

^{13}C — $\{^1\text{H}\}$ Nuclear Magnetic Resonance Spectroscopy of Polyacrylonitrile

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ABSTRACT: The natural abundance ^{13}C — $\{^1\text{H}\}$ high-resolution nuclear magnetic resonance spectra were measured for polyacrylonitrile. The sample used were three tactically different polymers. The spectra of carbons of methine and cyano groups clearly split into three peaks. These splittings were assigned to triad configurations.

It was concluded that the nuclear Overhauser effect due to total proton decoupling did not affect the relative intensities of the resonances of carbons which differ only in stereochemical configurations. The spectra of methylene carbon was rather broad but with a single peak.

KEY WORD Polyacrylonitrile / ^{13}C — $\{^1\text{H}\}$ NMR / Configuration / Nuclear Overhauser Effect / Tacticity /

The studies on the tactic structure of polyacrylonitrile (PAN) were started by the use of X-ray diffraction,¹ infrared absorption,^{2,3} and electron diffraction.⁴ Recently many studies on the estimation of the microtacticity of PAN have been made using proton nuclear magnetic resonance (^1H NMR).⁵⁻¹⁴ All the possible dyad and triad configurations of PAN have been detected using selectively deuterated polymers.

In the case of raw samples, *i.e.*, non-deuterated PAN, the spectra are very complicated due to the spin-spin coupling, and further, the meso methylene protons are magnetically non-equivalent in some solvents.^{10,12,13}

Therefore a detection and a quantitative evaluation of configurational sequences of raw polymer are not easy, even for the dyad sequences, by ^1H NMR.

The ^{13}C — $\{^1\text{H}\}$ high-resolution NMR is of great interest for the study of higher order stereochemical placements of vinyl polymers,¹⁵ because carbon is the most essential atom constituting the skeletal bonds of a polymer chain.

Recently, we have reported a detailed analyses of the ^{13}C — $\{^1\text{H}\}$ spectra of poly(methyl methacrylate)¹⁶ and polypropylene.¹⁷

In this paper, the assignments of ^{13}C — $\{^1\text{H}\}$ NMR spectra were shown, and quantitative estimations of the triad tacticity were done from these spectra.

EXPERIMENTAL

Material

PAN samples were offered by Dr. M. Murano of the Textile Research Institute, Toyobo Co. Ltd., Katata, Otsu, Japan. PAN-A was prepared using urea canal complexes of acrylonitrile by gamma-ray irradiation at -78°C . PAN-B was prepared with lithiumnaphthalene as catalyst in dimethylformamide at 0°C . PAN-C was prepared with an azobisisobutyronitrile as catalyst in benzene solution at 60°C .

Methods

The ^1H NMR spectra were observed at 100 MHz in dimethylsulfoxide- d_6 solution at 120°C . Tetramethylsilane was used as an internal reference.

The ^{13}C — $\{^1\text{H}\}$ spectra were observed by an external lock field sweep in absorption mode at 25.14 MHz, in 20% (w/v) solution for PAN-A and in 40% (w/v) solution for PAN-B and -C, in dimethylsulfoxide and dimethylformamide solutions at 140°C . These spectra were measured by means of a Japan Electron Optics Laboratory JNM PS-100 spectrometer. Total proton decoupling was done using JNM IS-100 and JNM SD-HC equipment.

The drifts of the field were automatically corrected by a signal trigger technique using a JEC-5 spectrum computer.

The samples for $^{13}\text{C}\text{--}\{^1\text{H}\}$ measurement were contained in 8 mm o.d. glass tubes. Chemical shifts of $^{13}\text{C}\text{--}\{^1\text{H}\}$ resonance were represented in terms of parts per million using the enriched carbonyl carbon of $\text{CH}_3^{13}\text{COOH}$ as a reference. Effective signal-to-noise ratio was improved by means of a multiple scan average technique using a JEC-5 spectrum computer. Each scan was taken at a sweep rate 27 ppm/250 sec. The number of scans employed is indicated in the caption for each spectrum. The microtacticity was determined from the relative intensities of the corresponding peaks.

RESULTS AND DISCUSSION

The ^1H spectrum of PAN-C is shown in Figure 1. The spectrum consists of the quintet

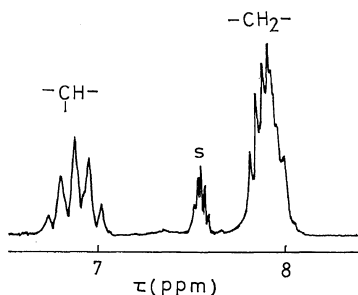


Figure 1. ^1H spectrum of PAN-C observed at 100 MHz, in 5% (w/v) solution in dimethylsulfoxide- d_6 at 140°C . The signals designated s were protons in solvent.

assigned to the resonance of the α -proton at the lower field and the multiplet assigned to that of the β -proton at the higher field. The latter was considered to consist of overlapping triplets. But it is not easy to evaluate the tacticity from this spectrum.

$^{13}\text{C}\text{--}\{^1\text{H}\}$ resonance of methylene carbon of PAN was rather broad but with a single peak, as shown in Figure 2.

These spectra show that the methylene carbon is little affected by the polymer configuration. In ^1H NMR, the meso methylene protons are magnetically non-equivalent in dimethylsulfoxide and equivalent in dimethylformamide.^{10,12,13} In $^{13}\text{C}\text{--}\{^1\text{H}\}$ NMR, however, there is no difference between in the dimethylsulfoxide and in the dimethylformamide. These results are inter-

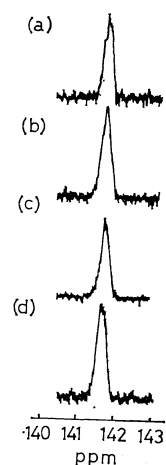


Figure 2. $^{13}\text{C}\text{--}\{^1\text{H}\}$ spectra of methylene carbon of PAN observed at 25.14 MHz, at 140°C : (a) PAN observed in dimethylsulfoxide (256 scans); (b) PAN-A in dimethylsulfoxide (128 scans); (c) PAN-B in dimethylsulfoxide (128 scans); (d) PAN-C in dimethylformamide (128 scans).

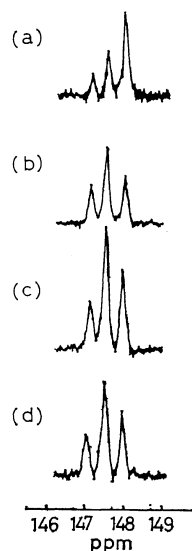


Figure 3. $^{13}\text{C}\text{--}\{^1\text{H}\}$ spectra of methine carbon of PAN observed at 25.14 MHz, at 140°C : (a) PAN-A in dimethylsulfoxide (256 scans); (b) PAN-B in dimethylsulfoxide (128 scans); (c) PAN-C in dimethylsulfoxide (128 scans); (d) PAN-C in dimethylformamide (128 scans).

esting in the study of solvent effect.

$^{13}\text{C}\text{--}\{^1\text{H}\}$ resonance of methine carbon is split into three components, attributable to

triad resonance as shown in Figure 3. The relative intensities of these three components may reflect the triad tacticities of each polymer. It is well known that the PAN prepared using urea canal complexes of acrylonitrile with gamma-ray irradiation at -78°C is highly isotactic.^{12,13}

Therefore the highest field peak of the methine carbon of PAN-A in Figure 3(a) could be reasonably assigned to the isotactic (*I*) triad. Then the central and the lowest peak could be assigned to the heterotactic (*H*) and syndiotactic (*S*) triad, respectively. The profile of these spectra are like those of the D-decoupled ¹H spectra of PAN-β, β-d₂.¹⁴

¹³C—¹H} resonance of cyano carbon is also split into three components as shown in Figure 4. The profile of these splittings gives the same triad pattern as the methine carbon (Figure 3), apart from wholly reversing the line ordering from the lower to the upper field. Therefore these peaks could be assigned to isotactic, heterotactic, and syndiotactic triads, respectively, from the lower to upper field. The spectra of methine carbon are spread over about two-fold greater range in chemical shifts than those of cyano carbon. This means that the latter are less affected by the polymer configuration than the former. The line width of each triad peak of cyano carbon is approximately equal to that of methine carbon. So the line broadening brought about by spin-spin coupling between the ¹³C and ¹⁴N or by quadrupole moment of ¹⁴N is considered to be small.

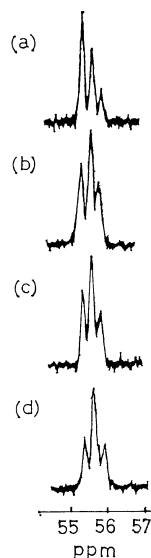


Figure 4. ¹³C—¹H} spectra of cyano carbon of PAN observed at 25.14 MHz, at 140°C: (a) PAN-A in dimethylsulfoxide (512 scans); (b) PAN-B in dimethylsulfoxide (256 scans); (c) PAN-C in dimethylsulfoxide (256 scans); (d) PAN-C in dimethylformamide (256 scans).

The triad tacticity of the polymers determined from the relative intensities of the peaks is tabulated in Table I. The triad tacticities determined from the methine carbon coincide with those from the cyano carbon within possible experimental error. These facts show that the nuclear Overhauser effect caused by the total proton decoupling did not affect the

Table 1. The triad microtacticity of polyacrylonitrile obtained from the ¹³C—¹H} spectra reproduced in Figures 3 and 4

	Polymerization condition	Solvent used for NMR measurement	Specified group	Triad tacticity, %			4I/S/H ²
				<i>I</i>	<i>H</i>	<i>S</i>	
PAN-A	γ-ray irradiation on urea canal complex, -78°C	Dimethylsulfoxide	$\begin{cases} \text{C}\equiv\text{N} \\ \\ \text{—CH—} \\ \end{cases}$	56	32	12	2.6
				56	33	11	2.3
PAN-B	Li naphthalene in dimethylformamide at 0°C	Dimethylsulfoxide	$\begin{cases} \text{C}\equiv\text{N} \\ \\ \text{—CH—} \\ \end{cases}$	30	47	23	1.2
				28	49	23	1.1
PAN-C	AIBN in Benzene at 60°C	Dimethylsulfoxide	$\begin{cases} \text{C}\equiv\text{N} \\ \\ \text{—CH—} \\ \end{cases}$	29	50	21	1.0
				30	48	22	1.1
		Dimethylformamide	$\begin{cases} \text{C}\equiv\text{N} \\ \\ \text{—CH—} \\ \end{cases}$	28	50	22	1.0
				30	48	22	1.1

relative intensities among the peaks assigned to the chemically equivalent carbons except for the stereochemical configurations even for ^{13}C — $\{^1\text{H}\}$ resonance.

Furthermore the triad tacticity of PAN-C determined from the spectrum observed in the dimethylsulfoxide solution coincides with that observed in the dimethylformamide solution. If the propagation reaction is controlled by Bernoullian statistics, the following relation must be held.¹⁸

$$4IS/H^2 = 1$$

This relation is held satisfactorily for the PAN-B and -C as listed in the last column of Table I. Thus the propagation mechanisms of PAN-B and -C were reasonably assumed to be controlled by the Bernoulli trial process. In the PAN-A, however, the above relation is not held. This may be caused by the special orientation of the monomer in the urea canal complexes.

In conclusion, the ^{13}C — $\{^1\text{H}\}$ NMR analysis for polyacrylonitrile configuration may be one of the most suitable means, because it is not necessary to use any deuterated sample. The totally spin-decoupled ^{13}C spectra are rather simple, and then the analyses of the spectra may be carried out more easily than those of the ^1H spectra.

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REFERENCES

1. C.R. Bohn, J.R. Schaefgen, and W.O. Statton, *J. Polym. Sci.*, **55**, 531 (1961).
2. H. Tadokoro, S. Murahashi, R. Yamadera, and T. Kamei, *ibid.*, *Part A*, **1**, 3029 (1963).
3. R. Yamadera, H. Tadokoro, and S. Murahashi, *J. Chem. Phys.*, **41**, 1233 (1964).
4. P.H. Lindenmeyer and R.H. Hoseman, *J. Appl. Phys.*, **34**, 42 (1963).
5. R. Yamadera and M. Murano, *J. Polym. Sci.*, *Part B*, **3**, 821 (1965).
6. K. Matsuzaki, T. Uryu, K. Ishigure, and M. Takeuchi, *ibid.*, *Part B*, **4**, 93 (1966).
7. J. Bargon, K.-H. Hellwege, and U. Johnsen, *Kolloid-Z.*, **213**, 51 (1966).
8. K. Matsuzaki, T. Uryu, M. Okada, K. Ishigure, T. Ohki, and M. Takeuchi, *J. Polym. Sci.*, *Part B*, **4**, 487 (1966).
9. R. Yamadera and M. Murano, *ibid.*, *Part B*, **5**, 333 (1967); *ibid.*, *Part A-1*, **5**, 1059, 1855 (1967).
10. T. Yoshino, H. Kenjo, and K. Kubo, *ibid.*, *Part B*, **5**, 703 (1967).
11. G. Svegliado, G. Talamini, and G. Vidotto, *ibid.*, *Part A-1*, **5**, 2875 (1967).
12. M. Murano, *Makromol. Chem.*, **112**, 281 (1968).
13. K. Matsuzaki, T. Uryu, M. Okada, and H. Shiroki, *J. Polym. Sci.*, *Part A-1*, **6**, 1475 (1968).
14. K. Matsuzaki, M. Okada, and T. Uryu, Lectured at the 19th Discussional Meeting of the Polymer Society of Japan, October 1970, Kyoto.
15. L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).
16. Y. Inoue, A. Nishioka, and R. Chûjô, *Polymer J.*, **2**, 535 (1971).
17. Y. Inoue, A. Nishioka, and R. Chûjô, *Makromol. Chem.*, in press.
18. R. Chûjô, *J. Phys. Soc. Japan*, **21**, 269 (1966).