High-Resolution Pulsed Carbon-13 Nuclear Magnetic Resonance Analysis of Polyacrylonitrile

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ABSTRACT: Fourier transforms of the noise-decoupled, natural abundance, 22.6-MHz ^{13}C nmr free induction decays of some polyacrylonitriles have been obtained. The spectra are interpreted in terms of the steric configurations of triads and pentads of units in the chain. The ^{13}C nmr analysis indicates that atactic polyacrylonitrile is almost a completely random polymer while the material prepared with an organometallic catalytic system has a modestly increased stereoregular content.

The proton nmr analysis of the steric configuration of polyacrylonitrile, $\mathrm{+CH_2CH(CN)+_{\it x}}$, has been a very difficult problem. The use of deuterated polymers and model oligomers,[1] exotic solvent systems,[2] and extensive homonuclear spin–spin decoupling techniques,[2] all in efforts to simplify the spectra, have still left uncertainties in the determinations of the relative concentrations of steric dyads and triads in the chain. These uncertainties are largely due to the insensitivity of the methine proton spectra of polyacrylonitrile to steric configuration and the likely inability to interpret properly the methylene proton spectra in terms of dyads in the chain (rather than both dyads and tetrads) even though only two spin-decoupled lines are observed.

Analysis of the ^{13}C nmr spectra of polyacrylonitrile circumvents these problems. The nmr spectra of the nitrile carbon can be interpreted in terms of steric triads and pentads. From these spectra it can be shown that atactic polyacrylonitrile is essentially a random polymer.

Experimental Section

High-resolution pulsed ^{13}C nmr spectra were obtained using the Bruker spectrometer as described in the preceding paper.[3] Samples for nmr investigations were prepared from 20% (w/v) solutions of the polymer in dimethyl sulfoxide.

Two different samples of polyacrylonitrile were investigated. The first was prepared in a water slurry using a persulfate–bisulfite redox system as a free-radical initiator. The second was obtained by polymerization of the monomer at 15° in dimethyl sulfoxide using a catalyst system which consisted of equimolar amounts of $NaAlEt_4$ and ethyl alcohol. The polyacrylonitrile produced in this way had been considered, on the basis of its dissolution and crystallization behavior, to possess a higher degree of chain regularity than the redox-generated polymer.[4] Both are high-molecular-weight materials.

Results and Discussion

The noise-decoupled, natural abundance ^{13}C nmr spectrum of the polyacrylonitrile initiated by the free-radical catalyst is shown in Figure 1. The very intense line at δ_C 40.4 ± 0.2 is due to the dimethyl sulfoxide solvent. The nitrile carbon resonance of polyacrylonitrile appears at δ_C 120.0, the methylene carbon at δ_C 32.6, and the methine carbon at δ_C 27.0. One feature of this spectrum is the absence of any broadening or reduction in intensity of the nitrile carbon resonance (relative to the other polymer carbon lines) resulting from coupling to the ^{14}N quadrupole. High polymers are subject to various motional restrictions which shorten the ^{14}N relaxation time and so effectively decouple the carbon. (For a small molecule such as acetonitrile, the coupling is important and results in a nitrile carbon resonance almost an order of magnitude broader than the methyl carbon resonance.)

An expanded version of the nitrile carbon spectrum of polyacrylonitrile is shown in Figure 2a. Three lines are clearly resolved and are attributed to the three possible steric triad configurations. The relative intensities of approximately 3:5:2 are consistent with this polymer having essentially a random configuration. (Comparing intensities of ^{13}C nmr lines directly is permissible when the carbons involved differ only in the steric configuration of neighboring units.[3])

The three lines are assigned to iso-, hetero-, and syndiotactic triads, in order of increasing field, from left to right. The assignment of the lowest field, nitrile carbon line to isotactic triads in the chain is made by comparison to the ^{13}C nmr spectra of the corresponding carbons of other vinyl polymers. We suggest that this procedure is reasonable on the basis of the following argument.

The spectra of the carbons directly bonded to the methine carbons in both polystyrene and polypropylene are interpreted by assignments in which the average position of lines due to sequences with central isotactic triads is at lower field than the averages for corresponding hetero- and syndiotactic sequences.[5] Unlike the situation for polyacrylonitrile, these assignments can be made completely unambiguously because crystalline polymers, identified as isotactic by other physical techniques, are available for comparison. Even though these carbons of polystyrene and polypropylene are functionally quite different, the steric configuration of the chain is reflected in their spectra in approximately the same way. This

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(1) K. Matsuzaki, T. Uryu, M. Okada, and H. Shiroki, *J. Polym. Sci., Part A-1*, **6**, 1475 (1968).

(2) J. Bargon, K. H. Hellwege, and U. Johnson, *Kolloid-Z. Z. Polym.*, **213**, 51 (1966).

(3) J. Schaefer, *Macromolecules*, **4**, 98 (1971).

(4) R. Chiang, *J. Polym. Sci., Part A*, **3**, 2019 (1965).

(5) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).

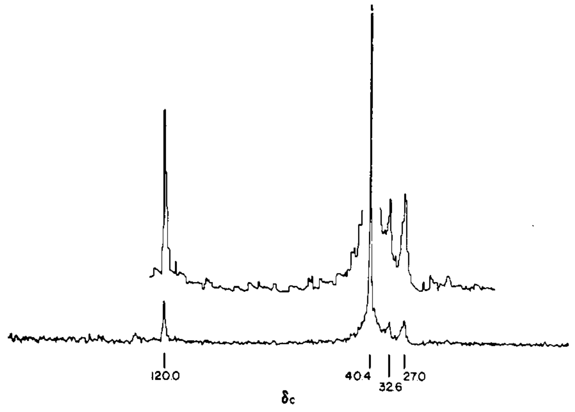

Figure 1. Fourier transform of the noise-decoupled, natural abundance ^{13}C nmr free induction decay from a solution of polyacrylonitrile in dimethyl sulfoxide. The free induction decay was obtained by sampling the receiver output using 1024 channels of a time averaging computer internally swept at a rate of 100 μsec/channel; 2500 scans were accumulated in a little over 4 min. The transform required about 30 sec.

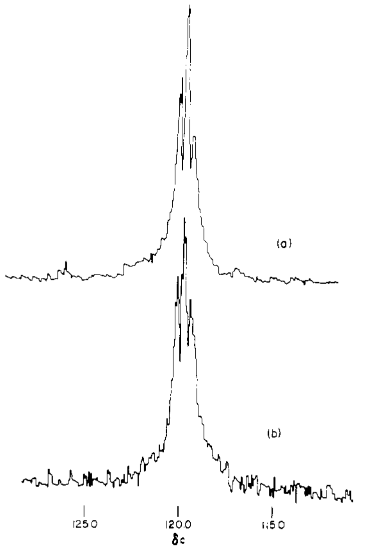

Figure 2. Fourier transform of the noise-decoupled, natural abundance ^{13}C nmr free induction decay from a dimethyl sulfoxide solution of polyacrylonitrile generated by (a) a free-radical catalyst system and (b) an organometallic catalyst system. Only the nitrile carbon resonance is shown. The free induction decay was obtained by sampling the receiver output using 2048 channels of a time averaging computer internally swept at a rate of 400 μsec/channel; 16,000 scans were accumulated in about 4 hr. The transform required 1 min.

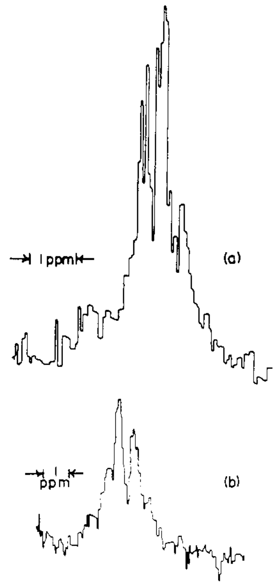

Figure 3. (a) A spectrum similar to that shown in Figure 2a except the concentration of the solution has been reduced by more than a factor of 3 and the horizontal display scale has been increased by a factor of 2. (b) The methine carbon resonance of the polyacrylonitrile initiated by the free-radical catalyst system. The spectrum was obtained as described in the caption to Figure 2 except that only 2500 scans were accumulated.

is related to the absence of a strong dependence of the nmr spectra of carbons in or near the main chain of a polymer on through-space magnetic interactions, magnetic anisotropies, and most solvent effects, none of which have a strong influence on the electron density distribution in the backbone of the chain. Such spectra are strongly dependent, however, on the skeletal form of the chain segment in solution, that is, on its conformation. For segments of different vinyl polymers[6] of the type $-\!\!\left[CH_2CHR\right]\!\!-_x$ (where R is always of modest size) and of the same steric configuration, the conformation in solution is qualitatively the same.[7] This means that carbons of different polymers but in the same relative locations in the main chains of segments of the same configuration will have similar conformational environments. For all of these polymers, making the same change in the segmental steric configuration will then produce a similar change in the conformational environment, the key factor in determining relative ^{13}C nmr chemical shifts. This means that if the methine carbon line of an isotactic triad is at low field relative to a heterotactic triad for one of these polymers, the same relative positions will hold for triads in all other polymers of this type as well. This is true for the *average* position of lines arising from central triad sequences even though the details of the spectra (for example, the relative shifts due to next-nearest neighbors) may vary from polymer to polymer. The similarity in spectra permits the assignment of the α-carbon, isotactic triad line of polyacrylonitrile relative to the heterotactic line by comparison with the spectra of α-carbons of other vinyl polymers.

The nitrile carbon spectrum of the polyacrylonitrile generated by the organometallic catalyst system is shown in Figure 2b. Both the iso- and syndiotactic triad concentrations have measurably increased relative to

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(6) Synthetic polyelectrolytes, for the moment, are explicitly excluded both because water is an unusual solvent and, more importantly, because the unusual effects of charge on the chemical shifts of polyanions are not yet very well understood.

(7) The conformations of polystyrene and polypropylene have been discussed recently: P. J. Flory and Y. Fujiwara, *Macromolecules*, 2, 327 (1969); Y. Fujiwara and P. J. Flory, *ibid.*, 3, 43 (1970). Despite differences in conformation, especially important with respect to the proton nmr spectra of these polymers, it seems clear that the physics involved in the two systems is the same. Major differences in conformation which would alter the basic, qualitative argument being presented here seem unlikely.

the heterotactic triad concentration. The increased stereoregular content of the polymer is consistent with its relatively high dissolution temperature.[4] The relative intensities of the three lines are now about 3:4:3 which is difficult to analyze in terms of a homogeneous distribution in a single chain. There are two possible explanations. The first is that the complex catalyst system involves several different types of catalytic sites, each producing a different type of polymer. That is not likely since the catalytic system is homogeneous, but it is not impossible. The second explanation is that the nitrile carbon region is not strictly interpretable in terms of triads alone, an explanation which can be tested by examining the spectrum under conditions of higher resolution.

By reducing the concentration of the polyacrylonitrile solution to about 5% (w/v), the resolution of the nitrile carbon spectrum can be substantially improved to the point where now steric next-nearest configurational neighbors, or pentads, can be resolved. The spectrum of the free-radical-initiated polymer obtained under these conditions is shown in Figure 3a. Each of the major triad lines is resolved into two or three pentad lines. At least six of the possible nine pentad lines are discernible. The resolution and sensitivity are not quite good enough to permit accurate quantitative measurements, but the spectrum is useful in showing that the more poorly resolved spectra of Figure 2 may not have been properly interpreted in terms of triads alone. This is true because the average spacing between the pentad lines is comparable to that between the groups of lines assigned to triads, especially the hetero- and syndiotactic triads. In other words, some of the next-nearest neighbors of syndiotactic triads may cause a downfield shift of the central nitrile carbon line in these sequences so that some of the syndiotactic triad intensity may, in fact, be incorrectly counted as heterotactic in an interpretation based on triads alone. Such an error, while small (on the order of 10% or less for this polymer), would still be sufficient to change the relative line intensities of Figure 2b enough to permit a statistical description in terms of a single homogeneous distribution in which syndiotactic placements are now slightly preferred.[8]

An expanded version of the methine carbon spectrum of the more concentrated solution of the free-radical-initiated polymer is shown in Figure 3b. Five lines are observed and are related to the various possible pentad configurations. The general appearance of this spectrum is the mirror image of that of the nitrile carbon. The identification of these lines as due to methine carbons was made by off-resonance decoupling experiments Because of the considerable extent of overlapping, any assignment of the methylene carbon tetrad lines would not be unique.

Acknowledgment. The author thanks Mr. Eli Perry, Central Research Department, Monsanto Co., for preparation of the polyacrylonitrile samples.

(8) These are summarized in F. A. Bovey, "Polymer Conformation and Configuration," Academic Press, New York, N. Y., 1969.

High-Resolution Pulsed Carbon-13 Nuclear Magnetic Resonance Analysis of the Monomer Distribution in Acrylonitrile–Styrene Copolymers

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ABSTRACT: Fourier transforms of the noise-decoupled, natural abundance, 22.6-MHz ^{13}C nmr free induction decays of some acrylonitrile–styrene copolymers have been obtained. Well-resolved lines arising from both kinds of monomer units are observed and interpreted in terms of the monomer distribution in the chain. Observed and theoretically calculated concentrations of triads are in agreement. The aromatic C_1 carbon of the styrene units is especially sensitive to the configuration of the chain and can be used to distinguish between two copolymers of the same composition (prepared using different catalysts) but differing in the minor details of their long-range steric and structural configuration.

The chief advantage of the analysis of copolymers by ^{13}C rather than proton nmr is the relative simplicity of the spectra. The simplicity results from large chemical shifts, the absence of any spin–spin coupling, and relatively narrow lines not severely broadened by dipolar interactions.[1] In some systems this simplicity is more than just a convenience but is essential to the analysis. While the proton nmr spectra of copolymers of acrylonitrile and styrene are so poorly resolved that a detailed interpretation is impossible, the ^{13}C nmr spectra are well resolved and can be quantitatively interpreted in terms of the monomer distribution in the chain.

Experimental Section

High-resolution pulsed ^{13}C nmr spectra were obtained using the Bruker spectrometer as described in the preceding paper.[2] Samples for nmr investigations were prepared

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(1) J. Schaefer, *Macromolecules*, **2**, 210 (1969).

(2) J. Schaefer, *ibid.*, **4**, 98 (1971).