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Determination of Stereoregularity of γ-Irradiation Canal Polymerized Polyacrylonitrile by ^{1}H 2D *J*-Resolved NMR Spectroscopy

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Introduction

The determination of the stereoregularity of polyacrylonitrile (PAN) is difficult. Even for ordinary free radically prepared PAN, inconsistent results have been presented: syndiotactic,[1,2] syndiotactic rich,[3–6] and atactic.[7,8] The reason for this inconsistency has not been clarified.

Recently, ^{13}C NMR measurements have been carried out for many polymer systems. The first ^{13}C NMR spectra of PAN were reported by Schaefer,[9] and the peak assignments were given based on conformational considerations. Many researchers have used the assignments in an interpretation of their ^{13}C NMR spectra[10–15] without direct verification of the stereoregularity of PAN. In this Note, to clarify the stereoregularity of PAN, ^{1}H 2D *J*-resolved NMR measurements were carried out. In particular, urea canal polymerized PAN, which is estimated to be highly stereoregular (see Figure 1), was taken and investigated in detail. The applicability of this projection technique for vinyl polymers has been demonstrated by Gippert and Brown for poly(vinyl alcohol).[16]

Experimental Section

Materials. The samples were prepared by urea canal polymerization (C-1) and anionic polymerization (A-1). Characterization is given in Table 1. Details of sample preparation conditions are described in ref 15.

^{13}C and ^{1}H NMR Measurements. A JEOL JNM GX-500 NMR spectrometer was used with the following conditions: solvent, dimethyl-d_6 sulfoxide; concentration, 1%; temperature, 60 °C. Besides ordinary ^{13}C and ^{1}H NMR measurements, ^{1}H 2D *J*-resolved NMR measurements were made as follows. The spectra were obtained by diagonal projection of 2D *J*-resolved absolute value spectra as given in ref 17. The *J*-resolved experiment was carried out with a recycle time of 3.0 s using a $90°-t_1-180°-t_1-t_2$ pulse sequence. A total of 16 transients was accumulated for each t_1 value. The data matrix consisted of 32 spectra of 2048 points and was zero-filled to 128 × 2048 points covering 50 and 1000 Hz in the F_1 and F_2 dimensions, respectively.

Results and Discussion

Anomalous NMR Behavior of PAN among Vinyl Polymers. Generally, characterization of PAN is quite difficult with respect to its molecular structure and various physical and chemical properties.[18–20] Because of this difficulty, the structure of PAN has been discussed inclusively in analogy with other vinyl polymers such as poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA). However, we have obtained recently several experimental results which cast doubt on this point; various modified free radical and anionic polymerizations did not ensure stereoregular PAN,[21] although these conditions surely permitted stereoregular polymers in other vinyl monomers, including MMA.

Table 1. Characterization of Samples[a]

	polymerization conditions					
code	method	initiator	solvent	temp (°C)	viscosity (η (dL/g))[b]	T_{sol}[c] (°C)
C-1	canal	γ-ray		−78	0.82	138
A-1	anionic	DSTPB	THF	−60	2.26	20

[a] Key: DMF, *N,N*-dimethylformamide; THF, tetrahydrofuran; DSTPB, 1,4-disodio-1,1,4,4-tetraphenylbutane. [b] DMF, at 25 °C. [c] Dissolution temperature in DMF (see ref 14).

It is also clearly indicated in the correlation diagram of the CH$_2$ and CH groups in the ^{13}C NMR spectra (Figure 2). In this figure is indicated the variation of the chemical shift of the CH$_2$ and CH groups for vinyl polymers $-(CH_2-CHX)_n-$ as a function of the type of side groups. In the case of polymers having electron-donating side groups, such as CH_3, $CH{=}CH_2$, and C_6H_5, the methine signals appear at higher magnetic field than the methylene signals, whereas in polymers having electron-withdrawing side groups, such as Cl, OH, and OCH$_3$, the methine signals appear at lower magnetic field than the methylene signals (Figure 2). Although PAN has electron-withdrawing side groups, the methine signals appear at higher magnetic field than the methylene signals. This may be due to the anisotropic magnetic shielding effect of the $C{\equiv}N$ triple bond attached to the methine carbon.[12] This anomalous NMR behavior of PAN among vinyl polymers suggests that we must be cautious in the discussion of the structure and properties of PAN. Although Figure 2 was taken from a well-known NMR monograph,[22] this odd behavior of PAN has never been discussed in relation to the molecular structure of PAN.

Tacticity Characterization by ^{1}H NMR Measurements. If PAN has a regular head-to-tail linkage, ^{1}H NMR measurements will be very effective for this purpose. As far back as the 1960s, Bovey and Tiers reported that the stereoregularity of PMMA can be determined by high-resolution ^{1}H NMR spectra.[23] The CH$_2$ protons in isotactic diads are magnetically nonequivalent, while those in syndiotactic diads are magnetically equivalent.

^{1}H NMR spectra of two kinds of PAN are shown in Figures 3 and 4 (top). Although the two spectra are very different, particularly in the methylene proton signals, the remarkable difference (numbers of peak splitting) as has been observed in the spectrum of PMMA was not observed in this case. The spectral assignment of PAN from ordinary ^{1}H NMR spectra is impossible, and decoupling experiments are needed.

^{1}H 2D *J*-Resolved NMR Spectral Projection of Two Kinds of PAN. The 2D *J*-resolved NMR spectral projections are shown in Figures 3 and 4 (bottom). The methylene protons show multiplet signals in the 1D spectra due to the overlapping of several spin-coupled signals (Figures 3 and 4 (middle)). However, the 2D *J*-resolved NMR spectral projections became simple, which correspond to homonuclear broad-band spectra. Two main peaks at 2.11 and 2.19 ppm with almost equal intensity were observed in urea canal polymerized PAN as shown in Figure 3 (bottom), which should be assigned to nonequivalent methylene protons (the appearance of the

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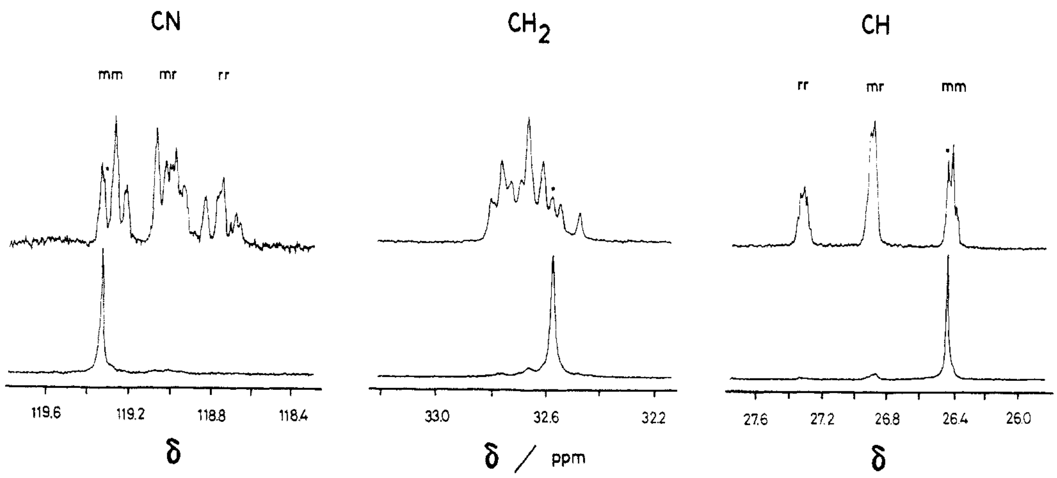

Figure 1. Comparison of 125-MHz ^{13}C NMR spectra of two kinds of PAN. Peak assignments were made according to Schaefer.[9] The ^{13}C NMR spectra of the samples differ significantly. Urea canal polymerized PAN (bottom) is estimated to be highly stereoregular, as evidenced also by the difference of solubility in solvent (see Table 1).

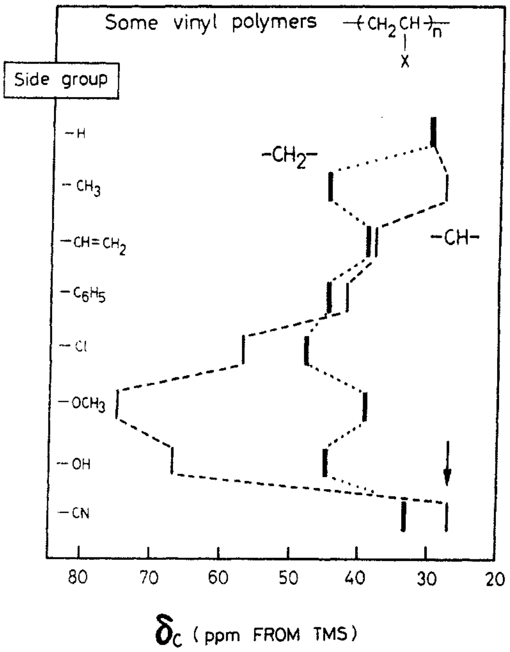

Figure 2. ^{13}C NMR chemical shift correlation diagram of the CH_2 and CH groups for some vinyl polymers.[22] Signals from methylene (CH_2) appear in the range 30–50 ppm, whereas those from methine (CH) vary significantly from 25 to 75 ppm. The chemical shifts of the former group are relatively constant, but the latter depend greatly on the type of side groups.

two peaks indicates that the predominant stereosequence in the γ-ray canal PAN is isotactic). Other minor signals observed in the background arise mostly from strong J-coupling between the geminal methylene protons,[24] although the minor contributions from the additional pairs of nonequivalent geminal protons which are different in longer tactic sequences might not be neglected. In the case of the anionic PAN (Figure 4, middle), it was also difficult to evaluate the tacticity from the methylene proton signals in the ordinary 1D spectrum. Three main peaks were observed in the projection spectrum, two (2.10 and 2.19 ppm) due to nonequivalent methylene protons of meso diads and one (2.13 ppm) due to the equivalent methylene protons of racemo diads. Thus, anionic PAN contains both nonequivalent (meso) and equivalent (racemo) methylene protons and has a low stereoregularity. The different chemical shifts for the meso methylene protons of these two PAN samples indicate that the chemical shift is sensitive to longer stereochemical sequences.

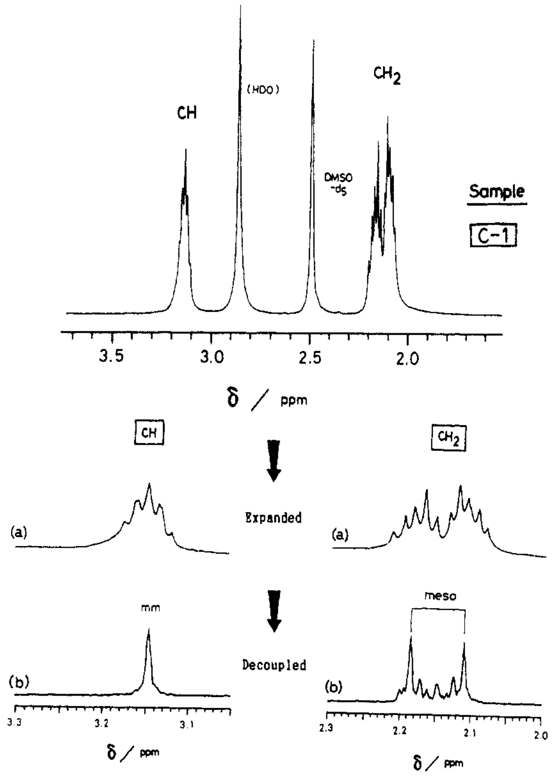

Figure 3. 500-MHz ^{1}H NMR spectra of urea canal polymerized PAN: (top) ordinary ^{1}H NMR spectra of the whole range; (middle) expanded spectra of the CH_2 and CH regions; (bottom) decoupled spectra of the CH_2 and CH regions. The decoupled spectra were obtained by projecting the 2D J-resolved spectrum onto the w_2 axis as described in ref 17.

The decoupled methine proton signals can also be reasonably explained in terms of the tacticity. In the γ-ray canal PAN, only one peak was observed at 3.15 ppm (Figure 3 (bottom)). This indicates a highly isotactic configuration, with the observed singlet attributed to mm triads. The methine signals of anionic PAN are broad multiplets (Figure 4 (bottom)). In the projection spectrum, three main peaks with small splittings were observed at 3.15, 3.17, and 3.19 ppm. Since the first one is due to mm triads, the other two can be assigned to be mr and rr triads,[25] respectively. From the above results, the anionic sample was much less stereoregular, though the tactic fractions could not be derived from the projection due to the lack of quantitativeness. The results obtained here strongly suggest that the tacticity assignments of PAN by Schaefer[9]

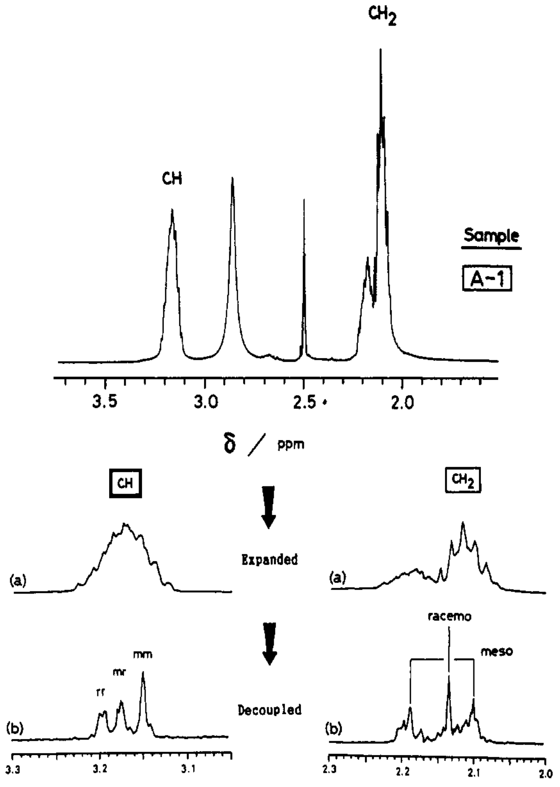

Figure 4. 500-MHz ^{1}H NMR spectra of anionic PAN. The symbols and their meanings are the same as those in Figure 3.

based on conformational consideration of ^{13}C NMR spectra are true.

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(25) These assignments are in good agreement with those shown in Figure 1. Strictly speaking, however, further detailed direct experimental confirmation is necessary for the mr and rr assignments, as criticized by one of the Reviewers.