13}C nuclear magnetic resonance to the study of crosslinking in poly(sodium acrylates) has been investigated. Solid samples have been examined using the cross-polarization/magic-angle spinning technique. Additional resonances associated with the cross-linking moiety have been identified. Solvent-swollen samples have been examined using a high-resolution instrument. The linewidths of some of the resonances increase sharply with the degree of crosslinking. It is suggested that this increase in linewidth may provide a convenient empirical measure of the extent of the crosslinking.

(Keywords: ^{13}C nuclear magnetic resonance; superabsorbent; crosslinking; poly(sodium acrylates))

INTRODUCTION

Crosslinked poly(sodium acrylates) (PSA) are commercially important superabsorbent polymers[1]. They have penetrated a significant part of the health-care product market[2] and are candidates for a wide range of other applications; for example, in packaging, public works, forestry and gardening. Their potential large-scale uses for the drying of organic solvents, for moisture retention in agriculture and as water-sealing agents in the construction industry have also been investigated.

In the above applications, the degree of crosslinking plays an important role because it affects profoundly the water absorbency of the polymer[3]. To the present ^{13}C n.m.r. studies of crosslinked PSA have not been reported, although there has been considerable n.m.r. work on the corresponding linear polymer[4-8] and related water-soluble polymers such as poly(acrylic acid)[5,6,9,10] and polyacrylamide[5-8,11-17].

Recently, a combination of cross-polarization (CP) and magic-angle spinning (MAS)[18,19] with high-power proton decoupling has provided a great deal of ^{13}C n.m.r. information about various solid crosslinked polymers such as epoxy[20] and phenolic[21,22] resins as well as polyimides[23]. ^{13}C n.m.r. spectra can be obtained on high-resolution instruments without recourse to the CP/MAS technique by using crosslinked polymers that have been highly swollen in good solvents[24-27]. This technique has the advantage that the measurements are made on samples in the same physical state in which the superabsorbent polymers are utilized.

In the present paper, we report the ^{13}C n.m.r. spectra of a series of divinyl-crosslinked poly(sodium acrylates) with various degrees of crosslinking. Measurements on dry polymers as well as on samples in the hydrogel state are reported. These spectra show systematic changes with crosslinking monomer content, which provide a method for estimating the concentration of divinyl crosslinks in these materials.

EXPERIMENTAL

Poly(sodium acrylate) samples

N,N'-Methylenebisacrylamide (MBAM) was used as a crosslinking monomer because of its industrial importance. This monomer has the structure $(CH_2{=}CH.CO.NH)_2CH_2$. The synthesis of the crosslinked PSA samples was based on a method reported previously[28]. Deionized, distilled water and chemicals of high purity were used. Each mixture of freshly distilled acrylic acid and MBAM was fully neutralized with aqueous sodium hydroxide solution and subjected to a freeze–thaw procedure to remove trace oxygen. Polymers were prepared in aqueous solution at 60°C in a Pyrex glass ampoule by using potassium persulphate as initiator. The initial concentrations of sodium acrylate and potassium persulphate were $4.7\,\mathrm{mol\,l^{-1}}$ and $0.5\,\mathrm{mmol\,l^{-1}}$, respectively. A reaction time of 24 h was allowed for each polymerization to ensure at least 99% conversion. All of the samples were precipitated in an equimolar solution of acetone and methanol, washed thoroughly with distilled water, precipitated again and dried under vacuum at 40°C. Each crosslinked polymer underwent Soxhlet extraction with water for 24 h and was dried again under vacuum. All of these extractions yielded sol fractions below 0.2 wt%.

For the sake of comparison, a linear PSA was also synthesized in the above manner. A series of four solutions of this polymer were prepared in water. From viscosity measurements on these solutions and by using Mark–Houwink constants obtained previously[28], we estimated a molecular weight of 1 475 000.

^{13}C nuclear magnetic resonance spectroscopy

The spectra of the crosslinked polymers were recorded in the dry condition by using CP/MAS and in the gel state under normal high-resolution conditions. Gel samples were prepared by slowly adding 5 ml D_2O to 0.5 g dry

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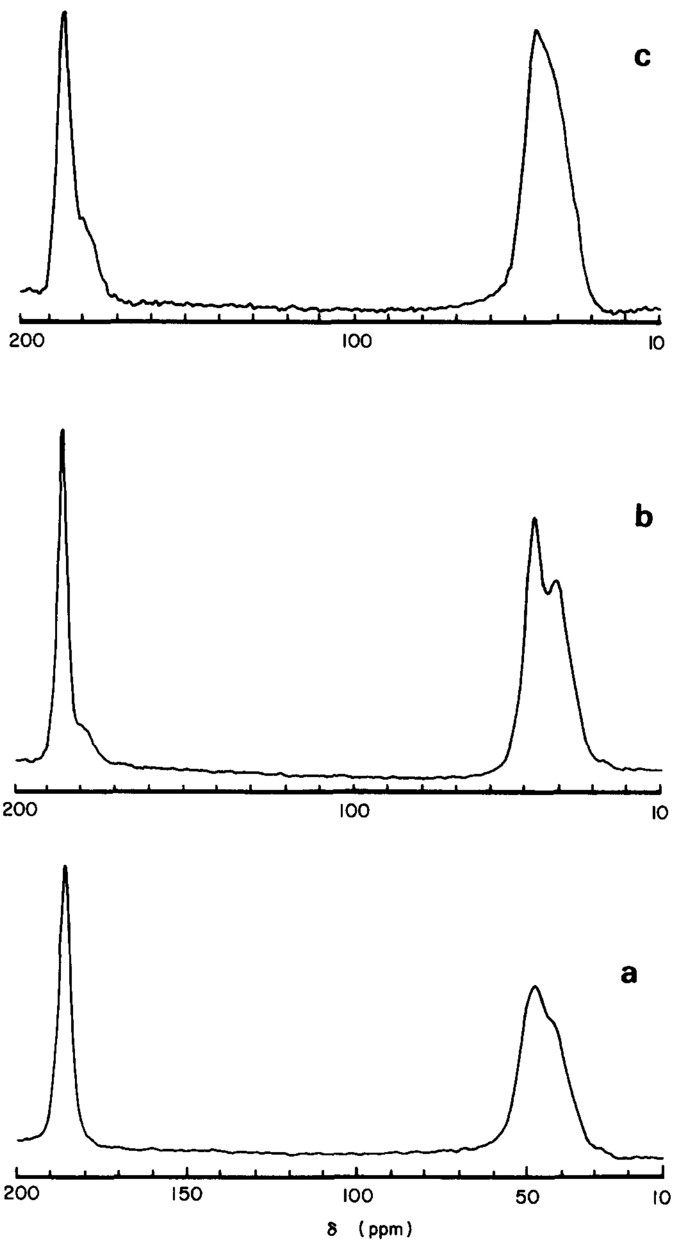

Figure 1 CP/MAS ^{13}C n.m.r. spectra of (a) linear poly(sodium acrylate) and of two crosslinked poly(sodium acrylate) samples containing (b) 0.0494 and (c) 0.1348 mole fraction crosslinking monomer (*N,N'*-methylenebisacrylamide). Each sample was measured as a dry powder

polymer powder while the mixture was stirred magnetically. The gels were measured about 24 h after preparation to allow time to attain complete swelling. The linear PSA sample was measured as a dry powder by using CP/MAS and in 9.96 wt% solution in D_2O.

The CP/MAS spectra were obtained at 25.14 MHz and ambient temperature on a Bruker MSL 100 spectrometer operating at 2.349 T with high-power proton decoupling. The samples were spun at about 4.0 kHz in a dual-bearing magic-angle spinning probe. The optimum conditions for data collection of CP/MAS spectra for quantitative purposes were found to be 1 ms contact time and 1 s delay between pulse sequences, and all the data were collected using these parameters. The ^{13}C and ^{1}H 90° pulses were 4 ms. An acquisition time of 72.7 ms was employed. Resolution enhancement was achieved with the 'Gaussian multiplication' feature included in the Bruker MSL software. Each CP/MAS spectrum contained 8000 data points over a 7042 Hz frequency range with 40 000 to 60 000 acquisitions.

Gel- and solution-state ^{13}C spectra were recorded at 62.89 MHz and ambient temperature on a Bruker WM 250 spectrometer operating at 5.87 T in the pulsed Fourier transform mode with broad-band proton decoupling. The ^{2}H resonance of the diluent was employed for frequency lock. Sample spinning rates were about 20 Hz. Sample height was at least 40 mm. The ^{13}C pulsewidth and acquisition time were 7 ms (20° pulse) and 0.442 s, respectively. Each gel- or solution-state spectrum contained 16 000 data points over a frequency range of 18 518 Hz with 120 000 to 160 000 acquisitions.

All of the ^{13}C chemical shifts are reported relative to tetramethylsilane (TMS). Spin–lattice relaxation times were determined for a representative crosslinked PSA gel and for a comparable linear PSA solution by the inversion recovery method[29].

RESULTS AND DISCUSSION

Cross-polarization/magic-angle spinning spectra

The solid-state ^{13}C n.m.r. spectra of two crosslinked poly(sodium acrylates) are shown in *Figure 1*, together with the solid-state spectrum of a linear PSA synthesized under the same conditions. The corresponding assignments are summarized in *Table 1*. The carboxylate, methine and methylene resonances occur at about the same chemical shifts in all three spectra. These peaks have been assigned on the basis of recent solution ^{13}C n.m.r. work involving PSA[5,6] and poly(ammonium acrylate)[16]. Despite the CP/MAS technique employed, the methine and methylene peaks tend to overlap and could not be resolved completely. A similar limitation was reported for the overlapping backbone ^{13}C peaks of linear poly(acrylic acid) in a recent solid-state study[10]. In addition, a weak, somewhat broad, peak appears in the spectra of the crosslinked polymers shown in *Figures 1b* and *1c*. This peak is absent from the spectrum of linear PSA (*Figure 1a*). Although it overlaps with the stronger carboxylate peak, its intensity clearly increases as the crosslinking monomer content increases. Furthermore,

Table 1 ^{13}C chemical shifts (relative to TMS) for crosslinked and linear poly(sodium acrylates) in solid state and in D_2O

	Chemical shift (ppm)			
Sample	$-CO_2^-$	$-C(O)NH-$	$-CH-$	$-CH_2-$
Linear PSA, solid state[a]	185	[e]	46	37
Crosslinked PSA, solid state[a]	185	180	46	37
Crosslinking monomer[b]	[e]	175, 168[f]	[e]	41
Linear PSA, solution[c]	184.5	[e]	[g]	[h]
Crosslinked PSA, gel[d]	185	[i]	46	37

[a] Recorded on dry samples by using CP/MAS and high-power proton decoupling

[b] *N,N'*-Methylenebisacrylamide, CP/MAS, olefinic carbon peaks appear at 135, 132 and 130 ppm

[c] 9.96 wt% in D_2O, broad-band proton decoupling

[d] 0.5 g polymer and 5 ml D_2O, broad-band proton decoupling

[e] Absent

[f] Doublet of approximately equal peak intensities

[g] 48.8(*rr*), 46.6(*mr*), 45.8(*mr*), 44.7(*mm*)

[h] 38.5, 36.4, 35.5

[i] Could not be resolved from CO_2^- peak

Table 2 Solid-state intensities and hydrogel linewidths of crosslinked poly(sodium acrylates)

Mole fraction crosslinking monomer[a]	Relative intensity at 180 ppm (CP/MAS)[b]	Linewidth (Hz) for hydrogels[c]	
		$-CH-$	$-CH_2-$
0[d]	0	10.55[e,f]	17.71[g,h]
0.0071	[i]	78.96	143.85
0.0191	[i]	181.39	261.58
0.0290	[i]	178.26	229.98
0.0311	[i]	176.87	283.34
0.0339	[i]	195.40	280.73
0.0391	[i]	196.36	290.05
0.0494	0.1001	207.52[j]	304.46[k]
0.0599	0.1182	[i]	[i]
0.0762	0.1416	236.24	358.97
0.1046	0.1922	239.31	365.10
0.1348	0.2662	233.48	362.65

[a] *N*,*N'*-Methylenebisacrylamide
[b] Area of the 180 ppm peak divided by the sum of the areas of this peak and of the 185 ppm peak
[c] Measured on gels containing 0.5 g polymer and 5 ml D_2O
[d] Linear poly(sodium acrylate)
[e] Measured at 44.7 ppm for 9.96 wt% solution in D_2O
[f] $T_1 = 174 \pm 28$ ms
[g] Measured at 38.5 ppm for 9.96 wt% solution in D_2O
[h] $T_1 = 51 \pm 12$ ms
[i] This peak could not be resolved
[j] $T_1 = 179 \pm 16$ ms
[k] $T_1 = 96 \pm 9$ ms

its position falls within the range common to amides of carboxylic acids[31] and nearly coincides with the chemical shift reported for the carbonyl carbon in polyacrylamide[15-17]. For comparison with the above results, the solid-state ^{13}C spectrum of the crosslinking monomer (MBAM) was also recorded, and the chemical shifts are reported in *Table 1*. It displays two peaks in the carbonyl region, to high field of 180 ppm, namely at 175 and 167 ppm. The peak at 180 ppm in the spectra of crosslinked poly(sodium acrylates), therefore, cannot be attributed to unreacted crosslinking monomer. The change in chemical shift relative to the monomer is, however, consistent with the change of the neighbouring unsaturated carbons to alkyl carbons. Such a change is generally assumed to occur during vinyl–divinyl copolymerization[32-34]. Thus, because of its chemical shift and its absence from the spectra of linear PSA and from the crosslinking monomer, we have attributed the 180 ppm peak to the carbonyl carbons of the MBAM units in the crosslinked polymer.

If our assignments in the carbonyl region are correct, the intensity of the 180 ppm peak provides a measure of the number of crosslinking MBAM repeat units. It would be reasonable to compare the intensity of this peak to that of the other copolymer carbonyl peak at 185 ppm if they have approximately the same NOE (nuclear Overhauser effect) factors. This supposition is supported by the observation that analogous peaks in polyacrylamide[5] have similar NOE values. Accordingly, the relative intensity of the 180 ppm peak was determined by dividing its area by the sum of both (180 and 185 ppm) carbonyl peak areas.

These intensities are presented in *Table 2* and are plotted against the mole fraction of the crosslinking monomer in *Figure 2*. This mole fraction (x) corresponds to that of the reaction mixture. It is not expected to differ largely from the MBAM repeat-unit mole fraction of the crosslinked and extracted poly(sodium acrylates) because at least 99% conversion was attained and all of the sol fractions were extremely low. In turn, we have designated the final mole fraction of MBAM repeat units as (ax), while anticipating the proportionality factor (a) to be close to one. Since each MBAM repeat unit contains two carbonyl groups, the intensities of the 180 and 185 ppm peaks may be assumed to be proportional to $2ax$ and $(1-ax)$, respectively. This assumption yields a simple approximate relationship between crosslinking monomer content and the relative intensity of the 180 ppm peak:

$$r = 2ax/(1+ax) \tag{1}$$

This relationship is compared to ^{13}C intensity data in *Figure 2*. Least-squares analysis of these data supports this model. This analysis also results in a proportionality factor close to one ($a = 1.069$), which confirms that the MBAM comonomer content of each crosslinked poly(sodium acrylate) sample is nearly equal to that of the respective reaction mixture.

Hydrogel and solution spectra

The CP/MAS approach is somewhat limited in the present case by the overlap of the two carbonyl peaks (*Figures 1b* and *1c*), which restricts its application to samples with a fairly high degree of crosslinking. To complement the CP/MAS results, we have also measured

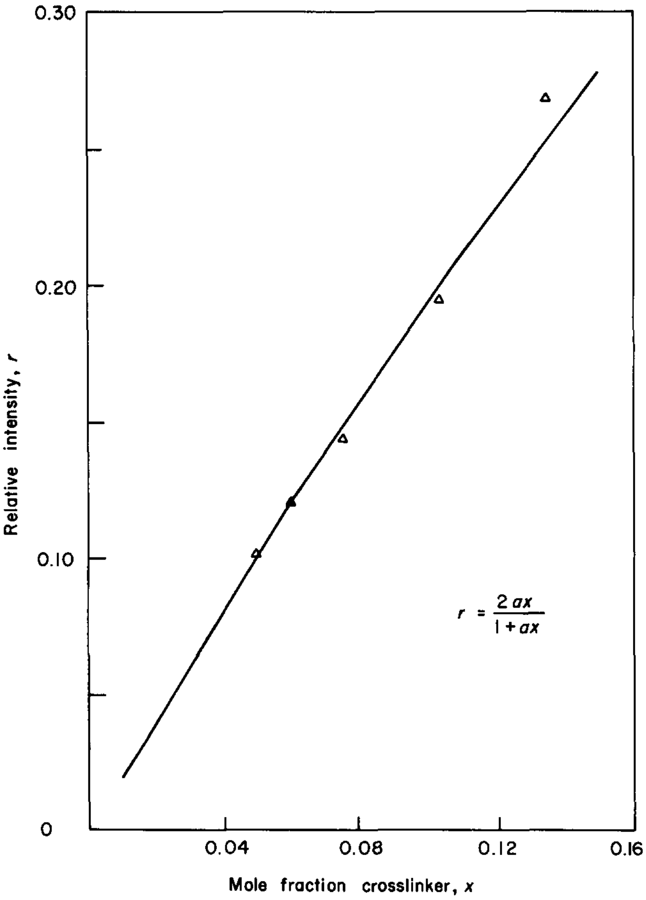

Figure 2 Relative intensity of the CP/MAS ^{13}C n.m.r. peak at 180 ppm (r) plotted as a function of the mole fraction of crosslinking monomer (x). The curve was calculated by least-squares analysis of the data shown using equation (1). This analysis yielded 1.069 as the best-fit value of parameter a

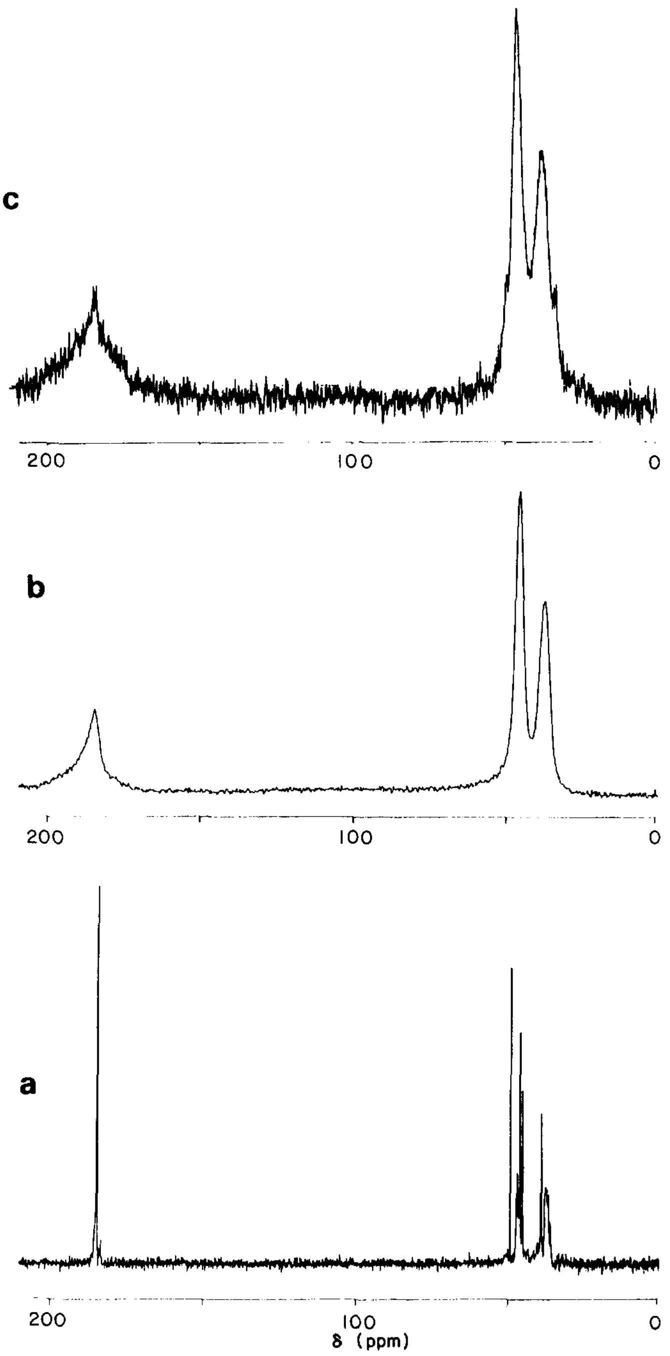

Figure 3 ^{13}C n.m.r. spectra of (a) a D_2O solution of linear poly(sodium acrylate) and of two crosslinked poly(sodium acrylate) samples swollen in D_2O, the latter containing (b) 0.0494 and (c) 0.1348 mole fraction crosslinking monomer in the dry condition

the same superabsorbent polymers as highly swollen hydrogels. The ^{13}C n.m.r. spectra of two of these hydrogels are presented in *Figure 3* together with the solution spectrum of a linear PSA synthesized in the same way. Assignments for these spectra are proposed in *Table 1* on the basis of recent work on the linear polymer[5-7]. As reported, the carbonyl region of linear PSA appears to be relatively insensitive to tacticity. In contrast, the methine and methylene resonances tend to split according to odd and even monomer sequence lengths, respectively[35]. This splitting was discussed in terms of triad resolution for the methine region by Truong *et al.*[6] Their spectra and assignments agree with ours, with the exception of a methine peak at 48.8 ppm, which was not reported by them. Nevertheless, Truong *et al.*[6] predicted a methine peak to appear somewhat downfield from 47 ppm, which would correspond to a syndiotactic triad sequence (*rr*). This sequence may be attributed to the 48.8 ppm peak in our linear PSA spectrum (*Figure 3a*). This assignment seems plausible partly because it matches the above prediction and partly because it also fits the sequence distribution pattern for the polyacrylamide methine region by Lancaster and O'Connor[14], namely, that the lowest- and highest-field peaks correspond to syndiotactic and isotactic sequences, respectively, at the triad level. In the same manner and in accord with Truong *et al.*[6], we have attributed the highest-field methine peak to an isotactic sequence and the central two, somewhat overlapping, methine peaks to heterotactic sequences. (The absence of the 48.8 ppm peak from a previous PSA spectrum[6] probably stems from the somewhat different synthetic approach taken in that study.)

Comparison of *Figures 1b* and *1c* with *Figures 3b* and *3c* reveals good agreement between CP/MAS and hydrogel spectra apart from the relatively weak CP/MAS peak at 180 ppm. In the gel measurements, this peak could not be resolved from the very broad CO_2^- peak centred around 185 ppm. If, in *Figure 3*, spectra *3b* and *3c* are compared to spectrum *3a*, the strong line broadening in the spectra of crosslinked PSA becomes obvious. Furthermore, the linewidths appear to increase with increasing crosslink density (i.e. from *3b* to *3c*). A similar effect was reported for crosslinked polystyrene gels that contained chloroform as diluent[26,27].

We have investigated the possibility that the line broadening described above might act as an empirical measure of the extent of crosslinking. For this purpose, the ^{13}C n.m.r. spectra of a series of MBAM-crosslinked PSA hydrogels were measured. Since the linewidths of some other gel spectra had been found to depend on diluent concentration[24], we have maintained a constant D_2O content in our hydrogel samples. The methine and methylene linewidths of these swollen polymers are listed in *Table 2* and are plotted against crosslinking monomer content in *Figure 4*. The extent of methine peak broadening remains considerably below that of the methylene peak broadening in the entire composition range examined. Both of these peaks reveal the same trend, namely, that they broaden sharply up to about 0.02 mole fraction crosslinking monomer but, above this limit, both linewidths tend to level off until they reach a maximum at about 0.08 mole fraction crosslinking monomer content.

The origin of this line broadening is not unambiguous. It may be due in part to an increasing diversity of environments, and hence of chemical shifts, with increasing crosslinking. Alternatively, more restricted mobility in the crosslinked polymer may result in shorter relaxation times and hence broader lines. It is also possible that the broadening is greater for some carbons than for others (depending on their position in the chain relative to the crosslinks) and that the apparent limiting linewidth reflects the inability to measure a very broad component at high crosslinking. We would suggest, though, that measurement of the linewidth could provide an empirical measure of the extent of crosslinking at low crosslinking. Thus the gel measurements complement the CP/MAS measurements to the extent that the latter only

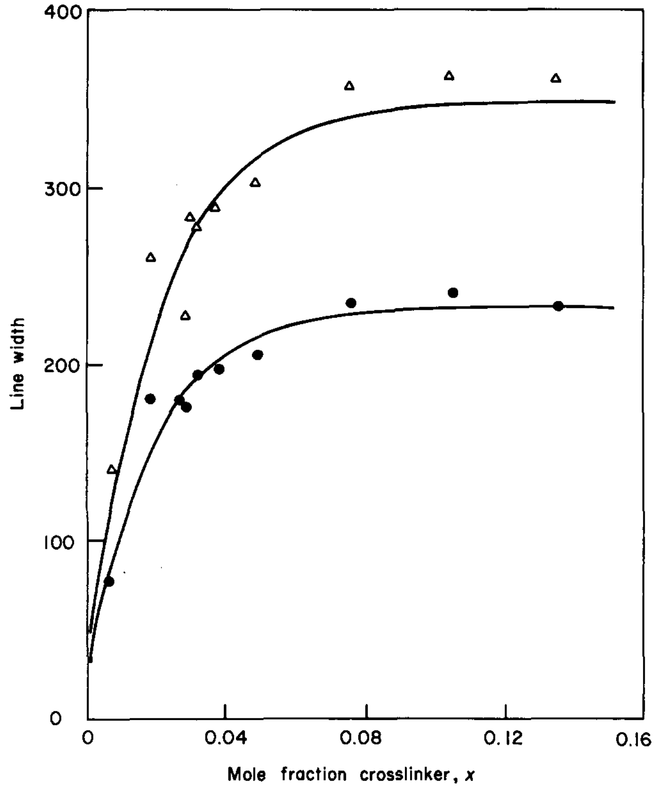

Figure 4 Linewidths (Hz) of the CH (●) and CH_2 (△) ^{13}C resonances (*w*) of crosslinked poly(sodium acrylate) samples swollen in D_2O *versus* the mole fraction of crosslinking monomer (*x*)

provide useful information on the extent of crosslinking at high crosslinking. Data shown in *Table 2* indicate that there is relatively little change of T_1 with crosslinking. There have been varied reports on this topic in the literature[36–44]. This observation would favour a chemical shift explanation for the line broadening.

CONCLUSIONS

The present study indicates that ^{13}C n.m.r. spectroscopy can provide useful information about crosslinked polymers. By using CP/MAS on dry, solid PSA-based superabsorbent polymers, the chemical nature of the crosslinks has been confirmed and a definite relationship has been obtained between the degree of crosslinking and the relative intensity of the 180 ppm peak in the spectra of these polymers. The degree of crosslinking also shows some correlation with the halfwidths of both backbone carbon peaks in the spectra of highly swollen hydrogels of the same polymers. This correlation may be suitable for estimating the crosslink density of industrial PSA samples in a rapid fashion. Preliminary results from this laboratory suggest that the ^{13}C spectra of methyl methacrylate–ethyleneglycol dimethacrylate copolymers follow a similar trend. A CP/MAS peak at 64 ppm in the spectra of these copolymers is absent from the spectra of poly(methyl methacrylate) and seems to be characteristic of the $-CH_2-CH_2-$ bridge in crosslinking ethyleneglycol dimethacrylate repeat units. Furthermore, the backbone carbon peaks in the spectra of chloroform-swollen copolymer gels broaden strongly as the crosslinking monomer content increases.

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