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Assignment of finely resolved ^{13}C NMR spectra of polyacrylonitrile

Kaname Katsuraya[a,*], Kenichi Hatanaka[a], Kei Matsuzaki[a,1], Masatomo Minagawa[b]

[a]*Institute of Industrial Science, University of Tokyo, Roppongi, Minatoku, Tokyo 106-8558, Japan*
[b]*Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa 992-8510, Japan*

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Abstract

Finely resolved ^{13}C NMR spectra of atactic and isotactic-rich polyacrylonitriles were determined. Assignments of nitrile carbon spectra with pentads were quantitatively confirmed. Methylene carbon spectra were assigned with hexads. Radically obtained polymer obeyed Bernoullian statistics. The polymerization mechanism of isotactic-rich polymer obtained from urea–canal complex is complicated and both the first and the second-order Markov statistics do not hold. The chemical shifts of nitrile carbon signals moved considerably toward up-field as the temperature is raised, due to change of solvation.

Keywords: Polyacrylonitrile; ^{13}C NMR assignment; Solvation

1. Introduction

Since Bovey et al. [1] and Nishioka et al. [2] determined proton NMR spectra of poly(methyl methacrylate), both proton and ^{13}C NMR spectra of most vinyl polymers have been measured. Matsuzaki et al. [3] summarized NMR spectra of polymers and their assignments. However, since the NMR spectra of even simple vinyl polymers have not been fully assigned, reinvestigation of the NMR spectra with a high frequency apparatus (500–600 MHz) and with new NMR techniques such as heteronuclear chemical shift correlation–total correlation spectroscopy (HETCOR–TOCSY) seems necessary. In our previous article [4,5], ^{13}C NMR spectra of poly(vinyl acetate) and poly(vinyl alcohol) were reinvestigated and new assignments were given. In this paper we reinvestigated ^{13}C NMR spectra of polyacrylonitrile (PAN).

The stereoregularity of PAN was first determined by Matsuzaki et al. [6–8] from proton NMR spectra of deuterated polymers and established that the radically obtained polymer has an atactic structure. Yoshino et al. [9], Matsuzaki et al. [7,8] and later Minagawa et al. [10] established that PAN obtained by X-ray or gamma-ray irradiation polymerization of urea–canal complex [11] has an isotactic-rich structure. The observation of ^{13}C NMR spectra of PAN confirmed the above conclusion. The nitrile carbon spectrum was assigned with triads [12], pentads [13] and partly with heptads [14]. The methine carbon spectrum was assigned with triads [15]. The methylene carbon was assigned with tetrads [16] but the spectra were not shown.

In the course of our investigation [17], it was found that methine proton signals (triads) in DMSO-d_6 split into pentads with increasing temperature from 120 to 150°C. In the present paper, finely resolved spectra of PANs with atactic and isotactic-rich structures were assigned. Further, the problem whether splitting of carbon signals take place or not at high temperatures, is investigated.

2. Experimental

2.1. Samples

Radical polymerization of acrylonitrile gives only atactic polymers independent of polymerization temperature and solvents [7]. Anionic polymerization usually gives atactic polymers as radical polymerization [14]. In contrast, with radiation polymerization of urea–canal complex, a little isotactic-rich to highly isotactic polymers (mm = 87%)are obtained by varying polymerization conditions [14,18]. Two samples were used. An atactic polymer (A-PAN) was obtained by radical polymerization of the monomer in toluene at 60°C with azobisisobutyronitrile as catalyst. An isotactic-rich polymer (I-PAN) was obtained by gamma-ray irradiation of urea–canal complex at −78°C. The triads of the polymers are shown in Table 1 as determined from methine carbon spectra.

* Corresponding author. Tel.: +81-3-3402-3060; fax: +81-3-3402-3067.
E-mail address: katuraya@iis.u-tokyo.ac.jp (K. Katsuraya).
[1] Present address: 4-10-10, Naritahigashi, Suginamiku, Tokyo 166-0015, Japan.

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Table 1
Assignment for methine carbon spectra of PAN

Peak no.	Chemical shift (ppm)	Assignment	A-PAN observed[a]	I-PAN observed[b]
1	27.31	rr	0.238	0.152
2	26.88	mr	0.503	0.366
3	26.40	mm	0.259	0.482

[a] $P_{mr} = 0.493$, $P_{rm} = 0.514$ and $P_{mr} + P_{rm} = 1.006$.
[b] $P_{mr} = 0.275$, $P_{rm} = 0.546$ and $P_{mr} + P_{rm} = 0.821$.

2.2. NMR measurements

The 1D ^{13}C NMR spectra were recorded with a JEOL 500 LA spectrometer on DMSO-d_6 solution at 120 or 150°C. The data points were increased by zero-filling from 32 to 64 K.

3. Results and discussion

As shown in Figs. 1–3, finely resolved spectra, which enable quantitative determination of even pentads and hexads, are obtained. Fig. 1 shows methine carbon spectra indicating a tendency to splitting but not enough for detailed assignments. Table 1 shows triad tacticities of the samples, obtained from the spectra. For the assignments of other carbons, the intensities of n-ads were calculated assuming Bernoullian statistics for radically obtained polymer and first-order Markov statistics for I-PAN obtained from urea–canal complex.

Fig. 2 shows nitrile carbon spectra. The assignments with pentads made by previous investigators [13] were quantitatively confirmed for A-PAN by comparing the observed intensities with the calculated, as shown in Table 2.

For I-PAN, it was found that the observed intensities of rr (peaks 7–9) are larger than that obtained from methine carbon spectra. This is due to a larger intensity of rrrr pentad (peak 9) as shown in Fig. 2, but the reason is not clear at present. Therefore, the intensities of mm (peaks 1–3) and mr (peaks 4–6) pentads were adjusted to those obtained

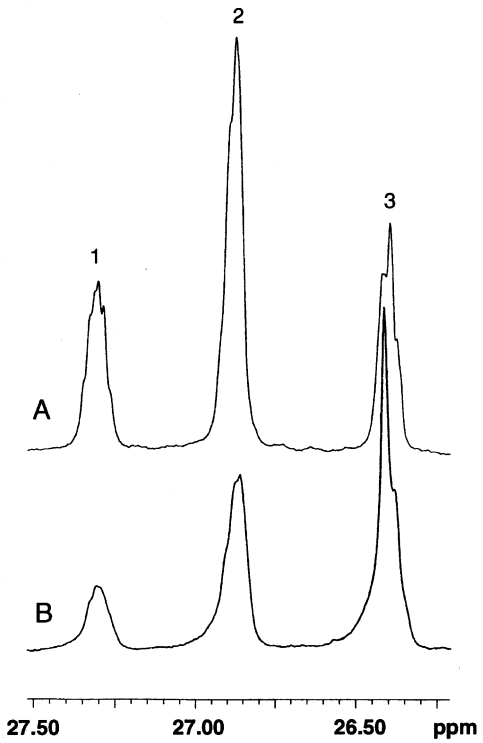

Fig. 1. ^{13}C NMR spectra of methine carbon region of PANs in DMSO-d_6 at 120°C: (A) atactic PAN(A-PAN); (B) isotactic-rich PAN(I-PAN).

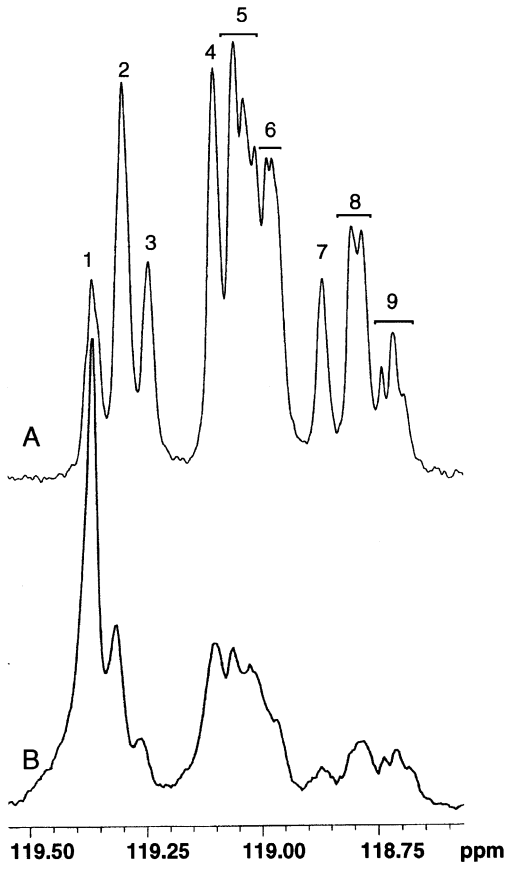

Fig. 2. ^{13}C NMR spectra of nitrile carbon region of PANs in DMSO-d_6 at 120°C: (A) atactic PAN(A-PAN); (B) isotactic-rich PAN(I-PAN).

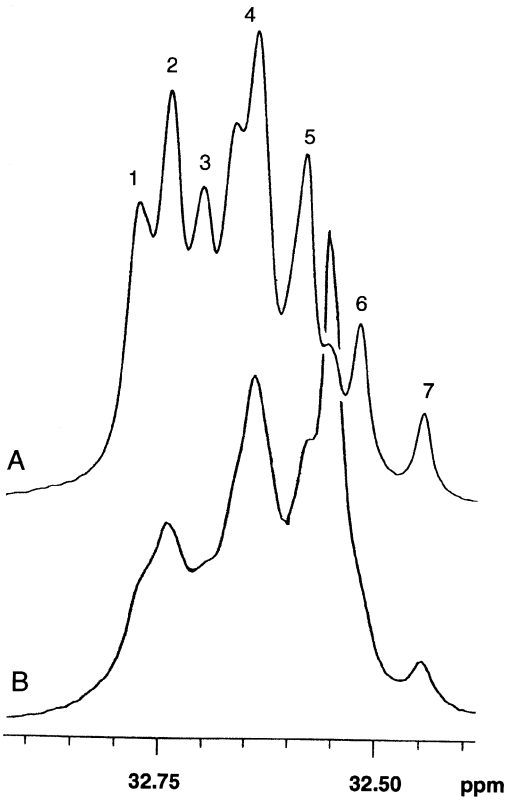

Fig. 3. ^{13}C NMR spectra of methylene carbon region of PANs in DMSO-d_6 at 120°C: (A) atactic PAN(A-PAN); (B) isotactic-rich PAN(I-PAN).

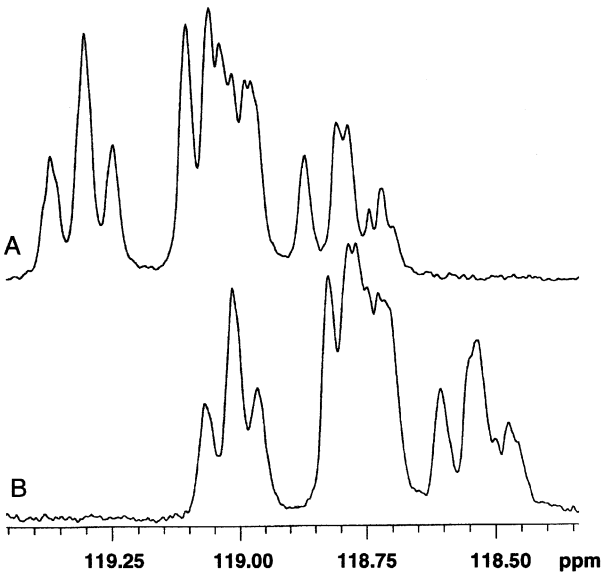

Fig. 4. ^{13}C NMR spectra of nitrile carbon region of atactic PAN in DMSO-d_6 at (A) 120°C; (B) 150°C.

from methine carbon spectra, that is, 0.482 and 0.366, respectively. In Table 2, the observed intensity of mmmm pentad is much larger than the calculated, indicating blocky formation of m linkages. Assumption of the second order Markov statistics for mmmm pentad gives $mmmm = mmm(P_{mmm}) = mm(P_{mmm})^2$. Putting the observed mmmm value in Table 2 and mm value in Table 1 into the equation leads to $P_{mmm} = 0.824$, which is much higher than $P_{mm} = 1 - P_{mr} = 0.725$. However, the calculated intensities of mmmr and rmmr assuming $P_{mmm} = 0.824$ did not agree with the observed. The polymerization mechanism of isotactic-rich PAN seems complicated.

Fig. 3 indicates methylene carbon spectra. The assignment has been carried out with tetrads [16] but the tetrads were not enough for the assignment. Careful inspection of Fig. 3 and comparison of the calculated hexad intensities with the observe intensities resulted the assignment shown in Table 3. Assignment for the pentamer model [13] was also taken into consideration. It is noteworthy that tetrads except rrr tetrad split into hexads constituting triplets with the same intervals (9.1 Hz). The agreement of the calculated intensities

Table 2
Assignment for nitrile carbon spectra of PAN

Peak no.	Chemical shift (ppm)	Assignment	A-PAN		I-PAN	
			Observed	Calculated[a]	Observed[b]	Calculated[c]
1	119.37	mmmm	0.071	0.067	0.327	0.253
2	119.30	mmmr	0.124	0.129	0.108	0.192
3	119.25	rmmr	0.067	0.063	0.046	0.037
4	119.10	mmrm	0.131	0.131	0.366	0.366
5	119.06	mmrr + rmrm	0.242	0.251		
6	119.98	rmrr	0.127	0.121		
7	118.86	mrrm	0.058	0.063	0.046	0.045
8	118.79	mrrr	0.112	0.119	0.066	0.075
9	118.72	rrrr	0.066	0.056	0.064	0.031

[a] Assuming Bernoullian statistics for $P_m = 0.510_5$.
[b] After adjusting mm and mr values to those obtained from methine carbon spectra.
[c] Assuming first-order Markov statistics for $P_m = 0.665$, $P_{mr} = 0.275$ and $P_{rm} = 0.546$.

Table 3
Assignment for methylene carbon spectra of PAN

Peak no.	Chemical shift (ppm)	Pentad	Assignment	A-PAN		I-PAN	
				Observed	Calculated[a]	Observed	Calculated[b]
1	32.78	rrr, rmr	rrr + mrmrm	0.155	0.148	0.216	0.255
2	32.75	mmr, mrr	mmmrm + mmrrm	0.147	0.130		
3	32.71	rmr, mrm	mrmrr + mmrmm	0.113	0.095	0.359	0.335
4	32.64	rmr, mmr, mrr, mrm	rrmrr + mmmrr + rmmrm + mmrrr + rmrrm + mmrmr	0.301	0.344		
5	32.59	mmr, mrr, mrm, mmm	rmrmr + rmmrm + rmrrr + mmmmm	0.181	0.185	0.424	0.411
6	32.52	mmm	mmmmr	0.069	0.066		
7	32.31	mmm	rmmmr	0.034	0.032	(0.037)	(0.027)

[a] Assuming Bernoullian statistics for $P_m = 0.510_5$.
[b] Assuming first-order Markov statistics for $P_m = 0.665$, $P_{mr} = 0.275$ and $P_{rm} = 0.546$.

with the observed is satisfactory for A-PAN except peaks 3 and 4. The discrepancy may be due to further splitting of the signals. For I-PAN, the agreement of the calculated intensities with the observed is good when considered that the calculated intensities of the signals are approximate.

In contrast to proton NMR spectra, change of the splitting of carbon signals with temperature (120 and 150°C) was not observed. However, at 150°C, a large up-field shift (0.28 ppm) of nitrile carbon absorptions (Fig. 4) was indicated. This is due to change of solvation of DMSO, which strongly bound to nitrile groups by dipole–dipole interactions, with increasing temperatures. Methine and methylene absorptions did not show a large change of chemical shifts; 0.12 ppm up-field for methine absorptions and almost zero for methylene absorptions.

References

[1] Bovey FA, Tiers GVD. J Polym Sci 1960;44:173.
[2] Nishioka A, Watanabe H, Abe K, Sono Y. J Polym Sci 1960;48:241.
[3] Matsuzaki K, Uryu T, Asakura T. NMR spectroscopy and stereoregularity of polymers. Tokyo and Basel: Japan Scientific Societies Press and Karger, 1986.
[4] Katsuraya K, Hatanaka K, Matsuzaki K, Yamaura K. Makromol Chem, Rapid Commun 2000;21:697.
[5] Katsuraya K, Hatanaka K, Matsuzaki K, Amiya S. Makromol Chem, Rapid Commun, in contribution.
[6] Matsuzaki K, Uryu T, Okada M, Ishigure K, Ohki T, Takeuchi M. J Polym Sci 1966;B4:487.
[7] Matsuzaki K, Uryu T, Okada M, Shiroki H. J Polym Sci 1968;6(A-1):1475.
[8] Matsuzaki K, Okada M, Uryu T. J Polym Sci 1971;9(A-1):1701.
[9] Yoshino T, Kenjo H, Kuno K. J Polym Sci, Polym Lett 1967;5:703.
[10] Minagawa M, Ute K, Kitayama T, Hatada K. Macromolecules 1994;27:3669.
[11] White DM. J Am Chem Soc 1960;82:5678.
[12] Schaefer J. Macromolecules 1971;4:105.
[13] Balard H, Fritz H, Meybeck J. Makromol Chem 1977;178:2393.
[14] Minagawa M, Yamada H, Yamaguchi K, Yoshii F. Macromolecules 1992;25:503.
[15] Inoue Y, Nishioka A. Polym J 1972;3:149.
[16] Neukam T, Wendish D. Angew Makromol Chem 1980;88:223.
[17] Matsuzaki K, Okada M. J Polym Sci 1972;10(A-1):823.
[18] Minagawa M, Miyano K, Takahashi M, Yoshii F. Macromolecules 1988;21:2387.