4526 *Macromolecules* **2000,** *33,* 4526−4531

Conformation Effect and FT-IR Diffuse Reflection Spectroscopy of Stereoregular Isotactic Poly(acrylonitrile) Prepared by Urea Clathrate Polymerization

Masatomo Minagawa,*,† Toshiki Taira,† Kimikazu Kondo,† Satoshi Yamamoto,† Eiji Sato,‡ and Fumio Yoshii§

Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa 992-8510; Perkin Elmer Japan Company, Ltd., K.N. Bldg., Nishi-ku, Yokohama 220-0004; and Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute (JAERI), Takasaki 370-1292, Japan

Received August 9, 1999; Revised Manuscript Received January 28, 2000

ABSTRACT: The conformation effect on the infrared intensity of the characteristic bands (1230/1250 cm^{-1}) of stereoregular isotactic poly(acrylonitrile) (PAN) was studied by the diffuse reflection (DR) and KBr disk methods. The DR spectroscopic features of isotactic PAN were briefly discussed. The intensity ratios (D_{1230}/D_{1250}) of the IR bands in the original sample (A) and the dissolution-recovered sample (B) were compared: the intensity of the latter sample decreased more than that of the former, the extent of which was larger when the stereoregularity of the sample was higher. Little difference was observed in atactic PAN. These intensity variations were summarized as a function of the isotacticity of PAN, from which the effect of both conformation and configuration was quantitatively evaluated. The intensity difference between the DR and KBr disk results was also reasonably explained in terms of conformation. The IR behavior of other bands (1100 and 540 cm^{-1} region) was briefly noted.

Introduction

Infrared (IR) spectroscopy is a successful analytical procedure for the elucidation of the structure and properties of polymers.[1−4] The diffuse reflection (DR) method is a useful technique for the study of surface and interfacial problems, although its application to the actual polymer system is relatively rare.

There have been several IR spectroscopic studies of poly(acrylonitrile) (PAN) including a stereoregular one.[5−9] With regard to the latter, we have carried out detailed IR measurements by the KBr disk method.[9] The presence of IR characteristic bands (1230/1250 cm^{-1}), which are sensitive to the stereochemical configuration of PAN, and their possible assignments, were discussed. Later, the solvent casting effect of the IR characteristic bands (1230/1250 cm^{-1}) was found in solvent cast PAN film:[10] the strength of the dissolution power of the solvents used for the film preparation was directly related to the intensity ratio of the IR bands of PAN. This fact indicates that the intensity ratio would be a good measure for the conformation problems of PAN.

In this article, the effect of both conformation and configuration on the IR intensity of stereoregular isotactic PAN was quantitatively discussed. The usefulness of the DR method under carefully controlled conditions is demonstrated, although its ambiguity due to the spectroscopic difference, reflection spectra (DR), and absorption spectra (KBr), has been excessively emphasized. The results presented here are quite important for the clarification of the structure−properties relationships of this polymer.

Experimental Section

Materials. Stereoregular PAN samples were prepared by urea clathrate polymerization in the solid state at low temperatures (−78 °C). Details of the practical preparation conditions have been described in refs 11−13. Various modifications were carried out to attain different isotacticity, such as by the combination of the insource and the post polymerization methods. The samples were obtained in the form of a fine powder. The extent of stereoregularity (triad tacticity) was from 25% to 83%. Characterization is given in Table 1.

Table 1. Characterization of Samples[h]

			NMR results			
		viscosity $[\eta]^a$	triad tacticity (%)			
polymerization	code	(dL/g)	I	H	S	$4IS/H^2$
canal[b]	C-1	1.52	83	14	3	5.08
canal[b]	C-2	1.73	80	15	5	7.11
canal[b]	C-3	1.19	74	20	6	4.44
canal[c]	C-4	1.44	67	25	8	3.43
canal[c]	C-5	4.96	48	36	16	2.37
anion[d]	A-3	2.17	30	43	27	1.75
radical[e]	R-2	1.97	28	46	26	1.38
radical[f]	W-3	6.03	29	49	22	1.06
radical[g]	B-4	6.87	26	47	27	1.27

[a] DMF, at 25 °C. [b] γ-Irradiation post polymerization. [c] γ-Irradiation insource polymerization. [d] Prepared in THF by sodium−naphthalene, at −78 °C. [e] Aqueous redox slurry (H_2O/APS−$NaHSO_3$, at 40 °C). [f] Aqueous solution (H_2O/APS, at 50 °C). [g] Bulk (UV-irradiated, at 14 °C). [h] Key: THF, tetrahydrofuran; APS, ammonium peroxodisulfate.

NMR Measurements. The stereoregularity was determined by ^{13}C NMR spectra. Details of the NMR conditions are given in ref 14. The peak area of methine carbon (CH) signals was used for the determination of isotacticity based on three monomer units (mm).

Wide-Angle X-ray Diffraction (WAXD) Measurements. The Rigaku Rotaflex RAD-rA diffractometer (Rigaku Corp. Ltd.) was used under the following conditions: acceleration voltage, 50 kV; current, 200mA; divergence slit, 1 mm^{ϕ}; and receiving slit,1 mm^{ϕ}.

FTIR-DR Measurements and Data Treatment. Three different FT-IR spectrometers, a Perkin-Elmer (Paragon 1000), a JASCO (type 7300), and a JEOL (JIR-1000), were used in addition to the one used previously.[9] These IR spectrometers

---

[†] Yamagata University.
[‡] Perkin Elmer Japan Company.
[§] JAERI.

10.1021/ma991328j CCC: $19.00

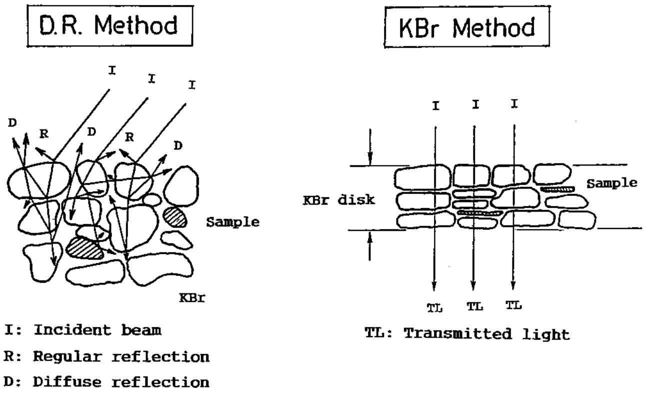

Figure 1. Illustration of two different IR methods. In the KBr method, the sample is ground with KBr to a fine powder and then pressed to a disk under high pressure. In the DR method, this high-pressure application is avoided (the left-hand side of the figure was reproduced with permission from ref 3. Copyright 1986 Tokyo Kagaku Dojin).

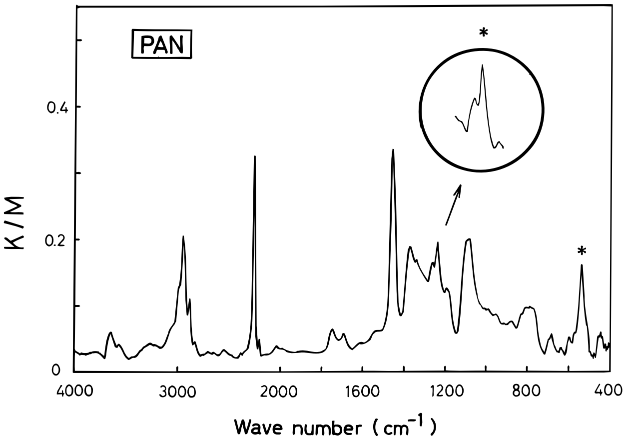

Figure 2. Typical FTIR-DR spectra of isotactic PAN. An asterisk indicates the characteristic bands, which are sensitive to the stereochemical configuration of PAN.

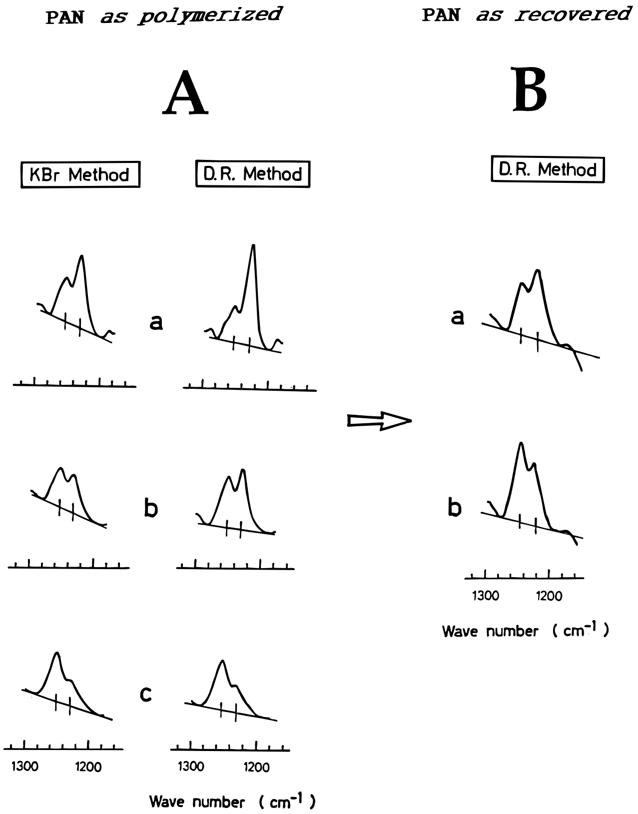

Figure 3. Expanded DR spectra of the 1300−1200 cm^{-1} region. Left: Polymerized sample (A). Right: Recovered sample (B). The isotacticity of these samples was 83% (a), 48% (b), and 28% (c). Samples B were recovered from dimethyl sulfoxide (DMSO) solution (see Figure 4). The intensity ratio of the bands (D_{1230}/D_{1250}) was 1.35, 0.82, and 0.54 (KBr), 2.26, 1.04, and 0.77 (DR, left), and 1.25 and 0.92 (DR, right), respectively.

are a standard type, having the following common performances; resolution, 4 cm^{-1}; detector, TGS; accumulation, >32 counts. PAN (fine powder, 30 mg) was mixed with KBr (100mesh, 300 mg) and ground in an agate mortar until it became a uniform powder. The Kubelka−Munk calibration was employed for each measurement. The DR method is excellent for a limited amount of powder:[16] (1) No external pressure is applied to the sample, and therefore little conformational distortion will be introduced (Figure 1). (2) Careful observation using the Kubelka−Munk calibration can reveal a minute difference in the IR intensity due to the conformational difference of PAN, as demonstrated here.

The absorbance of the IR characteristic bands (D_{1230}/D_{1250}) was determined by a baseline method, as shown typically in Figure 3. To summarize the experimental data in terms of a straight line,[17] the following IR total relationship was employed

$$D_{1230}/(D_{1230} + D_{1250}) = A + B(X) \qquad (1)$$

where D is the absorbance of each band, A and B are constant, and X is the extent of isotacticity (mm).

Results and Discussion

3.1. Typical FTIR-DR Spectra of Stereoregular PAN. Figure 2 shows the IR-DR spectra of isotactic PAN. The DR spectra of PAN are quite similar to those of ordinary IR absorption spectra obtained by the KBr disk method.[5,9] The difference in stereoregularity appears in the IR bands in the region of 1300−1200 and 540 cm^{-1} as indicated by an asterisk. The former is a methine (CH) deformation vibrational mode coupled with other components, while the latter is a deformation vibrational mode of C−C≡N groups.[5,6,9] Strange to say, there was no characteristic bands inherent to the isotactic PAN molecular chain, such as the 1058 cm^{-1} band for syndiotactic poly(methyl methacrylate)[18] and 995 and 841 cm^{-1} bands for isotactic poly(propylene).[19,20]

3.2. IR Characteristic Bands (1300−1200 cm^{-1}) and IR Methods. Figure 3 (left) shows the expanded spectra in the 1300−1200 cm^{-1} region. The presence of a couple of bands (1250/1230 cm^{-1}), which are sensitive to the stereochemical configuration of PAN, is obvious. When the stereoregularity was increased, the intensity of the 1230 cm^{-1} band was enhanced, and in some cases an inverse relationship was observed.

In the comparison of both DR and KBr disk results, the former method ensured a higher intensity of the 1230 cm^{-1} band than the latter. In the atactic sample, however, there was little difference between them. Although the enhancement of the 1230 cm^{-1} band accompanied a small extent of the high-frequency shift of the 1250 cm^{-1} band (see later), there was very little difference in the peak position of these two bands due to the different methods. We consider that the intensity difference between them is caused mainly by the difference of molecular conformation of PAN in both states.

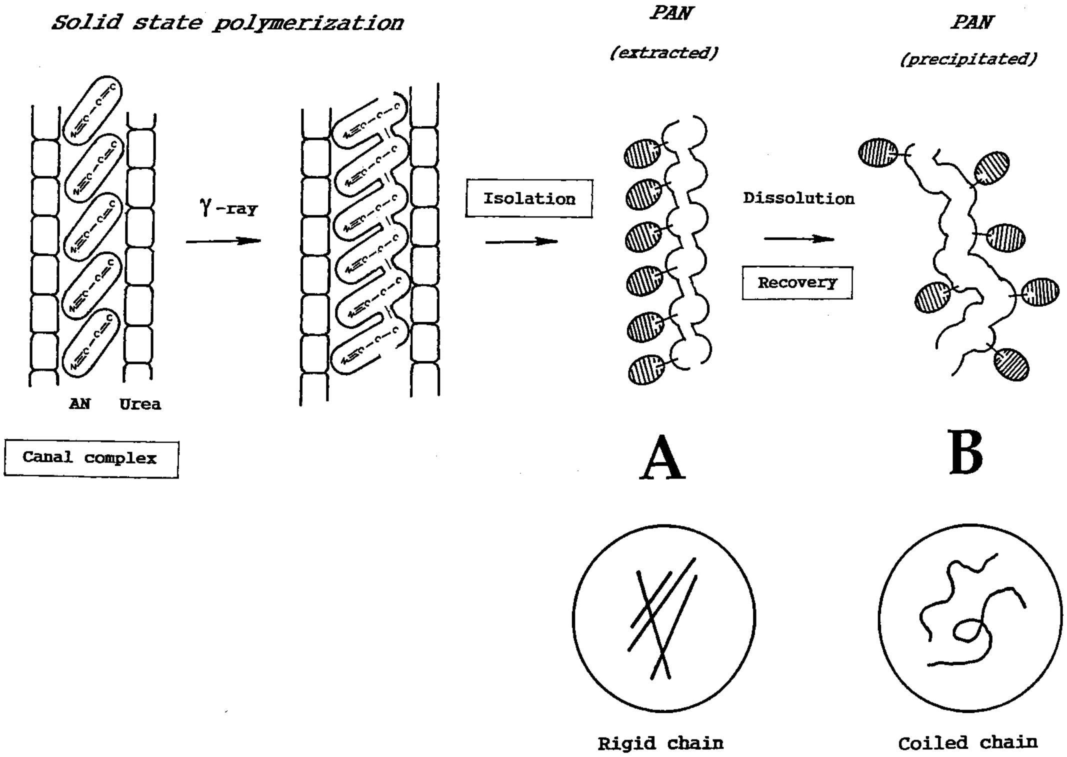

Figure 4. Schematic representation of the sample preparation process.

In the KBr disk method, PAN molecules are probably highly distorted due to the external high-pressure applied during KBr disk preparation (6000kg/cm^2), and the extent of this distortion will be reflected in the IR intensity (Figure 1). One may argue that such pressure sensitive IR results have never been observed except in peptide polymers, such as amide (II) bands and the like.[21] This is not surprising, however, as nobody has ever studied the IR spectra of urea canal polymers from such a point of view.

3.3. Sample Preparation Process and IR Characteristic Bands. The above estimation is directly supported by the comparison of the IR results of the original sample (A) with the recovered sample (B). Figure 4 shows a flow sheet for the sample preparation process: canal polymerization is carried out by γ-irradiation at low temperatures (-78 °C), and the resulting polymer retains its original one-dimensional oriented conformation. To remove urea, reactants are poured into an excess amount of methanol, washed by hot water and then isolated (sample A). This orientation cannot be destroyed even after the sample is boiled in a hot water.

However, when PAN samples are dissolved in a suitable solvent (DMSO) and recovered,[22] conformational changes are introduced (sample B). Although there is very little change in the appearance of the powder specimen except in the apparent bulk density and the like,[24] the difference in the WAXD pattern in Figure 5 clearly indicates the drastic change in the microscopic molecular cohesion state of PAN. That is, a sharp main peak at about 17° broadened and a minor second peak at 29.5° disappeared. The morphological change of PAN powder from a crystalline state to an amorphous state is evident from this figure. The above IR intensity change should be understood in connection with this morphological change in the PAN powder.

We will return to the intensity problem in Figure 3. In the recovered sample (Figure 3, right), the IR intensity ratio was reduced: the extent of this reduction was larger when the stereoregularity of the sample was higher. There was very little change in atactic PAN. It is sure that this intensity reduction is caused by the conformational change of urea clathrate PAN, as can be understood intuitively by Figures 4 and 5.

3.4. Conformational Effect on the Quantitative IR Data. One can evaluate the effect of molecular factors on the IR intensity of PAN as follows: when the IR data were summarized as a function of isotacticity, Figures 6 and 7 were obtained. In both cases, a pair of crossed straight lines resulted. In the former (DR method), the data for the original sample (A) produced a steeper line, while the recovered sample (B) produced a gentle line. The net difference between these two was evidently due to the conformation effect: the decrease in the IR intensity was caused by the introduction of conformational change around the isotactic PAN molecular chain, and the extent of its effect was unexpectedly large.

In the latter (KBr disk method), the effect of both conformation and configuration can be separated quantitatively as shown in Figure 7. Strictly speaking, the latter term (configuration) in Figure 7 may contain some excess contribution from the kinked conformation and the like,[25] this large conformation effect will provide a significant key for the clarification of the specific nature in the structure-properties relationships in isotactic PAN.

$$\text{IR intensity } (D_{1230}/D_{1230} + D_{1250}) = \text{conformation effect} + \text{configuration effect} \quad (2)$$

Thus, the IR intensity was proved to be defined by the above two molecular factors through the eq 2. Although

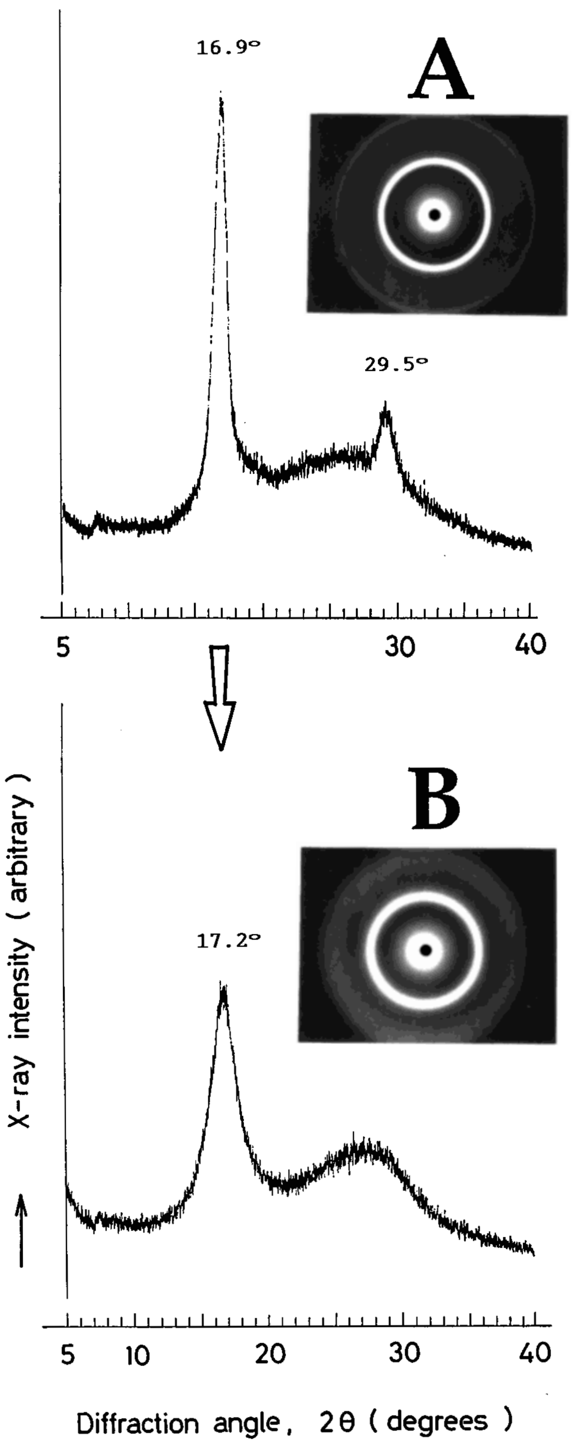

Figure 5. Typical WAXD results of isotactic PAN (83%) before (A) and after dissolution (B). Half-width value of the main peak at 17° was 1.2° (A) and 2.4° (B), respectively.

there was a considerable peak shift, particularly in the 1250 cm^{-1} bands (Figure 8), this observation does not affect the conclusion obtained here. From these results, it is possible to summarize that (i) the dependence of the IR characteristic bands on both configuration and conformation was evaluated quantitatively and (ii) the highly extended structure of the isotactic PAN molecular chain ensures a higher intensity ratio, while the introduction of conformational change around the isotactic chain drastically reduces the intensity ratio.

3.5. The IR Behavior of Other Bands in Isotactic PAN. Figure 9 shows the FTIR-DR spectra in the 1100

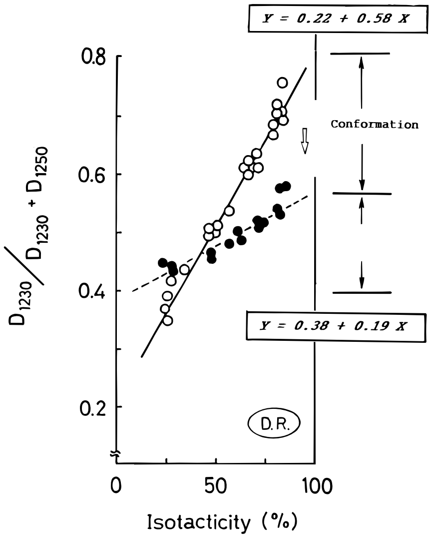

Figure 6. Quantitative IR results of PAN by the DR method. The open circle indicates the data for the polymerized sample (A), while the solid circle does so for the recovered sample (B). The significance of the conformation effect is clearly known by the extent of the reduction of the IR intensity at 100% isotacticity.

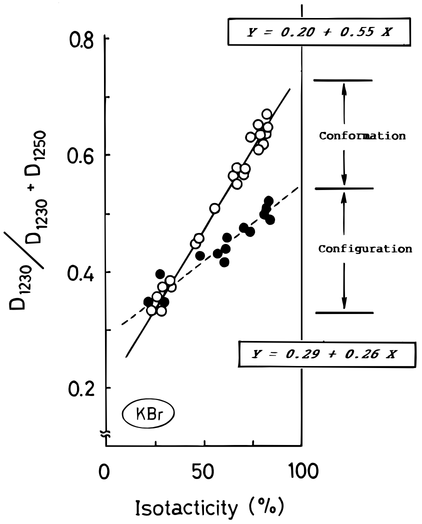

Figure 7. Quantitative IR results of PAN by the KBr disk method. The meaning of the symbols is the same as given in Figure 6.

and 540 cm^{-1} regions. On the left of Figure 9, the overlapping of the two components (1107/1074 cm^{-1}) is obvious. The former is enhanced and appears as a single independent peak, when the stereoregularity is increased. A simple computer simulation enables one to separate these two components semiquantitatively (Figure 10).

On the right of Figure 9, the half-width value of the 540 cm^{-1} band decreased proportionally with the increase in stereoregularity. More specifically, at least three components overlap (570/540/520 cm^{-1}), and the second one is enhanced when the stereoregularity is increased.

Conclusions

1. The FTIR-DR measurements were carried out for a series of isotactic PAN. The DR spectroscopic features

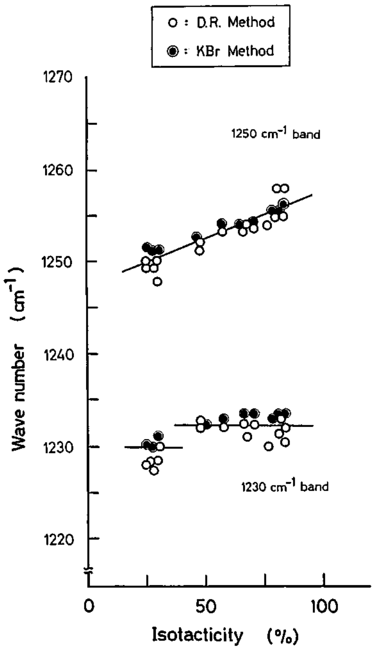

Figure 8. Peak shift in the IR bands of PAN.

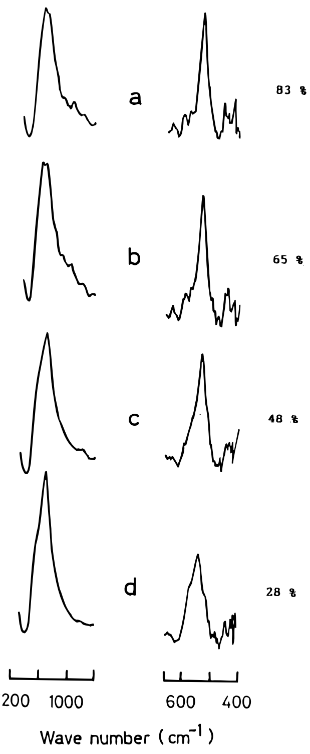

Figure 9. FTIR-DR spectra in the 1100 and 500 cm^{-1} region.

of PAN were discussed in comparison with the IR results for the atactic sample.

2. The intensity of the IR bands (1230/1250 cm^{-1}) was studied in terms of the sample preparation process. WAXD results imply the significance of the conformation effect before and after the dissolution of PAN.

3. The relative contribution of both configuration and conformation on the IR bands was quantitatively obtained. The effectiveness of the DR method for the conformational problems of PAN was suggested.

4. The IR behavior of several other bands (1100 and 540 cm^{-1}) was observed, and explained in terms of the overlapping of two or three components.

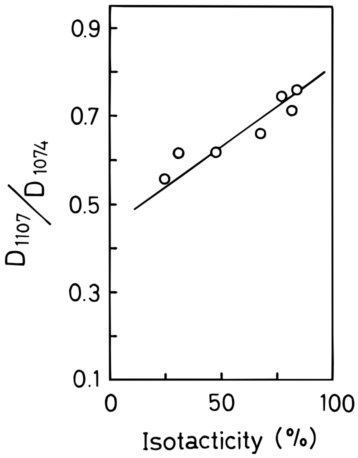

Figure 10. Separation of the overlapping peaks in the 1100 cm^{-1} region.

Acknowledgment. We wish to express sincere thanks to Mrs. F. Kaneuchi and Mr. T. Matsuno (JASCO) for their many suggestions regarding the DR measurements. Thanks are also expressed to Prof. M. Tasumi (University of Tokyo) for his valuable input.

References and Notes

(1) Zvinden, R. *Infrared Spectroscopy of High Polymers*; Academic Press Inc.: New York, 1964.

(2) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapmann and Hall, Ltd.: London, 1975.

(3) Tasumi, M. *Introduction to FT-IR Spectroscopy* (Jpn. ed.); Tokyo Kagaku Dojin Co., Ltd.: Tokyo, 1986.

(4) Koenig, J. L. *Spectroscopy of Polymers*; ACS Professional Reference Book; American Chemical Society: Washington, DC, 1992.

(5) Liang, C. Y.; Krimm, S. *J. Polym. Sci.* **1958**, *31*, 513.

(6) Liang, C. Y.; Peaesons, F. G.; Marchessault, R. H. *Spectrochim. Acta.* **1961**, *17*, 568.

(7) Ogura, K.; Kawamura, S.; Sobue, H. *Macromolecules* **1971**, *4*, 79.

(8) Ohta, K.; Iwamoto, R.; Miya, K. *Nippon Kagaku Kaishi* **1985**, No. 6, 1200.

(9) Minagawa, M.; Miyano, K.; Takahashi, M.; Yoshii, F. *Macromolecules* **1988**, *22*, 2387.

(10) Minagawa, M.; Yoshida, W.; Kurita, S.; Takada, S.; Yoshii, F. *Macromolecules* **1998**, *30*, 1782.

(11) Yoshii, F.; Abe, T.; Yoda, O. *Kobunshi Ronbunshu (Engl. Ed.)* **1975**, *4*, 516.

(12) Yoshii, F.; Abe, T.; Yoda, O. *Kobunshi Ronbunshu (Engl. Ed.)* **1975**, *4*, 625.

(13) Minagawa, M.; Yamada, H.; Yamaguchi, K.; Yoshii, F. *Macromolecules* **1992**, *25*, 503.

(14) Minagawa, M.; Nouchi, K.; Tozuka, M.; Chujo, R.; Yoshii, F. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 665.

(15) Minagawa, M.; Iwamatsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 481.

(16) Westra, J. G.; van Woerken, P. C. M. In *Laboratory Methods in Vibrational Spectroscopy*, 3rd ed.; Willis, H. A., van der Maas, J. H., Miller, R. G. J., Eds.; John Wiley & Sons Ltd.: Essex, England, 1987.

(17) When the relative intensity (D_{1230}/D_{1250}) was plotted against isotacticity, a curved relationship was obtained, whereas when the following total intensity ($D_{1230}/D_{1230} + D_{1250}$) was plotted, a valid straight line was obtained (see ref 9).

(18) Baumann, U.; Schreiber, H.; Tessmar, K. *Makromol. Chem.* **1959**, *36*, 81.

(19) Luongo, J. P. *J. Appl. Polym. Sci.* **1960**, *36*, 81.

(20) Tadokoro, H.; Kobayashi, M.; Ukita, M.; Anpuku, K.; Murahashi, S.; Torii, T. *J. Chem. Phys.* **1965**, *42*, 1432.

(21) Miyazawa, T. In *Polyamino Acid, Polypeptide, and Proteins*; Stahmann, M., Ed.; Wisconsin University Press: Madison, WI, 1962.

(22) The best solvent (with the highest dissolution power) was DMSO from the solvent characterization at high temperatures toward isotactic PAN.[23]

(23) Minagawa, M.; Hashimoto, K.; Shirai, H.; Morita, T.; Yoshii, F. *Macromolecules*, in press.

(24) The apparent density decreased when the sample was recovered as a precipitant from DMSO solution.

(25) We estimate that external high pressure in the KBr disk preparation may exert a restrained conformation change in PAN molecules, which are detectable by IR spectroscopy (see ref 26).

(26) Minagawa, M.; Taira, T.; Sugiura, M.; Kondo, K.; Yoshii, F. Manuscript in preparation.

MA991328J