Polymer Journal, Vol. 17, No. 12, pp 1291—1295 (1985)

NOTES

Pentad Tacticity of Polyacrylonitrile Polymerized by γ-Ray Irradiation on Urea–Acrylonitrile Canal Complex at −78°C

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(Received January 30, 1985)

KEY WORDS Polyacrylonitrile / Canal Complex / Pentad Tacticity / ^{13}C NMR spectrometer / Bernoulli Statistics / First-Order Markov Statistics /

Very recentry, we have successfully assigned all the CN carbon NMR peaks of polyacrylonitrile (PAN), prepared by radical polymerization with a redox catalyst (hereafter, referred to as R-PAN), proposing a method for evaluating its pentad tacticity by ^{13}C NMR analysis.[1] The stereoregularity of R-PAN was proved to obey the Bernoulli statistics. However, the CN carbon peaks responsible for the pentad sequences of mmrr and mrmr (here, m and r denote meso and racemo diads, respectively) in the R-PAN/deuterated dimethylformamide (DMF-d_7) system overlapped heavily with each other, thus preventing the correct assignment of the peaks of these pentad sequences.

This note, as an extension of the previous study,[1] intends (1) to evaluate the pentad tacticity of PAN, prepared by γ-ray irradiation on the urea-acrylonitrile canal complex at −78°C (hereafter, referred to as γ-PAN) and (2) to assign correctly the peaks for mmrr and mrmr sequences.

EXPERIMENTAL

Deuterated dimethyl sulfoxide (DMSO-d_6) was chosen as a solvent for ^{13}C NMR measurements on γ-PAN as well as R-PAN, because the solubility of γ-PAN into DMSO is unconditionally better than that in DMF at room temperature and the γ-PAN/DMSO system has no gel-like particles often found in a γ-PAN/DMF system.

γ-PAN was prepared in the following manner: One part of AN purified by extracting inhibitor (hydroquinone methyl ether) originally existing in AN with 2 wt% aq. Na_2CO_3 soln., and one part of urea recrystallized from methanol–water (1 : 4, v/v at 25°C) was mixed slowly at −20°C. The mixture was stored in the dark at −78°C for 6 days to give a urea canal complex. The complex thus obtained was wrapped with an aluminum foil and irradiated by γ-ray (total dose, 1.5 Mrad) at −78°C. The resultant was washed with excess water several times, dissolved in DMSO, and the whole polymer was precipitated with methanol. It was fractionated by a modified successive solution refractionation method into 20 fractions using DMSO as solvent and toluene as non-solvent. A fraction (polymer code 5—2) was employed because of relatively better resolution of NMR peaks. Note that the ratio of the integrated peak intensities for other fractionated γ-PAN samples is not significantly different from that for the γ-PAN used here. The γ-PAN used here had a weight-average molecular weight M_w of 26.3×10^4, determined by the light scattering method in DMSO at 25°C. The molecular characteristics of γ-PAN samples having almost the same stereoregularity in solution will be described elsewhere.[2]

A whole R-PAN sample used without fractionation was the same as employed in the previous work ($M_w = 16.8 \times 10^4$).[1]

^{13}C NMR measurements were made on an FT-NMR (JEOL, FX-400) spectrometer under the following operating conditions: Polymer concentration, 5 wt%; temperature, 80°C; pulse repetition, 5 s; pulse width, 10 μs (45°); number of pulse, 64 × 50. The strongest central methyl carbon peak (39.60 ppm) among septet peaks of DMSO-d_6 was taken as the reference. The fraction of the integrated peaks was estimated as follows: The NMR spectra with integrated curves, in which each peak position was definitively assigned with an arrow mark, were distributed to five staffs in our laboratories for fraction analysis. They independently estimated the fraction from the spectra and integrated curves by their own judgement (see, Figure 1c). The data reported were in good agreement within reading errors and finally the averaged values were taken in this work.

RESULTS AND DISCUSSION

Figure 1 shows the CN carbon region spectra of R-PAN/DMSO-d_6 and γ-PAN/DMSO-d_6. The figure contains the spectrum of R-PAN/DMF-d_7 reported elsewhere.[1] NMR pat-

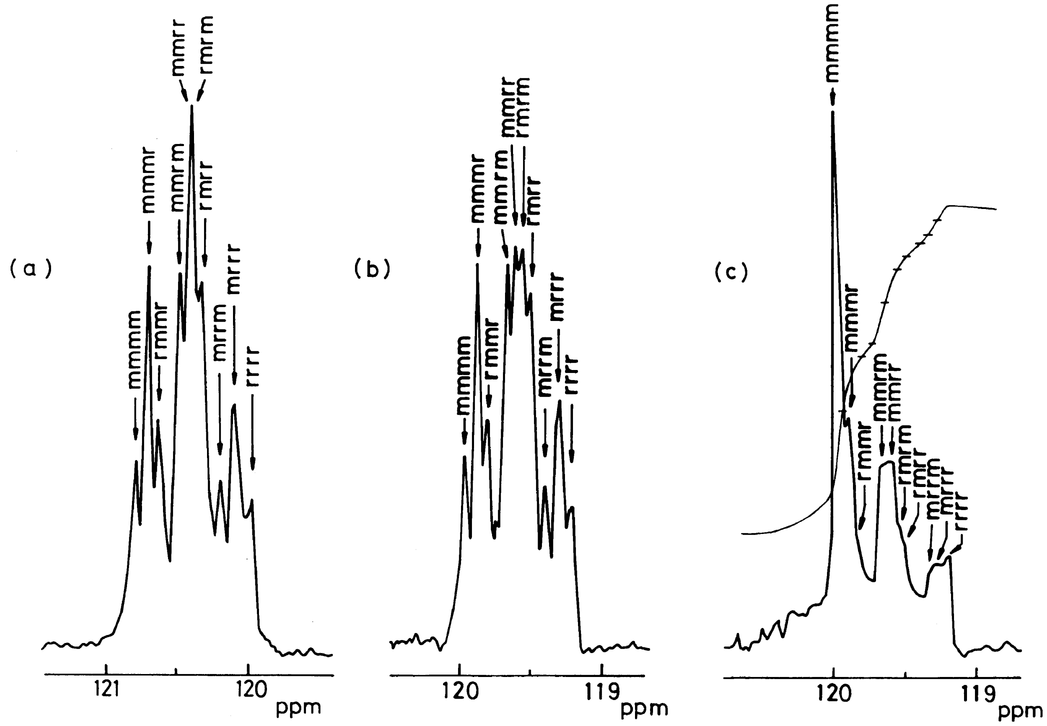

Figure 1. ^{13}C NMR spectra of polyacrylonitrile polymerized with a redox catalyst (R-PAN) and by γ-ray irradiation on the urea canal complex (γ-PAN) for CN carbon region. a, R-PAN in DMF-d_7; b, R-PAN in DMSO-d_6; c, γ-PAN in DMSO-d_6 (an example of an integral curve for the evaluation of pentad tacticity is shown). m and r mean meso and racemo configurations, respectively.

terns for R-PAN/DMF-d_7 and R-PAN/DMSO-d_6 are quite similar and all the CN carbon peaks in the R-PAN/DMSO-d_6 system appear by 0.76—0.86 ppm higher than those in the R-PAN/DMF-d_7 system. This strongly suggests that the assignment previously made for the CN carbon peaks in the R-PAN/DMF-d_7 system can be applied to the R-PAN/DMSO-d_6 system without serious modification. The smaller but still significant difference in the chemical shifts of R-PAN in two solvents can be explained by the solvent effect[3] at least in part. The peaks due to mmrr and mrmr sequences of both R- and γ-PAN in DMSO-d_6 separate definitely, in contrast with the case of R-PAN/DMF-d_7 system. The chemical shifts of the CN carbon peaks for the γ-PAN/DMSO-d_6 system are almost the same as those for the R-PAN/DMSO-d_6 system (Table I). Accordingly, the peak assignment given for the R-PAN/DMF-d_7 system is also applicable to the γ-PAN/DMSO-d_6 system. Thus, the pentad tacticity of γ-PAN can be estimated by analyzing the intensity of the peaks assigned based on the pentad configurations. Table I summarizes the peak assignment for R-PAN/DMF-d_7, R-PAN/DMSO-d_6, and the γ-PAN/DMSO-d_6 systems. Concerning the peaks for mmrr and mrmr pentads, the lower magnetic field peak was assigned for the former, as explained later.

The second and 6th columns of Table II list the fractions of various pentad sequences of γ-PAN and R-PAN in DMSO-d_6, determined

Table I. Peak assignment of CN carbon for R-PAN and γ-PAN in different solvents

Base triad	Pentad sequence	R-PAN (ppm) DMF-d_7	R-PAN (ppm) DMSO-d_6	γ-PAN (ppm) DMSO-d_6
I	mmmm	120.81	119.95	119.96
	mmmr	120.71	119.87	119.89
	rmmr	120.64	119.80	119.80
H	mmrm	120.47	119.65	119.66
	mmrr	120.40	119.60	119.59
	rmrm		119.56	119.55
	rmrr	120.30	119.50	119.51
S	mrrm	120.18	119.39	119.34
	mrrr	120.06	119.29	119.27
	rrrr	119.96	119.20	119.19

Table II. Comparison of the observed pentad fractions for γ-PAN and R-PAN with those calculated by Bernoulli and first-order Markov statistics

Pentad sequence	γ-PAN/DMSO-d_6 Observed	γ-PAN/DMSO-d_6 Theoretical Bernoulli (Triad method)[a]	γ-PAN/DMSO-d_6 Theoretical 1st-order Markov (Triad method)[b]	γ-PAN/DMSO-d_6 Theoretical 1st-order Markov (Pentad method)[c]	R-PAN/DMSO-d_6 Observed	R-PAN/DMSO-d_6 Theoretical Bernoulli (Triad method)[d]
mmmm	0.373	0.332	0.359	0.374	0.077	0.073
mmmr	0.162	0.221	0.191	0.185	0.125	0.134
rmmr	0.041	0.033	0.025	0.023	0.068	0.062
mmrm	0.121	0.211	0.137	0.121	0.125	0.134
mmrr	0.101	0.067	0.105	0.110	0.097	0.125
rmrm	0.041	0.067	0.036	0.030	0.149	0.125
rmrr	0.043	0.021	0.028	0.027	0.129	0.116
mrrm	0.025	0.033	0.038	0.036	0.055	0.062
mrrr	0.046	0.021	0.058	0.065	0.112	0.116
rrrr	0.047	0.003	0.022	0.029	0.065	0.054
$\delta \times 10^3$	—	13.11	5.19	4.58	—	4.39

[a] $P_m=0.759$; [b] $P(r/m)=0.210$, $P(m/r)=0.565$; [c] $P(r/m)=0.198$, $P_m(m/r)=0.524$; [d] $P_m=0.519$.

experimentally from the integral curve under the corresponding NMR peaks. Here, mmmm fraction includes a peak envelope appeared at the lower magnetic field than the peak for mmmm sequence. The reading errors included in determining the fractions for mmmm, mmmr, rmmr, mmrm, mmrr, rmrm, rmrr, mrrm, mrrr, and rrrr are ± 1.7, 3.6, 10.0, 5.3, 6.3, 16.0, 13.3, 26.6, 13.3 and 12.5%, respectively.

We calculated the fractions of pentad sequence of γ-PAN and R-PAN in DMSO-d_6 by assuming Bernoulli or first-order Markov statistics. For this, the following fundamental parameters should be evaluated in advance: the probability of meso arrangement, P_m, in Bernoulli statistics and the probabilities that a monomer unit adds to a meso sequence in a racemo arrangement, P(r/m), and that a monomer unit adds to a racemo sequence in a meso arrangement, P(m/r), in the first-order Markov statistics.

P_m, P(r/m) and P(m/r) can be readily derived using the isotactic (I), heterotactic (H) and syndiotactic (S) triad fractions.[4] The summation of the experimentally determined fractions of mmmm, mmmr, and rmmr was used for the I fraction, the summation of the fractions of mmrm, mmrr, rmrm, and rmrr for the H fraction and the summation of the fractions of mrrm, mrrr, and rrrr for the S fraction. The method to obtain the parameters P_m, P(r/m), and P(m/r) from the observed triad fractions is simply referred to as the triad method. We obtained I=0.576, H=0.306, and S=0.118 for γ-PAN. These values are quite different from those for R-PAN (*i.e.*, I=0.27, H=0.500, and S=0.232). From these results, meso diad fractions of γ- and R-PAN were estimated to be about 70 and 50%, respectively.

In the third and 4th columns of Table II, the theoretical fractions of the pentad sequence for γ-PAN, evaluated by the triad method, are compiled. In the seventh column, theoretical (by Bernoulli statistics) fractions for the R-PAN/DMSO-d_6 system is also included.

In order to judge which statistics are more reasonable to explain the pentad sequence of the polymer, we introduce a parameter δ, defined by

$$\delta=\frac{\sqrt{\sum_{i=1}^{N}(X_i-Y_i)^2}}{N} \tag{1}$$

where X_i and Y_i are the experimental and calculated fractions for a specific pentad sequence, respectively, and N is the total number of pentad sequence (*i.e.*, 10). δ values obtained by the triad method are shown in Table II.

There is an alternative approach to estimate P(r/m) and P(m/r), utilizing directly the experimental pentad fraction data (this is referred to as the pentad method). We can determine the most probable combination of P(r/m) and P(m/r) so as to minimize δ. Here, Y_i in eq 1 is calculated assuming arbitrary values of P(r/m) and P(m/r).

Figure 2 shows the correlation between P(r/m), P(m/r), and δ for γ-PAN. The number on the line denotes the value of $\delta\times10^3$. The filled mark is the most reasonable combination of P(r/m) and P(m/r) (*i.e.*, P(r/m)=0.198 and P(m/r)=0.524) and the unfilled mark is the corresponding value evaluated by the triad method (*i.e.*, P(r/m)=0.210 and P(m/r)=0.565).

Using the most reasonable combination of P(r/m) and P(m/r) thus obtained, the theoretical fractions of pentad sequence were calcu-

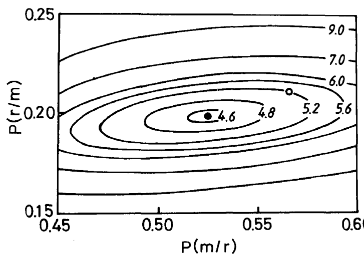

Figure 2. Correlationships between P(r/m), P(m/r) and δ: ○, the combination of P(r/m) and P(m/r) determined from the observed triad fractions; ●, the most reasonable combination of P(r/m) and P(m/r); number on each line denotes value of $\delta\times10^3$.

lated. The results are shown in the 5th column of Table II.

δ for the first-order Markov statistics is quite smaller than that for Bernoulli statistics (13.11×10^{-3}), even if the error contained in determining the observed triad fractions (± 3, 8, and 15% for I, H, and S, respectively) is taken into consideration. This measn that the pentad sequence of γ-PAN obeys approximately the first-order Markov statistics. In the case of γ-PAN, δ value (5.19×10^{-3}) for the triad method is a little higher than that (4.58×10^{-3}) for the pentad method, but the difference is not so significant. When the reading errors contained in the observed pentad and triad fractions are considered, the values of P(r/m) and P(m/r) for γ-PAN calculated by the triad method may have an uncertainty of ± 0.018 and 0.055 and those calculated by the pentad method may have an uncertainty of ± 0.008 and 0.012, respectively. The difference in P(r/m) (or P(m/r)) between the two methods is negligible within the above uncertainty, leading to the conclusion that both the triad and pentad methods give reasonable values of P(r/m) and P(m/r). The pentad sequence of R-PAN can be explained by Bernoulli statistics because the summation of $P(\mathrm{r/m}) = 0.519$ and $P(\mathrm{m/r}) = 0.488$ calculated by triad method is almost unity.

The calculated fractions for mmrr and mrmr in γ-PAN based on Markov statistics indicate that the intensity for the mmrr peak should be higher than that for the mrmr peak. It is concluded for the assignment of mmrr and mrmr pentads that a lower magnetic field peaks is assigned to the mmrr pentad and a higher magnetic field peak to the mrmr pentad.

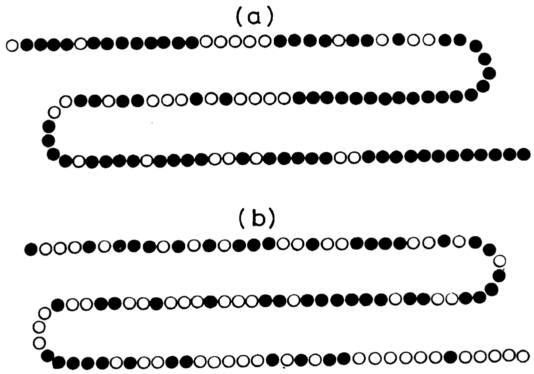

Figure 3. Examples of γ-PAN (a) and R-PAN (b) sequences: ○, racemo diad; ●, meso diad.

Figure 3 shows examples of the computer-simulated sequences for γ-PAN and R-PAN, satisfying the observed pentad fractions. In the figure, the open circle denotes the racemo diad and the closed circle, the meso diad. It is obvious that the γ-PAN molecule has a long meso sequence as block parts.

The detailed data on pentad tacticity of γ-PAN, presented here, will be very helpful for a better understanding of its polymerization mechanism and its characteristics molecular properties in solution.

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