A study of the C-Cl stretching region of the Raman spectrum of PVC

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The C–Cl stretching regions of the Raman spectra of a number of samples of PVC prepared by various methods which lead to differences in tacticity, conformational content and crystallinity have been studied. It is shown that the spectra of all samples can be fitted well with a set of nine Lorentzian peaks whose positions and widths are the same for each spectrum. Two of these peaks are attributable to the A_g and B_{3g} species vibrations of crystalline material and the remaining seven may be assigned with reasonable confidence to specific structures in the amorphous regions, three of which are associated with isotactic placements. The area under the A_g and B_{3g} peaks may be used to estimate the crystallinity of the samples and the area under the peaks assigned to isotactic material may be used to estimate the tacticity of the polymer.

INTRODUCTION

The detailed microstructure of PVC is very important in determining its physical properties and processing characteristics and the properties of the products. Configurational and conformational content, degree of crystallinity and distribution of orientations of amorphous and crystalline components can all be important. Configurational, and to a lesser degree conformational, content has been studied in great detail by means of high resolution n.m.r. spectroscopy (see e.g. refs 1–4). The chief drawback of this method is that it is at present applicable only to polymers in solution. Polymers of high syndiotactic content are virtually insoluble, and even for polymers which are soluble the conformational distribution in solution may not be representative of that in even the amorphous regions of the solid polymer. The technique which has so far given the most detailed information about the configurational and conformational content of solid PVC is infra-red spectroscopy (see e.g. refs 5–9).

The carbon–chlorine stretching region of the infra-red spectrum of PVC is particularly sensitive to the detailed structure of the polymer chains. Three approaches have been followed previously in elucidating, either qualitatively or quantitatively, the effects of different configurational or conformational contents on the spectrum. In the first approach the spectra of polymers which were known, from n.m.r. studies or otherwise, to have different configurational contents (degrees of tacticity) have been studied. Observation of the changes in the spectrum from one sample to another, or within one sample as it was mechanically worked or as its temperature was changed, have been used to associate particular features of the spectrum with isotactic or syndiotactic sequences or with energetically favourable or unfavourable conformations[6–9]. These studies have been closely associated with the second approach, the study of the spectra of small secondary chlorides[5,10,11]. For each of these molecules the possible configurations and conformations are known and, by comparing the spectra of a large number of them, Shipman *et al.*[11] showed that the most important influence on the frequency of the stretching vibration of a particular carbon–chlorine pair is the nature of the two atoms *trans* to the chlorine atom across both neighbouring C–C bonds.

The notation S_{HC} was used[11] to represent a conformation of a secondary chloride in which chlorine is *trans* to hydrogen across one of these bonds and to carbon across the other, with a corresponding meaning for S_{HH} and S_{CC}. The S_{CC} conformation is of very high energy and is unlikely to occur in secondary chlorides to any measurable extent. The range of frequencies of the S_{HC} conformations was observed to be approximately 655–674 cm^{-1} and that of the S_{HH} vibrations 608–637 cm^{-1}. The notation S_{HH} was restricted to planar zig-zag structures of at least five carbon atoms with the chlorine atom on carbon atom 3 and the notation S'_{HH} was used for bent structures. The ranges of S_{HH} and S'_{HH} vibrations were observed to be approximately 608–615 cm^{-1} and 627–637 cm^{-1}, respectively. Using these assignments it is possible to understand many of the features of the spectra of solid PVCs, but it is necessary to note first that the secondary chlorides used as model compounds are liquids and that conformations not present in the liquid state may be present in the solid polymer and secondly, that the frequencies found for small molecules may not be transferable directly to polymer molecules.

The third approach has been to attempt to calculate the vibrational frequencies for both ordered and disordered chains[12–14]. Once again, some results from small molecules must be used, but now force constants are assumed to be transferable from them to the polymer, rather than vibrational frequencies. This is undoubtedly a great step forward in principle, but in practice errors in the calculated frequencies can arise because of the choice of an insufficiently de-

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Table 1 Polymers studied

Polymer	Polymerization temperature (°C)	Commercial or experimental
M80/50		Commercial
S110/10		Commercial
5°C	5	Experimental
M–E	–30	Commercial
TR37ICH		Experimental
JLB237	–62	Experimental
U–C		Experimental

tailed and complete set of force constants. This may be particularly important when calculating the frequencies of disordered structures. An additional difficulty is that although frequencies of vibrational modes can be calculated for any molecular structure and assumed set of force constants it is not yet possible to calculate intensities with any degree of reliability, since studies of the transferability of information about dipole moments (or Raman tensors) from one molecule to another are still at an early stage. We therefore think that the empirical approach to the understanding of the effects of the detailed microstructure on the vibrational spectrum is still of great importance. The results of such an understanding are immediately applicable to practical problems and are also invaluable in testing the predictions of any calculations of the spectrum.

As already indicated, a great deal of effort has been devoted previously to the C–Cl stretching region of the infrared spectrum. The Raman spectrum has received very little attention, in comparison, and no detailed study of the C–Cl stretching region has been made except on spectra from a highly ordered polymer made in a urea–canal complex[15]. Although most of the vibrational frequencies of disordered molecular species are expected to be active in both infra-red and Raman spectra, because of the low symmetry of such species, Raman spectroscopy nevertheless has certain advantages over infra-red spectroscopy. An important advantage for certain kinds of samples is that no special preparation is required, such as microtoming thin slices off a thick sample or casting a film from solution. This means that thick specimens and powders can be studied without the risk of changing the molecular conformations during the preparation of samples.

A second advantage is that even an isotropic sample, provided that it is optically homogenous and does not produce polarization scrambling, can yield two different spectra, depending on whether the polarizations of the exciting and observed scattered radiations are parallel or perpendicular to each other. This provides information about the symmetry species of the vibrational modes and also helps in the resolution of overlapping peaks, because the relative intensities of two peaks will in general be different in the two spectra. Four different spectra can be obtained from an oriented sample, even for the simplest type of distribution of orientations. (In principle there are five different spectra but only four can be readily obtained experimentally for samples of moderately high birefringence[16].) In addition to providing yet further different spectra from the same sample for the purpose of band resolution this means that more information can be obtained about the distribution of molecular orientations than can be obtained from i.r. studies where only two different spectra can be obtained from an oriented sample.

We therefore decided to undertake a detailed quantitative study of the C–Cl stretching regions of the Raman spectra of a wide range of PVCs of varying tacticity, plasticizer content and degree of molecular orientation in order to elucidate as fully as possible the influence of molecular configuration, conformation and orientation on the spectra. In this paper we describe the analysis of the Raman spectra by digital computation into sets of overlapping peaks and discuss the origins of the peaks. The conclusions support, but with a sounder quantitative basis, most of those previously drawn from the evidence of i.r. spectroscopy and help to elucidate some outstanding difficulties. The results discussed in this paper are for randomly oriented samples. Some work on oriented samples will be reported in a separate publication.

EXPERIMENTAL

Samples

The types of polymer from which the samples were derived are shown in *Table 1* and further details of them are given below.

(i) M80/50: a commercial polymer made by BP Chemicals Ltd, using the mass polymerization process. $M_n = 42\,000$; $M_w = 84\,000$.

(ii) S110/10: a commercial polymer made by BP Chemicals Ltd, using the suspension polymerization process. $M_n = 57\,000$; $M_w = 150\,000$.

(iii) An experimental polymer polymerized at 5°C using the suspension polymerization process. $M_n \sim 108\,000$; $M_w \sim 865\,000$.

(iv) M–E: a commercial polymer made by the Montecatini–Edison Company. It was polymerized at –30°C using the mass polymerization process and has a viscometrically determined molecular weight of 60 000.

(v) TR37ICH: an experimental polymer of low molecular weight prepared by using a Grignard reagent as catalyst. The polymer was subsequently extracted using cyclohexanone and the sample used was the insoluble part. It is thus expected to be of rather high crystallinity.

(vi) JLB237: an experimental polymer of high molecular weight prepared at –62°C in a redox emulsion in methanol and water.

(vii) U–C: an experimental highly syndiotactic polymer made in a urea–canal complex[17].

Except for TR37ICH, the samples are listed in the order in which the syndiotactic content was expected to increase because of the decreasing temperature of polymerization or because of special polymerization conditions. TR37ICH was expected to be somewhere between the M–E and U–C polymers in syndiotactic content but whether it was of higher or lower syndiotactic content than JLB237 was not known initially.

The spectrum of each of these polymers was studied using the powder as received from the maker. Spectra were also obtained from clear sheets made from the M80/50 polymer. These sheets were prepared in the following way. 500 g of polymer in powder form was mixed with 20 g stabilizer (Mellite 831D) and the appropriate weight of plasticizer (dioctyl sebacate) to give one of the compositions specified in *Table 2*. The mixture was blended in a high speed mixer operating at 2000 rev/min for 5 min. From this blend 150 g was taken and milled between rollers to form a 'pelt' 1–2 mm thick. The rollers, which were heated by oil to 160°C, rotated at 20 rev/min and the pelt cooled in air to room temperature after leaving the rollers. When small

Table 2 Sheet samples

Sample	Plasticizer (g)/PVC(100 g)	Annealing time (min)
A	0	30
B	5	30
C	10	5
D	15	5
E	20	5
F	20	30

pieces cut from these pelts were examined between crossed polarizers it was clear that there were residual strains within them. The strains were relieved in the following way. A small piece cut from the pelt was placed between aluminium plates which were allowed to heat up in a press to 180°C. Sufficient pressure was then applied to make good contact between the polymer and the plates. The pressure was then removed but the heated plates remained in contact with the polymer for either 5 or 30 min. The plates and sample were then quenched in water at room temperature. Details of the samples produced in this way are given in *Table 2.*

Samples for spectroscopy were made from the annealed sheets by cutting off small pieces and polishing the surfaces through which the incident or scattered light would pass, using fine grade emery paper initially and finishing off with diamond paste.

Spectrometer and recording system

The spectra were obtained using a Coderg PHO double grating spectrometer and a Coherent Radiation Laboratories 52A argon ion laser tuned to 488 nm. The S-20 photomultiplier was cooled to −30°C and an axial magnetic field was applied in order to improve the signal-to-noise ratio. The signal from the p.m. was amplified by a low-noise amplifier and the output voltage was recorded both on a chart recorder and digitally on paper tape by means of a Solartron Data Transfer Unit (*DTU*). The spectrometer is scanned by means of a stepper motor which advances one step for every 0.125 cm^{-1}. An output pulse is produced in synchronism with the pulse to the stepper motor and this was applied to the *DTU* via a pulse divider so that readings of the output voltage from the spectrometer amplifier were punched onto the tape at equal intervals which could be selected to be any multiple of 0.125 cm^{-1}. For the spectra to be discussed the interval used was 1 cm^{-1} and the spectrum was recorded over the range 500–800 cm^{-1}. The output from a power meter which monitored the intensity of the laser beam, via a beam splitter, was also recorded on the tape immediately following each recording of the output from the spectrometer. The laser power drifted very slowly and usually by only ~1% during the running of any spectrum. In subsequent data analysis the first operation was always to divide the spectrometer output corresponding to any wavenumber by the power meter output at the corresponding wavenumber and multiply it by the power meter output at the lowest wavenumber recorded.

Before reaching the sample the laser beam passed through a $\lambda/2$ plate, which could be used to rotate the polarization of the incident beam from its initial vertical direction (V) to the horizontal direction (H), and then through an interference filter with a narrow pass band, which blocked plasma lines from the laser. Raman-scattered light was collected at right angles to the direction of the incident laser beam and then passed through an analyser which could be set to transmit either vertically or horizontally polarized light (v or h). After the analyser the light passed through a $\lambda/4$ plate which reduced the difference between the sensitivities of the spectrometer to vertically or horizontally polarized light to a negligible level.

Sampling for powders

The spectrum of a powder was recorded by packing a small quantity of it into the open end of a thin-walled glass capillary tube of internal diameter 1 mm and partly focussing the incident laser beam into the powder so that the beam was travelling parallel to the axis of the tube. The laser power at the sample was ~0.2 W and the spectrometer slit width was equivalent to ~2 or 4 cm^{-1}.

Sampling for sheets

The sheet samples were mounted so that the plane of the sheet was vertical, the laser beam was incident on the face of the sheet and the Raman light was collected from the edge of the sheet. The incident beam passed through the sheet, which was 0.5–1 mm thick, about 1 mm inside the edge from which the Raman light was collected. This arrangement was used so that the incident and scattered light each passed through only a small thickness of sample and polarization scrambling by residual inhomogeneities was minimized. The laser power at the sample was again ~0.2 W and the spectrometer slit width was equivalent to ~2 cm^{-1}.

Spectra of stabilizer and plasticizer

Raman spectra of the pure plasticizer and stabilizer were run. In the region of interest, 500–800 cm^{-1}, the largest peak in the spectrum of the plasticizer was at 770 cm^{-1} and the stabilizer had two peaks at 515 and 600 cm^{-1} with intensities in the approximate ratio 1:1.5. The spectrum of the sample of PVC with the highest plasticizer content, 20 pph, showed possible evidence of a peak at ~770 cm^{-1}, but the height of this peak was certainly $< 2\%$ of the height of the spectrum at its greatest value, at ~640 cm^{-1}. There was no evidence of a peak at 515 cm^{-1}. It was therefore concluded that the direct effects of the plasticizer and stabilizer on the spectrum of all sheets were negligible.

ANALYSIS OF SPECTRA

Introduction

In their analysis of the C–Cl stretching region of the i.r. spectrum of PVC, Pohl and Hummel[9] made the assumption that the observed absorbance can be regarded as the sum of a discrete set of symmetrical peaks of absorbance. They also assumed that all peaks in the complex have the same shape, that all peaks in the S_{HH}, S'_{HH} region have the same half-intensity width and that all peaks in the S_{HC} region have the same half-intensity width. The shape of the peaks was determined, and the separation made, by assuming that the outer sides of the peaks at the extreme ends of the complex are almost undistorted, so that after subtraction of a background they can be reflected about a perpendicular to the frequency axis through the peak and subtracted from the complex. The same was then done with the remaining complex and so on until complete separation was achieved. Although this procedure seems somewhat arbitrary, a fairly successful separation appeared to be made and a plausible assignment was given to each of the peaks found.

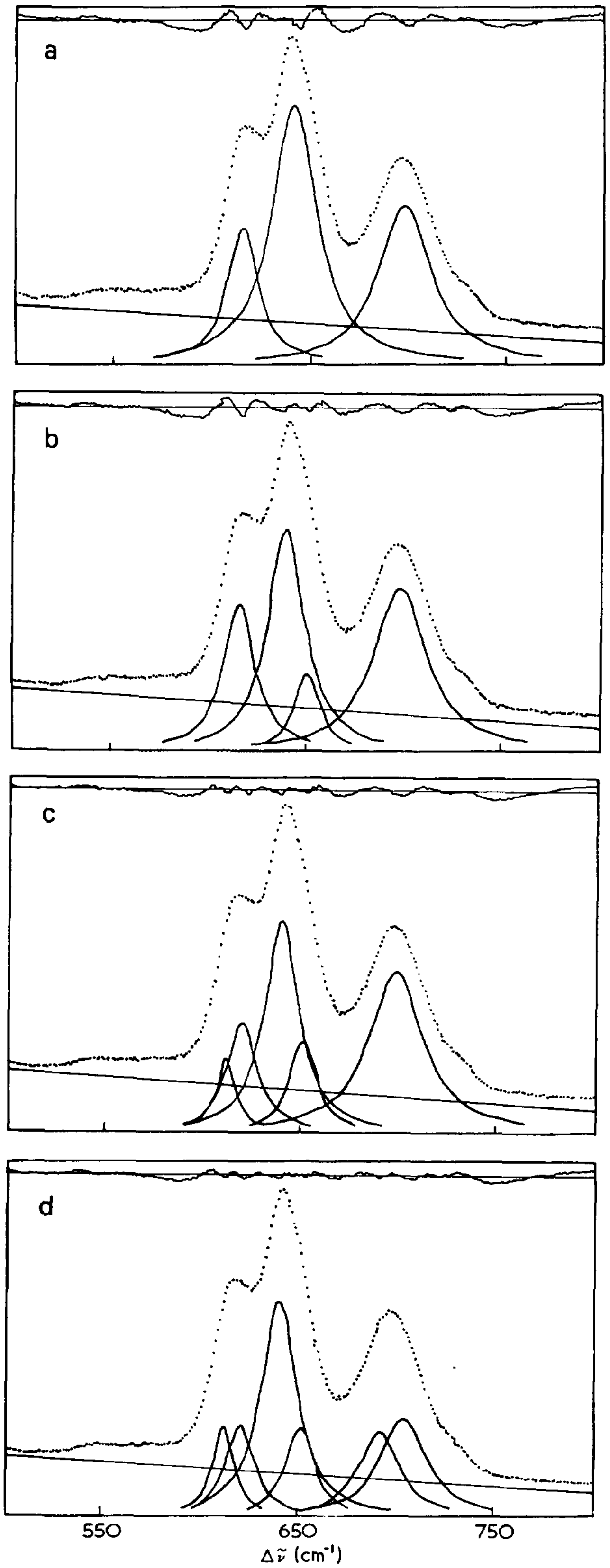

Figure 1 Fits to spectrum of M–E powder using (a) three; (b) four; (c) five; (d) six major peaks. ...., are the experimental intensities; ———, show the Lorentzian peaks and linear background and above each spectrum is shown the deviation of the experimental points from the sum of the fitted peaks and background. For clarity the minor peaks included in the fit, at ~545, 570, 730 and 760 cm^{-1}, are not shown in the Figure

In the present work assumptions somewhat similar to those made by Pohl and Hummel in analysing the i.r spectra were used in analysing the Raman spectra. First, it was assumed that the observed scattered intensity was the sum of a linear background and a set of overlapping Lorentzian peaks. This is at first sight an even more arbitrary assumption and it was made as a working hypothesis which it was hoped would be justified, at least to a fair approximation, by the results obtained. It had the practical advantage of giving each peak a simple mathematical shape requiring only three parameters, viz. height, width and position of centre, to specify it completely. In addition it has been shown that this line shape is usually a good fit to isolated infra-red peaks[18,19] and it has also been used successfully in the analysis of the Raman spectrum of a polymer[20]. With one exception, to be noted later, no restriction was placed on the half-intensity widths allowed.

In Pohl and Hummel's work the fitting was done by a graphical procedure, whereas in the present work a digital computer was used to find a 'best fit'. It was thus necessary to decide, before making each fit, how many peaks were to be used. Since a large number of samples with a wide variety of degrees of configurational and conformational order was available, which provided a correspondingly wide range of shapes for the C–Cl stretching complex, the criterion adopted was that the number of peaks used should be the minimum required to permit the fitting of the spectra from all the samples with the positions and widths of corresponding peaks the same for each sample. This meant that some samples were eventually fitted with a larger number of peaks than would have been necessary for obtaining an almost equally good fit to an individual sample. Some further constraints placed on the form of the fit will be discussed in the following sections.

Fitting procedures

The linear background and set of Lorentzian peaks were fitted to the observed intensity distribution in the spectrum using an iterative 'damped least squares' procedure[21,22]. In this procedure an initial set of estimated values of the various parameters in the function describing the fitted spectrum are refined using the first derivative of the function with respect to each of the parameters to estimate the effect of a change in that parameter on the fit.

It was clear from visual inspection of the spectra that in addition to the major peaks required in the fit four small peaks were present at approximately 545, 570, 730 and 760 cm^{-1}. The parameters describing these small peaks were not allowed to vary in the fitting procedure. If they had been allowed to vary freely they could have interferred seriously with the fitting of the major peaks and background.

Spectra of powders

Every sample showed the need for at least three major peaks at approximately 615, 640 and 700 cm^{-1}. An attempt to fit the spectrum of the M–E powder, which is of intermediate order, immediately showed, however, that only a rather poor fit could be obtained unless at least six major peaks were used. Fits using 3, 4, 5 and 6 major peaks are shown in *Figure 1* and the positions of the centres of the fitted peaks are shown in *Table 3*, together with the r.m.s. deviations of the fits expressed as a percentage of the maximum observed intensity.

The three extra peaks could also be justified by examination of the spectra of other samples. The spectrum of the

Table 3 Fits to M–E powder spectrum

No of peaks fitted	Peak positions, $\Delta\bar{\nu}$(cm^{-1})			100 X r.m.s. deviation/peak height
3	614	641	697	1.8_2
4	614	638 649	697	1.5_0
5	610 618	638 649	696	1.1_7
6	610 619	638 649	690 702	0.9_7

U–C sample could only be fitted well using Lorentzian peaks if four peaks at ~608, 638, 647 and 700 cm^{-1} were used. The peaks at 608 and 638 cm^{-1} have previously been interpreted as being due to the B_{3g} and A_g vibrations, respectively, of crystalline syndiotactic material[15,23]. It was thus reasonable to expect that a good fit to the spectrum of the M–E powder would require peaks in the 608 and 647 cm^{-1} regions, as found. An indication that at least two peaks were required in the 700 cm^{-1} region was provided by the crossed polarizer spectra of sheet samples, which suggested a peak near 675 cm^{-1}.

Having obtained fairly good fits to the spectra of the M–E and U–C samples when they were fitted separately an attempt was made to fit the two spectra simultaneously, constraining corresponding peak positions and widths to be the same in each spectrum. A poor fit was obtained in the region 600–650 cm^{-1}, particularly for the M–E powder (*Figure 2a*). This was attributed to the fact that the spectrum of the U–C sample consisted of two very well-defined peaks, assigned to the crystal vibrations, and only rather small contributions from peaks due to disordered structures. The two crystal peaks thus dominated the fit to the two spectra. It was clear from the spectra that there was a large contribution in the spectrum of the M–E sample at slightly lower frequency than the A_g crystal peak at 638 cm^{-1}, since the actual maximum of intensity was at a lower frequency than for the spectrum of the U–C sample. The introduction of a further peak, even when fitting two spectra together, seemed likely to produce a meaningless fit unless some additional constraint was introduced at the same time. It was therefore assumed that the part of the spectrum due to the crystalline regions could be represented by two peaks of equal width. The width and separation of these peaks were allowed to vary but were constrained to be the same for all spectra fitted together. Initially, the peak heights were left free. When this composite peak and five other major peaks were used to fit the two powder spectra a far superior fit was obtained. The ratios of the heights of the A_g and B_{3g} species crystal peaks were, however, found to be slightly different for the two spectra, viz. 1.70 for the M–E sample and 1.85 for the U–C sample. It was decided to constrain the fit so that the value of this ratio was free to vary but was the same for each spectrum of the pair. A good fit was still obtained (*Figures 2b* and *2d*) and the ratio required was 1.71. A third peak was used in this fit in the S_{HC} region, since the attempts to fit the spectra of sheets with only two peaks in the region 675–700 cm^{-1} had shown that the 'best fit' positions of these two peaks were at about 690 and 705 cm^{-1} and that an excess of intensity was left near 675 cm^{-1}. The addition of this third peak produced a slight improvement in the fit to the M–E sample but the positions of the peaks in this region are best determined from other samples since the U–C and M–E samples show weaker scattering in this region. The fit showed the centres of the crystal peaks to be at 609 and 638 cm^{-1} and those of the other peaks to be at 618, 631, 647, 681, 690 and 701 cm^{-1}. It is important to note that although eight peaks are available for fitting each spectrum, only four remain with any significant intensity in the 'best fit' to the spectrum of the U–C powder.

In order to test the wider applicability of this fit, which uses the composite crystal peak and six other major peaks, four powder spectra were fitted simultaneously. The two additional powders were the commercial sample M80/50, which is of lower order than the M–E sample, and the experimental powder TR37ICH, expected to be of order intermediate between that of the M–E and U–C powders. A moderately good fit was obtained but significant deviations were observable in the 620 cm^{-1} regions of the spectra of both the M80/50 and M–E samples. The effect of replacing the peak near 620 cm^{-1} by two peaks was therefore investigated and a very good fit was obtained (*Figure 3*). The overall fit of all four spectra was now good and it is thus suggested that a minimum of nine major peaks is required in order to obtain a simultaneous good fit to spectra obtained from samples of widely differing order.

A second simultaneous fit to the spectra of four powders, which were now chosen as M80/50, S110/10, 5°C and JLB237 was therefore made using nine major peaks. In this fit the A_g and B_{3g} species peaks were constrained to be in the same positions and to have the same ratio of peak heights as found in the fit to the first set of four powders, since that set contained the spectrum of the U–C polymer which defines these fairly precisely. The positions of the other seven major peaks and the widths and heights of all the peaks were allowed to vary freely, except for the constraint that the two crystal peaks were to be of equal width. The peak positions and widths found in this fit were slightly different from those obtained in the first fit and in order to obtain sets of comparable fits for the spectra of all seven powders each set of four was refitted with the positions and widths of the peaks constrained to be the same as those found in the first fit to the other set. *Table 4* shows the mean positions and half-widths of the peaks found in the two fits and the mean areas, expressed as a percentage of the total area under the C–Cl stretching region. The uncertainties shown are simply half the differences between the values obtained in the two fits.

The percentage area of a peak will be assumed in the following section to be a measure of the concentration of the structure to which the peak corresponds. This assumption is equivalent to the assumption that the total area under the C–Cl stretching region is proportional to the total number of $-CH_2-CHCl-$ units contributing to the spectrum, irrespective of the degree of configurational or conformational order of the sample or of its crystallinity. As shown in *Figure 3*, the shape of the C–Cl region of the spectrum changes very considerably from sample to sample because of the relatively strong dependence of the C–Cl stretching frequency on these factors, which is precisely why this region of the spectrum is useful in studying them, and it might be expected that there would be equally serious effects on the Raman activities. The C–H stretching region shows a very much smaller change from one sample to another and it might therefore be expected that the total area under this region of the spectrum would be a better measure of the total number of $-CH_2-CHCl-$ units contributing to the spectrum. This region of the spectrum was therefore recorded for each powder and the area under it was compared with that under the C–Cl stretching region, using measurements made by means

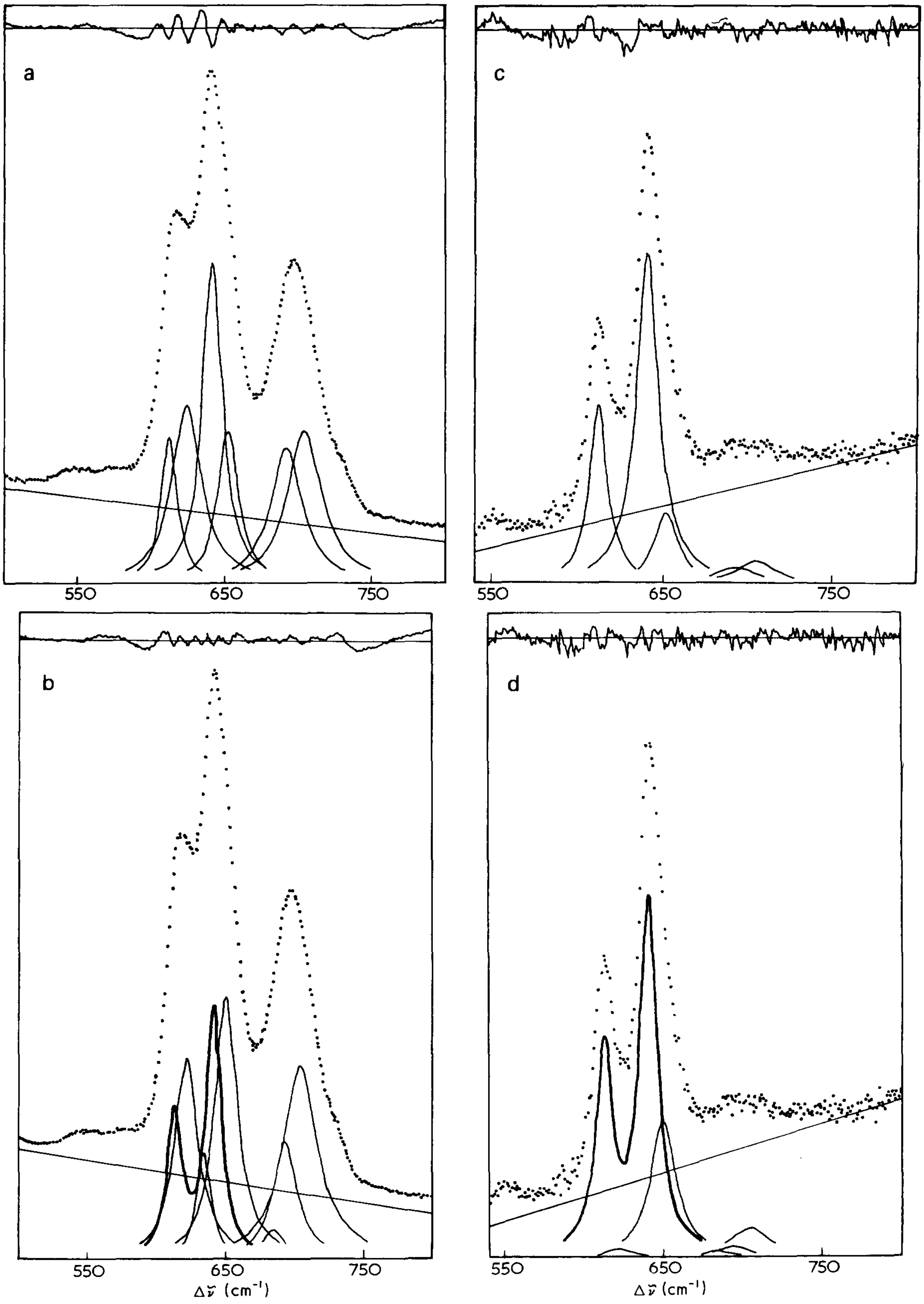

Figure 2 Simultaneous fits to spectra of M–E (a,b) and U–C (c,d) powders. (a) and (c) without composite crystal peak; (b) and (d) with composite crystal peak. Notation, etc., as in *Figure 1*

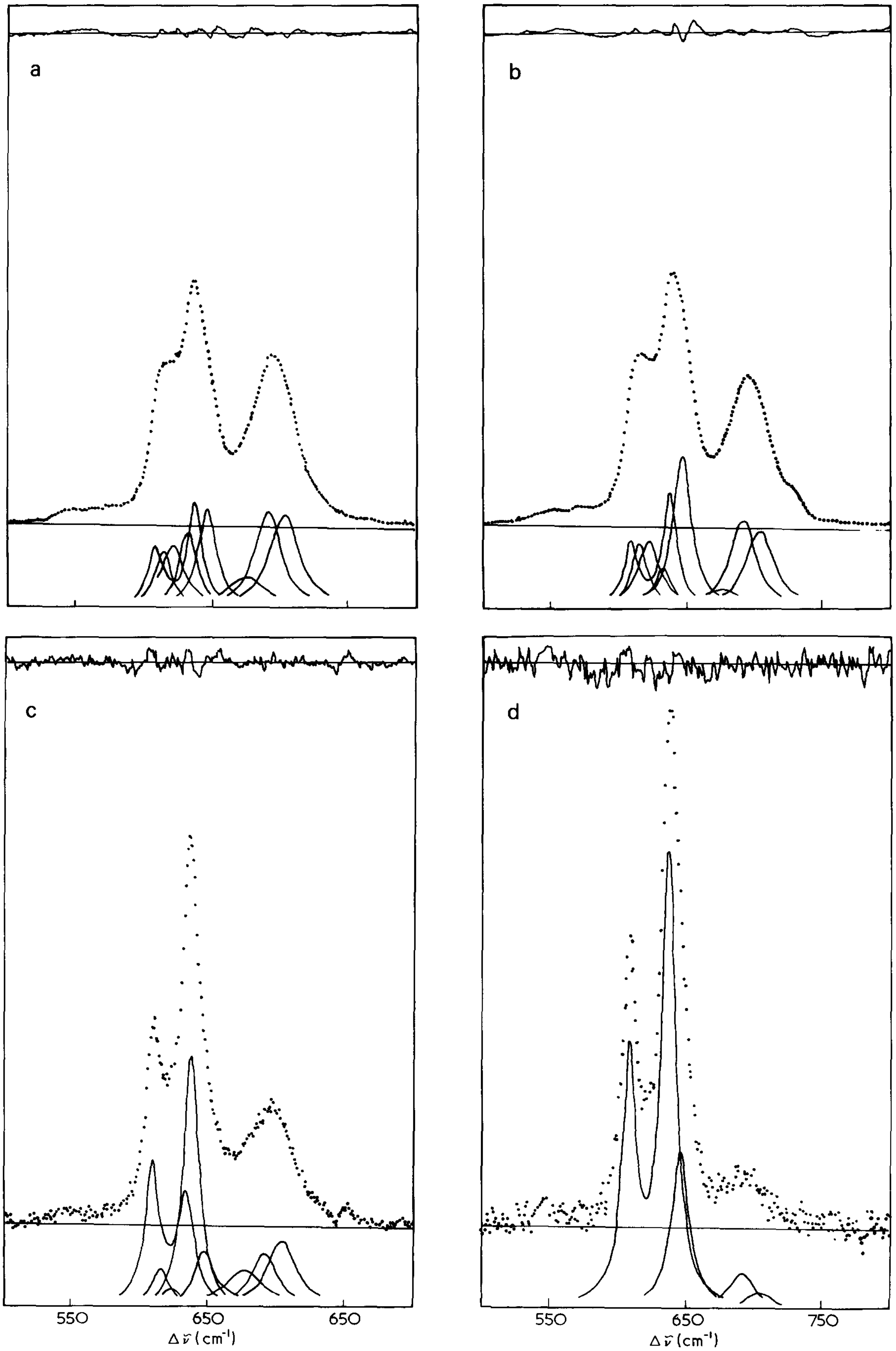

Figure 3 Simultaneous fits to spectra of (a) M80/50; (b) M–E; (c) TR37ICH; (d) U–C powders. All four spectra are normalized to the same area. Notation, etc., as in *Figure 1*

Table 4 Fits to spectra of powders

Centre (cm^{-1})	608.3	614.0 ±0.6	622.9 0.7	634.4 1.0	637.6	646.5 0.7	679.5 1.6	692.4 0.6	704.3 0.4
Half-width (cm^{-1})	12.2 ±0.4	13.6 0.1	17.6 1.2	14.6 4.2	12.2 0.4	19.6 2.0	34.1 15.0	23.8 1.8	25.4 0.8
Polymer	Areas of peaks (%)								
S110/10	4.4 ±0.9	7.9 0.1	9.5 0.2	11.9 5.6	7.3 1.5	14.6 0.6	7.6 1.7	18.5 2.0	16.1 1.3
M80/50	4.3 ±0.8	7.4 0.2	10.0 0.1	11.0 5.3	7.1 1.4	15.0 0.3	8.2 2.3	17.6 1.7	16.8 1.3
5°C	4.6 ±0.5	7.7 0.5	10.3 0.3	8.3 3.9	7.7 1.0	19.3 0.3	7.1 1.3	16.6 1.3	16.0 1.0
M–E	5.2 ±0,4	8.3 0.8	10.2 0.6	6.0 2.8	8.6 0.5	22.9 0.5	4.9 1.4	16.7 1.4	13.6 0.7
JLB237	3.3 ±0.0	8.8 1.3	11.6 1.3	3.7 1.4	5.5 0.1	28.2 1.8	6.8 3.7	15.0 0.1	14.6 0.6
TR37ICH	12.0 ±0.6	5.0 0.4	4.6 0.9	16.4 6.4	20.0 1.0	8.8 1.2	10.2 4.1	9.6 0.2	12.2 1.1
U–C	23.9 ±0.8	0.7 0.7	0.2 0.2	0.1 0.1	39.9 1.3	24.7 0.5	0.0 0.0	7.0 0.9	2.5 0.2

Table 5 Comparison of areas under C–Cl and C–H stretching regions

Polymer	Area under C–H/area under C–Cl
S110/10	1.00
M80/50	0.90
M–E	0.99
TR37ICH	0.96
U–C	1.03

of a planimeter, and the results are shown in *Table 5*. The approximate constancy of the ratio of the two areas implies that the use of the total area under the C–Cl stretching region for normalizing the areas of individual peaks is justified to a first approximation.

Spectra of sheets

The series of sheets of M80/50 containing different quantities of plasticizer (*Table 2*) were ideal for testing the effects of changes of conformational order without any changes of configurational order. The following fitting procedure was adopted so that the results for six samples could be compared. The V_v spectra* of samples A, C, and E were fitted simultaneously using the following constraints on the two crystal peaks:

(i) the widths of the peaks are identical, but variable;

(ii) the separation between the peaks = 29.3 cm^{-1};

(iii) the centre of the B_{3g} species peak is at 608.3 cm^{-1};

(iv) the ratio of the height of the A_g species peak to that of the B_{3g} species peak = 3.6.

The V_v spectra of samples B, D and F were then fitted by a program which constrained the peak positions and widths to be identical to those found from the fit to the first three spectra.

The V_v spectra were used for the comparison because they are much more intense than the V_h spectra, so that the signal-to-noise ratio is better. In addition, the difference between the samples appeared to be reflected somewhat more strongly in these spectra. The V_h spectra were, however, used in determining the value of the ratio of the heights of the A_g and B_{3g} species peaks assumed in the fit to the V_v spectra. In the V_h spectra both crystal peaks are of similar intensity to the other peaks (the B_{3g} species peak is the most intense peak in the V_h spectrum) and thus the ratio of the heights could be determined with reasonable accuracy. In the V_v spectrum, however, the B_{3g} species peak is usually one of the smaller peaks and its intensity, and thus the ratio of the two intensities, cannot be determined very accurately without the application of some constraint. The ratio of the heights of the A_g and B_{3g} species peaks for the V_v spectrum was therefore determined by using the theoretical depolarization ratio of 0.75 for the B_{3g} species peak, and the observed values of the ratios of the heights of the A_g and B_{3g} species peaks for the V_h spectra of sheets and of powders, which were 0.38 and 1.7, respectively. The assumption was made that the powder spectrum of the crystalline regions should be identical to that of the weighted mean of the V_v and V_h spectra for an isotropic sheet, the weighting being 2:1 in favour of the V_h spectrum. This assumption is justified by the fact that a powder spectrum is effectively taken with completely unpolarized incident light and completely scrambled scattered light because of multiple scattering. Constraints (ii) and (iii) were derived from the results of the fit to the four powder spectra described in the last section.

ASSIGNMENTS

In the previous section a description has been given of the purely empirical approach made to fitting the spectra of the

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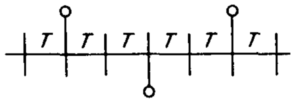
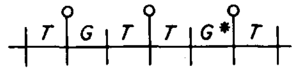
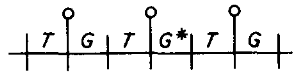
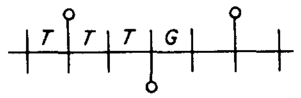
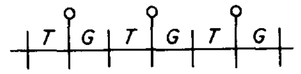
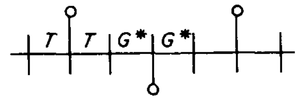
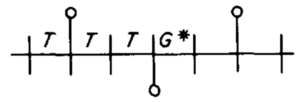
* See Experimental section for explanation of V_v etc.

Table 6 Assignments of peaks due to disordered structures

Configuration	Structure[a]	Type of C–Cl	Frequency (cm^{-1}) Krimm *et al.* (i.r.)	Pohl and Hummel (i.r.)	Rubcic and Zerbi (calc.)	This work (Raman)
s		S_{HH}	612	613		614
i		S_{HH}	622	624		623
i		S'_{HH}	635			634
s		S'_{HH}			650–655	647
i		S_{HC}	685	695	695–700	692
s		S_{HC}	693	677		680
s		S_{HC}			695–700	704

[a] In the diagrams illustrating the structures the planar zig-zag chain is imagined to be viewed so that the Cl atoms (indicated ⚲) are on the side of the chain nearest the eye for those structures where it is necessary to make this distinction. *T* stands for a *trans* bond, *G* for a right-handed *gauche* bond (i.e. the fifth structure represents a right-handed helix) and *G** stands for a left-handed *gauche* bond

C–Cl stretching region and in particular to deciding how many peaks to use. It will now be shown that the fitted peaks can be assigned to different configurational and conformational isomers of PVC with some degree of certainty. Since the present data have not been obtained for as wide a range of physical treatments of the samples as have some of the previous i.r. data, nor have model compounds been studied, it will be necessary to take the conclusions of earlier work into account in making assignments, and they will therefore be summarized here.

Table 6 shows the assignments made by Krimm and his coworkers[5,6] and by Pohl and Hummel[9]. It should be noted that Krimm *et al.* did not undertake curve resolution, whereas Pohl and Hummel did. The structures shown are those considered by Krimm *et al.*, on the basis of studies of model compounds, to be the most likely disordered structures present in PVC which could account for the observed frequencies. Also shown in the Table are frequencies calculated by Rubcic and Zerbi[13] for some of these structures. In addition to the frequencies shown in the Table, Pohl and Hummel also inferred the presence of a peak at 633 cm^{-1} which they assigned to 'an isotactic S'_{HH} structure' and observed a peak at 647 cm^{-1} which they assigned to a 'high energy syndiotactic structure'.

If we consider the results of the analyses of the powder spectra, shown in *Table 3*, the most obvious trends are for the 647 cm^{-1} peak to increase rapidly as the syndiotactic content increases and for the 634 cm^{-1} peak to decrease rapidly. These trends suggest that the 647 and 634 cm^{-1} peaks should be assigned, respectively, to syndiotactic and isotactic structures. This is consistent with the presence of a strong peak at 647 cm^{-1} in the spectrum of the U–C sample and the absence of the peak at 634 cm^{-1} and is in agreement with the assignments of these two peaks to the different configurational isomers by Pohl and Hummel. The 634 cm^{-1} peak is within the region 627–637 cm^{-1} generally assigned to S'_{HH} vibrations and the most reasonable assignment is thus to isotactic S'_{HH}.

The close agreement of the observed frequency 647 cm^{-1} with the frequency 650–655 cm^{-1} calculated by Rubcic and Zerbi for the syndiotactic *TTTG* structure strongly suggests that the observed peak should be assigned to this structure. This is not inconsistent with the assignment by Krimm *et al.* of part of the intensity of the 635 cm^{-1} region to the *TTTG* structure, since the peak at 647 cm^{-1} is not resolved, even as a shoulder, from the two overlapping peaks at 634 and 638 cm^{-1} in any of the spectra. The presence of a third peak in this region was therefore not suspected by Krimm *et al.* who merely observed changes in intensity and peak position of the whole complex of peaks in the region 630–650 cm^{-1}. It is not possible to make any other clear assignments with the help of the powder spectra alone and we now turn to the spectra of the annealed, plasticized sheets.

Table 7 shows the positions, widths and % areas of the various peaks for samples A–F after they had been subjected to various annealing treatments as described earlier. Unfor-

Table 7 Fits to spectra of annealed M80/50 sheets

Centre (cm^{-1})			608.3	613.3	621.3	633.1	637.6	646.5	683.4	694.2	705.9
Half-width (cm^{-1})			12.4	14.3	15.7	15.6	12.4	19.8	20.8	20.9	22.5
Sample	Plasticizer (g)/PVC (100 g)	Annealing time (min)	Area (%)								
A	0	30	1.5	5.6	7.2	10.5	1.5	23.4	10.6	18.4	16.4
B	5	30	1.7	4.5	7.9	9.1	1.7	24.1	9.5	19.2	16.8
C	10	5	2.6	4.0	7.7	7.6	2.6	23.1	8.8	19.1	16.8
D	15	5	3.4	3.8	7.1	8.3	3.4	20.6	9.0	18.2	16.3
E	20	5	3.6	3.2	7.3	8.4	3.6	20.0	8.9	18.6	16.3
F	20	30	2.6	5.5	5.8	12.2	2.6	19.7	10.6	16.4	17.0

tunately it was not possible to produce isotropic sheets with only 5 min annealing time for samples containing 5 pph plasticizer or less. It was in general undesirable to use long annealing times, because of the increase in thermal degradation. The more highly plasticized sheets degrade more rapidly and the time of 5 min was therefore used for samples C–E, since it gave reasonably isotropic samples with only moderate degradation. Sample F had the same plasticizer content as sample E but was annealed for 30 min and could be seen to be significantly more degraded than the other samples by its much darker colour, although the level of degradation is unlikely to exceed 0.1%[24]. The results for all except this sample are fairly consistent and show a steady increase in the intensity of the two crystal peaks and a corresponding decrease in intensity of the 647 cm^{-1} syndiotactic peak with increasing plasticizer content. Of the two peaks in the S_{HH} region not so far assigned, that at 614 cm^{-1} decreases markedly in intensity, whereas that at 623 cm^{-1} remains approximately constant in intensity*. This strongly favours the assignment of the 614 cm^{-1} peak to short planar zig-zag syndiotactic segments which can be incorporated into crystallites, and the 623 cm^{-1} peak to isotactic material, in agreement with the assignments of Krimm *et al.* and of Pohl and Hummel.

The behaviour of the intensities for sample F, which contained 20 pph plasticizer and was annealed for 30 min contrasts strongly with that for sample E, which had the same plasticizer content but was annealed for only 5 min. In particular, the intensities of the crystal peaks dropped significantly, possibly because this darker sample may have been appreciably heated by the laser beam during the running of its spectrum. Nevertheless, it is reasonable to assume that the only difference between samples E and F is in conformational and crystalline content, and some further assignments are suggested. Apart from the strong decrease in intensity of the crystal peaks, the peaks at 614, 634 and 680 cm^{-1} increase markedly in intensity, that at 704 cm^{-1} shows a small increase in intensity and those at 692 and 623 cm^{-1} decrease in intensity. The increase in intensity of the 634 cm^{-1} isotactic peak requires a corresponding decrease in intensity of other contributions from isotactic structures. There is a small decrease in the 623 cm^{-1} isotactic peak, but it seems likely that this is not enough and there is thus a very strong suggestion that the 692 cm^{-1} peak is due to isotactic material, since it is the only other peak to show a significant decrease in intensity. The increases in the intensities of the peaks at 683 and 706 cm^{-1} would then be consistent with their being due to bent syndiotactic structures which increase in concentration when the crystallinity falls. These assignments are consistent with those of Pohl and Hummel, who assigned peaks at 695 and 677 cm^{-1} to the isotactic _TGTGTG_ (regular helix) structure and the syndiotactic _TTG*G*_ structure, respectively, but not with those of Krimm *et al.* who reverse these assignments. Neither of these sets of authors mentions a peak at 704 cm^{-1}, but a third peak, possibly at about 710 cm^{-1}, is clearly indicated by the i.r. spectra of a 72% syndiotactic sample obtained by Germar[25], although he does not assign it.

If it is accepted that the peaks at 680 and 704 cm^{-1} are due to the two S_{HC} syndiotactic structures, the fact that the 680 cm^{-1} peak is much the weaker of the two in all the spectra and also shows a decrease in intensity with increasing plasticizer content suggests that it is due to a structure of higher energy than that at 704 cm^{-1}. Of the syndiotactic structures likely to give rise to these two peaks, viz. _TTG*G*_ and _TTTG*_, the latter is the more stable structure[5] and we thus tentatively assign the 704 cm^{-1} peak to _TTTG*_ and the 680 cm^{-1} peak to _TTG*G*_.

The final assignments for the peaks due to disordered structures are shown in the last column of *Table 6*.

DISCUSSION

General

The results of the previous two sections show that to a good approximation the Raman spectrum of the C–Cl stretching region of PVC may be regarded as the sum of a series of symmetrical overlapppng peaks, two of which have been interpreted as being due to crystalline syndiotactic material and the remainder of which have been interpreted as being due to specific structures in the amorphous regions. The positions of the peaks due to amorphous material are in most instances close to those found in a similar interpretation of the infra-red spectrum and the present results support most of the previous assignments but some changes and additional assignments are suggested.

The deviations of the observed spectra from the sums of the fitted peaks are small but systematic and this may be attributed to at least three possible causes. First, the number of peaks fitted may not be sufficiently large, but the use of additional peaks would require further constraints if meaningful fits were to be obtained. Secondly, the shape of peak assumed in the present fits, viz. Lorentzian, may not be exactly the correct shape. Thirdly, the spectrum may not be correctly fitted as a sum of discrete components. The presence of defects may cause the activation of modes with-

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* Note that the positions of the peaks quoted are those obtained from the powder spectra as these are probably more reliable than the slightly different values obtained from the sheets

Table 8 Syndiotactic content and crystallinity

Polymer	Syndiotactic content From n.m.r.	 From Raman (1)	 From Raman (2)	Crystallinity From X-rays	 From Raman
S110/10	0.54	0.60	0.55	0.08–0.10	0.12
M80/50	0.55	0.61	0.56	0.08–0.10	0.11
5°C	0.59	0.65	0.59		0.12
M–E	0.61	0.67	0.61	0.25	0.14
JLB237		0.70	0.62	0.30	0.09
TR37ICH		0.69	0.66		0.32
U–C		0.93	0 93	0.63	0.64

in the C–Cl stretching band of the syndiotactic chain which are not optically active for the infinite perfect chain and which could give rise to infra-red absorption or Raman scattering over broad ranges of frequency[26]. At the moment there seems to be no clear experimental evidence that such effects must be taken into account in interpreting the C–Cl stretching regions of the vibrational spectra of PVC and the simpler interpretation is therefore preferable at present. We shall now consider two applications of that interpretation.

Tacticity

If the naive assumption is made that the total percentage area under the peaks assigned to isotactic material is equal, at least approximately, to the percentage of isotactic linkages, then the fractions of syndiotactic linkages shown in the third column of *Table 8* are obtained for the powders. These values are qualitatively in agreement with those found by means of n.m.r. spectroscopy[27], shown in column two, but are quantitatively rather high.

At least two clear reasons can be suggested for this discrepancy. The first is that the Raman intensities may not be proportional, even as a fairly good approximation, to the number of chlorine atoms principally involved in a particular vibration. Evidence that the approximation may be a reasonable one is, however, provided by the fact mentioned earlier that the integrated intensity under the C–Cl stretching region bears a constant ratio to the integrated intensity under the C–H stretching region for all samples. The second possible reason for the discrepancy is that not all the isotactic structures shown in *Table 6* produce a single chlorine atom of the specified type (S_{HH} etc.) if only one isotactic diad is present. The only structure that requires at least a triad is the isotactic *TGTTG*T* structure, but it contains only one S_{HH} chlorine atom. If the corresponding peak is given double weight in evaluating the isotactic content the syndiotactic contents shown in the fourth column of *Table 8* are found. The excellent agreement of these figures with the n.m.r. data is probably to some extent fortuitous, particularly as giving double weight to the triad tacitly assumes that the diads included in it do not contribute individually at other frequencies. Nevertheless, it is clear that a good indication of tacticity can be obtained from the Raman data.

Figure 4 shows the percentage areas of the various peaks for the powder spectra plotted against the syndiotactic content deduced from the Raman data. The lines drawn are merely meant to indicate general trends. The Figure shows that the intensities of the individual peaks vary in a reasonably systematic way with syndiotactic content except for those of the polymer TR37ICH, which is an insoluble fraction and was not expected to fit into the same pattern as the other samples. One apparently anomalous feature is that the intensity of the 623 cm^{-1} peak, assigned to a structure requiring at least an isotactic triad, appears to increase with decreasing isotactic content. It is possible, but unlikely, that this is a real effect. A more likely explanation is that short syndiotactic sequences, which have been assumed to produce the peak at 614 cm^{-1}, produce intensity over a wide range of frequencies in the S_{HH} region and that some of the intensity at 623 cm^{-1} has this origin. If this is assumed, the apparent rather slow increase in the number of short syndiotactic sequences with increasing syndiotactic content indicated by the slow increase in intensity of the 614 cm^{-1} peak could be accounted for at the same time as the apparent in-

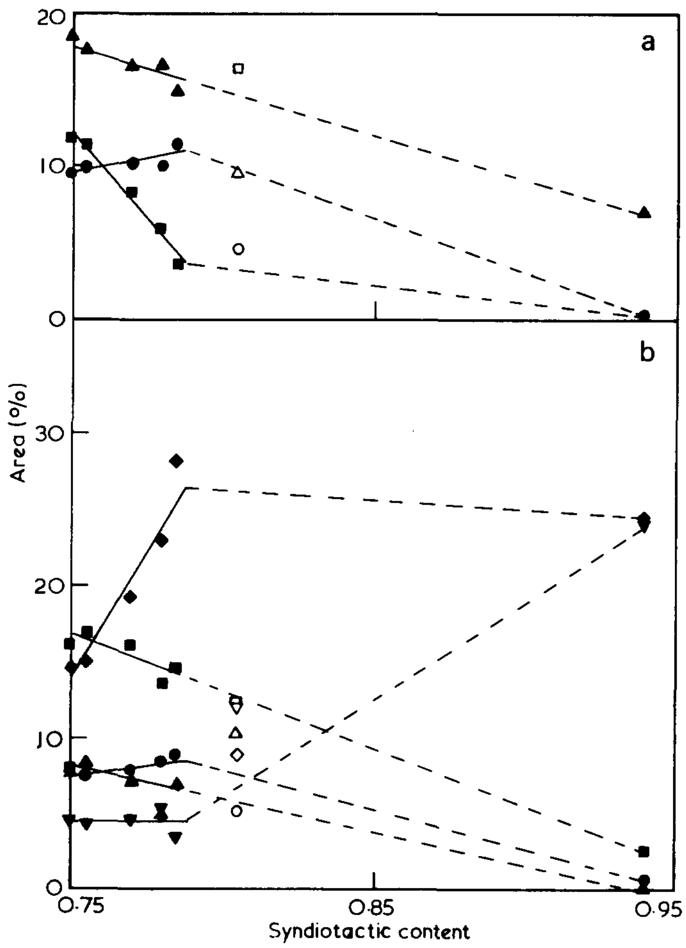

Figure 4 Percentage areas of peaks from fits to spectra of powders plotted against syndiotactic content deduced from Raman spectra (Raman 2). (a) Peaks assigned to isotactic material: ▲, 692 cm^{-1}; ●, 623 cm^{-1}; ■, 634 cm^{-1}. (b) Peaks assigned to syndiotactic material: ◆, 647 cm^{-1}; ■, 704 cm^{-1}; ●, 614 cm^{-1}; ▲, 680 cm^{-1}; ▼, 608 cm^{-1}. The 638 cm^{-1} peak is not shown as its area is a constant multiple of that of the 608 cm^{-1} peak. The open points refer to TR37 ICH

crease in the content of the isotactic *TGTTG*T* structure with decreasing isotactic content. Such an interpretation would add extra uncertainty to the calculation of the isotactic content from the Raman spectra.

Crystallinity

If the two peaks that have been called the A_g and B_{3g} crystal peaks are truly due to crystalline material and not simply to regular material (cf. a discussion by Zerbi *et al.*[28]) then the fractional area of these peaks should be equal to the crystalline fraction of polymer using the approximation that was used when discussing tacticity in the previous section. The values for the crystallinity deduced in this way are compared with those deduced from X-ray measurements[29], where available, in the last two columns of *Table 8*. For the S110/10, M80/50 and U–C polymers the agreement is seen to be good, whereas for the M–E and JLB237 polymers it is rather poor. The reason for this is not understood but it may be connected with the approximation that fractional areas of peaks are proportional to concentration of corresponding species or to the assumption that the peaks at 608 and 638 cm^{-1} do not include contributions from regular but non-crystalline material.

Evidence that the two peaks in question are due to crystalline material and do not include significant contributions from long planar zig-zag syndiotactic segments in amorphous regions is provided by the fact that the corresponding peaks in the i.r. spectrum, and in particular the B species peak, do not coincide exactly in frequency with those in the Raman spectrum. The difference is approximately 7 cm^{-1} and this has been interpreted previously[23] as correlation splitting due to the interaction between the two chains per unit cell in the crystal. The implication of the clear splitting seems to be that there are not many long planar zig-zag syndiotactic segments in the amorphous reigons, since these would presumably give rise to intensity in the regions between the B_{3g} and B_{1u} crystalline frequencies. Further studies will, however, clearly be required before Raman spectra can be used to give completely reliable measures of crystallinity.

CONCLUSION

The conclusion to be drawn from the present study is that the C–Cl stretching region of the Raman spectrum of PVC may, to a good approximation, be regarded as the superposition of nine Lorentzian peaks. Two of these peaks are attributable to the A_g and B_{3g} species vibrations of crystalline material and the remaining seven may be assigned with reasonable confidence to specific structures in the amorphous regions, three of which are associated with isotactic placements. The area under the A_g and B_{3g} peaks may tentatively be used to estimate the crystallinity of the samples and the area under the three isotactic peaks may be used to estimate the tacticity of the polymer.

Raman spectroscopy has the advantage over infra-red spectroscopy for this kind of study because no special sample preparation is required which might change the conformational content or crystallinity.

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