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Line Broadening in the Carbon-13 NMR Spectra of Cross-Linked Polymers

A. D. Bain, D. R. Eaton,* A. E. Hamielec, M. Mlekuz, and B. G. Sayer

Department of Chemistry and Institute for Polymer Production Technology, McMaster University, Hamilton, Ontario, L8S 4M1, Canada.

Received July 25, 1988; Revised Manuscript Received February 15, 1989

ABSTRACT: The ^{13}C NMR spectra of cross-linked poly(sodium acrylate) in a swollen gel have been examined. As has been reported by other investigators, the line widths of the resonances increase with the degree of cross-linking. The origin of the broadening has been examined in some detail. Spectra have been obtained at six different field strengths, and a number of relaxation and "hole burning" experiments have been performed. All of the results are consistent with the proposition that the increased width is due to unresolved chemical shift structure arising from the presence of the cross-links rather than from shorter relaxation times associated with decreased polymer mobility.

Introduction

NMR has become one of the more versatile techniques for investigating polymer structure. High-resolution NMR has revealed many details regarding the microstructure of polymer molecules. The advent of two-dimensional methods promises further applications.[1] There are however some limitations particularly in the case of cross-linked polymers. These arise from the low solubility of such compounds. To some extent, that has been overcome by the use of the CPMAS (cross-polarization/magic angle spinning) technique for obtaining well-resolved spectra of solid samples.[2] However, the resolution obtained is still less than that normal for solution spectra and the finer structural details such as information on tacticity are usually lost. An alternative, which is available at relatively low levels of cross-linking, is to obtain the NMR spectra of solvent-swollen samples on a high-resolution instrument. The spectra obtained are usually significantly broader than solution spectra but can provide valuable information.[3-7] We have previously used the line widths in such spectra to provide an empirical measure of the degree of cross-linking.[8]

The origin of the line broadening of cross-linked polymers compared to their straight-chain analogues is not unambiguously known. Two different causes have been suggested. One possibility is that the cross-linking reduces the mobility of the polymer, leading to longer correlation times and hence shorter relaxation times and broader lines. A recent study by Errede et al.[9] on the swelling of styrene/divinyl benzene cross-linked polymers in chloroform reported that the line broadening increased exponentially with cross-linking and concluded that the increase was caused by a relaxation effect. Chemical shift anisotropy relaxation was suggested as the most likely mechanism. The alternative explanation is that the increased line width arises from unresolved structure due to the greater multiplicity of chemical environments introduced by the cross-linking. Mohanraj and Ford[10] studied cross-linking in poly[(chloromethyl)styrene]/divinyl benzene and favored this explanation on the basis that the apparent line width increased by approximately a factor of 3 on changing the resonance frequency from 25 to 75 MHz. If the origin of the broadening is chemical shift dispersion, the widths should be proportional to frequency whereas relaxation due to chemical shift anisotropy increases with the square of the frequency. There is, of course, no reason why there should be a single cause of the line broadening, and Mohanraj and Ford do indeed suggest that dipolar coupling effects become significant at high cross-linking ratios.

It is of some interest and of practical value to establish the nature of this broadening. If it originates in a relaxation effect due to changes in polymer mobility, it might be anticipated that similar results would be obtained for a wide range of cross-linked polymers and that a general empirical correlation with the degree of cross-linking might be established. If, on the other hand, the origin lies in chemical shift effects, these are likely to be different for each different polymer, and no general correlation would be anticipated. In the present paper the question of the origin of the line broadening observed in gels containing cross-linked polymers has been investigated.

Experimental Section

Cross-linked sodium acrylate polymers were prepared as described previously.[8] *N,N'*-Methylenebis(acrylamide) was used as the cross-linking monomer. The details of the preparation of these polymer samples will be described elsewhere.[13]

Gel samples were prepared directly in 10-mm NMR tubes. The spectra of the gels were recorded 24 h after preparation to allow time for complete swelling. A constant concentration of 10% polymer by weight with D_2O or H_2O was used for all the poly(sodium acrylate) spectra discussed in the present paper. The use of D_2O rather than H_2O has no observable effect on the spectra. A number of samples were also run at 2, 4, 6, and 8 wt

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* Author to whom correspondence should be addressed.

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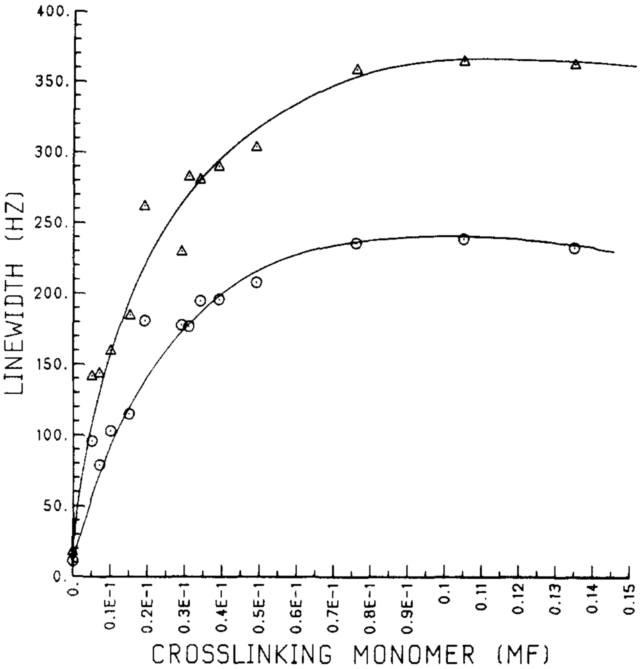

Figure 1. Variation of CH (circles) and CH_2 (triangles) line widths with mole fraction of cross-linking monomer.

%. There is a small decrease in line width at lower concentrations. The higher concentration was adopted to minimize data acquisition time. Each sample was prepared in duplicate and run two or three times to ensure that the line widths were reproducible. Differences between duplicate runs were always less than 10%.

The ^{13}C NMR spectra were recorded under normal high-resolution conditions using a 90° pulse of 35 μs on a Bruker WM250 instrument operating at 62.8 MHz for ^{13}C NMR. Since the T_1's were found to be around 100–200 ms, a delay of 1 s (more than $5 \times T_1$) was allowed between each 90° pulse during data acquisition. A total acquisition time of approximately 1 h was needed to obtain acceptable spectra.

For the variable-field study the samples were also examined on Bruker AM500, AM400, AM300, AC200, and WP80 spectrometers operating at 125.72, 100.58, 75.43, 50.29, and 20.12 MHz, respectively. Spin–lattice relaxation times (T_1) for the CH and CH_2 resonances were determined at 5, 30, and 70 °C on both the WM250 and AM500 spectrometers using the standard inversion recovery method.[11] Spin–spin relaxation times (T_2) for the CH and CH_2 resonances were obtained at 30 °C on the WM250 spectrometer using the Carr–Pucell–Meiboom–Gill (CPMG) pulse sequence.[11] The "hole burning" experiment was carried out on the WM250 instrument at 30 °C, employing a modified DANTE pulse sequence.[12] Presaturation was achieved using 150 3° pulses at 1 ms intervals prior to spectral acquisition.

All of these relaxation experiments and field-dependence studies were performed on cross-linked poly(sodium acrylate) samples containing the same mole fraction (0.01) of cross-linking monomer.

Results

Our earlier studies in this area involved aqueous gels of poly(sodium acrylate) cross-linked with *N*,*N*′-methylenebis(acrylamide). It was observed that both the methine and methylene peaks showed substantial broadening with increasing cross-linking. In both cases the line widths increased rapidly up to about 0.02 mole fraction of cross-linking monomer and then more slowly to reach a maximum at about 0.08 mole fraction of cross-linking monomer. A maximum width of approximately 20 times the original width was observed. Plots of line width versus mole fraction of cross-linking agent were smooth and reproducible.

Experiments to determine the mechanism of line broadening were carried out on the poly(sodium acrylate) system. Initially some additional data at low levels of cross-linking were obtained, and the errors and accuracy of the experiments were carefully examined. The procedures adopted are described in the Experimental Section. The results confirmed those previously reported, and a plot of line width versus percentage of cross-linking monomer is shown in Figure 1. Spectra illustrating the broadening effect are shown in Figure 2.

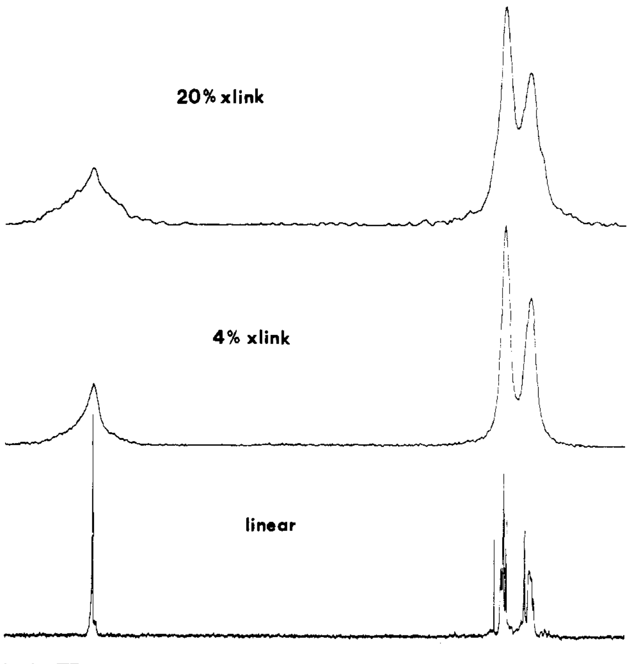

Figure 2. ^{13}C NMR spectra of linear poly(sodium acrylate) in D_2O solution of cross-linked poly(sodium acrylate) swollen with D_2O.

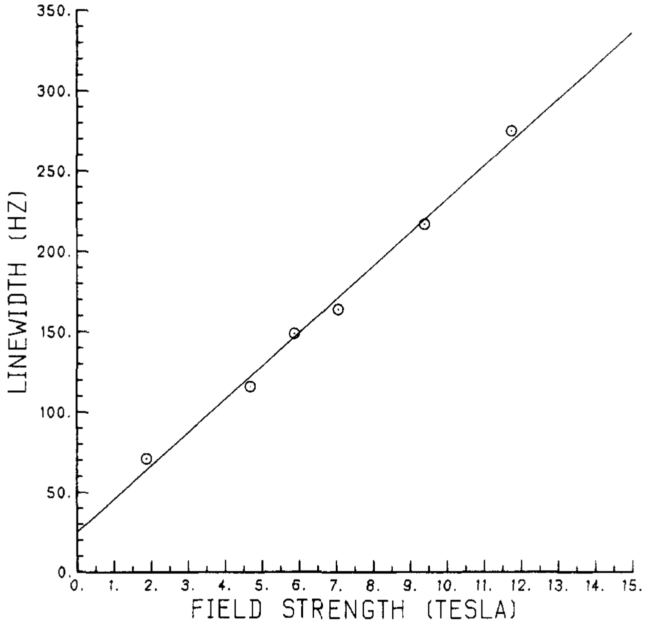

Figure 3. Variation of CH_2 line width with spectrometer field strength.

A number of different experiments have been carried out to investigate the source of this broadening. As indicated above it could be either a relaxation or a chemical dispersion effect. The latter should be linearly dependent on field. Figure 3 shows a plot of line width versus field strength for six different NMR frequencies. It is clear that the major part of the broadening is field dependent. The intercept at zero field is approximately 25 Hz. This rep-

Table I
Relaxation Times of Cross-Linked Poly(sodium acrylate)

field strength, Tesla	temp, °C	T, ms CH	T, ms CH_2
5.87	5	158 T_1	87 T_1
5.87	30	181 T_1	105 T_1
5.87	30	29 T_2	26 T_2
5.87	70	267 T_1	168 T_1
11.74	5	321 T_1	192 T_1
11.74	30	319 T_1	179 T_1
11.74	70	441 T_1	211 T_1

resents the "true" line width and is only slightly larger than the width of the lines in the linear polymer. Thus at low cross-linking it appears that there is very little increase in relaxation due to lower mobility in the cross-linked polymer. This agrees with the conclusion of Mohanraj and Ford[10] from their study of cross-linking in poly[(chloromethyl)styrene] swollen with chloroform. Further evidence on the origin of the line broadening was obtained from relaxation measurements. A number of such measurements were made, and the results are given in Table I.

Finally, hole burning experiments have been performed on both the methine and methylene resonances. The results are illustrated in Figure 4. In these experiments the center of the line is irradiated with a DANTE sequence of weak pulses. In this way saturation of a narrow band of frequencies is achieved. A single powerful pulse would inevitably cover a wider band of frequencies. If the line shape results from homogeneous broadening due to a short relaxation time, the overall intensity of the peak will decrease. If, on the other hand, the line shape is due to a distribution of different structural types causing a range of chemical shifts, a "hole" will appear at the frequency of the saturating field. In the present case the latter explanation is unambiguously demonstrated.

Discussion

The above experimental evidence shows quite clearly that the major cause of the line broadening observed in solvent-swollen cross-linked polymer NMR spectra is chemical shift dispersion. The results do not preclude a contribution from relaxation effects at high cross-linking levels, but such contributions are negligible in the samples examined. If the origin had been physical rather than chemical, i.e., longer correlation times resulting from lower polymer mobility, it would have been reasonable to anticipate approximately the same amount of broadening from chemically different samples. In this case, a rather general relationship between line broadening and degree of cross-linking could have been anticipated and a general empirical relationship between the two perhaps developed. Since the origin is chemical, it is to be anticipated that the effect will be quantitatively quite different for chemically different polymers. This is consistent with some of our preliminary results comparing the sodium acrylate and methyl methacrylate polymers. Qualitatively, a maximum in the broadening with increasing cross-linking is also anticipated. When tacticity considerations are neglected, with no cross-linking all sites will be equivalent. If all the monomer units were cross-linked, again all sites would be equivalent. At intermediate degrees of cross-linking there will be a distribution of monomer units at one, two, and three positions distant from the nearest cross-link and hence of chemical shifts. Thus a maximum in the observed line width is anticipated. However, as the cross-link density increases beyond the range studied here, mobility effects may well become important, and the source of the observed line broadening may be the relaxation effects.

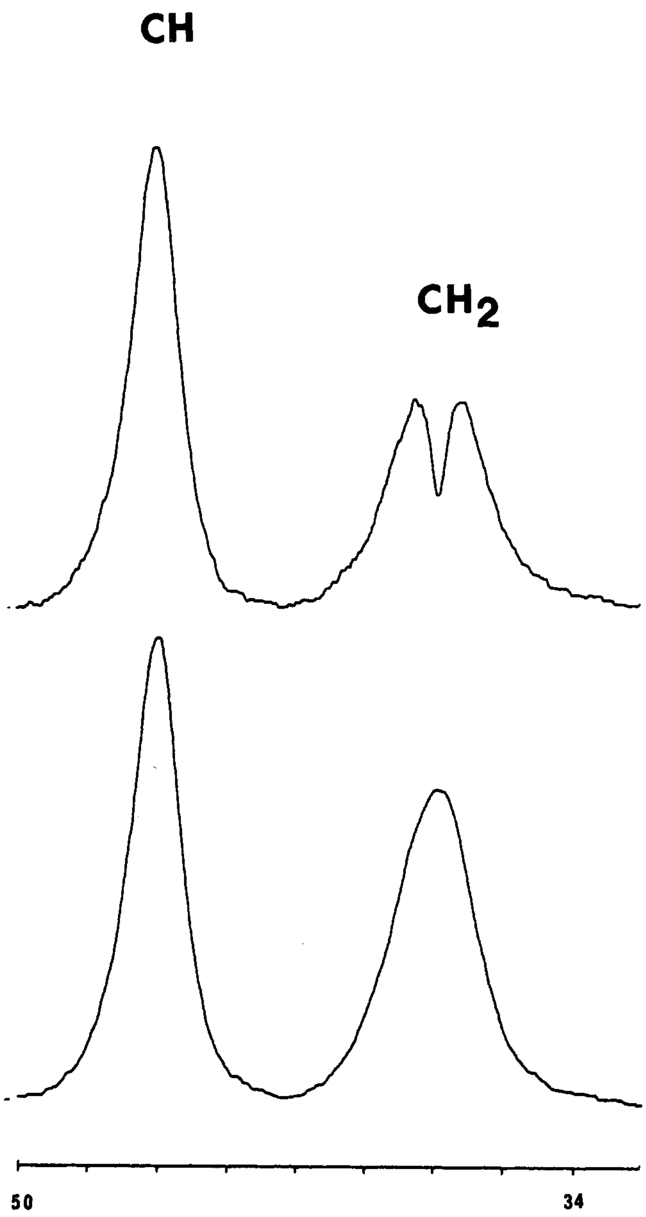

Figure 4. Spectra obtained by "hole burning" experiment. Bottom spectrum is unperturbed; top spectrum has been presaturated.

The detailed interpretation of relaxation measurements in a polymer system is a very complex procedure, since all the parameters are averages over distributions of correlation times, etc. However, the relaxation times reported here do give a qualitative indication of the type of relaxation occurring in this system.

It should first be noted that there is probably a distribution of relaxation times for a given composite resonance, and hence the significance of the values obtained by normal-pulse sequences cannot be used quantitatively. However, qualitative conclusions can be drawn. The fact that T_1 increases with increasing temperature indicates that the spin system is above the T_1 minimum; i.e., the effective correlation time is shorter than the reciprocal of the Larmor frequency. In this case, the value of T_2 should be of the same order as T_1, as shown in Table I. This value of T_2 is consistent with the intercept of the line width vs field plot in Figure 3. However, if the line broadening were homogeneous, i.e., caused by relaxation, T_2 would have to be a few milliseconds. This would not be consistent with the data in Table I. Therefore, the relaxation data support the other evidence that the line broadening is inhomogeneous.

This combination of relaxation studies, the field dependence of the line width, and the hole-burning experiment provides convincing evidence that in cross-linked poly(sodium acrylate) the NMR lines are inhomogeneously broad. The cross-linking creates a distribution at different chemical environments, which is reflected in the distribution of chemical shifts.

Acknowledgment. We are indebted to the Natural Science and Engineering Research council of Canada for financial support of this research and to Bruker Spectrospin (Canada) Ltd. for the use of the AM400, AM300, and AC200 spectrometers located in their Milton (Ontario) laboratories.

Registry No. (Sodium acrylate)(*N,N'*-methylenebis(acrylamide)) (copolymer), 25359-44-8.

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Photophysics of Nominally Alternating Copolymers of 2-Isopropenylnaphthalene and Maleic Acid in Aqueous Solution

John L. Sturtevant and S. E. Webber*

Department of Chemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712.

Received September 20, 1988; Revised Manuscript Received February 21, 1989

ABSTRACT: A copolymer of maleic anhydride (MAn) and 2-isopropenylnaphthalene (2IPN) has been prepared and found to be water soluble over a wide pH range. The copolymer composition has been determined to be dependent upon the monomer feed ratio in a manner suggesting a 1:1 alternating sequence distribution. The fluorescence spectrum exhibits monomer and excimer emissions at high pH and shifts dramatically over the pH range 5-3 to a nearly pure excimer spectrum. At high pH, the excimer emission is ascribed to nearest-neighbor naphthalene-naphthalene diads which are present in small quantities as "defects". Excitation spectra and 77 K fluorescence spectra demonstrate that this static excimer component persists for all pHs, and dynamic excimer component arises upon acidification. This is attributed to the collapse of the coil structure as the acid groups are neutralized. Experiments utilizing an environmentally sensitive optical probe (1,8-anilinonaphthalene sulfonate) supported this picture as did anthracene sensitization and copper(II) quenching studies. It is proposed that electronic energy transport between chromophores is efficient, especially at low pH. Dynamic light scattering studies gave evidence for polymer aggregation at high concentration.

Introduction

Studies on polymer-bound chromophore systems have shown that the details of photoprocesses are highly dependent upon the microenvironments of the chromophores. Of particular interest are aqueous solutions of amphiphilic polyelectrolytes incorporating various levels of hydrophobic aromatic groups.[1-4] For low loadings, intramolecular chromophore interaction is avoided, but as the chromophore content is increased, such interaction becomes significant. The solution behavior of these systems is not fully understood, but possibly they can be viewed as organized assemblies similar to micelles or vesicles.

An interesting class of amphiphilic copolymers is alternating copolymers, which in some cases represent the upper limit of hydrophobic character with continued water solubility. Relatively few photophysical studies have been conducted on these systems, and the results are ambiguous. In 1974, Fox et al. reported no excimer fluorescence for alternating copolymers of 2-vinylnaphthalene and styrene with methyl methacrylate.[5] Mikawa and co-workers[6] likewise found no evidence of excimer formation in *N*-vinylcarbazole alternating copolymers in organic solution. Webber et al. found exclusively monomer emission in an alternating copolymer of methyl methacrylate and 4-vinylbiphenyl in THF.[1b] In 1975, however, Wang and Morawetz[7] reported prominent excimer emission for an alternating acenaphthalene-maleic acid system. In recent studies, excimer fluorescence has been observed for aqueous solutions of alternating copolymers of 2-vinylnaphthalene with methacrylic acid and maleic acid. Very recent results from this laboratory and Morishima et al. indicate that, for these polymers, excimer formation is critically depedent upon the precise monomer sequence distribution.[8] Thus, it is possible that a comparison of different "alternating" copolymers is misleading. It is expected that factors such as hydrophilic spacer group, molecular weight, coil conformation, and sequence defects will all influence the manner in which chromophores communicate via energy migration and/or excimer formation. The present paper focuses on the photophysical behavior of a previously unstudied nominally alternating copolymer of maleic anhydride and 2-isopropenylnaphthalene. This polymer also represents an interesting comparison to 2-vinylnaphthalene maleic acid copolymers because of the additional methyl groups on the α-carbon