

Infrared Spectrum and Chain Conformation of Poly(vinylidene Fluoride)

By GIUSEPPE ZERBI and GABRIELE CORTILI

(Centro Nazionale di Chimica delle Macromolecole del CNR; Istituto di Chimica Industriale del Politecnico,
Pza. L. Da Vinci, 32, Milano, Italy)

THE structure of poly(vinylidene fluoride) has not been previously determined. As part of the work on the vibrational spectra of fluorinated polymers we have studied the vibrational spectrum of poly(vinylidene fluoride). It has been previously reported¹ that the infrared spectrum of a cast film of poly(vinylidene fluoride) is drastically different at room temperature and above 170°. We report here on the infrared spectrum of a cold stretched sheet of highly crystalline poly(vinylidene fluoride) examined from 4000 to 70 cm.⁻¹ with Perkin-Elmer 221, 125, and 301 spectrometers. The dichroism of the spectrum has been studied with conventional polarizers (Perkin-Elmer) in the spectral region 4000—650 cm.⁻¹.

For a polymer chain obtained by a head-to-tail addition* of the $\cdot\text{CH}_2\cdot\text{CF}_2$ units several chain conformations can be postulated and the corresponding selection rules predicted: (a) helix with many chemical units and several turns per identity period as in the case of teflon.² For such a helix we expect 8 A_2 (IR, \parallel) and 17 E_1 (IR \perp) modes. (b) C_2 helix [Reinhardt's model of poly(vinylidene chloride)]³ 16 $A \parallel$, 16 $B \perp$. (c) C_s helix (Fueller's model of PVC2)⁴ 18 $A' \perp$, 14 $A'' \parallel$. (d) C_{2v} planar zig-zag chain 5 $A_1 \perp$, 4 $B_2 \perp$, 3 $B_1 \parallel$, 2 A_2 (inactive).

The simplicity of the observed spectrum suggests that the chain may possess a high symmetry. For a polymer chain whose line group is isomorphous with C_{2v} point group the expected 14

* Recent studies of the n.m.r. spectra of poly(vinylidene fluoride)^{5,6} suggest that 5—10% of the monomer linkages may be reversed from the usual head-to-tail sequence. These structural defects will give rise to spurious weak bands in the infrared spectrum. Our structural analysis is only based on the strong bands observed in the spectrum.

¹ T. Wentink, Jr., L. J. Willwerth, and J. P. Phaneuf, *J. Polymer Sci.*, 1961, **55**, 551.

² C. Y. Lyang and S. Krimm, *J. Chem. Phys.*, 1956, **25**, 563.

³ R. C. Reinhardt, *Ind. Eng. Chem.*, 1943, **35**, 422.

⁴ C. S. Fueller, *Chem. Rev.*, 1940, **26**, 143.

⁵ C. W. Wilson, *J. Polymer Sci., Part A, General Papers*, 1963, **1**, 1305.

⁶ R. E. Naylor and S. W. Lasoski, *J. Polymer Sci.*, 1960, **44**, 1.

normal modes can be described in terms of approximated group frequencies as follows:

$A_1 \perp$: $\text{CH}_2 \nu_s$, $\text{CH}_2 \delta$, $\text{CF}_2 \nu_s$, $\text{CF}_2 \delta$, $\text{CC } \nu_s$

$B_2 \perp$: $\text{CH}_2 \nu_a$, $\text{CH}_2 \text{ rock}$, $\text{CF}_2 \nu_a$, $\text{CF}_2 \text{ rock}$.

$B_1 \parallel$: $\text{CH}_2 \text{ wag}$, $\text{CC } \nu_a$, $\text{CF}_2 \text{ wag}$.

A_2 (inactive): $\text{CH}_2 \text{ twist}$, $\text{CF}_2 \text{ twist}$.

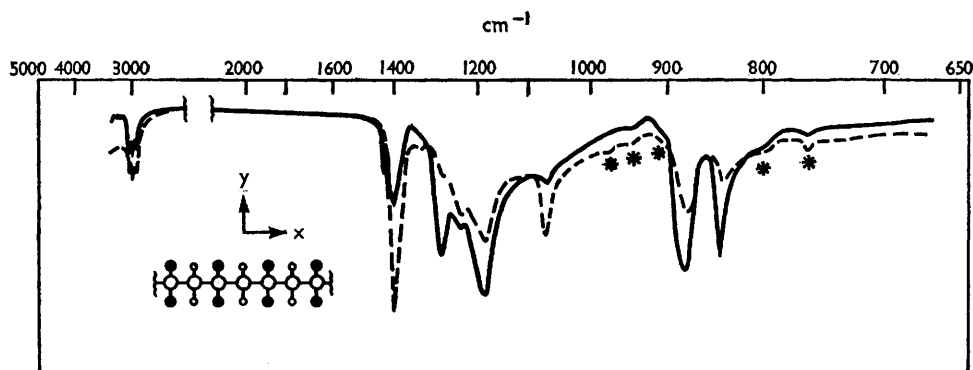
Accordingly in the frequency range 1450—700 cm^{-1} we should find five perpendicular and two parallel bands of strong or medium intensity. $\text{CF}_2 \delta$, $\text{CF}_2 \text{ wag}$, and $\text{CF}_2 \text{ rock}$ should occur as medium or strong bands below 600 cm^{-1} . Five perpendicular and two parallel bands in the right positions are actually observed from 1450 to 700 cm^{-1} in the spectrum of a cold stretched poly(vinylidene fluoride) sample. Three strong bands are found in the far infrared at 509, 480, and 298 cm^{-1} .

These experimental findings are good evidence that the polyvinylidene chain under suitable

conditions may take up a planar zig-zag conformation with one monomer unit per identity period, the length of which should be of about 2.54 Å.

It must be pointed out that in the infrared spectrum of a hot pressed sample of poly(vinylidene fluoride), as recorded by us, many strong bands occur especially in the far-infrared region. This fact proves that the molecular chain may take up at least another conformation which must be either helical or with a symmetry lower than C_{2v} . Leshchenko *et al.* have suggested a helical structure for poly(vinylidene fluoride) with an identity period of 25.4 Å.⁷

The decision of the precise type of the previously discussed chain conformations is not straightforward because it is based on small differences in the selection rules and polarization of some of the fundamentals. A more complete discussion of the chain conformation of poly(vinylidene fluoride) determined from its infrared spectrum and the corresponding vibrational assignment and normal-coordinate calculations will be reported elsewhere.



Infrared spectrum of cold stretched film of poly(vinylidene fluoride). [—] radiation polarized perpendicular to orientation direction; [---] radiation polarized parallel to orientation direction. Bands with asterisks belong to the spectrum of the helical form (present as impurity) and are not considered in the present discussion.

(Received, April 27th, 1965.)

⁷ S. S. Leshchenko, V. L. Karpov and V. A. Kargin, *Vysokomol. Soedineniya*, 1959, **1**, 1538; *Chem. Abs.*, 1960, 15998e.

Addendum

Unusual Co-ordination of the Palladous Ion in the Structure of *trans*-Di-iodobis(dimethylphenylphosphine)palladium(II)

N. A. BAILEY, J. M. JENKINS, R. MASON, and B. L. SHAW

Chem. Comm., 1965, 237.

Further refinement of the X-ray data ($R = 0.075$) has rotated the second phenyl ring of the Figure to a position where its β -carbon hydrogen is now positioned only 2.9 Å from the palladous ion, which is therefore effectively seven-co-ordinate.