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.

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(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).

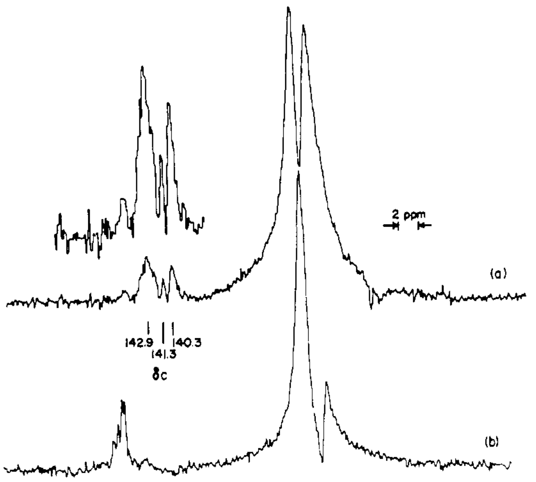

Figure 1(a). Fourier transform of the noise-decoupled, natural abundance ^{13}C nmr free induction decay from a 20% (w/v) solution of an acrylonitrile–styrene copolymer (Monsanto Lustran A-21 containing 40 mol % acrylonitrile) in dimethyl sulfoxide. Only the aromatic and nitrile carbon regions are shown. 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 400 μsec/channel; 16,000 scans were accumulated in about 2 hr. The transform required 30 sec. (b) A similar spectrum of a dioxane solution of polystyrene from an accumulation of 4000 scans. The δ_C scale does not apply to this spectrum. The relative positions of the major resonances of polystyrene relative to the copolymer were determined from a spectrum of the latter in solution in dioxane.

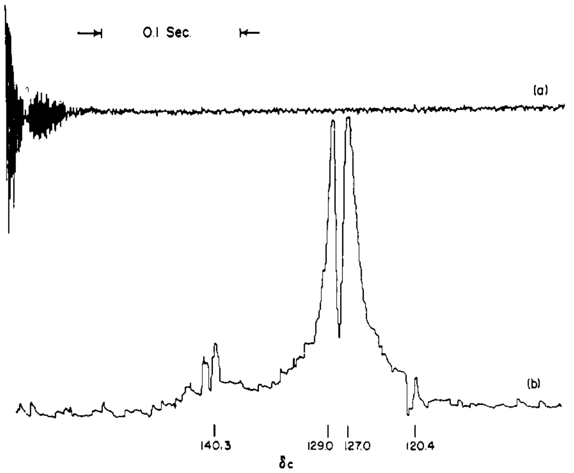

Figure 2. (a) The noise-decoupled, natural abundance ^{13}C nmr free induction decay from a 20% (w/v) solution of a high-conversion acrylonitrile–styrene copolymer (containing 50 mol % acrylonitrile) in dimethyl sulfoxide and (b) its Fourier transform. The free induction decay was obtained as described in the caption to Figure 1a. Only the aromatic and nitrile carbon regions are shown.

from 20% (w/v) solutions of the copolymers in dimethyl sulfoxide.

Acrylonitrile–styrene copolymers were prepared by a free-radical polymerization of the monomers using azobisisobutyronitrile as initiator. The polymerization was performed in a water slurry in the presence of Triton X-200 suspending agent and a mercaptan chain-transfer agent. The pH of the slurry was controlled by the addition of SO_2. When high-conversion copolymers were produced, monomer was continuously added to the mixture to maintain the initial ratio of reactants. The copolymer was purified in the usual way.

A material thought to be a completely alternating copolymer of acrylonitrile and styrene was prepared by copolymerization of the monomers in the presence of zinc chloride and the absence of solvent or any other initiators.[3]

Two commercially available materials were also investigated, one a polystyrene, Monsanto Lustrex, and the other an acrylonitrile–styrene copolymer, Monsanto Lustran A-21 (containing 40 mol % acrylonitrile). Both are prepared using free-radical catalysts.

All of these materials are high polymers with weight-average molecular weights on the order of 200,000.

Results and Discussion

The noise-decoupled, natural abundance ^{13}C nmr spectra of a dioxane solution of polystrene and of a dimethyl sulfoxide solution of an acrylonitrile–styrene copolymer (containing 40 mol % acrylonitrile) are presented in Figure 1. Only the aromatic and nitrile carbon regions are shown.[4] The regions to higher field are partially obscured by the solvent peaks.

The C_1 carbon resonance of polystyrene appears at low field (and is sensitive to the stereochemistry of the chain), the C_4 carbon line appears at high field, and the C_2 and C_3 carbon lines appear together at intermediate

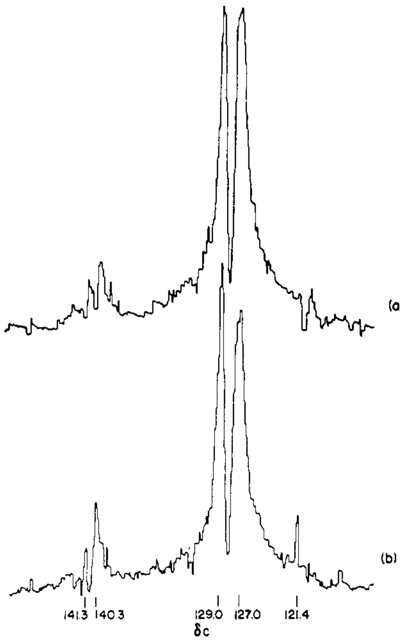

Figure 3. The ^{13}C nmr spectrum of a dimethyl sulfoxide solution of an acrylonitrile–styrene copolymer (containing 50 mol % acrylonitrile) obtained (a) from a low-conversion, free-radical-initiated polymerization and (b) from a high-conversion, $ZnCl_2$-catalyzed polymerization. The spectra were obtained as described in the caption to Figure 1a. Only the aromatic and nitrile carbon regions are shown.

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(3) S. Yabumoto, K. Ishii, and K. Arita, *J. Polym. Sci., Part A-1*, 7, 1577 (1969).

(4) The aromatic carbon resonances from hexafluorobenzene also appear in the low-field region. By using sufficiently small amounts of C_6F_6, these were negligible compared to the polymer lines; C_6F_6 is used in the field-frequency control.

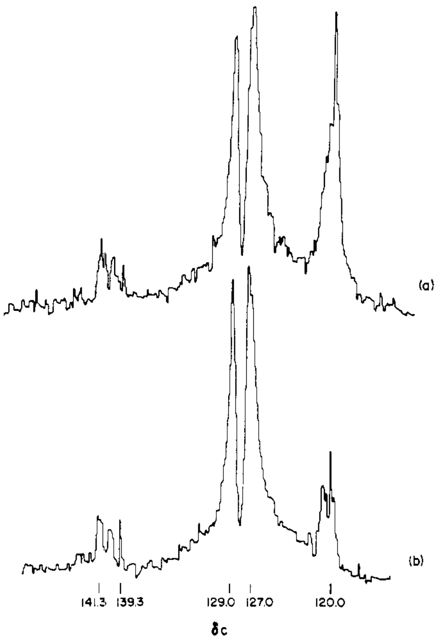

Figure 4. The ^{13}C nmr spectrum of a dimethyl sulfoxide solution of an acrylonitrile–styrene copolymer containing (a) 85 mol % acrylonitrile and (b) 64 mol % acrylonitrile. The spectra were obtained as described in the caption to Figure 1a. Only the aromatic and nitrile carbon regions are shown.

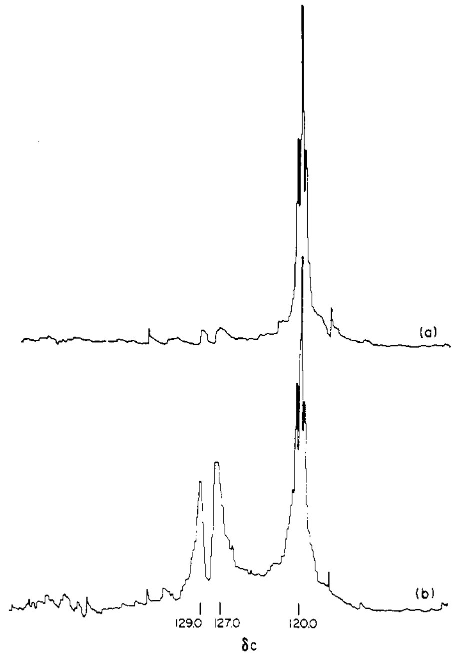

Figure 5. The ^{13}C nmr spectrum of a dimethyl sulfoxide solution of an acrylonitrile–styrene copolymer containing (a) 98 mol % acrylonitrile and (b) 92 mol % acrylonitrile. The spectra were obtained as described in the caption to Figure 1a. Only the aromatic and nitrile carbon regions are shown.

field[5] (Figure 1b). The positions of the major resonances of the copolymer relative to polystyrene (as shown in Figure 1) were determined by obtaining a spectrum of the copolymer of Figure 1a in dioxane. A single solvent which was satisfactory for both polystyrene and all the copolymers was not available.

Just as for the homopolymer, the C_1 carbon of the styrene units in the copolymer are sensitive to the structure of the chain. The lowest field line (δ_C 145.1) is assigned to the C_1 carbon in B*B*B triads (where B is styrene and A is acrylonitrile) and the lower field portion of the line at δ_C 142.9 to these carbons in B*B*A, A*B*B triads; all higher field lines (up to δ_C 139) are assigned to C_1 carbons in A*B*A triads. The multiplicity of lines in these triad assignments is due to the sensitivity of the C_1 carbon in the styrene units to steric as well as structural configuration. No attempt will be made to assign those features of the spectra attributable to either steric or long-range structural configuration. Because styrene units prefer to add to acrylonitrile in the copolymerization (the reactivity ratios differ by an order of magnitude) even the copolymer rich in styrene contains a high concentration of ABA sequences. The C_2, C_3, and C_4 carbon lines together appear as a doublet (δ_C 129.0 and 127.0) which arises, for the most part, from A*B*A triads. Which carbon produces which line is not clear. Resonances from these carbons in the other much less probable sequences are not resolved. In this copolymer virtually all the acrylonitrile units are in B*A*B sequences, and the nitrile carbon resonance from these sequences appears as a shoulder on the high-field side of the aromatic carbon doublet.

Figure 2 shows the ^{13}C nmr spectrum of a high-conversion copolymer richer in acrylonitrile. Now the only C_1-aromatic carbon lines observed are those in A*B*A sequences. Furthermore, the nitrile carbon resonances are more apparent and the line at δ_C 120.4 is assigned to nitrile carbons in A*A*B,B*A*A sequences. This carbon is sensitive to steric as well as structural features of the chain. However, the amount of acrylonitrile in the chain is still too small to observe any large concentrations of consecutive acrylonitrile units.

Because of the restricted chain mobility, the nitrile carbon resonance is not affected by any ^{14}N quadrupole coupling.[6] The nitrile carbon line is as narrow and intense as the aromatic C_1 carbon line. This particular comparison is reasonable because the resonance of the C_1 carbon (which, like the nitrile carbon, has no directly bonded protons) is not significantly affected by the nuclear Overhauser enhancement normally obtained upon noise decoupling of the protons.[7]

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

(6) J. Schaefer, *ibid.*, 4, 105 (1971).

(7) The sensitivity of these experiments was not sufficient to determine if the C_1-carbon resonance was enhanced during noise decoupling by a relaxation mechanism involving a dipolar coupling to nondirectly bonded protons [see A. J. Jones, D. M. Grant, and K. F. Kuhlmann, *J. Amer. Chem. Soc.*, **91**, 5013 (1969)]. However, the line shapes and relative intensities of the C_1 and nitrile carbon lines were not affected by the introduction of long delays between pulses, by changes in the pulse power of more than a factor of 2, or by significant offsets of the ^1H and ^{13}C irradiating frequencies. Thus, selective relaxation mechanisms affecting the intensity of the aromatic C_1 carbon line but not the nitrile carbon line appear to be absent and any small nuclear Overhauser enhancement is probably about the same for both. In any event, a problem in comparing intensities in the ^{13}C nmr spectra of copolymers is only critical when sequences with different central units are compared. Changes in the structural or steric configuration of nearest or next-nearest neighbors will, under most circumstances, have no effect on the signal intensity arising from the carbons in the central unit of a sequence.

The spectra of two copolymers each of which contain about 50 mol% acrylonitrile are shown in Figure 3. One is a low-conversion (less than 8%) copolymer prepared using a free-radical initiator while the other was prepared using a $ZnCl_2$ catalytic system which has been credited with producing a completely alternating chain.[3] The two spectra are similar, with the apparent differences attributed to differences in the steric configurations of A*B*A and B*A*B, to possible differences in the long-range structural configuration, and to the presence of a small concentration of AAB,BAA sequences in the free-radical initiated polymer. No significant concentrations of sequences containing consecutive styrene or acrylonitrile units are observed in the $ZnCl_2$-catalyzed copolymer.

The ^{13}C nmr spectra of copolymers very rich in acrylonitrile are shown in Figures 4 and 5. Intense nitrile carbon lines, assigned to A*A*B,B*A*A sequences, are observed at δ_C 120.4 (Figure 4), while the nitrile carbon lines due to A*A*A sequences centered at δ_C 120.0 are the dominant feature of the spectrum of the copolymer containing 98 mol % acrylonitrile[8] (Figure 5a). The aromatic doublet in copolymers very rich in acrylonitrile is shifted downfield about 0.4 ppm relative to its position in styrene-rich copolymers and in the alternating copolymer catalyzed by $ZnCl_2$. This is probably the result of each line of the doublet arising from carbons in a variety of sequences, the resonances of some of which are sensitive to next-nearest neighbors. Changing these next-nearest neighbors produces the shift.

Using the above line assignments, the relative concentrations of sequences of triads in acrylonitrile–styrene copolymers can be experimentally determined with an accuracy of about ±10%. The rather large error limit reflects the difficulty in measuring widely differing intensities in amplitude Fourier transform spectra.[1] As an example, the values for the low-conversion copolymer of Figure 4b are presented in Table I and compared to those obtained from a calculation[9] in which the experimentally known ratio of reactants was equal to 20, r_1 equal to 0.04, and r_2 equal to 0.41.[10] The agreement is reasonable. This means that the monomer distribution can now be determined by ^{13}C nmr analysis for those acrylonitrile–styrene copolymers prepared under such poorly characterized reaction conditions of conversion and drastically changing concentrations of reactants that theoretical calculations of the distribution are not possible.

TABLE I
RELATIVE CONCENTRATIONS OF TRIADS IN THE ACRYLONITRILE–STYRENE COPOLYMER OF FIGURE 4b

Sequence	Relative concn Obsd	Relative concn Calcd
B*B*B	0	0.001
B*B*A,A*B*B	0	0.1
A*B*A	3.0	2.7
B*A*B	1.0	1.2
A*A*B,B*A*A	2.0	2.0
A*A*A	1.0	0.8

Acknowledgment. The author thanks Mr. Eli Perry, Central Research Department, Monsanto Co., for the preparation of the acrylonitrile–styrene copolymers.

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[8] A discussion of the assignment of the three A*A*A lines to the steric configurations of these sequences is given in the preceding article.

[9] F. P. Price, *J. Chem. Phys.*, **36**, 209 (1962).

[10] See, for example, P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 188, for representative values for the reactivity ratios.

High-Resolution Pulsed Carbon-13 Nuclear Magnetic Resonance Analysis of Some Cross-Linked Polymers

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ABSTRACT: Fourier transforms of the noise-decoupled, natural abundance, 22.6-MHz ^{13}C nmr free induction decays of some polymeric gels have been obtained. The gels were formed both from mixtures of a high-molecular weight poly(vinyl chloride) in a moderately poor solvent at low temperature and from a copolymer of ethylene and maleic anhydride cross-linked with 3 mol % of a difunctional monomer. Despite the restricted mobility of the chains in these systems, the ^{13}C nmr spectra are well enough resolved to reveal details of the microstructure. Proton nmr spectra of the gels provided no usable, high-resolution signal.

Duch and Grant[1] have shown that relatively narrow ^{13}C nmr lines are obtained from solid polybutadienes and polyisoprenes when the spectra are obtained above the glass transition temperatures of the polymers. This result can be atrributed to the substantial segmental mobility of rubbery chains at these temperatures and to the absence in ^{13}C nmr spectra of a strong dependence on those dipolar interactions not averaged to zero by the motion of the chains.[2]

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[1] M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).

[2] J. Schaefer, *ibid.*, **2**, 210, 533 (1969).