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

	Relative concn	
Sequence	Obsd	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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Received September 8, 1970

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).

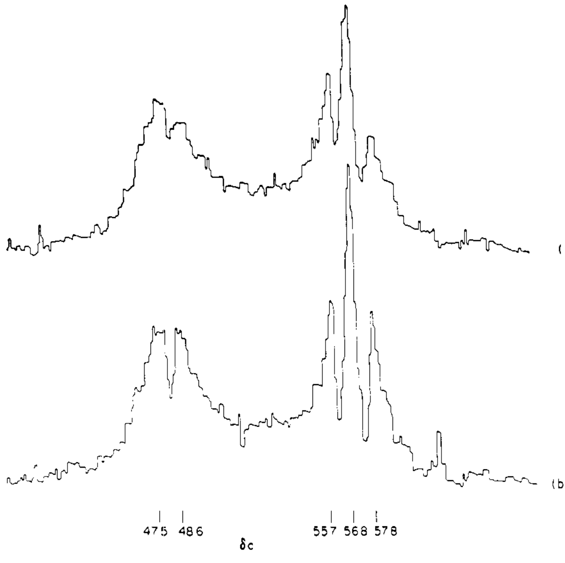

Figure 1. Fourier transform of the noise-decoupled, natural abundance ^{13}C nmr free induction decay of a chlorobenzene gel at 40° containing (a) 20% and (b) 10% by weight of a high-molecular-weight poly(vinyl chloride). In order to avoid the strong aromatic signal due to chlorobenzene, the irradiating pulse was offset to the high-field side of the methine and methylene carbon regions of the polymer. The aromatic carbon signal was then removed by a low-pass analog filter. Because of the offset the magnetic field increases from right to left. 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; 25,000 scans were accumulated for (a) and 100,000 for (b), the latter requiring 11 hr. Its transform was performed in 30 sec.

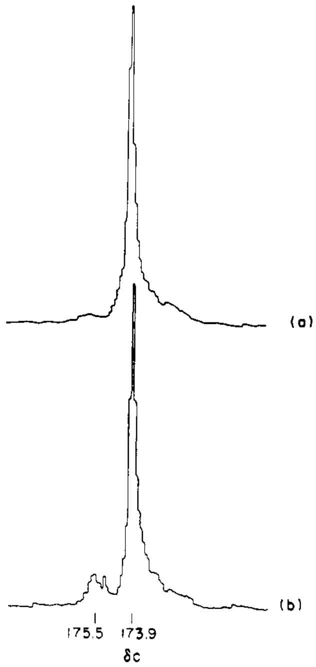

Figure 2. Fourier transform of the noise-decoupled, natural abundance ^{13}C nmr free induction decay from a dimethylformamide (a) solution and (b) gel containing 20% (by weight) ethylene–maleic anhydride copolymer. Only the carbonyl carbon resonances are shown. The copolymer in the gel has been cross-linked with 3 mol % 3,3′-(methylimino)bispropylamine. The magnetic field increases from left to right. 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; 8000 scans were accumulated for both spectra in less than 1 hr each. Each transform was performed in 30 sec.

High-resolution ^{13}C nmr spectra can also be obtained from polymers below their glass transition temperatures even though the polymers are not soluble in a convenient solvent at the operating temperatures of the spectrometer. Two examples include a high-molecular-weight poly(vinyl chloride) (Monsanto Opalon 660, melting point greater than 200°) and an ethylene–maleic anhydride copolymer cross-linked with 3 mol % 3,3′-(methylimino)bispropylamine.

Figure 1a shows the noise-decoupled, natural abundance ^{13}C nmr spectrum of a mixture of 20% (by weight) poly(vinyl chloride) $+\!\mathrm{CH_2CHCl}\!+_x$ and 80% chlorobenzene obtained at 40° using a Bruker pulsed nmr spectrometer.[3] The sample was first heated to 175° to form a uniform solution and then allowed to cool to the nmr probe temperature. At this temperature the mixture formed a swollen gel which could be handled as a solid. Since chlorobenzene is not a particularly good solvent for poly(vinyl chloride), the gel probably consists of two phases with some of the amorphous polymer forming an extremely viscous true solution and connecting (or cross-linking) regions of higher molecular weight, more crystalline polymer only swollen by the chlorobenzene.[4] In any event, the ^{13}C nmr spectrum is sufficiently well resolved to reveal the stereochemical microstructure of the chain. The methine carbon resonance appears at low field and is split into three lines attributed to iso-, hetero-, and syndiotactic triads. (Note that the magnetic field in Figure 1 increases from right to left.) The intensity ratios of the three lines are about 1:2:1, consistent with the known, approximately random steric configuration of poly(vinyl chloride).[5] The methine carbon is not quadrupole coupled to the chlorine because of the lack of chain mobility,[6] so the methine carbon resonances are as intense as those due to the methylene carbons. The latter appear at higher field, consist of two lines of about the same intensity, and are attributed to iso- and syndiotactic dyads.

Figure 1b is a similar spectrum of the same material now reduced in concentration by a factor of 2 relative to the solvent. At 40° the polymer still formed a solid gel with chlorobenzene, although a considerably less rigid gel. The ^{13}C nmr spectrum, obtained from a data accumulation four times as long, is somewhat better resolved. The fact that the levels of the signal intensities in the two spectra are the same indicates that

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

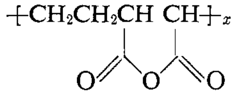
(4) See, for example, P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 574.

(5) F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963); F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Fornegay, *J. Phys. Chem.*, **71**, 312 (1967).

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

most of the carbons in both the concentrated and dilute gels are contributing to the observed nmr signals.

Figure 2a shows the noise-decoupled, natural abundance ^{13}C nmr spectrum of the carbonyl region of a solution of 20% (by weight) ethylene–maleic anhydride (A) in dimethylformamide. Only a single, narrow line



A

is observed corresponding to the single type of carbonyl carbon in the completely alternating copolymer. If this material is cross-linked through the ring by a difunctional monomer, it is no longer soluble in dimethylformamide (in any concentration) but rather forms a swollen gel or slurry which remains visibly inhomogeneous despite heating to elevated temperatures. Nevertheless, a narrow carbonyl line is still observed from the gel, containing 20% (by weight) polymer and 80% dimethylformamide (Figure 2b). The level of signal intensity obtained from the gel is comparable to that obtained from the true solution. (The new lines at low field are probably the result of rearrangements during the heat treatment, but may contain information about the cross-linking sites.)

Apparently the segmental chain motion in these gels is sufficient to eliminate much of the dipolar interaction responsible for the broadening of the nmr spectra of polymers, at least to the extent that high-resolution ^{13}C nmr spectra can be obtained. This is true even for polymers which are not rubbery and are, in fact, characterized by a modest degree of crystallinity. Proton nmr spectra of the gels provided no usable, high-resolution signal.

Determination of Intermolecular Potentials from Crystal Data. II. Crystal Packing with Applications to Poly(amino acids)[1]

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Received July 27, 1970

ABSTRACT: A technique used to study the crystal packing of both small molecules and biopolymers is presented, and the development of an internally consistent set of intermolecular potentials is described. Using this set of potentials for all intermolecular interactions together with a previously reported set of intramolecular potentials, the conformation and crystal packing energies of the β structure of poly-L-alanine and the ω-helix of poly(β-benzyl-L-aspartate) were calculated. The internal torsional energies, as well as both the intramolecular and intermolecular nonbonded, hydrogen-bonded, and electrostatic energy contributions, were included in these computations. Energy minimization was carried out with respect to both the intramolecular variables (*i.e.*, the backbone and side-chain dihedral angles) and also variations in the intermolecular orientations and crystal packing of the homopolymers. In general, the conformation and crystal packing of both polymers, predicted from the computed energies, were in agreement with the reported crystallographic results. For poly-L-alanine, the observed packing, as calculated here, is caused primarily by intermolecular interactions, *viz.*, the intermolecular hydrogen bonds and the nonbonded side-chain interactions, with very little influence from the intramolecular interactions. Not only were the conformation and the lattice constants in good agreement with results from crystal studies, but, further, from a comparison of the calculated energies for a number of "similar" crystal structures, a statistical model as proposed from the X-ray diffraction studies was verified. For the packing of the ω-helix of poly(β-benzyl-L-aspartate), the major contribution to the total interaction energy arises from the intramolecular interactions, although the observed conformation and packing results from contributions from both the intermolecular and intramolecular interactions.

It is necessary to have accurate potential functions for calculating conformational energies of macromolecules.[3,4] For this purpose, much effort has been devoted in recent years[5–9] to calculating the forces

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[1] This work was supported by research grants from the National Science Foundation (GB-7571X and GB-17388), from the National Institute of General Medical Sciences of the National Institutes of Health, U. S. Public Health Service (GM-14312), from the Eli Lilly, Hoffmann-LaRoche, and Smith Kline and French Grants Committees, and from Walter and George Todd.

[2] (a) NIH Postdoctoral Trainee, 1968–1969; Postdoctoral Fellow of the National Institute of General Medical Sciences, National Institutes of Health, 1969–1971; (b) Postdoctoral Fellow of the National Institute of General Medical Sciences, National Institutes of Health, 1965–1968; (c) Special Fellow of the National Institute of General Medical Sciences, National Institutes of Health, 1968–1969; (d) Predoctoral Fellow of the National Institute of General Medical Sciences, National Institutes of Health, 1967–1971; (e) on leave from the Weizmann Institute of Science, 1966–1969; (f) to whom requests for reprints should be addressed.

[3] H. A. Scheraga, *Advan. Phys. Org. Chem.*, **6**, 103 (1968).

[4] H. A. Scheraga, Nobel Symposium 11 on "Symmetry and Function of Biological Systems at the Macromolecular Level," Stockholm, Aug 26–29, 1968, A. Engstrom and B. Strandberg, Ed., Almqvist and Wiksell, Stockholm, 1969, p 43.

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[9] A. Warshel and S Lifson, *J. Chem. Phys.*, **53**, 582 (1970.