An Anomalous Tacticity−Crystallinity Relationship: A WAXD Study of Stereoregular Isotactic (83−25%) Poly(Acrylonitrile) Powder Prepared by Urea Clathrate Polymerization

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Received December 21, 2000

ABSTRACT: A detailed wide-angle X-ray diffraction (WAXD) study was carried out for a series of stereoregular poly(acrylonitrile)s (PANs) having different isotacticities (83−25%). The degree of crystallinity did not depend on the extent of their isotacticity, as confirmed by three WAXD evaluation procedures reported previously. However, the main peak shifted from 17.1 to 16.8°, and the half value width of the main peak decreased (1.70 to 0.97°) with an increase in stereoregularity. Drastic WAXD changes were observed when PAN was dissolved in a good solvent and recovered. The specific tacticity−crystallinity independent relationship of stereoregular PAN powder is discussed in connection with the polymerization mechanism in the urea clathrate at low temperatures.

Introduction

Stereoregular poly(acrylonitrile) (PAN) can be prepared by urea clathrate polymerization in its solid state at low temperatures.[1] The PAN obtained in this way has been proved to be essentially isotactic.[2−4] Although the samples are obtained in the form of a crystalline white powder, the morphological structure and various other physical properties in the solid state have never been investigated as a function of the extent of the steroregularity of PAN. The lack of such a basic study makes it difficult to understand the structure and properties of this unique polymer.

In this article, a wide-angle X-ray diffraction (WAXD) study of stereoregular isotactic PAN powders obtained by urea clathrate polymerization in the solid state has been described. In contrast with the behavior of other stereoregular polymers, the degree of crystallinity of PAN obtained by urea clathrate polymerization is independent of its stereoregularity.

Experimental Section

Samples. Isotactic PAN was prepared by γ-irradiation solid state polymerization as described in refs 5 and 6. Atactic PAN was prepared by free radical and anionic polymerization.[7] The PAN powder was passed through a 100 mesh sieve. Characterization is given in Table 1. For comparison, two other kinds of stereoregular polymers were used: isotactic poly(styrene) (PSt) and isotactic poly(propylene) (PP). The former was supplied by Polymer Laboratories Ltd. (U.K.), and the latter was supplied by Dr. T. Aoki (Tonen, Co. Ltd.). These are characterized in Table 2.

Tacticity Determination. The JEOL JNM GX-270, GX-400, and α-500 NMR spectrometers were used under similar conditions as given in ref 8. The triad tacticity mm was determined from the intensity of ^{13}C NMR signals from methine carbon (CH).

WAXD Measurements. A Rigaku Rotaflex (type RAD-rA) was used under the following conditions: accelerating voltage, 50 kV; current, 200 mA; divergent slit, 1 mm o.d.; receiving slit, 1 mm o.d. Step interval scanning was also employed for the precise determination of the main peak position.

Table 1. Characterization of Several PAN Samples[g]

			NMR results triad tacticity (%)			
type	code	viscosity $[\eta]^f$	mm	mr	rr	$4IS/H^2$
canal[a]	C1	0.74	83	14	3	5.08
canal[a]	C2	0.99	80	15	5	6.54
canal[a]	C3	1.54	78	17	5	5.40
canal[b]	C4	1.99	62	28	10	3.16
canal[b]	C5	3.06	58	31	11	2.66
canal[b]	C6	1.84	54	34	12	2.24
canal[b]	C7	4.96	48	36	16	2.37
anion[c]	A1	2.26	33	43	24	1.31
radical[d]	R1	3.30	30	48	22	1.30
radical[e]	R2	1.84	28	50	22	0.99

[a] γ-Irradiation post-polymerization. [b] γ-Irradiation in source polymerization. [c] Prepared in tetrahydrofuran using phenylmagnesium bromide, at −78 °C. [d] Aqueous zinc chloride solution ($H_2O-ZnCl_2/(NH_4)_2S_2O_8$, at 55 °C). [e] Aqueous redox slurry ($H_2O/(NH_4)_2S_2O_8-NaHSO_3$, at 60 °C). [f] In *N*,*N*-dimethylformamide (DMF), at 25 °C. [g] More than 20 samples were used. The experimental data for several selected samples are given here.

Table 2. Characterization of Stereoregular PSt and PP Prepared by the Ziegler−Natta Method

polymer	type[c]	form[d]	T_m^e (°C)	IR data D_{974}/D_{995}^f	tacticity (%)	crystallinity (%)
PST-1[a]	iso	CG	243.0		>90	54
PST-2[b]	atact	AP				
PP-1	iso	CG	172.8	1.00	98[g]	81[h]
PP-2	iso	CG	165.3	1.07	93	80
PP-3	iso	CG	159.7	1.20	67	58
PP-4	iso	CG	155.5	1.24	64	53
PP-5	iso	CG	148.5	1.48	57	40

[a] Poly(styrene) standard, crystalline sample (Polymer Laboratories Ltd.). $[\eta] = 1.21$ (*o*-dichlorobenzene, at 25 °C). [b] Poly(styrene) standard, amorphous monodisperse sample (no. 8). $M_p = 490\,000$; $M_w/M_n = 1.10$; $T_g = 100$ °C. [c] Key: iso, isotactic; atact, atactic. [d] Key: CG, crystalline granules; AP, amorphous powder. [e] DTA method. [f] IR characteristic bands. [g] IR method by Luongo.[9] [h] WAXD method by Natta.[20]

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10.1021/ma002173e CCC: $20.00
Published on Web 04/26/2001

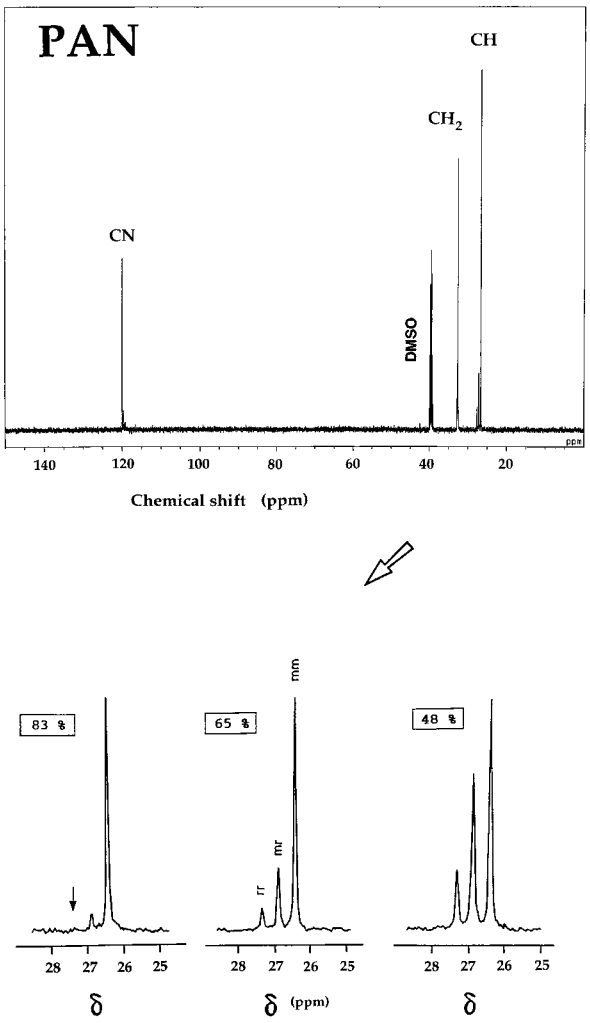

Figure 1. ^{13}C NMR spectra (125 MHz) of isotactic PAN. Only the methine carbon region is expanded (bottom).

Infrared (IR) Measurements. The Hitachi double beam IR spectrometer (type A-630) was used. The stereoregularity of isotactic PP was evaluated by the KBr disk method as described by Luongo.[9]

Preparation of Highly Crystallized Sample (Crystallites). To evaluate the crystallinity of PAN, crystallites were obtained according to the manner of Holland et al.[10] That is, isotactic PAN powder was dissolved in γ-butyrolactone at a high temperature (150 °C) and was allowed to crystallize at 110 °C. The crystallites were recovered as an aggregate of fine platelets.

Results and Discussion

1. ^{13}C NMR and WAXD Results of Isotactic PAN. Figure 1 shows the typical ^{13}C NMR spectra of stereoregular isotactic PAN. Three kinds of carbon species are observed: methine (CH), methylene (CH_2), and nitrile carbon (CN), with a decreasing magnetic field.[2−4] The methine carbon (CH) signals can be used for determining the tacticity of PAN. The extent of isotacticity (mm) of these samples was 83%, 65%, and 48%, respectively. Although further detailed information on the tactic structure of PAN can be obtained from nitrile carbon signals,[11,12] discussion of this is omitted here.

Figure 2 shows WAXD results of PAN. Two clear coaxial rings were observed in isotactic PAN, whereas only one diffuse ring was observed in atactic PAN. When the extent of the stereoregularity was increased, the main peak at about 17 degrees sharpened, shifting from 17.1 to 16.8°. This is more clearly demonstrated by the step interval scanning in Figure 2: the shift of the main peak to a lower angle, together with its broadening with a decrease of tacticity. These results are summarized in Figures 3 and 4.

The spacings corresponding to the diffraction peaks were linear in the percent isotacticity (Figure 3) and could be extrapolated to a value of 5.27_5 Å for a perfectly isotactic PAN. The rigid nature of isotactic PAN molecules results in a wider intermolecular distance and a smaller fluctuation in the alignment of rodlike molecules (see later section). (Interestingly, the position of the main peak was slightly different according to the details of the recovery procedure, as shown by a short vertical line in Figure 3. This problem is discussed in ref 13.)

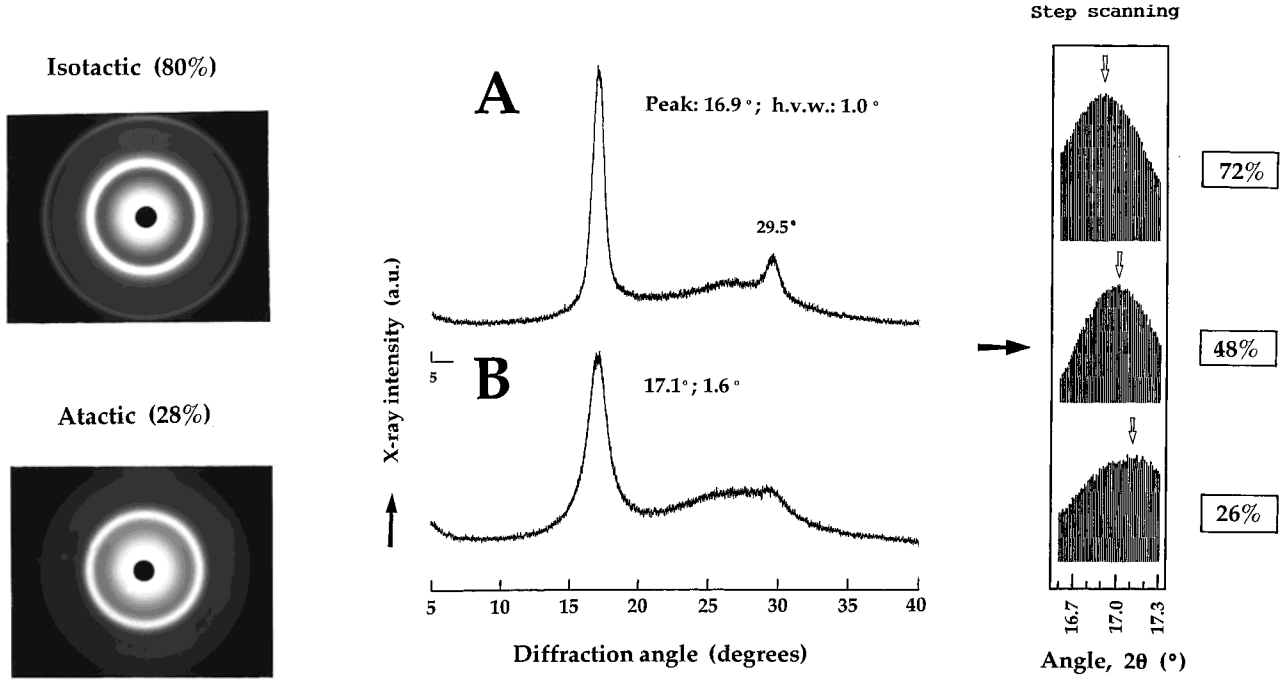

Figure 2. Comparison of WAXD results of PAN powder: (A) C-2, 80%; (B) R-2, 28%. Step interval scanning (right) indicates the variation of the main peak position.

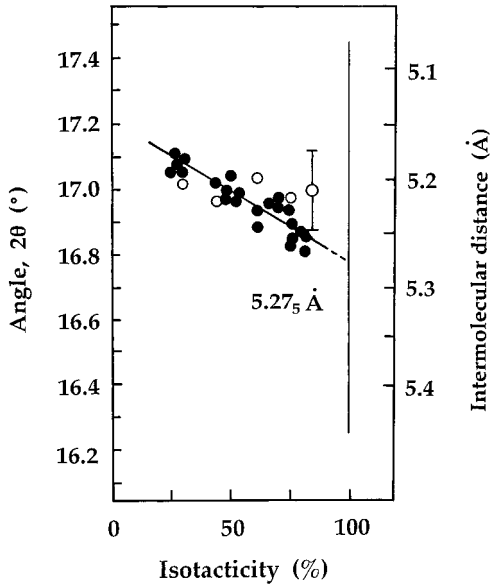

Figure 3. Summary of WAXD results (shift of the main peak). Open circle indicates the results for recovered sample (see Figure 6, middle).

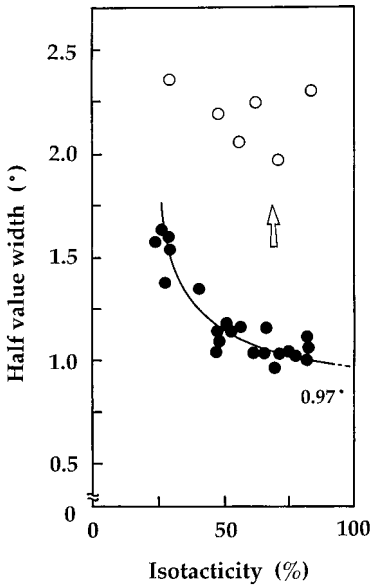

Figure 4. Summary of WAXD results (hvw of the main peak). The meaning of the open circle is the same as in Figure 3.

2. Evaluation of Crystallinity of PAN by WAXD Analysis. The degree of crystallinity can be presented from the WAXD results by three procedures (Figure 5, top): Hinrichsen,[14] Bell and Dumbleton,[15] and Gupta et al.[16,17] In the third case, in particular, not only the crystallinity but also a minor peak at about 30° has been evaluated adequately from a detailed WAXD analysis of copolymers (AN−methyl methacrylate, and AN−methacrylonitrile). The difference between these three procedures is how the contribution from the crystalline region is characterized or how the crystalline diffraction is extracted from the WAXD pattern.

The results for a series of isotactic PAN having different isotacticities are summarized in Figure 5 (bottom). By all evaluation methods, the degree of crystallinity of PAN was almost constant irrespective of the isotacticity. (Strictly speaking, the results may be regarded as being fitted on rather decreasing lines: the PAN samples were isolated as fine powders after boiling in hot water to remove urea.[5,6] This boiling treatment may have caused some conformational differences in isotactic PAN.)

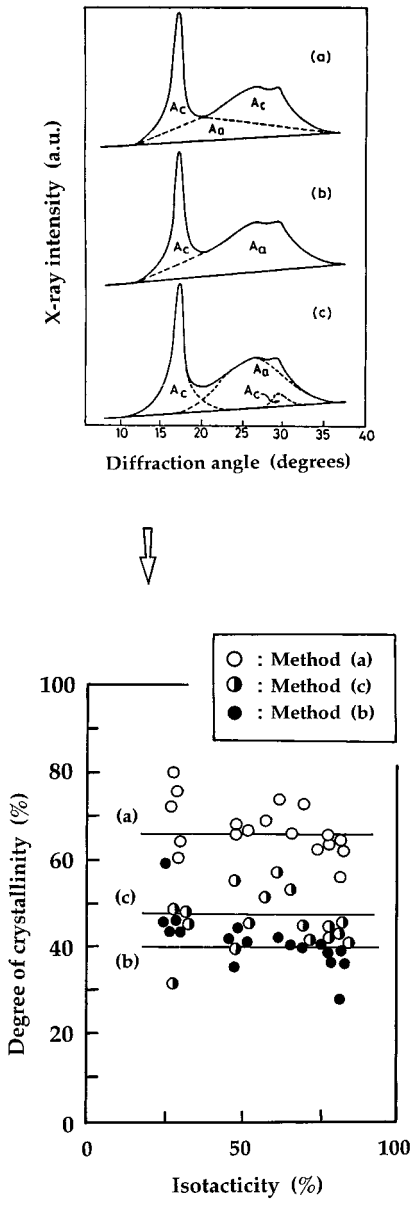

Figure 5. Evaluation of cystallinity by WAXD procedure. Top: Literature method (from ref 17). Hinrichsen (a),[14] Bell and Dumbleton (b),[15] and Gupta et al. (c)[16,17] Bottom: Results for PAN by the literature method.

However, we would like to define the crystallinity of PAN as shown in Figure 6. This evaluation method is very close to the third one above. The results by this definition are summarized in Figure 7. The degree of crystalliniy was almost constant. It is concluded that the crystallinity of the PAN powder does not depend on the extent of stereoregularity, although its inherent value, depending on the WAXD evaluation procedures, ranges from 40% to 70%.

3. Tacticity−Crystallinity Relationship in Connection with the Polymerization Mechanism. The above conclusion differs strikingly from the results with isotactic PSt and isotactic PP,[18,19] where the crystallinity depends on the extent of stereoregularity: (1) PSt does not crystallize without stereoregular isotactic sequence in its backbone (see Table 2), and (2) the crystallinity of PP is a unique function of isotacticity (Figure 8). The

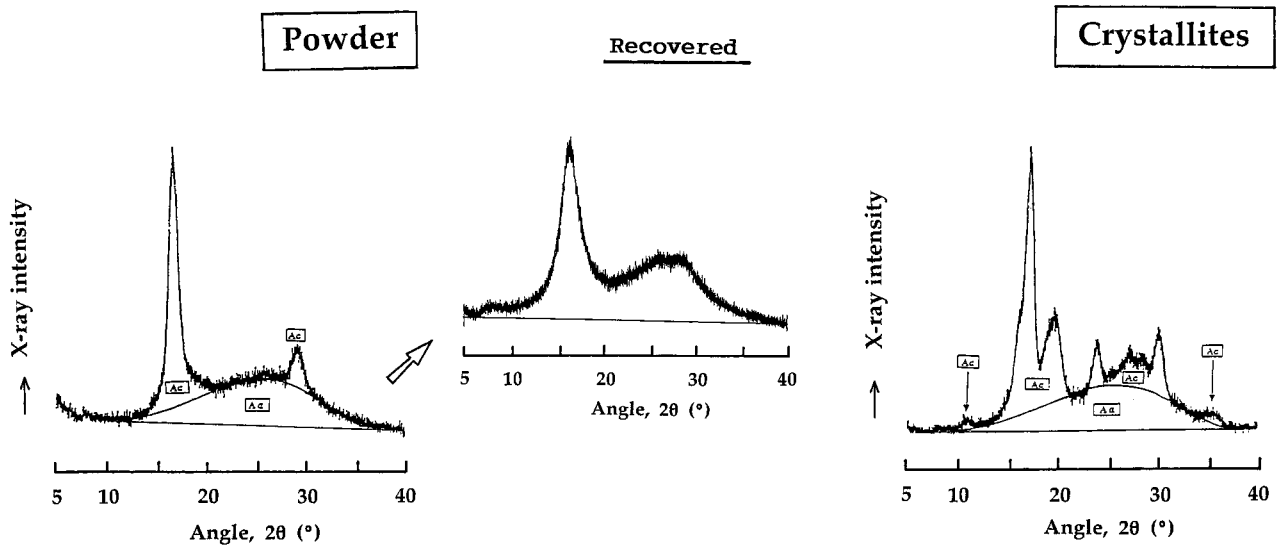

Figure 6. Definition of the crystallinity and comparison of WAXD pattern between powder and crystallites. Left: Isotactic PAN (C-1/powder). Middle: Recovered PAN (C-1/powder) from DMSO solution. Right: Isotactic PAN (C-1/crystallites). The degrees of crystallinity of these samples were about 42%, 40%, and 55%, respectively.

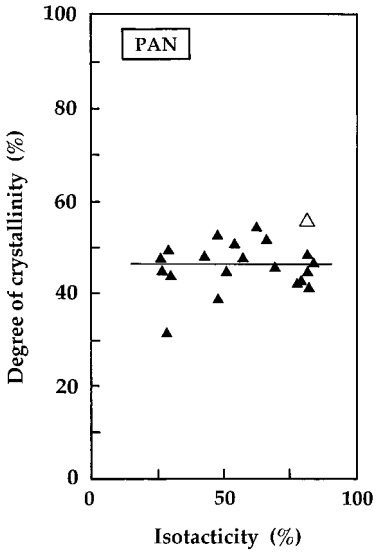

Figure 7. Tacticity−crystallinity relationship in PAN powders. The open triangle indicates the value of crystallites in Figure 6 (right).

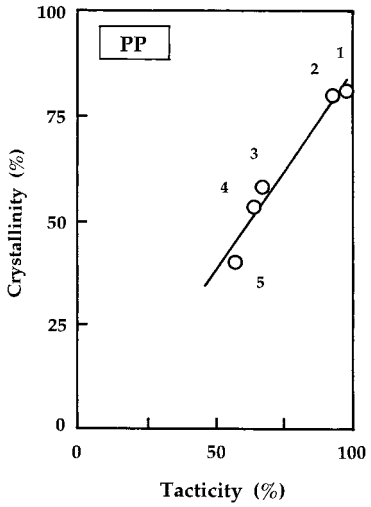

Figure 8. Tacticity−crystallinity relationship in isotactic PP. Numbers indicate the sample numbers in Table 2. The crystallinity was determined according to the manner of Natta.[20]

anomaly in the tacticity−crystallinity relationship in PAN is clearly demonstrated by the comparison of Figures 7 and 8.

These results can be understood by the urea canal polymerization of AN in its solid state: (i) the AN monomers align in a one-dimensional hexagonal lattice of urea separated from each other, (ii) polymerization occurs at a low temperature as low as −78 °C, and (iii) due to the immobility of the resulting polymer chain, crystallization does not take place. Isotactic PAN retains its original extended structure, as can be understood from WAXD results (Figures 3 and 4). A very important problem, the lack of longitudinal order along the main chain, as confirmed by no diffraction spots in a meridional direction, is discussed elsewhere.[21] At any rate, once the sample is dissolved in a good solvent (dimethyl sulfoxide, DMSO), the recovered sample shows drastic change in the WAXD pattern (Figure 6, middle).

It is also interesting to note that even though crystallization does not take place during polymerization, the polymer is inherently highly stereoregular, and it crystallizes easily when external conditions allow. Namely, when isotactic PAN is dissolved in a polar solvent (i.e., γ-butyrolactone) at a high temperature and is allowed to crystallize isothermally, crystallites having high crystalline order are obtained. A WAXD photograph of PAN crystallites in Figure 6 (right) indicates that the sample is highly crystallized, although a detailed structural analysis will be given in ref 22.

4. A Minor Second Peak at 30° in WAXD Pattern. One of the interesting things about the WAXD pattern of isotactic PAN powder is the existence of a minor second peak at about 30° (Figure 2). Since this peak does not exist in the WAXD pattern of ordinary atactic PAN, and it disappears when the sample is recovered from solution (Figure 6, middle), it is attributed to the diffraction from the crystalline structure of isotactic PAN. From the geometrical consideration of the rodlike

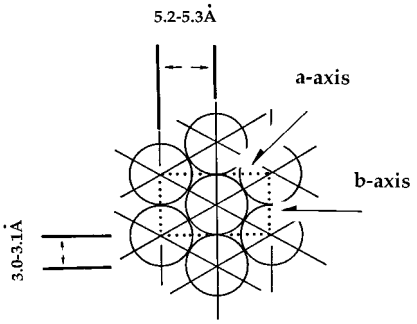

Figure 9. Geometrical considerations for molecular packing of rodlike isotactic PAN chain.[23−25]

molecules of PAN,[23−25] it is assigned to the [101] lattice plane (d = 3.0−3.1 Å) in hexagonal packing of PAN (close packing structure) (Figure 9).

It is also interesting that the relative intensity of this peak toward the main peak ($W_{29.5}/W_{17}$: peak area) showed a reasonable change: In atactic PAN, this value is in the range of 0−7%, while in isotactic PAN it increased from 10% to 15%, when the isotacticity was increased from 48% to 83%. There exists a proportional relationship between these two quantities. Further advanced considerations on this topic could be described in the future.

Conclusion

1. A detailed WAXD analysis of a series of isotactic PAN powders was carried out. The results were summarized as a function of the isotacticity of PAN (83−25%).

2. The crystallinity of urea clathrate PAN did not depend on the isotacticity. This was in a clear contrast with the results of other stereoregular polymers, such as isotactic PP and isotactic PSt.

3. The degree of crystallinity was inherently between 40% and 70% depending on the three WAXD evaluation procedures. The validity of these evaluation methods was discussed.

4. The values corresponding to a 100% isotactic sample were obtained: 5.27_5Å (intermolecular distance) and 0.97° (hvw of the main peak).

5. The specific relationship between tacticity and crystallinity was discussed in relation to the polymerization mechanism: besides the separation of each monomer by a urea wall, such a low temperature would prevent the mobility and crystallization of the resulting polymer.

6. The origin of a minor second peak at about 29.5° in the WAXD pattern was considered based on a geometrical consideration of close packed (hexagonal lattice) rodlike PAN molecules.

Acknowledgment. We wish to express our hearty thanks to Dr. T. Aoki (Tonen Co. Ltd.) for supplying stereoregular PP samples. This research was carried out under the support of JAERI (Takasaki)-University research cooperation.

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MA002173E