Polymer Journal, Vol. 17, No. 12, pp 1233—1239 (1985)

Stereoregularity of Polyacrylonitrile by High Resolution ^{13}C NMR Analysis

Kenji KAMIDE,* Hitoshi YAMAZAKI,* Kunihiko OKAJIMA,* and Kunio HIKICHI**

*Textile Research Laboratory, Asahi Chemical Industry Co., Ltd., 11-7 Hacchonawate, Takatsuki, Osaka 569, Japan
**Department of Polymer Science, Faculty of Science, Hokkaido University, Nishi 8, Kita 10, Kita-ku, Sapporo 060, Japan

(Received October 26, 1984)

ABSTRACT: A method for evaluating the pentad tacticity of polyacrylonitrile (PAN) was proposed by analyzing the splittings of the CN carbon NMR peak with high magnetic field ^{13}C NMR. The method was applied to PAN prepared by polymerization with a redox catalyst (R-PAN). The results showed that R-PAN is completely random in stereoregularity and the peak assignment for CN and CH carbons of R-PAN, formerly carried out for evaluating the triad tacticity, was confirmed as correct.

KEY WORDS Polyacrylonitrile / ^{13}C NMR / Triad Tacticity / Pentad Tacticity / Bernoulli Statistics /

So far numerous studies on the stereoregularity of polyacrylonitrile (PAN) have been carried out by ^{1}H NMR analysis.[1-12] By analyzing CH_2 proton signals of partially deuterated PAN in solvents which make the CH_2 proton magnetically equivalent or non-equivalent, Yoshino *et al.*[6] concluded that PAN prepared by γ-ray irradiation on the urea–acrylonitrile canal complex (γ-PAN) is rich in the meso (m) configuration in diad tacticity, compared with that of PAN prepared by a redox catalyst (R-PAN). Schaefer[13] and Inoue *et al.*[14] have recently proposed methods for determining the triad tacticity of PAN by using ^{13}C NMR technique at 25.14 MHz. They observed three peaks in both CN and CH carbon peak regions and assigned these three peaks from a lower magnetic field to isotactic (I), heterotactic (H), and syndiotactic (S) triads for CN carbon peaks and the reverse for CH carbon peaks, assuming that the largest peak in γ-PAN is attributable to I triad. Obviously, their assignment cannot be unconditionally accepted because an abundance of m diads in γ-PAN increases the intensity of the NMR peaks not only for the I triad but also the H triad and if the randomness of the R-PAN can be confirmed by other methods than NMR methods, the assignment can be rigorously performed.

Recently, we have found, by using a higher magnetic field (100.7 MHz) ^{13}C NMR spectrometer, that each peak attributable to I, H, and S triads in CN carbon region is moreover constituted of three or four peak components.

In this article, we elucidate the pentad tacticity of R-PAN and also discuss whether the attribution to I, H, and S signals, formerly proposed by other authors,[13,14] is acceptable or not.

EXPERIMENTAL

Material

R-PAN was prepared by polymerizing acry-

lonitrile in aqueous media for 4 h at 35°C with ammonium persulfate and sodium sulfite as the redox type initiator.

^{13}C NMR

The solution of R-PAN was made by dissolving 200 mg of R-PAN in a mixture of deuterated dimethylformamide (DMF-d_7) (Merck, West Germany)/DMF (guarantee grade, Kishida Chem., Japan) (=1/2, ml/ml). The spectrum was recorded on an FT-NMR spectrometer model JEOL FX-400 (100.7 MHz for ^{13}C nucleus) at 60°C. Measuring conditions are as follows: 45° pulse, width 10 μs, repetition 10 s, data point 16 K, number of pulse 64 × 67. The methyl carbon peak (31.00 ppm) of DMF on the higher magnetic field was taken as a reference.

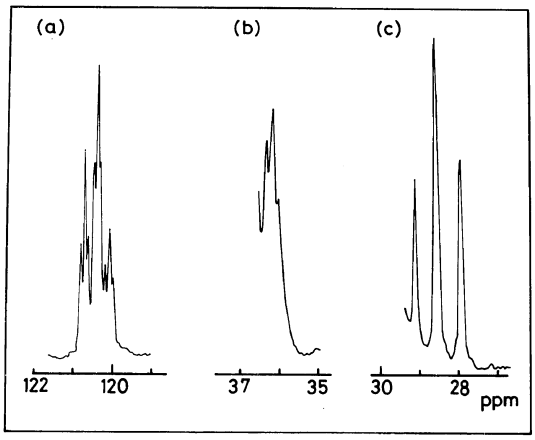


Figure 1. ^{13}C NMR spectra of polyacrylonitrile in DMF-d_7: a, CN carbon region; b, CH_2 carbon region; c, CH carbon region.

RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C NMR spectra for CN (a), CH_2 (b), and CH (c) carbon regions. CN carbon peaks in the range 120—121 ppm are approximately divided into three envelopes and each envelope is further split into 3 or 4 peaks. The CH_2 carbon peaks of R-PAN are constituted of 3 envelopes, although they are considerably overlapped with CH_3 or CD_2H carbon signals due to solvents. The CH carbon peaks of R-PAN in the range 28—29 ppm are clearly constituted of 3 peaks. The 3 envelopes for CN carbon and 3 peaks for CH carbon can be considered to reflect the triad tacticity of R-PAN and the fact that each envelope for CN carbon consists of 3 or 4 peaks might be related to the pentad tacticity of R-PAN.

First, we assume the following in order to assign the CN carbon peaks: (1) The racemo (r) part of R-PAN is energetically stable in a *trans–trans* conformation (see, Figure 3), as proposed for dicyanopentane as model compound for PAN.[15] (2) The meso (m) part of R-PAN takes a *trans–trans* or almost *trans–trans* conformation, in which the adjacent CN groups in m arrangement have double bond nature as a result of the interaction with each other (see, Figures 4 and 5). Although a *trans–gauche* conformation is reported to be stable for dicyanopentane,[15] we consider that a stable conformation for the model compound is not always applicable to the part of a polymer molecule when such a specific interaction is anticipated. The interaction might make the energy difference between *trans–trans* and *trans–gauche* conformations small and also make a slight rotation of the bond axis possible (see, Figure 5). (3) The interacted form with double bond nature in the m part in R-PAN is stable even in solution. (4) Intermolecular interaction of R-PAN in solution is negligibly small. (5) The CN carbon peak region roughly separates into 3 envelopes corresponding to I, H, and S triads and each envelope splits in a very small chemical shift range into 3 or 4 peaks due to pentad sequences.

Assumptions (2) and (3) can be proved by the facts that 1) the m part both in γ-PAN and R-PAN in DMF solution preferentially interacts with cupric ion,[16] 2) solubility of γ-PAN, which is rich in the m diad,[6] in DMF is poorer than that of R-PAN under the same conditions, and 3) the short range interaction

parameter A for γ-PAN in DMSO is larger than that for R-PAN.[17] Fact 1) shows that the m part is more anionic than the r part and facts 2) and 3) show that the m part is more rigid than the r part. For γ-PAN, it is reasonable to consider the existence of the ladder-like part in the m sequence. We think that it is also true for the conformation of the m part in R-PAN, described in assumption (2).

Essentially, the carbon nuclei of CN and CH groups of an isolated monomer unit is shielded by a magnetic field induced by a circular current as demonstrated in Figure 2. In an r sequence, the induced magnetic field from the adjacent CN groups are almost perpendicular to each other, resulting in no influence on a given CN or CH carbon (see, Figure 3). In an m sequence, the adjacent CN groups interact with each other and induce some conjugate double bond nature forming six-membered rings as exemplified in Figure 4.

First, the shielding effect originally existing on the CN and CH carbons of an isolated monomer unit in an r arrangement disappears. We define this apparent deshielding effect on a given CN and CH as δ and δ', respectively. These parameters are allocated only if the CN and CH groups of a monomer unit in question belong to an m or r sequence (in the latter case, $\delta=\delta'=0$). Since this effect is derived by the disappearance of the magnetic field shown in Figure 2, the magnitudes of δ and δ' are anticipated to be in the same order.

Secondly, the double bond nature inevitably leads to the diminishing of the electron density on a CN carbon, as compared with that on an isolated CN carbon in an r arrangement and this effect is expressed by the parameter σ. σ_1 and σ_2 are used for the CN carbon of a monomer unit located at the right and left ends in m and mm sequences, respectively. Electron density decreasing effect in an mm sequence is obviously larger than that in an m sequence. This means that σ_2 is larger than σ_1.

Third, the diminishing of electron density on a CN carbon results in decreasing electronegativity of the CN group, leading to an effect of increasing apparent electron density on a CH carbon belonging to the same monomer unit. This effect is expressed by parameter $-\omega$. $-\omega$ and -2ω are allocated for the CH carbon located at the right and left ends of an m sequence and for the CH carbon in the monomer unit located at the center of an mm sequence, respectively.

Next, the CN group having a double bond nature induces a magnetic field and gives a

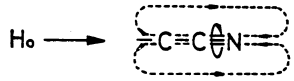


Figure 2. Schematic representation of the shielding effect on a carbon nucleus in an isolated CN group. H_0 denotes the external magnetic field: ----→, induced magnetic field; ——→, circular current.

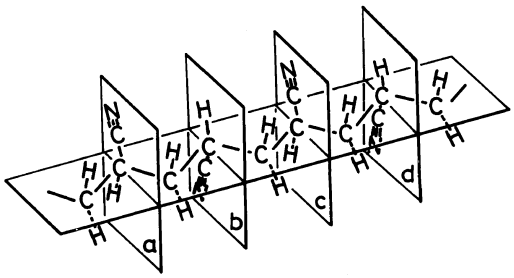


Figure 3. Schematic representation of a racemo sequence of polyacrylonitrile. The C–C≡N planes are almost parallel to each other and perpendicular to the molecular axis.

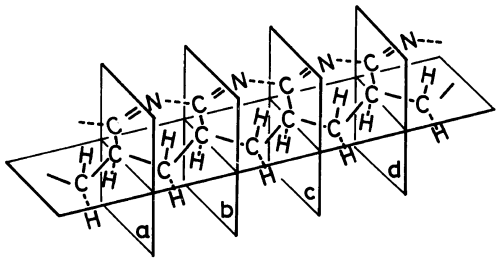


Figure 4. Schematic representation of a meso sequence of polyacrylonitrile in a *trans–trans* conformation. A CN group interacts with the adjacent CN group to form a six-membered ring and the CN group projects out of the plane *a—d*.

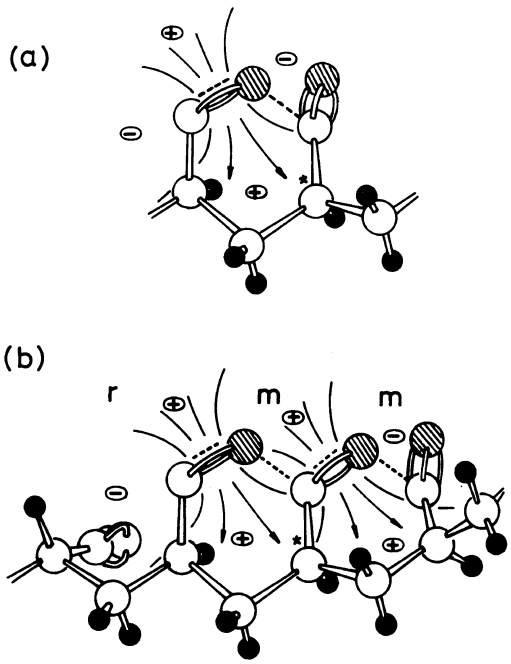


Figure 5. Schematic representation of the shielding (+) and deshielding (−) areas induced by the double bond nature of a CN group in an almost *trans–trans* conformation: a, the case of an m sequence (CH carbon marked by * is shielded); b, the case of rmm (CH carbon marked by * is shielded from two CN groups having a double bond nature and CN group in a monomer unit connected to an m sequence in an r arrangement is deshielded and further an m sequence does not influence the CH carbon in question). ○, carbon; ▨, nitrogen; ●, hydrogen.

Table I. Relative chemical shifts and relative positions of given CN carbons in the triad sequences of R-PAN

Triad sequence		Relative chemical shift[a]	Relative position[b]
Name	Schematic expression		
Syndiotactic	●r○*r●	0	1
Heterotactic	●r○*m○ ○m○*r●	$\delta+\sigma_1$	2
Isotactic	○m○*m○	$\delta+2\sigma_1$	3

[a] Relative chemical shift was given to the CN carbon in the monomer unit marked by *.
[b] Number was given from the higher magnetic field peak.
r and m means racemo and meso configurations, respectively.

Table II. Relative chemical shifts and relative positions of given CH carbons in the triad sequences of R-PAN

Trial sequence		Relative chemical shift	Relative position
Name	Schematic expression		
Syndiotactic	●r○*r●	0	3
Heterotactic	●r○*m○ ○m○*r●	$-\omega+\delta'-\varepsilon'$	2
Isotactic	○m○*m○	$-2\omega+\delta'-2\varepsilon'$	1

strong shielding effect on the CH carbon belonging to the adjacent monomer unit (see, Figure 5a). Contrary to this, a deshielding effect is caused on a CN group of the adjacent monomer unit which is connected to an m sequence in question in an r arrangement, as shown in Figure 5b. We define the former effect on the CH carbon as parameter $-\varepsilon'$ and the latter effect on the CN carbon as ε. Figures 5a and 5b were drawn by assuming a conformation slightly deviated from a *trans–trans* conformation. For the CH carbons shown in Figures 5a and 5b (symbolized by *), $-\varepsilon'$ and $-2\varepsilon'$ are assigned, respectively. For the CN carbon belonging to a monomer unit connected to an m or mm sequence in an r arrangement, only ε is assigned because its magnitude in both cases seems to be the same as shown in Figures 5a and 5b.

These parameters δ, σ, ε, δ' ε', and ω are positive and can be expressed in ppm unit. Using the assumptions (1)—(4) and parameters, we can qualitatively estimate the NMR peak position of a given carbon atom of CN or CH in a monomer unit, relative to that for the CN or CH carbon positioned at the center in an rr sequence. Tables I and II show the schematic expression of a triad configuration and relative chemical shifts of carbons belonging to CN and CH groups in a monomer unit

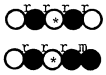
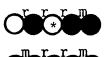
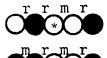
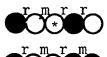
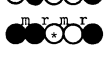
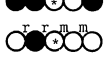
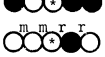
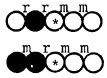
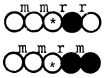
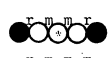
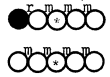
Table III. Peak assignment of CN and CH carbons in relation to triad tacticity of R-PAN and comparison of the observed fractions with thoery

Carbon species	Triad sequence	Peak in ppm	Observed fraction	Bernoulli statistics A[a]	Bernoulli statistics B[b]	$4IS/H^2$ [c]
CN	rr (S)[d]	120.06[g]	0.243	0.217	0.234	
	mr (H)[e]	120.40[g]	0.491	0.498	0.500	1.07
	mm (I)[f]	120.71[g]	0.266	0.285	(0.266)	
CH	mm (I)[f]	27.90	0.285	(0.285)	0.266	
	mr (H)[e]	28.53	0.490	0.498	0.500	1.07
	rr (S)[d]	29.09	0.225	0.217	0.234	

[a] Calculated by using pm′ = 0.534.
[b] Calculated by using pm = 0.516.
[c] Calculated from the observed fractions for triads.
[d] S means syndiotactic.
[e] H means heterotactic.
[f] I means isotactic.
[g] central peak.
Values in parentheses were used in calculation of pm and pm′.

(symbolized by $*$) centered at the triad configuration as well as the numbering of the peak positions from a higher magnetic field. For the CN carbon in mr (or rm), $\delta+\sigma_1$ is assigned because the CN carbon is involved in an m sequence ($+\delta$ for the disappearance of a shielding effect induced by the change of an isolated CN group to CN with a double bond nature) and its electron density decreases ($+\sigma_1$). For the CN carbon in an mm sequence, $\delta+2\sigma_1$ is assigned because the CN carbon is involved in an m sequence ($+\delta$) and influenced by the electron density decreasing effect from both sides of an m sequence ($+2\sigma_1$). Thus, it is obvious that CN carbon peaks must correspond to S, H, and I triad peaks from a higher magnetic field. For the CH carbon in mr (or rm), $-\omega+\delta'-\varepsilon'$ was assigned because of the disappearance of a shielding effect ($+\delta'$), the effect of increasing apparent electron density from one m sequence ($-\omega$) and the shielding effect from one m sequence ($-\varepsilon'$). In the same manner, $-2\omega+\delta'-2\varepsilon'$ was assigned to the CH carbon in a monomer unit at the center of an mm sequence. The constant term 2 for ω and ε' expresses the effect from two monomer units at both sides in an m sequence. The latter chemical shift is obviously smaller than the former one. Since δ' is thought to be nearly equal to δ, and δ is almost zero as explained latter, CH carbon peaks must correspond to the I, H, and S triad peaks from a higher magnetic field. These results suggest that the assignment given by Inoue *et al.*[14] is acceptable. On the basis of our assignment, the triad fraction was determined from the CN peak envelope or CH peak area ratio shown in the 4th column of Table III. In the same table, observed peak positions (in the 3rd column) and the calculated triad fractions, assuming the Bernoulli trial process, using pm and pm′ determined from the experimental I fractions (pm or pm′ $=I^{1/2}$) of CN and CH peak areas, respectively, are listed. Also the values of $4IS/H^2$, which become unity when the polymerization process obeys Bernoulli statistics, are included in the table. As seen from the table, the observed and calculated values are in good agreement and also $4IS/H^2=1$ with pm $\cong 0.5$, verifying the randomness of the polymerization employed here. From the observed peak

Table IV. Relative chemical shifts and relative positions of given CN carbons in the pentad sequences of R-PAN

Base triad	Schematical expression of pentad sequence		Relative chemical shift[a]	Relative position[b]
S			0	1
			ε	2
			2ε	3
H			$\delta+\sigma_1$	1
			$\delta+\sigma_1+\varepsilon$	2
			$\delta+\sigma_2$	3
			$\delta+\sigma_2+\varepsilon$	4
I			$\delta+2\sigma_1$	1
			$\delta+\sigma_1+\sigma_2$	2
			$\delta+2\sigma_2$	3

[a] Relative chemical shift was given to the CN carbon in the monomer unit marked by *.

[b] Number was given from the higher magnetic field peak within a pentad group constituted on a base triad. S, H, and I mean syndio-, hetero-, and isotactic, respectively. r and m mean racemo and meso configurations, respectively.

interval and relative chemical shift expressed by the parameters, the values of σ_1 and δ are estimated to be about 0.31 and 0.03, respectively. $\varepsilon'+\omega$ and δ' are estimated to be about 0.63 and 0.07, respectively. Thus, δ and δ' are nearly equal to zero.

Table IV shows the schematic expression of the pentad configurations constituted by adding a monomer unit in an m or r arrangement to both sides of the given triad sequences shown in Table I and the relative chemical shift of the carbon belonging to a CN group in a given monomer unit (symbolized by *) as well as the numbering of the peaks from a higher magnetic field. As an example of the calculation of the relative chemical shift, the case of the CN carbon located at the center of an mmrm sequence is shown as follows. Add δ because the CN carbon is involved in an m arrangement (disappearance of the shielding effect by the change of the isolated CN group to the CN group having a double bond nature), add σ_2 because the CN carbon in question has an mm sequence, and further add ε because the CN carbon-containing monomer unit is connected to an m sequence in the r arrangement; the total becomes $\delta+\sigma_2+\varepsilon$. Using assumption (5), it is very easy to number the relative chemical shifts expressed by δ, σ, and ε within a pentad sequence group constituted based on a given triad configuration (I, H, or S) except for the order of rmrm and mmrr sequences. Then, we can assign the observed CN carbon peaks schematically shown in Figure 6. From the observed peak intervals between rrrr and mrrr and between mmmm and mmmr peaks, we can estimate ε and $\sigma_2-\sigma_1$ to be equal to about 0.1 ppm. σ_1 and δ were already estimated to be about 0.31 and 0.03 ppm. Therefore, the peak interval between rmrr and mrrm ($\delta+\sigma_1-2\varepsilon$) and that between rmmr and mmrm ($2\sigma_1-\sigma_2-\varepsilon$) are always positive, showing that assumption (5) is valid. This means that the peak assignment shown in Figure 6 is reasonable. Then, the magnitudes of the parameters, estimated from the peak intervals between arbitrarily chosen two peaks are as follows: $0.07\leqq\varepsilon\leqq0.12$, $0.31\leqq\sigma_1\leqq0.42$, $0.38\leqq\sigma_2\leqq0.52$, and $0.03\leqq\delta\leqq0.06$, hence $\sigma_2>\sigma_1>\varepsilon>\delta$.

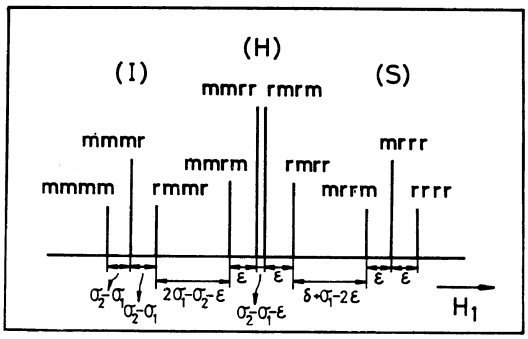


Figure 6. Schematic representation of relative chemical shifts in the CN carbon region by the parameters.

Table V shows the pentad configurations, their chemical shifts, their fractions experimen-

Table V. Peak assignment of CN carbons in relation to pentad tacticity of R-PAN and comparison of the observed fractions with theory

Base triad	Pentad sequence	Peak in ppm	Observed fraction	Bernoulli statistics[a]
	mmmm	120.81	0.076	0.070
I	mmmr	120.71	0.126	0.132
	rmmr	120.64	0.064	0.062
	mmrm	120.47	0.126	0.132
H	mmrr } rmrm }	120.40	0.268	0.250
	rmrr	120.30	0.097	0.118
	mrrm	120.18	0.064	0.062
S	mrrr	120.06	0.119	0.118
	rrrr	119.96	0.060	0.055

[a] Calculated by using pm = 0.516.

tally determined from the peak area ratios, and the theoretical fractions calculated by assuming the Bernoulli trial process using the pm employed before. Obviously, the experimental and calculated values are in excellent agreement, showing that our assignments and basic considerations are pertinent. The conformation for the m part of R-PAN introduced in this study is still tentative with only a little by-evidence and is open to further detailed study.

REFERENCES

1. R. Yamadera and M. Murano, *J. Polym. Sci., B*, **3**, 821 (1965).
2. K. Matsuzaki, T. Uryu, K. Ishigure, and M. Takeuchi, *J. Polym. Sci., B*, **4**, 93 (1966).
3. J. Bargon, K. H. Hellwege, and U. Johnsen, *Kolloid-Z.*, **213**, 51 (1966).
4. K. Matsuzaki, T. Uryu, M. Okada, K. Ishigure, T. Ohki, and M. Takeuchi, *J. Polym. Sci., B*, **4**, 487 (1966).
5. R. Yamadera and M. Murano, *J. Polym. Sci., B*, **5**, 333 (1967), *J. Polym. Sci., A-1*, **5**, 1095, 1855 (1967).
6. T. Yoshino, H. Kenjo, and K. Kuno, *J. Polym. Sci., B*, **5**, 703 (1967).
7. G. Svegliad, G. Talamini, and G. Vidotto, *J. Polym. Sci., A-1*, **5**, 2875 (1967).
8. M. Murano, *Makromol. Chem.*, **112**, 281 (1968).
9. K. Matsuzaki, T. Uryu, M. Okada, and H. Shiriki, *J. Polym. Sci., A-1*, **6**, 1475 (1968).
10. K. Matsuzaki, M. Okada, and T. Uryu, Preprint of the 19th Polymer Symposium of the Society of Polymer Science of Japan, October 1970 Kyoto 21D04.
11. K. Matsuzaki and M. Okada, *J. Polym. Sci., A-1*, **10**, 823 (1972).
12. K. Matsuzaki, M. Okada, and T. Uryu, *J. Polym. Sci., A-1*, **9**, 1701 (1971).
13. J. Schaefer, *Macromolecules*, **4**, 105 (1971).
14. Y. Inoue and A. Nishioka, *Polym. J.*, **3**, 149 (1972).
15. P. E. MoMahon and W. C. Tincher, *J. Mol. Spectros.*, **15**, 180 (1965).
16. K. Kamide, H. Yamazaki, K. Okajima, and K. Hikichi, unpublished result (to be submitted to *Polym. J.*).
17. K. Kamide, Y. Miyazaki, and H. Yamazaki, unpublished results.