SHORT COMMUNICATION

Carbon-13 NMR Analysis of the Tacticity of Polyacrylamide

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Polyacrylamide (PA) and its derivatives are of great use as polymer gels for electrophoretic analysis, polymer agglutinant, and paper reinforcement. Solution properties of PA have been extensively studied. However, no attempt has been made to elucidate quantitatively the microstructure of PA except by Gupta and Bansil.¹ These authors suggested qualitatively, on the basis of polarized Raman, Infrared, and proton NMR spectra, and group theoretical calculations, that a PA prepared by free-radical polymerization has a structure dominated by isotactic species.

In this letter, we wish to report the first determination of triad tacticity of PA by carbon-13

NMR. Two PA samples were used for this purpose. PA-A (reported degree of polymerization was about 18000) was obtained from Wako Pure Chemical Industries, Ltd. and used without further purification. PA-B was prepared by free-radical polymerization as follows: Acrylamide monomer was recrystallized from a benzene solution. The solution consisting of 270 mg acrylamide, 2 ml benzene, 1 ml dioxane, and 10 mg azobisisobutyronitrile was heated at 60°C for 4 h and the resulting PA was washed successively with methanol, acetone, and benzene. The final yield after drying *in vacuo* was 220 mg.

Carbon-13 NMR spectra of PA were obtained

Figure 1. Proton-decoupled carbon-13 NMR spectrum of 10% (w/v) PA-B in $^2\text{H}_2\text{O}$ at 25.1 MHz and 100°C, after 3000 accumulations of time domain signals with a 90° pulse recycle time of 1.5 s. Chemical shifts are expressed in ppm with respect to external tetramethylsilane.

with a 10% (w/v) solution in deuterium oxide at 100°C, using a JEOL JNM PS-100 spectrometer equipped with a PFT-100 Fourier transform system operating at 25.1 MHz, a JEC-100 spectrum computer, and a noise-modulated proton decoupler. The spectra incorporated 4096 data points with a sweep width of 5000 or 2000 Hz. Chemical shifts were measured with respect to the resonance of internal *p*-dioxane, which was taken as 67.7 ppm downfield from the resonance of external tetramethylsilane. Carbon-13 spin-lattice relaxation times of the methine and methylene carbons were measured roughly by null methods to be 290 and 150 ms, respectively. The 90° pulse recycle times were chosen to be at least 5 times greater than these relaxation times. The carbon-13 NMR spectra were measured soon after the preparation of the solutions which were placed in 8 mm O.D. glass tubes.

The proton-decoupled carbon-13 NMR spectrum of PA-B is shown in Figure 1. On the basis of chemical shifts, spin-lattice relaxation time, and proton-decoupled spectrum, we assigned each resonance to the corresponding carbon as shown in Figure 1. The side chain carbonyl carbon shows a sharp resonance without any splitting. The appearance of this resonance did not change during the spectrum accumulation, and no new peak appeared at the end of as long a time accumulation as about 12 h. This suggests that no hydrolysis of the amide group occurred. In contrast to the resonance of the carbonyl carbon, those of the methine and methylene carbons were split into many peaks. The expanded and refined spectra for these resonances are shown in Figure 2. The methine and methylene resonances fall into three distinct peaks with asymmetrical peak intensities. Furthermore, the methine resonance showed a slight resolution corresponding to pentad splitting. Three peaks of the methylene resonance may result from partial overlapping of the six possible tetrad peaks. The commercial polymer PA-A gave no significant spectral differences from that of PA-B. There are two possible assignments for the three major methine and methylene peaks. These are as follows.

First Assignment

According to Gupta and Bansil¹ who reported that a PA has a structure dominated by isotactic species, the three major peaks of the methine resonance can be assigned to isotactic (*mm*), hetero-

Figure 2. Proton-decoupled carbon-13 NMR spectra of (A) PA-A and (B) PA-B, after 10000 accumulations with a 90° pulse recycle time of 3 s.

Table I. Triad tacticity of PA estimated from methine carbon resonance

Peak No.	1	2	3	4 (<i>mm</i>)(<i>rr</i>)
Assignments	(<i>mm</i>)	(<i>mr</i>)	(<i>rr</i>)	(<i>mr</i>) ²
PA-A	0.33	0.47	0.20	1.2
PA-B	0.32	0.47	0.21	1.2

tactic (*mr*), and syndiotactic (*rr*) triads from low to high fields. Here, *m* and *r* stand for meso and racemic diads, respectively. The *mr* resonance was assumed to appear between *mm* and *rr* resonances. This triad line order is the same as that of the

Table II. Relative intensities and assignments of methylene carbon resonance of PA

Peak No.		4	5	6
PA-A	Obsd Intensities	0.33	0.47	0.20
	Calcd Intensities ^a			
	Assignments I	(<i>mmm</i>) + (<i>mrm</i>)	(<i>mmr</i>) + (<i>mrr</i>)	(<i>rmr</i>) + (<i>rrr</i>)
		0.30	0.50	0.20
	Assignments II	(<i>rrr</i>) + (<i>mrr</i>)	(<i>mrm</i>) + (<i>rmr</i>) + (<i>mmr</i>)	(<i>mmm</i>)
		0.32	0.52	0.16
PA-B	Obsd Intensities	0.29	0.55	0.16
	Calcd Intensities ^a			
	Assignments I	(<i>mmm</i>) + (<i>mrm</i>)	(<i>mmr</i>) + (<i>mrr</i>)	(<i>rmr</i>) + (<i>rrr</i>)
		0.32	0.49	0.19
	Assignments II	(<i>rrr</i>) + (<i>mrr</i>)	(<i>mrm</i>) + (<i>rmr</i>) + (<i>mmr</i>)	(<i>mmm</i>)
		0.29	0.52	0.19

^a Calculated using the single parameter P_m to be 0.55 for PA-A and 0.57 for PA-B and assuming Bernoulli statistics.

methine resonance of poly(vinyl alcohol),² and is the reverse of those of poly(vinyl chloride)³ and polyacrylonitrile.⁴ Chemical shift assignments should, therefore, be made independently for each vinyl polymer system examined.⁵ Based on the first assignment, triad tacticities of PA-A and PA-B were estimated from the intensities of peaks in the methine resonance, and are tabulated in Table I. The triad tacticities show that the simple Bernoullian statistics is adequate for describing the stereospecificity of the polymerization: *i.e.*, the relation⁶

$$4(mm)(rr)/(mr)^2 = 1$$

holds approximately as listed in the last column of Table I. These results are in agreement with the usual observation that free-radical polymerization of vinyl monomers is usually controlled by Bernoullian statistics.²⁻⁸

Next we tried the assignments of three peaks of the methylene resonance by comparing the relative intensities with tetrad tacticities calculated from Bernoulli statistics. In the calculation, 0.55 and 0.57 were used as the values of P_m for PA-A and PA-B, respectively, where P_m is the probability that a growing polymer end will form a meso sequence with an incoming monomer. The observed relative intensities and two possible sets of tetrad assignments with calculated intensities are shown in Table II. At the present stage we cannot decide which of the two tetrad assignments is valid.

Second Assignment

Alternative assignments were made on the basis of the general but not universal observation that many of free radical polymers are predominantly syndiotactic.^{2-5,8} In this case, the three methine peaks were assigned to *rr*, *mr*, and *mm* triads from low to high fields. Thus, the line order is the reverse of those of the first assignments. Consequently, in the assignments of tetrad methylene peaks, *m* and *r* should be interchanged by *r* and *m*, respectively. These interchanges do not remove the Bernoullian characteristics of the intensity distribution.

At the present time we have no positive reason to prefer the first over the second assignment.

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