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Solvent Casting Effect on the Infrared Characteristic Absorption Bands (1230/1250 cm^{-1}) of Stereoregular Isotactic Poly(acrylonitrile) Film

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ABSTRACT: The solvent casting effect on the infrared (IR) characteristic absorption bands of stereoregular isotactic poly(acrylonitrile) (PAN) film was studied in comparison with those of an atactic sample. The relative intensity of the IR characteristic bands (D_{1230}/D_{1250}) of PAN film was strongly dependent on the kind of dipolar aprotic solvent used in the film preparation. A higher intensity ratio was obtained when a good solvent such as dimethyl sulfoxide was used, whereas a lower value was obtained when a poor solvent such as malononitrile was used. A linear relationship between the intensity ratio of the IR bands and the dissolution power of nine different kinds of dipolar organic solvents was found. The IR characteristic bands of stereoregular PAN was dependent on not only configuration but also conformation through the difference of the molecular cohesion state in the solvent-cast film. The effect of configuration and conformation on the IR results was quantitatively studied as a function of the film preparation conditions.

1. Introduction

Infrared (IR) spectroscopy is a powerful analytical tool for the investigation of structure and properties of polymers.[1−3] However, its application to poly(acrylonitrile) (PAN) is not always sufficient,[4−7] particularly for stereoregular samples prepared by urea clathrate polymerization.

Previously, we have reported a detailed IR study of stereoregular isotactic PAN.[8] The presence of IR characteristic absorption bands (1230/1250 cm^{-1}), which are sensitive to stereochemical isotactic configuration, and their possible assignments were briefly discussed. In this connection, the solvent casting effect on the IR characteristic bands in PAN film is discussed herewith. That is, the relative intensity of these bands in the PAN film was strongly dependent on the kind of dipolar aprotic solvents used in the film preparation, and the dissolution power of these solvents is closely related to the IR results. Although the problem of the molecular cohesion state in PAN is evidently one of the significant subjects not yet sufficiently clarified, the results and the discussion presented here are closely related to this important problem. In this paper, as a preliminary study on the molecular cohesion state of PAN, the problem of how the IR absorption behavior of isotactic PAN film is defined by the film preparation conditions is described.

2. Experimental Section

Samples. The samples were prepared by free-radical polymerization or γ-irradiation canal polymerization (insource method). The former ensured atactic polymers, while the latter ensured isotactic polymers. These are characterized in Table 1.

^{13}C-NMR Measurements. NMR measurements were carried out as described in refs 9 and 10. The isotacticity discussed here is defined by three monomer units (triad tacticity).

Table 1. Characterization of Samples

sample polymerization	code	$[\eta]^a$ (dL/g)	IR D_{1230}/D_{1250}	NMR^b triad tacticity (%) I	H	S
canal^c	C-1	1.61	1.35	72	22	6
canal	C-2	1.34	1.22	66	25	9
canal	C-3	1.52	1.23	67	24	9
canal	C-4	4.96	0.85	48	36	16
canal	C-5	4.58	0.82	48	35	17
anion^d	A-1	2.17	0.60	30	43	27
radical (S)^e	R-1	2.14	0.53	25	51	24
radical (R)^f	R-2	1.73	0.54	28	46	26
radical (B)^g	R-3	6.87	0.51	28	50	22

[a] DMF, at 25 °C. [b] Peak intensity was calculated based on the methine carbon signal. [c] All of the canal samples were prepared by the insource method. [d] Prepared in THF using sodium−naphthalene, at −78 °C (taken from ref 8). [e] Homogeneous solution (DMSO/AIBN, at 55 °C). [f] Aqueous redox slurry (H_2O/APS−$NaHSO_3$, at 40 °C). [g] Bulk (UV photoinitiated, at 14 °C). Key: DMF, *N,N*-dimethylformamide; THF, tetrahydrofuran; DMSO, dimethyl sulfoxide; AIBN, azobis(isobutyronitrile); APS, ammonium peroxodisulfate.

Film Preparation. The film was prepared by the solvent casting method. That is, after preparation of a homogeneous solution of PAN at a higher temperature (~150 °C), a few drops of the solution were spread on a flat glass laboratory dish and evacuated by an aspirator at a temperature of 85−90 °C. To prevent instability of the solution (gel formation), the solution was maintained in a heating bath at the same temperature. The following nine kinds of solvents were used: dimethyl sulfoxide (DMSO), ethylene carbonate (EC), γ-butyrolactone (γ-BuL), tetramethylene sulfone (TMS), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), malononitrile (MaN), glutaronitrile (GuN), and succinonitrile (SuN). These were carefully distilled under reduced pressure prior to use.

To remove the residual solvent, all the films were boiled in hot water (more than 2 h) followed by immersion in methanol and dried under vacuum at 80 °C. Particular attention was paid to providing the samples with nearly equal thermal histories (boiling and drying). The thickness of the film was in the range of about 3−30 μm.

IR Measurements. Details of IR measurements are given in ref 8.

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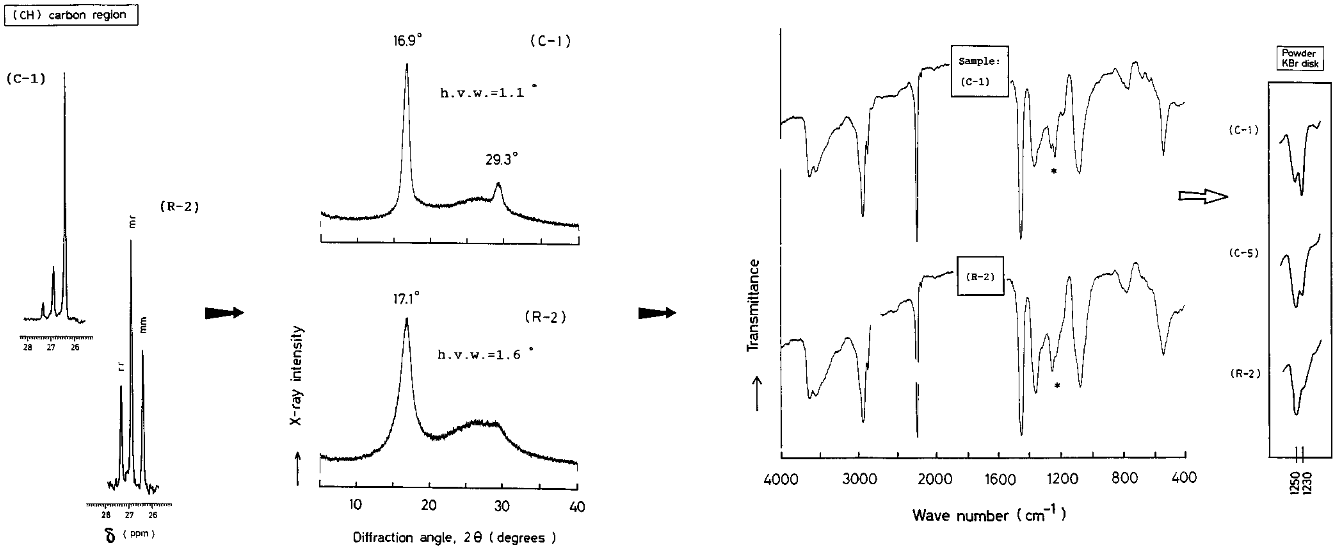

Figure 1. ^{13}C-NMR, WAXD, and IR spectra of PAN. (Left) Only the methine carbon region is presented. The isotacticity of these samples was 72% (C-1) and 28% (R-2), respectively. (Middle) Diffraction results should be compared with WAXD photograph in Figure 9. (Right) The intensity ratio of the IR characteristic bands (D_{1230}/D_{1250}) was 1.32, 0.82, and 0.64, respectively.

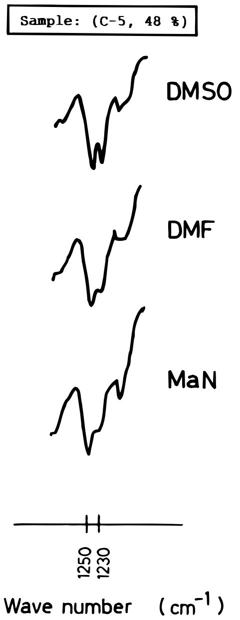

Figure 2. IR Characteristic bands of PAN film solvent cast from different solvents. The intensity ratio of the IR characteristic bands was 0.91, 0.83, and 0.67, respectively. Note that in the case of DMSO solvent a much higher intensity ratio than that of the original powder (0.82) was obtained (cf. Table 1).

Wide-Angle X-ray Diffraction (WAXD) Measurements. WAXD measurements were carried out for powder and film specimens as described in ref 11.

3. Results and Discussion

3.1. ^{13}C-NMR, WAXD, and IR Results for Isotactic PAN. Figure 1 shows ^{13}C-NMR, X-ray, and IR results for PAN. The molecular characteristics of PAN revealed by these measurements have been described previously.[8,11] In the WAXD pattern (middle), the main peak at about 17° was sharpened and the peak position slightly shifted to a lower angle. The results suggest that the stereoregular isotactic PAN molecular chain is very stiff and rigid. The IR characteristic absorption bands (indicated by asterisks) appearing in the region of 1300−1200 cm^{-1} also reflect the difference of the stereoregularity of PAN (right). When the isotacticity was increased, the 1230 cm^{-1} band was enhanced, and the value of the relative intensity between the 1250 and 1230 cm^{-1} bands increased remarkably. This intensity ratio, therefore, can be regarded as a measure of the stereoregularity of PAN, and there exists a valid quantitative relationship between the stereoregularity and the IR intensity ratio of the powder sample.[8]

Even in the case of solvent-cast PAN film, however, the relative intensity of these bands was strongly dependent on the kind of dipolar aprotic solvents used in the film preparation (Figure 2). That is, the intensity ratio was high when solvents such as DMSO and DMF were used, whereas the intensity ratio was low when solvents such as MaN and GuN were used. The results are quantitatively summarized in Figure 3. The IR intensity is closely related to certain properties of these solvents. It is necessary to clarify the following three points: (1) Why is such a specific IR absorption behavior observed (molecular mechanism)? (2) To what extent is the IR intensity varied (quantitative results)? (3) What kind of relationship exists between IR results and solvents through the film preparation process (practically important step)?

3.2. Relation between IR Results and Solvent Properties. The relationship between the IR intensity and the solvent properties was investigated. The dipole moment and solubility parameter, etc., had little significant relationship. However, when it was plotted against the dissolution temperature (T_{sol}), Figures 4 and 5 were obtained. The experimental values lay on a smooth straight line for the atactic sample, while for the isotactic sample the values fell on two smooth straight lines with different slopes.

In the latter case, particularly, since the dissolution temperature (T_{sol}) is directly related to the dissolution power of the solvents,[13] it is possible to say that the IR results are directly defined by the dissolution power of the solvents—i.e., a good solvent ensured a higher intensity ratio, whereas a poor solvent ensured a lower value. The reason why the IR results are related to the dissolution power of the solvents can be explained as follows: according to the molecular theory of polymer solutions,[14] the molecular dimension of a polymer chain in a solution is quite different according to the kind (or

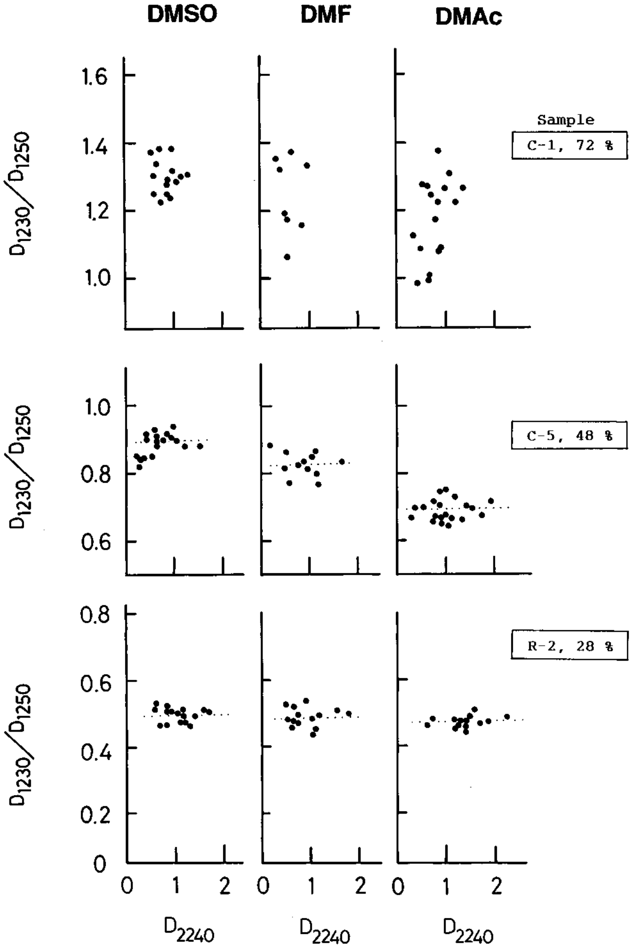

Figure 3. Quantitative IR results of PAN film indicating the solvent casting effect. The intensity ratio was obtained from IR spectra of PAN films having different thicknesses. The large scattering of the experimental data in the highly isotactic sample (72%) is closely related to the instability of the solution (see ref 12).

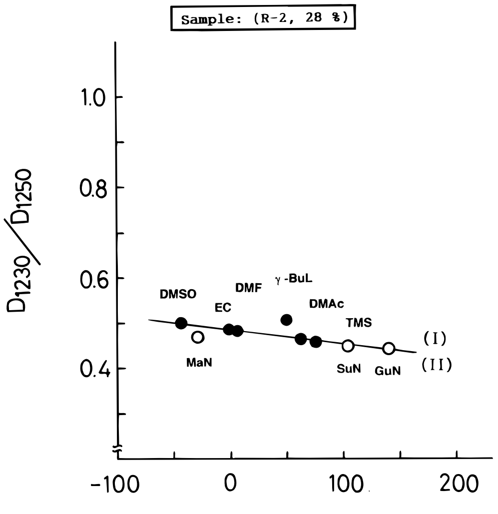

Figure 4. Relationship between T_{sol} and IR results for atactic PAN.

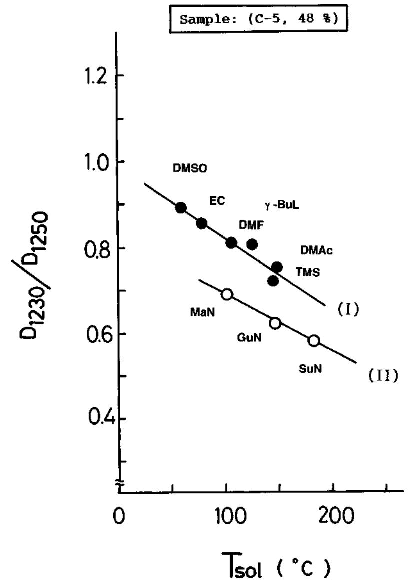

Figure 5. Relationship between T_{sol} and IR results for isotactic PAN.

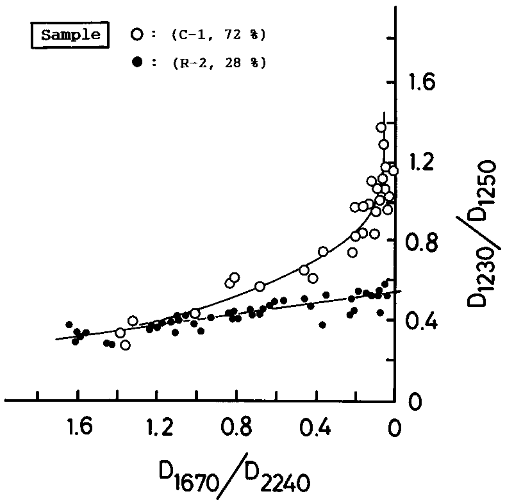

Figure 6. Variation of the IR intensity of PAN film in the solvent removal process. Solvent: DMF. The molecular weights of both samples are comparable enough (cf. Table 1).

type) of solvent. Generally, good solvents ensure an expanded dimension whereas poor solvents ensure a contracted dimension of a polymer chain. If the molecular dimension defined by the dissolution power of the solvents is directly retained in the solvent-cast film, the difference of molecular dimension in the solution will be reflected in the IR results of PAN through the difference of molecular conformation in the film. As a matter of fact, heat treatments of PAN film caused a significant variation of the IR intensity (see Figure 7).

3.3. IR Results and Film Preparation Conditions. The molecular conformation will depend on the film preparation conditions. The film preparation process consists of three elementary steps: (1) dissolution, (2) casting, and (3) solvent removal.

The first step (1) is of primary importance. The direct relationship between the T_{sol} and the IR results indicates that the molecular dimension of PAN is directly defined by the dissolution power of the solvent. The third step (3) is also significant from this point of view. One dilemma in the discussion of the structure–properties relationship in PAN is the residual solvent, since the intermolecular interaction between PAN and dipolar aprotic solvents is quite strong. One well-known empirical method for the effective removal of residual solvent is to boil the sample in hot water. This method is very effective and is used here.

The results are summarized in Figure 6. The progress of solvent removal from cast PAN film is clearly shown

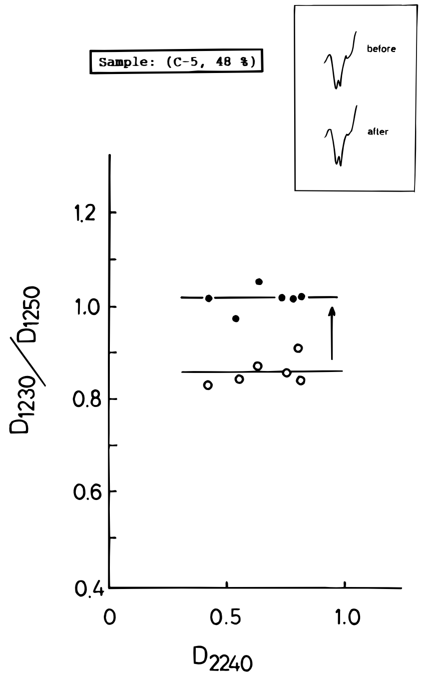

Figure 7. Variation of the IR bands before and after heat treatment. The film was heated to 200 °C under vacuum at a heating rate of 5 °C/min and rapidly quenched to ambient temperature.

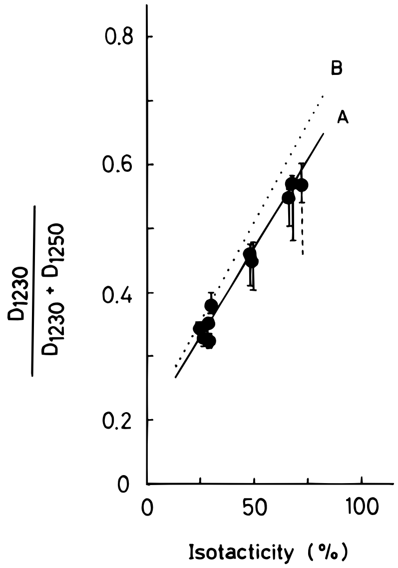

Figure 8. Effect of configuration and conformation on the IR results. The vertical line is due to the conformational effect. The results from a good solvent such as DMSO were very close to the results from the IR diffuse reflectance method (line B).[15] In a highly isotactic PAN (~70%), the intensity variation was very large, particularly toward the lower intensity region (see Figure 3).

in Figure 6 as the horizontal part of each line. The decrease of the carbonyl intensity ($\nu_{C=O}$) indicates the decrease of residual solvent from PAN film by boiling, although its intensity is normalized by dividing its intensity by that of the nitrile intensity ($\nu_{C\equiv N}$). It is obvious that in an ordinary atactic sample, the variation of the intensity ratio is relatively small, whereas in the isotactic sample, the intensity ratio increases gradually and rapidly rises in the final stage. That is, the intensity ratio is determined substantially at the final stage, where a trace amount of residual solvent is almost completely removed and where the molecular conformation of PAN is finally defined.

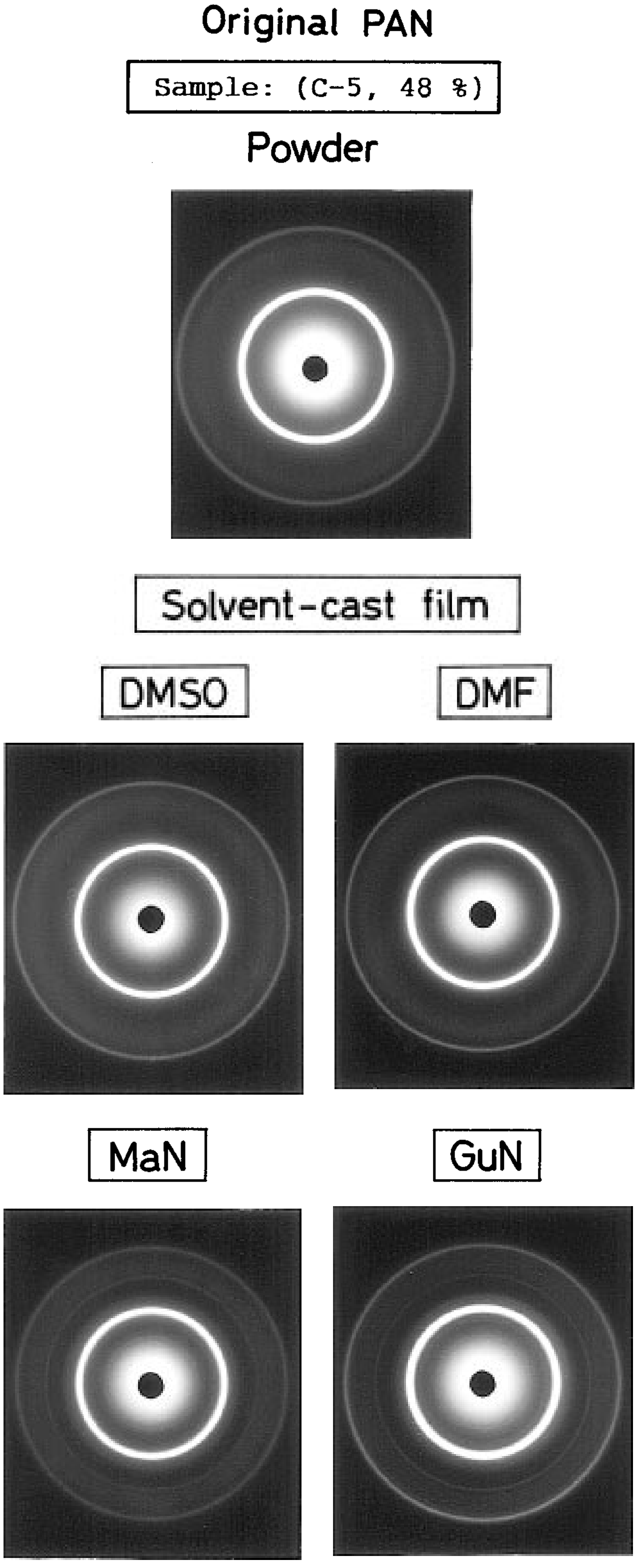

Figure 9. WAXD photographs of isotactic PAN film cast from different solvents. The existence of coaxial circles in the PAN film from poor solvents indicates that the sample is partially crystallized.

3.4. Effect of Thermal History on IR Results through Conformational Change. Thus, the IR characteristic absorption bands are strongly defined not only by configuration but also by conformation. Therefore, various experimental parameters relating to these will exert a significant effect on the IR results. Figure

7 shows the IR results of heat treatments for some cases. After the heat treatments, the 1230 cm^{-1} band was highly enhanced and the intensity ratio increased. The extent of this enhancement was larger when the stereoregularity of PAN was higher, and little effect was observed for the atactic sample.

In the above discussion (sections 3.1−3.3), the problem of residual solvent and the effect of thermal history can be neglected. This is because all the film specimens were prepared under carefully controlled conditions, particularly with respect to these two factors. In fact, no solvent carbonyl band was detected in the film and the IR intensity variation was relatively small, so long as the film was handled without any rapid thermal quenching, as shown in Figure 7.

All the experimental results obtained here are summarized in Figure 8. One can evaluate the relative contribution of both factors quantitatively. The solid circles are the results for a powder sample obtained previously.[8] A short vertical line indicates the experimental range of the variation of IR characteristic bands in the PAN film, the contribution from the conformation effect through the solvent casting and heat treatments.

It must be emphasized that the results obtained here have a significant meaning in the study of structure and properties relationships of PAN. This is because the most difficult problem in the study of PAN is the “molecular cohesion state and related problems”. As a matter of fact, as shown in Figure 9, quite different molecular cohesion states in PAN film are obvious from the WAXD results of solvent-cast films. By what mechanisms are these quite different structures formed? This problem is quite interesting and will be discussed in a forthcoming paper.[12]

4. Conclusions

The effect of film preparation conditions on the IR characteristic bands (1230/1250 cm^{-1}) of PAN film was studied. The IR bands were strongly affected by various experimental factors in the film preparation process. The primary factor was the kind of solvent used. The second factor was physicochemical factors relating to the solvent removal, including the thermal history etc. Thus, the IR intensity of PAN was dependent on not only configuration but also conformation, and the effect of both factors was quantitatively studied as a function of film preparation steps. It is suggested that there is considerable difference in the molecular cohesion state in PAN film according to the difference of the sample preparation conditions employed.

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