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Infrared Characteristic Absorption Bands of Highly Isotactic Poly(acrylonitrile)

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ABSTRACT: The infrared (IR) absorption spectra of highly isotactic poly(acrylonitrile) (PAN) prepared by γ-ray irradiation in a urea canal complex were studied in detail and compared with those of an atactic sample. It was found that there exist in the IR spectrum characteristic bands corresponding to the isotactic configuration of PAN. These are at 1250 and 1230 cm^{-1}. The relative intensity of these bands (D_{1230}/D_{1250}) is directly proportional to the content of isotactic triad units determined by ^{13}C NMR spectra. The relationship between the intensity of IR bands and NMR isotacticity percentage in triad units was obtained quantitatively. The assignment of the IR bands is briefly discussed based on halogen substitution experiments in the solid state, etc. Other IR spectroscopic features of isotactic PAN are briefly noted.

Introduction

It is well-known that highly stereoregular poly(acrylonitrile) (PAN) can be prepared by γ-ray irradiation in a urea canal complex of acrylonitrile.[1] The stereochemical structure of PAN prepared by such a method has been assigned to be an essentially isotactic configuration.[1,2] However, little infrared (IR) spectroscopic study of stereoregular PAN has been made. In this article, some IR spectroscopic features of highly isotactic PAN are described in relation to those of radically and anionically prepared PAN. The complete assignment of the IR bands of ordinary free radical PAN has already been made by Liang and Krimm.[3,4] Here we report that careful investigation of IR spectra can reveal the configurational differences of PAN molecules through the variation of the deformation modes of methine (CH) and methylene (CH$_2$) groups.

Experimental Section

Sample. Isotactic PAN was prepared in the manner of White[1] and Yoshii.[5] The sample was obtained in the form of a crystalline powder. For comparison, four different types of free radical samples[6] and one kind of anionically prepared sample were also used. These are characterized in Table I.

Table I
Characterization of Samples

sample polymerization	code	viscosity $(\eta)^a$	NMR results triad tacticity,[b] % I	H	S	$4IS/H^2$
canal[c]	C-1	1.61	72	22	6	3.44
canal	C-2	1.34	66	25	9	3.69
canal	C-3	1.52	67	24	9	3.99
canal	C-4	4.96	48	36	16	2.41
canal	C-5	4.58	48	35	17	2.60
anion[d]	A-1	2.17	30	43	27	1.82
radical	R-1[e]	2.14	25	51	24	0.94
radical	R-2[f]	1.97	28	46	26	1.35
radical	R-3[g]	6.03	29	49	22	1.07
radical	R-4[h]	6.87	26	47	27	1.32

[a] DMF, at 25 °C. [b] Peak intensity was calculated based on methine carbon. [c] All the canal samples were prepared by in-source method. [d] Prepared in THF by sodium–naphthalene, at −78 °C. [e] Homogeneous solution (DMSO/AIBN, at 55 °C). [f] Aqueous redox slurry (H_2O/APS-NaHSO$_3$, at 40 °C). [g] Aqueous solution (H_2O/APS, at 50 °C). [h] Bulk (photoinitiated, at 14 °C). THF, tetrahydrofuran; DMSO, dimethyl sulfoxide; AIBN, azobisisobutyronitrile; APS, ammonium peroxodisulfate.

^{13}C NMR Measurements. The JEOL NMR spectrometers JNM FX-90 Q and FX-100 were used. All the samples were measured in solution in deuteriated dimethyl sulfoxide (DMSO-d_6) at an elevated temperature. The conditions were as follows: frequency, 22.49 MHz; solvent, DMSO-d_6; concentration, 10–2%; temperature, 90 °C.

IR Measurements. The Hitachi double-beam grating IR spectrophotometers EPI-G$_2$ and A-285 were used. For quantitative purposes each spectrum was recorded at a sufficiently slow

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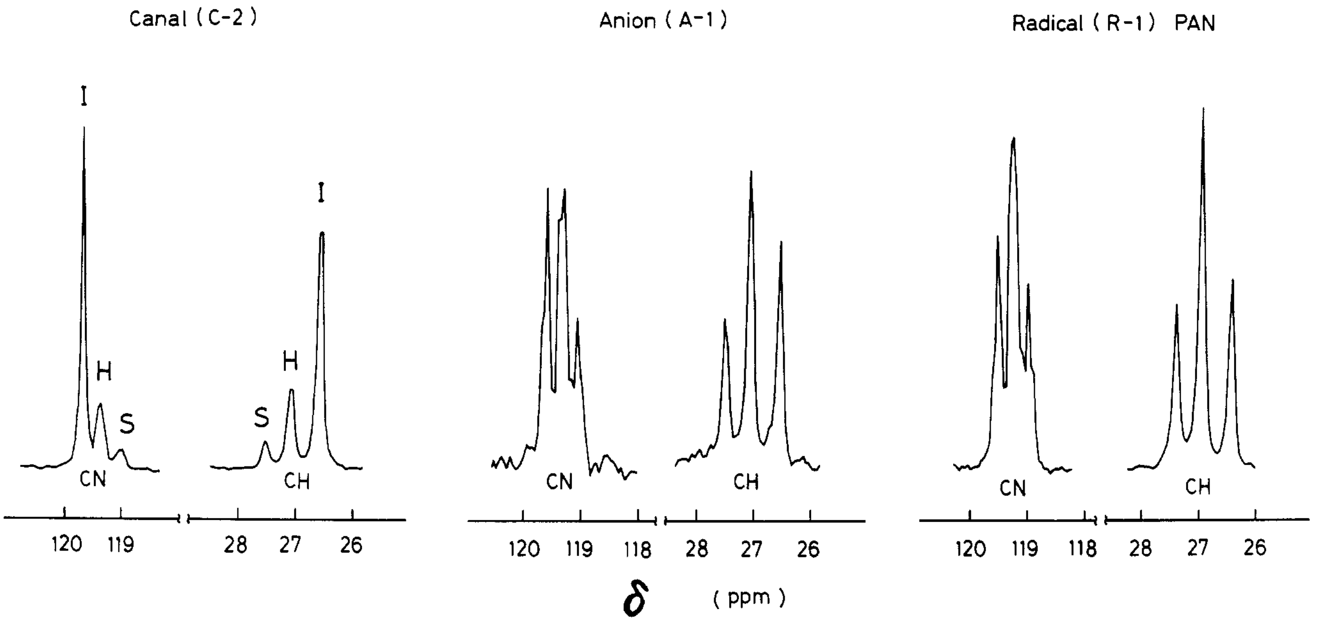

Figure 1. ^{13}C NMR spectra of three kinds of PAN. The notation given in ref 2 was used. That is, symbols I, H, and S indicate isotactic, heterotactic, and syndiotactic triad units. The isotacticity of these samples was 66%, 30%, and 25%, respectively.

scanning speed (16 min). The KBr disk method was mainly used for powders. In addition, direct measurements on solvent-cast films were carried out.

Results and Discussion

^{13}C NMR Spectra of Different Kinds of PAN. Typical ^{13}C NMR spectra are shown in Figure 1. It has been reported that differences in stereoregularity of PAN appear in the methine (CH) and nitrile (CN) carbons.[2,7] In the methine carbon, the isotactic peak appears at lower magnetic field, whereas in the nitrile carbon resonance it appears at higher field. The isotacticity is defined by three monomer units (i.e., triad tacticity) in this case. The isotacticity of ordinary radical and anionic samples was less than 30%. The canal polymerized sample showed a higher value. The highest value was 72% in our experiments (see Table I). Although there is some confusion about the stereochemical structure of PAN (i.e., syndiotactic,[8] syndiotactic-rich,[9,10] and atactic[11,12]), this confusion is excluded in the ^{13}C NMR results, as has been demonstrated by Schaefer.[7]

IR Absorption Spectra of Highly Isotactic PAN. Typical IR spectra are shown in Figure 2. In the stretching vibrational modes of the methylene (CH_2) and nitrile (CN) groups, little difference between samples was observed. For example, when the intensity of the methylene band was plotted against the nitrile band, a linear straight line was obtained. Any deviation from this linearity was quite small for isotactic and atactic PAN (Figure 3).

However, a noticeable difference was observed in the absorption bands appearing in the region 1300–1200 cm^{-1}. These are the 1250- and 1230-cm^{-1} bands, respectively (Figure 4). In ordinary atactic PAN, the former is stronger than the latter. However, in isotactic PAN, the latter is extremely enhanced, and in some cases the inverse relation was observed. It is likely that such anomalous IR absorption behavior is closely related to stereochemical differences.

Intensity of IR Bands and Stereoregularity of PAN. In order to obtain quantitative IR data, the relative intensity of these bands was determined by the base line method (see Figure 4). The results are summarized in Figure 5, in which a nearly straight line was obtained, although with some fluctuation. It is obvious that the relative intensity is independent of the weight of sample and is therefore dependent on the kind of PAN.

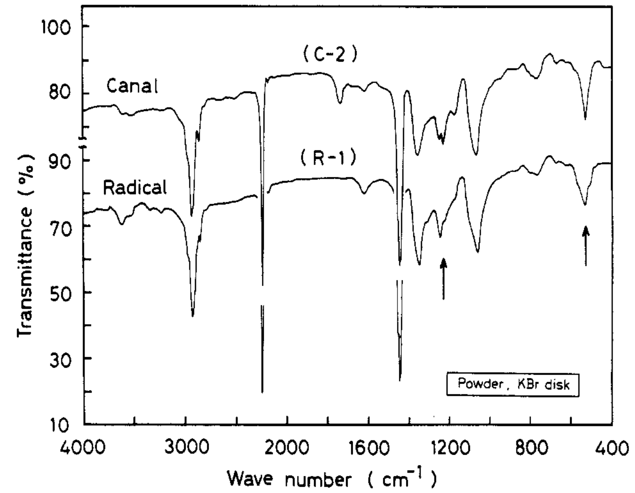

Figure 2. IR spectra of isotactic and atactic PAN. Arrows indicate the IR characteristic bands, which are sensitive to stereoregularity of PAN.

The IR results obtained in this way are plotted against the NMR results (Figure 6). A slightly curved relationship was obtained, as has been observed in the IR absorption behavior of other stereoregular polymers, such as isotactic polypropylene[13] and syndiotactic poly(methyl methacrylate).[14] It is apparent that when isotacticity is increased from 25% to 72% the intensity ratio increases from 0.5 to 1.4. When the results were normalized, Figure 7 was obtained. A linear relationship holds good in this case. The value of the normalized intensity increased linearly from 0.33 to 0.58. This can be expressed in the following numerical form:

$$Y = 0.21 + 0.51X \qquad (1)$$

where Y is the normalized IR intensity and X the fraction of isotactic triad units. The results indicate that if a completely isotactic (100%) PAN were prepared, the value of the normalized intensity would be 0.72, although such an ideal sample has not been obtained in our experiments. At any rate, from Figures 6 and 7, it is possible to conclude

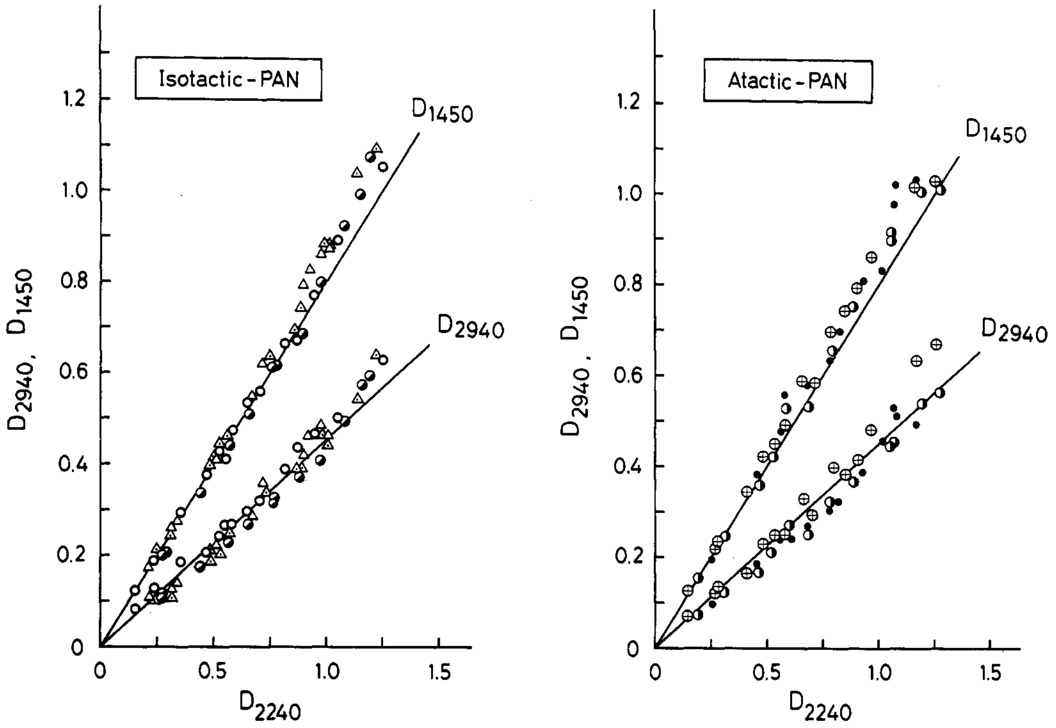

Figure 3. Quantitative IR results of CH_2 and CN bands. The meaning of each symbol is given in Figure 5.

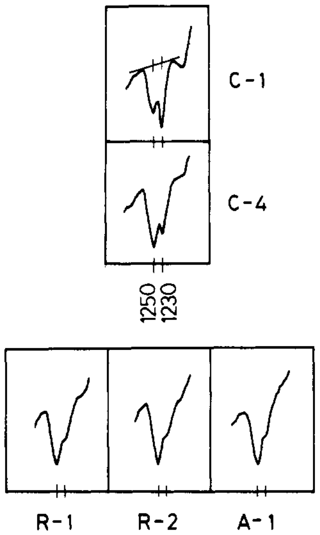

Figure 4. Difference of the IR bands in the region 1300–1200 cm^{-1}.

that the relative intensity or the normalized intensity of these bands is a direct measure of the stereoregularity of PAN.

Assignment of 1250- and 1230-cm^{-1} Bands. The complete assignment of the IR absorption bands of free radical PAN has already been given in ref 3 and ref 4, although the ambiguity of the bands in the region of 1400–400 cm^{-1} has been emphasized. According to Liang and Krimm,[3] the 1250-cm^{-1} band is assigned to the wagging mode of the methine (γ_w(CH)) group coupled with other bands, probably with the rocking mode of the methylene (CH_2) groups. The 1230-cm^{-1} band is due to the twisting mode of the methylene ($\gamma_t(CH_2)$) group coupled with the methine (CH) group. Although a different view point has been stated for the former coupling component,[9] the above assignments appear to be reasonable.

In order to confirm these assignments, a halogenation experiment in the solid state was carried out in the following way. As pointed out by Brandrup and Peebles,[15] when vinyl polymers, including PAN, are halogenated, the preferential attack of the halogen radical will occur in the β-position rather than the α-position. This effect, which is known as the directive effect of electronegative side groups in modern organic chemistry,[16] has been emphasized by the present authors.[17] Since the reactivity of radicals varies inversely as their selectivity,[18] if the most inert halogen such as iodine (I_2) is used, the most effective and selective halogenation in a β-position on a polymer backbone will be realized.

This halogen substitution reaction in the solid state was carried out on a PAN film, which was exposed to iodine vapor in an inert atmosphere at 230 °C. The results are shown in Figure 8. It is apparent that the 1250-cm^{-1} band is extremely enhanced and the 1230-cm^{-1} band depressed, which justify the above assignments and related considerations.

Strictly speaking, however, the assignment for the former is quite reasonable, but the assignment for the latter has some ambiguity. This is because the 1230-cm^{-1} band is overlapped in the slope of the 1250-cm^{-1} band, and exact calculation of the absorbance of the 1230-cm^{-1} band is impossible. One can consider other possibilities from a different point of view, such as the deformation vibrational mode of the methine (CH) group. That is to say, in comparing IR spectra of several vinyl polymers including poly(vinyl chloride) (PVC) and poly(vinyl fluoride) (PVF), the complete spectrum of PAN is close to that of PVF rather than PVC (see Figure 9). Specifically, (1) the relative intensity of the bands (1450, 1350, and 1250 cm^{-1}) in PAN is closer to that of PVF rather than PVC. (2) PVF shows a similar pair of bands (1250 and 1230 cm^{-1}) in this region similar to those of PAN. These similarities in IR spectra are probably due to the presence of structural disorder along the main chain in both polymers. Although the existence of such structural disorder in PVF is well-known,[20,21] similar structural disorder in PAN is not always well recognized. The present authors consider that PAN contains a considerable extent of longitudinal disorder along the main chain,[17] the extent of which is estimated to be more than 2.5 mol % in some typical cases.[22] (3)

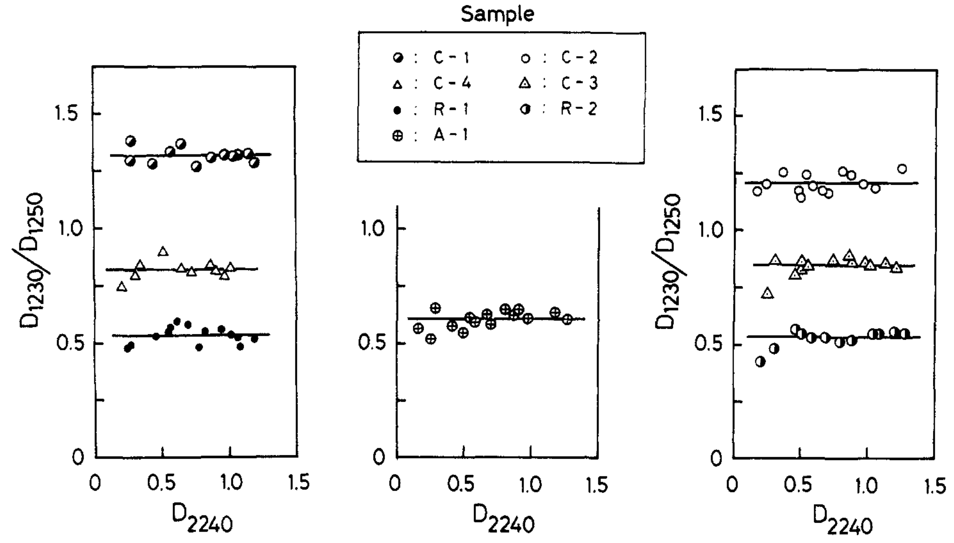

Figure 5. Determination of intensity ratio of the IR bands. To avoid confusion, experimental data of only 7 kinds of samples, which are selected from among 10 samples, are shown in Figures 3 and 5.

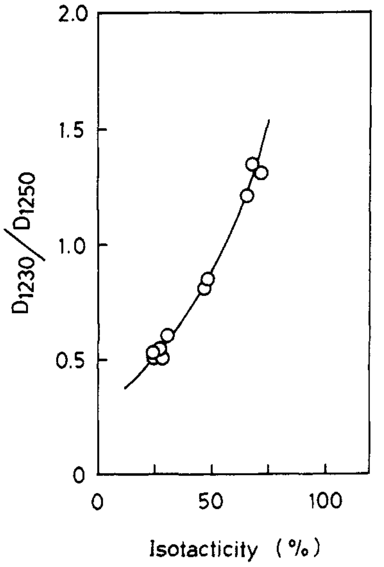

Figure 6. IR intensity ratio as a function of stereoregularity of PAN.

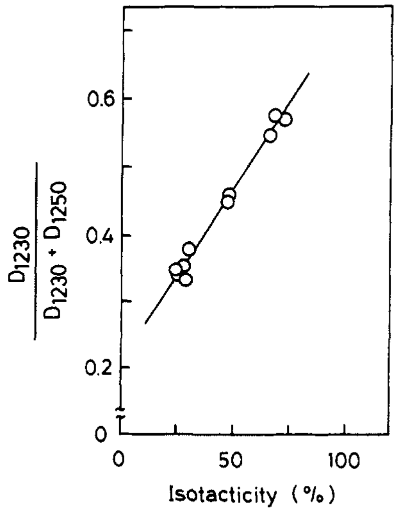

Figure 7. Normalized IR intensity versus stereoregularity of PAN.

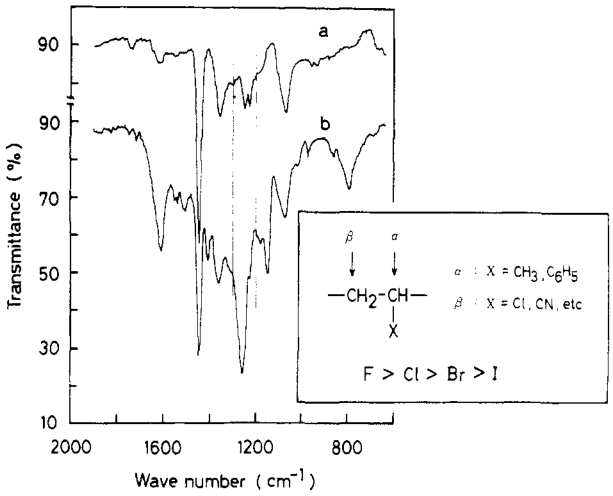

Figure 8. Change in IR spectra of PAN film before (a) and after halogenation reaction (b). Reaction conditions: 230 °C, 30 min, in N_2. The film was prepared by the solvent casting method from DMF solution.

Further, the assignment of the 1230-cm^{-1} band to the deformation vibrational mode of the methine (CH) group is also supported by the IR spectra of PVC (see Figure 9). In this case, ordinary radically prepared PVC shows the methine (CH) band at 1250 cm^{-1}. In stereoregular PVC, it splits into 1250- and 1220-cm^{-1} bands probably for internal stereochemical reasons. But it clear that these are deformation modes of the methine (CH) group.

In the above discussion, the important point is that the IR bands of vinyl polymers appearing in the region 1300–1200 cm^{-1} are generally assigned to the deformation vibrational mode of the methine (CH) group rather than the methylene (CH_2) groups. Of course, this consideration overestimates the methine (CH) band, and other possibilities may be considered. At any rate, in order to make the assignment of the 1230-cm^{-1} band and for the establishment of complete assignments of IR bands of PAN, more studies are necessary.

IR Absorption Behavior of 530-cm^{-1} Band. Other IR spectroscopic features of stereoregular PAN appear in the absorption band near 530 cm^{-1}. Although there is some confusion in the assignment of this band,[3,9] the effect of stereoregularity appears in this band. That is, when the isotacticity of PAN is increased, the intensity is enhanced and the half-value width decreases over a constant peak area (Figure 10). It is apparent that the half-value width of the 530-cm^{-1} band is directly related to the content of isotactic triad units in PAN, although the quantitative

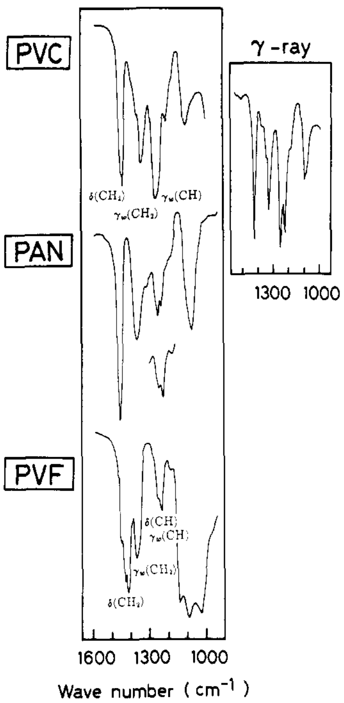

Figure 9. Comparison of IR spectra of several vinyl polymers. IR conditions: Powder, KBr disk method. The assignment of the bands in PVC and PVF was taken from ref 19 and 20.

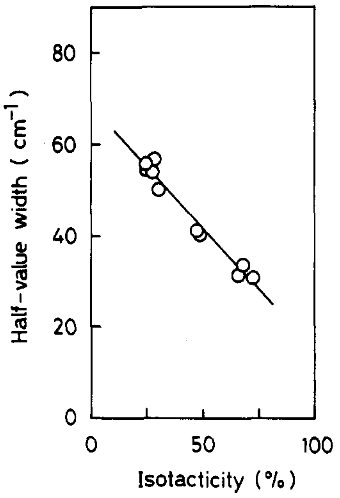

Figure 10. Half-value width of the 530-cm^{-1} band versus stereoregularity of PAN.

relationships to the sequence length, etc., are not clarified.

Conclusion

The existence and assignment of the characteristic IR absorption bands, which are sensitive to the stereochemical configuration of PAN, are briefly discussed. A comparison of IR spectra of various kinds of PAN reveals that there exist such characteristic IR bands appearing in the region 1300–1200 cm^{-1}. These are the 1250- and 1230-cm^{-1} bands. The relation between IR data and stereoregularity of PAN has been obtained quantitatively. The assignment of these bands is discussed on the basis of halogen substitution experiments. Other IR spectroscopic features of isotactic PAN are briefly discussed in relation to the half-value width of the 530-cm^{-1} band.

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