Studies of Poly-2-vinylpyridine. IV. Crystalline Bands in the Infrared Absorption Spectrum of Stereospecific Poly-2-vinylpyridine

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(Received June 12, 1967)

In 1960, Natta and others[1,2] reported systematic studies of the method and mechanism of the stereospecific polymerization of 2-vinylpyridine, and also of some properties of the polymer. They made use of the diffraction of X-rays as a direct method for the characterization of the crystals of poly-2-vinylpyridine. They also confirmed that the crystallized polymers are insoluble in hot acetone. However so far as this polymer is concerned, no method in which the infrared absorption spectrum is used for the characterization of the crystals has yet been reported. The present author has recognized that there are distinct absorption bands in the infrared spectrum at the wave numbers of 928 and 1180 cm^{-1}, which are characteristic of crystallized poly-2-vinylpyridine.

The stereospecific polymerization of 2-vinylpyridine and the purification of the polymer were carried out according to the method of Natta and others.[2] In the polymerization, phenylmagnesium bromide was used for the catalyst, and toluene for the diluent. A series of isotactic poly-2-vinylpyridines was then obtained by the same procedure, but by varying the concentrations of the catalyst and the polymerization temperatures. The crystallization of the polymer was effected by first maintaining the amorphous polymer for seven hours at 155—157°C under a nitrogen atmosphere, and by then treating the whole polymer in hot acetone. The polymerization conditions and some properties of the polymer, S-3, which was mainly used in this study are summarized in Table 1. As for the atactic, noncrystallizable poly-2-vinylpyridine, which was used for comparison, the G-2 fraction, described in the preceding paper,[3] was used.

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[1] G. Natta, G. Mazzanti, G. Dall'Asta and P. Longi, *Makromol. Chem.*, **37**, 160 (1960).

[2] G. Natta, G. Mazzanti, P. Longi, G. Dall'Asta and F. Bernardini, *J. Polymer Sci.*, **51**, 487 (1961).

[3] S. Arichi, This Bulletin, **39**, 439 (1966).

TABLE 1. THE POLYMERIZATION CONDITION AND THE PROPERTIES OF ACETONE INSOLUBLE FRACTION OF STEREOSPECIFIC POLY-2-VINYLPYRIDINE (SAMPLE No. S-3)

Monomer	C_6H_5MgBr	Toluene	Temp.	Time	Polymer	Yield	Acetone insoluble polymer				
							g/g of whole polymer %	Melting point °C	$[\eta]^{25°}_{\text{benzene}}$ d*l*/g	$[\eta]^{25°}_{\text{methanol}}$ d*l*/g	M_w by light scattering meas.
50 g	7.29 g	500 g	45°C	4 hr	45 g	90%	96.1	190—195	0.182	0.293	12.3×10^4

The Geiger-counter registration of the X-ray diffraction spectrum for the acetone-insoluble fraction of S-3 is shown in Fig. 1, and the photograph of the Debye-Scherrer ring for the same fraction, in Fig. 2. The crystal structure of S-3, characterized by an identity period of about 6.7 Å, which was estimated from Fig. 1, is essentially in accordance with the one reported by Natta and others.2) When the same X-ray examination was carried out of the atactic poly-2-vinylpyridine, G-2, neither peak nor ring such as is seen in Fig. 1 and Fig. 2 was observed.

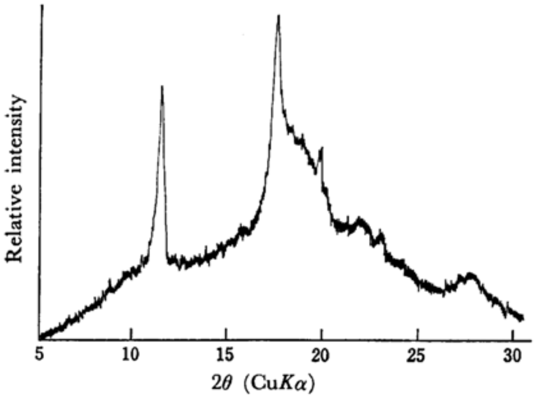

Fig. 1. Geiger counter registration of X-ray diffraction spectrum of the crystalline poly-2-vinylpyridine.

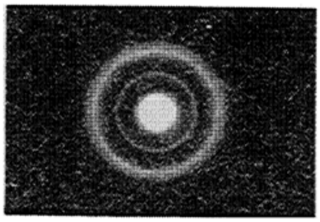

Fig. 2. Photograph of Debye-Scherrer ring for the crystalline poly-2-vinylpyridine.

The infrared absorption spectra of the crystallized poly-2-vinylpyridine, S-3, and the atactic poly-2-vinylpyridine, G-2, measured in the form of KBr pellets, are shown in Fig. 3. The characteristic absorption bands, shown in this figure, are observed in the spectrum of crystallized poly-2-vinylpyridine, S-3, at the wave numbers of 928 and 1180 cm⁻¹. These bands had been observed in the S-3 sample, neither before it was treated for crystallization nor when the acetone-soluble films which were prepared from a methanol or benzene solution of the S-3, sample, were examined without treatment for crystallization. The bands were, nevertheless, observed when the films had been treated in decalin at 120—130°C and proved to be acetone-insoluble.

The experimental results may allow us to conclude, at least qualitatively, that the characteristic absorption bands, especially the one at 928 cm⁻¹, can be used as an indicator of the degree of the crystallization of isotactic poly-2-vinylpyridine. The bands may even be useful in confirming the tacticity of poly-2-vinylpyridine.

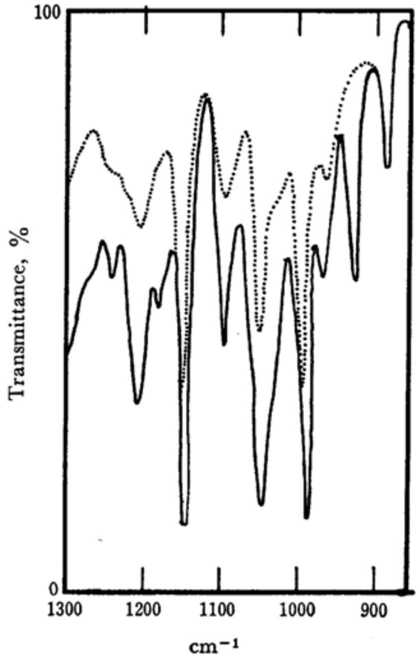

Fig. 3. Infrared absorption spectra of the crystalline (——), and atactic, (……), poly-2-vinylpyridine.

In spite of various attempts, we have not yet been successful in detecting any dichroism in the infrared absorption spectrum of the stereospecific poly-2-vinylpyridine. Further investigations of the quantitative relationship between the degree of crystallization and the intensity of the bands at 928 cm⁻¹ in the absorption spectrum are in progress.