IR Investigations of the Structure of PVC

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ABSTRACT

An infrared method has been developed to characterize the
double bond and crystallizable syndiotactic sequence content
of PVC. Good agreement was found for the double bond content
as determined by the IR method and chemical methods. The
IR crystallizable content was slightly greater than the x-ray
crystallinity, presumably because not all crystallizable
sequences actually crystallized.

Detailed knowledge of the structure and of the various structural
defects of PVC is very important for the characterization and develop-
ment of PVC products. This paper deals with an IR method that de-
scribes how to determine the content of double bonds and the amount
of so-called crystallizable syndiotactic monomer units.

EXPERIMENTAL

The samples under investigation were prepared at polymerization
temperatures of -78°C for the PVC urea complex up to +55°C. The
IR spectra were measured by the FTIR-15 B/D of Digilab Inc. and a
digitalized spectrometer 325-Model of Perkin-Elmer Co. The PVC
samples were pressed at room temperature to tablets of 300-1000
μm in thickness. Since it sometimes is impossible to press the

original PVC powder to homogeneous disks, we precipitate such samples from a 1,2-dichloroethane solution of 2%.

RESULTS AND DISCUSSION

The investigations of the dependence of concentrations of the different structural defects on the thermal stability of PVC have shown that the content of double bonds is presumably most important. There are different chemical methods to determine the C=C bonds in PVC, but the results obtained by those methods differ very much. Therefore we have investigated PVC samples, polymerized under various conditions, by FTIR and NMR. The NMR measurements shall not be discussed in this paper because much work has been done in this field by other scientific groups [1-5], but it is well known that there are at least three to five different signals in the C=C region of low molecular PVC extracts. The strongest of them is assigned to trans C=C. However, the IR spectra of thick PVC films mostly show only one absorption band at about 1667 cm^{-1} in the spectroscopic region of interest (Fig. 1). We compared the positions of that band with the absorption of C=C of low molecular weight model substances and assigned the absorption at 1667 cm^{-1} to the trans-$Cl-CH_2-CH=CH-$ endgroups. The absorption band at 1602 cm^{-1} is due to the water content of the PVC sample. It disappears after the deuteration with D_2O or after the drying of the sample.

Sometimes the absorption band shows an asymmetry and so we have calculated the first and second derivative of the spectra (Fig. 2). In the second derivative there appears another absorption band of very low intensity at about 1650 cm^{-1} (Fig. 3). In some of the PVC spectra there are some more absorption bands in the C=C region, e.g., a weak shoulder at 1640-1650 cm^{-1} and a weak absorption band at 1620 cm^{-1} and at about 1600 ± 20 cm^{-1}. The latter is probably the C=C stretching mode of aromatic starters or additives. We evaluated the intensity of the band at 1667 cm^{-1} as a peak height in the absorption mode and compared our results with the content of double bonds determined by a chemical method which was described by Hildenbrand et al. [6].

Very good agreement has been found between the results obtained by both methods.

It is well known that a commercial PVC, produced at temperatures between 50-60°C, is an atactic polymer with a content of syndiotactic diads of about 50-55%. And it is also well known that such a polymer is able to crystallize. Some years ago we therefore carried out some experiments to determine the crystallinity by IR and x-ray measurements. The IR measurements were performed by means of a digitalized Perkin-Elmer instrument. The curve fitting of the investigated spectral region was based on a somewhat altered program written by Jones. The values of syndiotacticity were determined by a ^{13}C-NMR
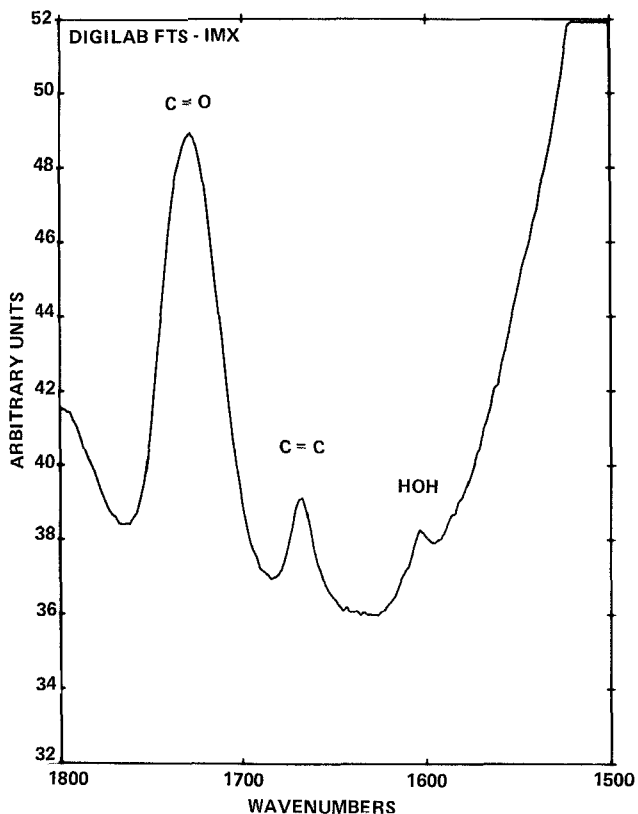
FIG. 1. IR spectrum of a 0.859-mm thick PVC sample.

measurement at elevated temperatures. Some typical IR spectra are
shown in Fig. 4.

   The well-known differences in the C–Cl stretching region are due
to the various chain configurations and conformations. The assign-
ment of the C–Cl absorption bands has already been given by other
spectroscopists [7-10] and therefore will not be discussed here.
For our measurements we assumed that only long syndiotactic se-
quences of at least four monomer units are able to form crystals
which cause the absorption at 602 and 638 cm^{-1} in the IR spectrum.
In such a case the intensity of these two bands should at least be pro-
portional to the crystallinity of the PVC sample. In order to evaluate
the intensity of these bands it is necessary to analyze the C–Cl band
complex. Pohl and Hummel [9, 11] have separated the overlapping
bands by a graphical method but they presumed the same width for
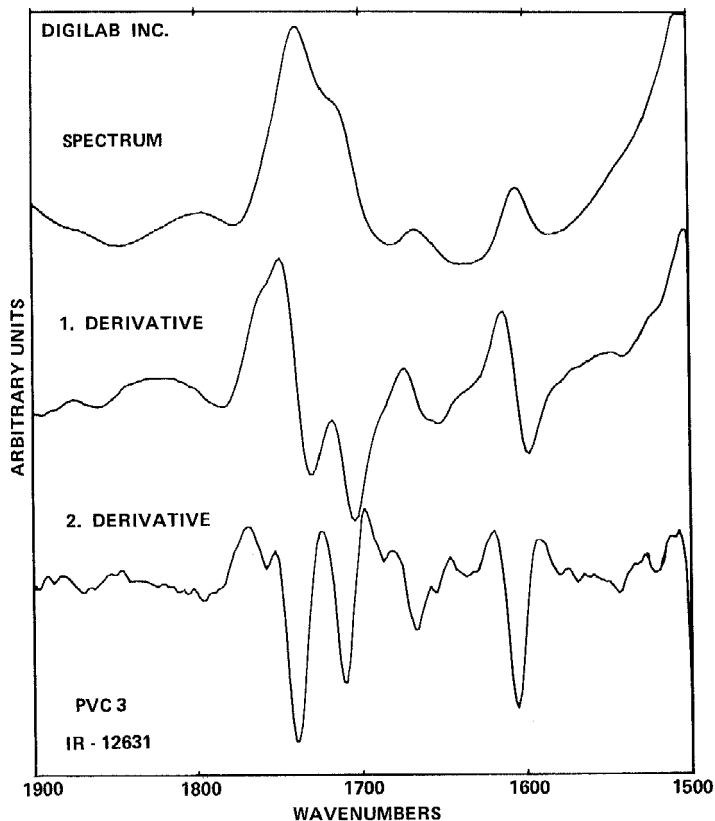all bands. Consequently they were unable to estimate the extinction

FIG. 2. IR spectrum of PVC and its first and second derivatives.

coefficients of the bands of interest. In order to separate these bands
by means of a computer it was necessary to know the number of bands
in the region in question, their positions, and their widths. We deter-
mined the positions and the widths of the two absorptions bands by
the experiment described in Fig. 5. In this experiment we compen-
sated a spectrum of a PVC sample in the solid state by the same
sample dissolved in THF. Since THF absorbs in the same region, we
had to compensate it, too.

We assumed that there are no long straight zigzag syndiotactic
chains left in the solution and that there are no significant changes
in the C–Cl frequencies. Since we had the same configuration of
chains in the solid film and in the solute, Spectrum D corresponds
only to the long straight linear syndiotactic chain sequences. After
a 20-min annealing of the PVC samples at 120°C the quantitative
measurement of the intensity of the 602 and 638 cm^{-1} absorption
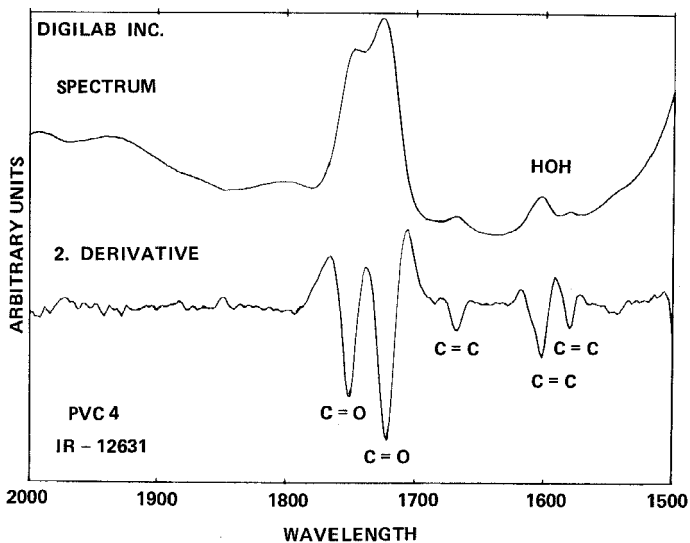
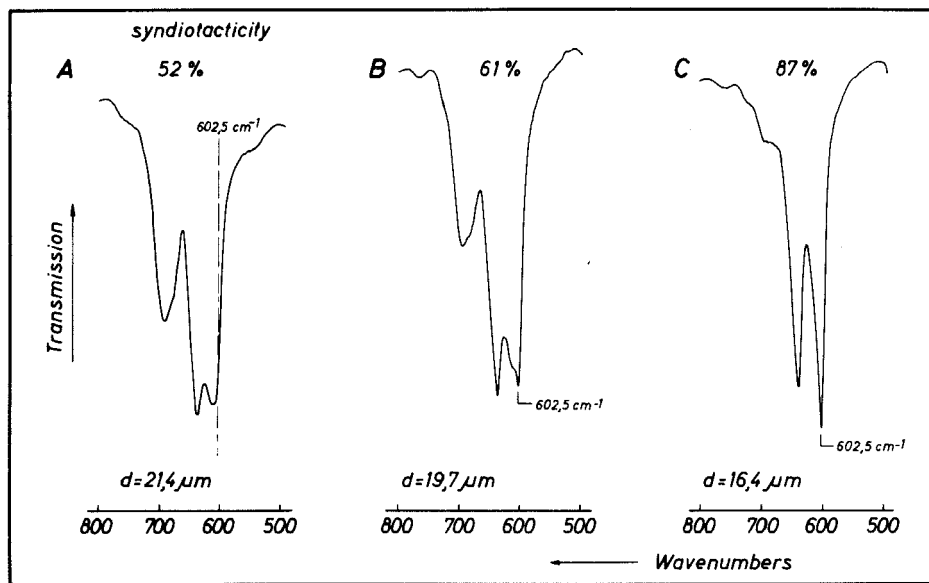FIG. 3. IR spectrum of PVC and its second derivative.

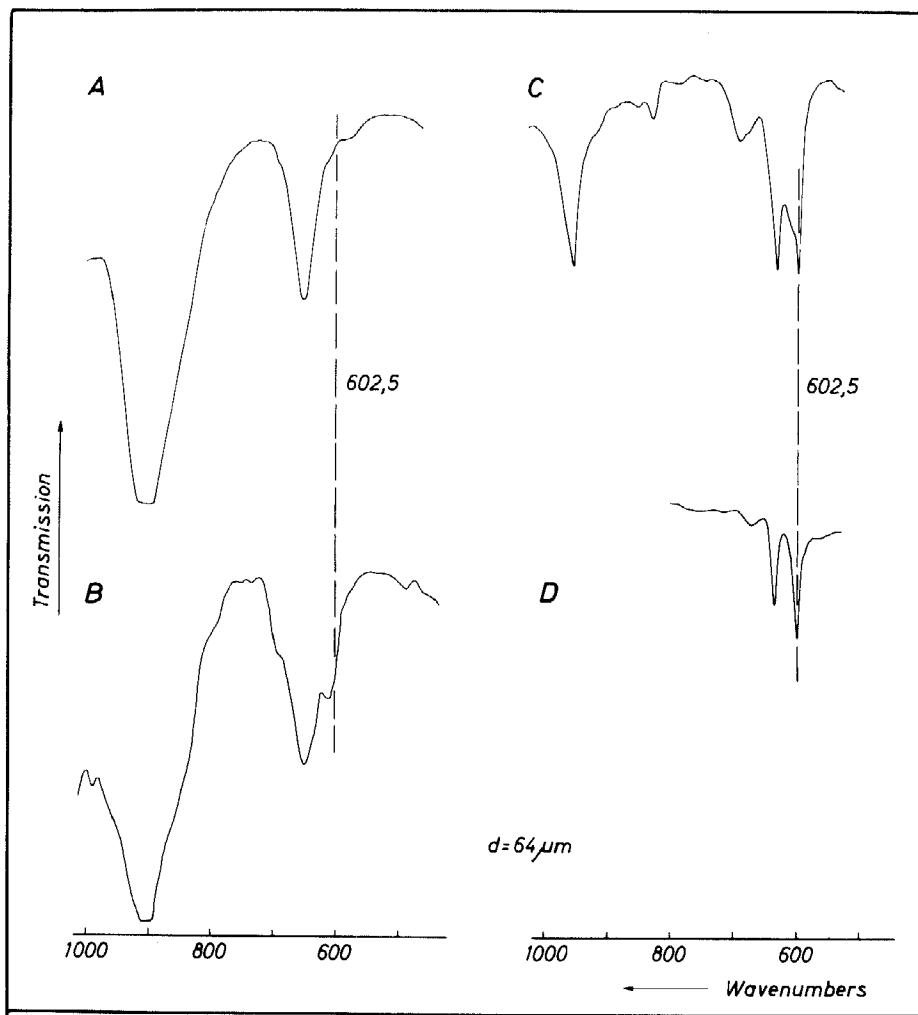FIG. 4. IR spectra of PVC. Syndiotacticity: (A) 52%, (B) 61%, (C) 87%.

FIG. 5. Spectrum A is the spectrum of THF, B is the spectrum of the solution, C is the spectrum of a solid film of PVC, and D is the difference of C minus A + B, i.e., it is the fully compensated spectrum.
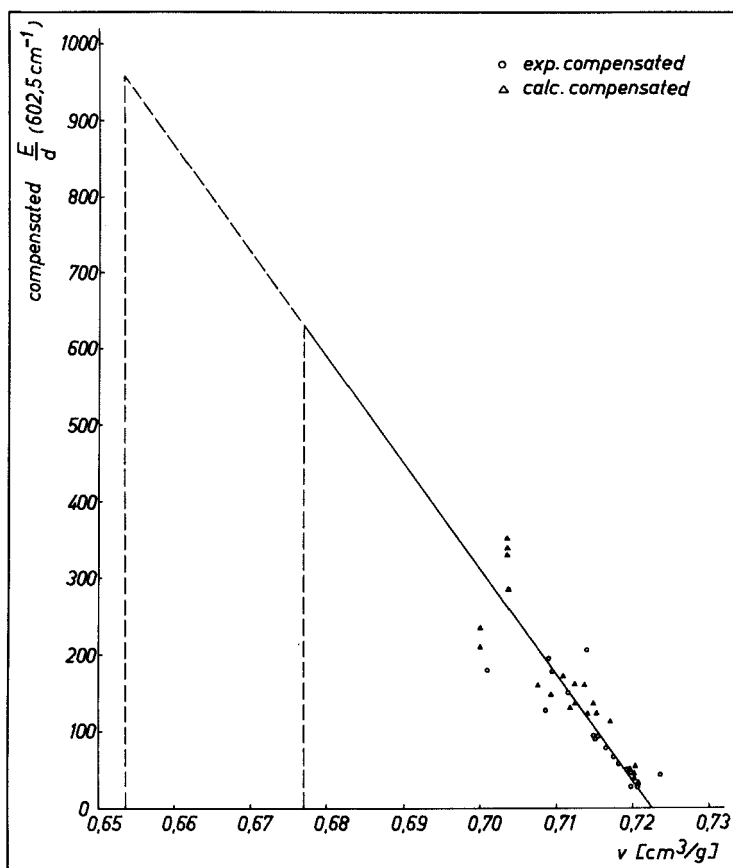
FIG. 6. Dependence of the band intensity of 602 cm^{-1} on the specific volume of the PVC samples.

bands should yield the amount of the so-called crystallizable syndio-tactic monomer units. In order to determine the extinction coefficients of these bands we measured the specific volume of different samples. In Fig. 6 the relationship between the specific volume and the intensity of the band is shown. The extrapolation to crystallinity equal to zero is easily done. We found a value of 0.722 cm^3/g which is in good agreement with the specific volume of amorphous PVC obtained by other methods. Nearly the same value was obtained by the extrapolation of the 938 cm^{-1} band. The described method does not work if the PVC sample is not soluble, especially in the case of high syndiotactic samples. So we did some comparative measurements
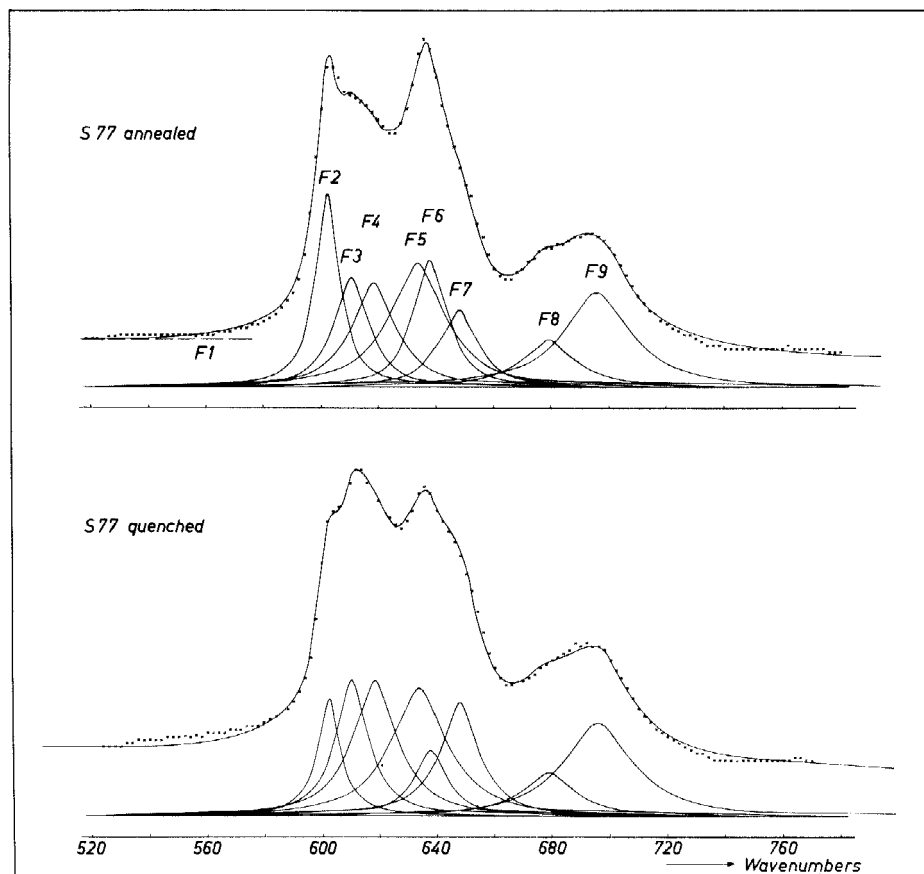
FIG. 7. Fitted IR spectra in the ν C–Cl region. Top: Annealed PVC. Bottom: PVC film quenched from the melt.

on soluble samples. We found that there is a linear relationship between the intensity of the band under investigation obtained by the described method and the direct measurement of the intensity at 602 cm^{-1} on thin PVC films after annealing. But there are some difficulties to estimate the band intensity of 100% crystalline PVC because in the literature [13, 14] different values are given. In consideration of the great differences in the specific volume of PVC crystals we had to determine the volume of each sample. First we proved if the sum of the C–Cl absorption band area, reduced to a definite thickness of the samples, alters with the different tacticities of the PVC samples. If the sum changes, we have to consider the extinction coefficients of these bands, i.e., the integrated band area divided by the thickness of the sample is different for the various C–Cl bands.

TABLE 1. The Positions and the Widths of the Computed Absorptions

Area	Position	Width (cm)
F2	602.5	9.6 (10)
F3	610.5	14.0
F4	618.6	18.6
F5	634	23.0
F6	638	13.4
F7	648	16.0
F8	679	22.6
F9	696	28.6

Fortunately, our results have shown the same sum of areas of C–Cl bands for all the samples. The deviations from the presumed constant sum are within the limits of experimental accuracy. The analysis of the C–Cl region with a set of Lorentzian peaks led to typical results shown in Fig. 7.

The agreement between the calculated and the experimental curves was a good one. Normally we needed less than 10 iteration steps to minimize the discrepancy between the experiment and the fitted curves.

The fitting procedure of spectra with different tacticities yielded the best results when the spectra were computed with eight peaks and the values of the positions and widths given in Table 1.

The number of bands within that region agrees with the work published by Hummel et al. [9, 11], but the widths of the bands differ very much.

In Fig. 8 we plotted the sums of the areas of the 638 and 602 cm^{-1} bands, divided by the corresponding thickness of the samples, versus the specific volume of those samples.

Unfortunately the plots show greater deviations than expected. It turned out that it is very difficult to get a somewhat larger range of the specific volume of PVC and that even small oxidation effects or a small quantity of additives falsify the density considerably. Despite such difficulties these results enable us to determine the specific volume of 100% crystalline PVC in approximation. The extrapolation of our diagram of the sum F_2 and F_6 to equal 100% leads to a value of the specific volume of 0.677 cm^3/g. The value obtained for the 100% amorphous material is nearly the same as that which we obtained from the diagram shown in Fig. 6. In comparison with the theoretical value evaluated by Wilkes [14] for PVC crystals, our specific volume is larger. We assume that the experimental value corresponds to the
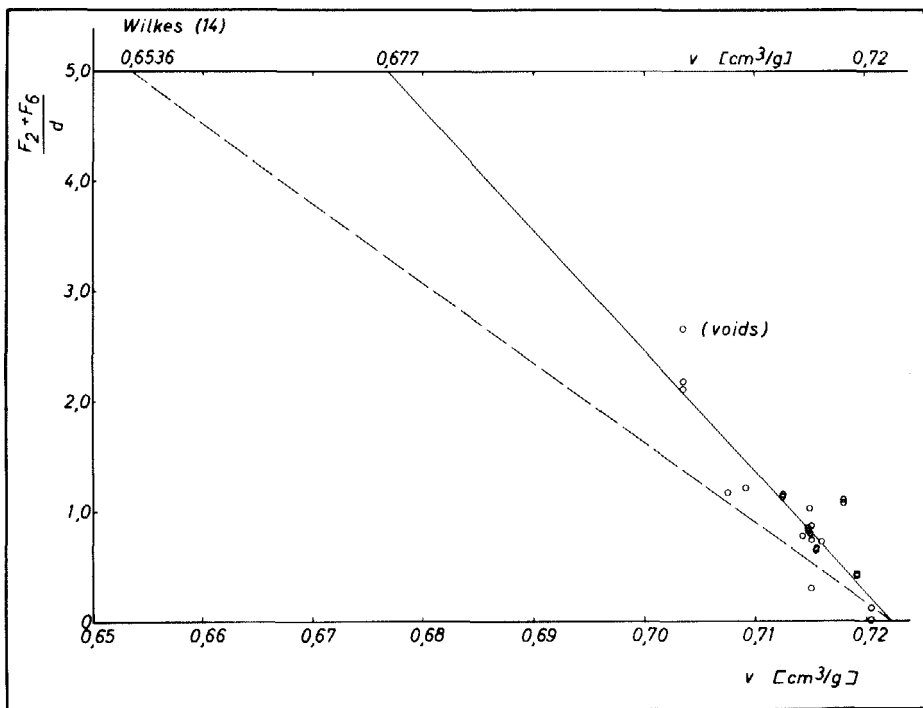
FIG. 8. Dependence of the sum of areas of the 638 and 602 cm^{-1}
absorptions on the specific volume of PVC.

TABLE 2

Poly-T (°C)	IR (%)	X-ray (%)	ΔH* (J/g)
+130	10	8	11
+70	13	7	14
−5	18	16	18
−52	24	22	−

specific volume of a real, poorly ordered PVC crystal. Knowledge of
the specific volume enables us to calculate the amount of crystalliz-
able syndiotactic units from the measurement of the intensity of the
602 cm^{-1} band after annealing.

Some results of the IR measurement obtained without any curve
fitting or compensation are given in Table 2.

The agreement of the results obtained by the IR and the x-ray method is good. The values obtained by IR measurements are somewhat greater than the results of x-ray measurements because not all of the chains are incorporated into the crystal.

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