

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Quantitative Conformational Studies on Poly(vinyl Chloride)

W. F. Maddams^a; P. B. Tooke^a

^a Group Research and Development Department, The British Petroleum Company Limited, Middlesex, England

To cite this Article Maddams, W. F. and Tooke, P. B.(1982) 'Quantitative Conformational Studies on Poly(vinyl Chloride)', *Journal of Macromolecular Science, Part A*, 17: 6, 951 – 968

To link to this Article: DOI: 10.1080/00222338208056495

URL: <http://dx.doi.org/10.1080/00222338208056495>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Quantitative Conformational Studies on Poly(vinyl Chloride)

W. F. MADDAMS and P. B. TOOKE

Group Research and Development Department
The British Petroleum Company Limited
Sunbury-on-Thames, Middlesex, England

ABSTRACT

Although curve fitting provides a method for obtaining intensity data for the individual components of overlapping band systems, the number of configurational and conformational bands in the C-Cl stretching region of the vibrational spectrum of poly(vinyl chloride) is such that many parameters have to be optimized. It is therefore desirable to impose constraints in the calculations, and prior knowledge of the number of component bands would be valuable. The potential of derivative spectroscopy for obtaining this information has been examined. It is shown that the superior resolution of second and fourth derivative spectra is partially offset by their inferior signal-to-noise ratio, a discriminatory effect against broader bands, and interference by subsidiary derivative peaks. The method has been used to examine the CH₂ deformation and C-Cl stretching modes of three PVC samples of different tacticity. With the former the overlapping system proves to be more complex than hitherto realized; hence, tacticity determinations based on the intensity ratio of two peaks only at 1428 and 1434 cm⁻¹ must be suspect. With the C-Cl stretching bands second derivatives are more useful than fourth derivatives, and the number and positions of the located bands are in broad agreement with the results from curve fitting, so providing confirmatory evidence for the correctness of the latter.

INTRODUCTION

There seems little doubt that the crystallinity and various other macroscopic properties of poly(vinyl chloride) (PVC) are dependent on both the configurational and conformational states of the molecule. With the availability of sound ^1H and ^{13}C NMR spectroscopic methods [1-3] for measuring syndiotacticity, it has become clear that the crystallinity increases with increasing syndiotactic content. X-ray diffraction measurements have shown that the crystalline regions of PVC are composed of syndiotactic chains with the planar conformation [4], although it is difficult to account for the observed crystallinity, about 10%, of commercial polymers solely in terms of this particular configurational/conformational combination [5]. The extent to which the various conformational isomers determine the macroscopic properties of the polymer has been little studied, primarily because it is difficult to measure their concentrations.

Although NMR spectroscopy has proved invaluable for quantitative configurational studies, its value for conformational work is very limited; the time scale of the NMR process is slow by comparison with the interconversion time of rotational isomers and the observed spectrum is a time-average weighted according to the proportions of the various conformers present. Information is available for simple model compounds such as 2,4-dichloropentane [6] and 2,4,6-trichloroheptane [7], but the configurational/conformational complexity of PVC virtually precludes this approach. It has been known for some years that the carbon-chlorine stretching region of the vibrational spectrum is characteristic for the various conformational isomers [8], and recent work has led to some updating of these assignments [9]. The difficulty in using this spectral region for quantitative work arises because the various bands overlap badly. Although it is possible to measure changes in the conformational structure by IR difference spectroscopy [10], quantitative measurements require the mathematical separation of the overlapping bands and this poses problems. Until recently only Pohl and Hummel [11] have attempted such calculations, and then only on the basis of simplifying assumptions which they did not justify.

This paper describes the current status of a detailed program of work with two objectives: 1) to develop suitable mathematical methods for separating the components of overlapping band systems, and 2) the application of these methods to quantitative conformational isomerism studies on PVC.

THE USE OF CURVE FITTING

The process of separating overlapping peaks by mathematical methods is known as curve fitting. Although simple analog methods such as the Du Pont 310 curve resolver are available, they have

considerable limitations and have largely been replaced by computer methods which are very much more flexible and vastly more rapid. In principle, the provision of the relevant software presents no problems but it has now become very clear [12-14] that there are considerable practical difficulties with multicomponent overlapping systems.

Five parameters are involved: the number and positions of the component peaks, their shapes and half widths and, usually, a base line to allow for background signal. The composite profile is fitted in terms of a set of component peaks, to a specified goodness of fit, by an iterative procedure based on damped least squares calculations. If a fit is attempted without prior knowledge of some of the variables it will, at worst, lead to nonconvergent calculations and no information and, at best, there are likely to be several equally plausible solutions in terms of a particular goodness of fit criterion.

It is therefore necessary to define values for some of the parameters or, at least, to constrain them within reasonable limits. In the case of vibrational spectra the band shape is the most amenable to this approach. Both IR and Raman bands usually approximate to the Lorentzian shape [15, 16], and when deviations occur it is possible to express them in a simple mathematical form convenient for calculation purposes [17]. On the other hand, it is very difficult to define or constrain band widths and these are best obtained by the computer optimization routine. The desirability of having some prior knowledge of the number of component bands has been stressed by Vandeginste and De Galan [12], and this point is attracting increasing attention.

In the case of a complex system of overlapping bands it may be possible to curve fit plausibly by building up from simpler systems. We have used this approach in the case of PVC [9]. The first step involves curve fitting the spectrum of the highly syndiotactic urea clathrate polymer in terms of three Lorentzian bands. This can be done with some confidence. This is then used as the basis of a fit for a somewhat less-ordered polymer by adding the minimum number of additional peaks required to obtain the requisite goodness of fit. By a further extension of this approach, fits were obtained for the spectra of commercial polymers, using nine peaks. Although this method does not necessarily avoid systematic errors, the results can be viewed with more confidence than those from an a priori nine-peak fit. Nevertheless, it is desirable to have an independent method for assessing, approximately, the number of component peaks, and the present study relates to the use of derivative spectroscopy.

THE PRINCIPLES OF DERIVATIVE SPECTROSCOPY

The visual recognition of individual peaks in a composite profile is based on the appearance of a discrete maximum or, at least, of an

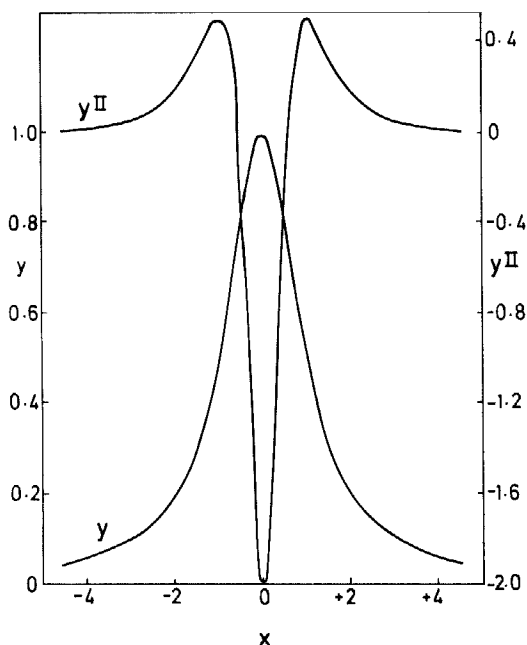


FIG. 1. The Lorentzian profile and its second derivative.

inflection or shoulder. The limit to the detection of such a peak is set by its width, usually expressed as the half-width, i.e., the width at half the maximum height, in relation to its separation from adjacent peaks. The latter is fixed but if the half width can be reduced, the effective resolution will be increased and peak identification will be made more certain. Derivative spectroscopy provides a potentially attractive approach to this problem.

This was noted as long ago as 1953 by Singleton and Collier [18] and the principles were discussed in rather more detail by Martin [19]. The essential points can be appreciated by reference to Fig. 1, which shows a Lorentzian peak together with its second derivative. The latter has three peaks, a strong negative one and two weaker positive ones symmetrically disposed about it. The former is of primary interest but the latter do have practical implications and will be considered below. The half-width of the negative peak of the second derivative is one-third that of the Lorentzian profile from which it derives, thus appreciably enhancing the resolution capability. This is demonstrated by Fig. 2 which gives the composite profile obtained by summing two Lorentzian peaks of equal half-width and height separated by 40% of their half-widths, together with the second derivative of this profile. The composite profile gives no indication for the

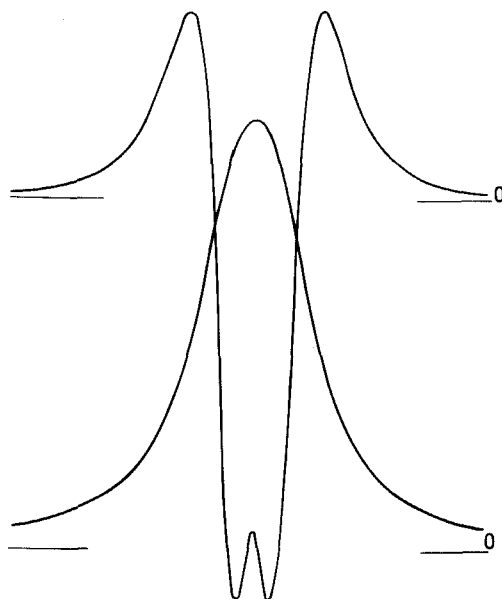


FIG. 2. The composite peak, and its second derivative, from two Lorentzian peaks of equal intensity and half width separated by 40% of this half width. The two curves have been displaced along the vertical axis for the sake of clarity.

presence of two peaks whereas this is very evident from the second derivative.

Three factors set the limit to what may be achieved by this approach. The first is the presence of the subsidiary peaks in the second derivative. These are situated at the half-width values along the abscissal axis and are one-quarter of the intensity of the main peak. It follows that if a composite profile consisting of two Lorentzian components separated by 50% of their half-widths with an intensity ratio of four to one is examined as its second derivative, there will be serious interference between the negative peak of one and the positive peak of the other, as is clear from Fig. 3. There is no direct evidence for the presence of the second component, although the distortion of the derivative pattern of the stronger component gives a reasonable indication that it cannot be that of a single symmetrical peak. In the case of multicomponent overlapping systems the recognition of such accidental cancellations is considerably more difficult. Hence the number of negative peaks in second derivative spectra may be less than the number of components present.

The second factor relates to the effect of unequal half-widths in

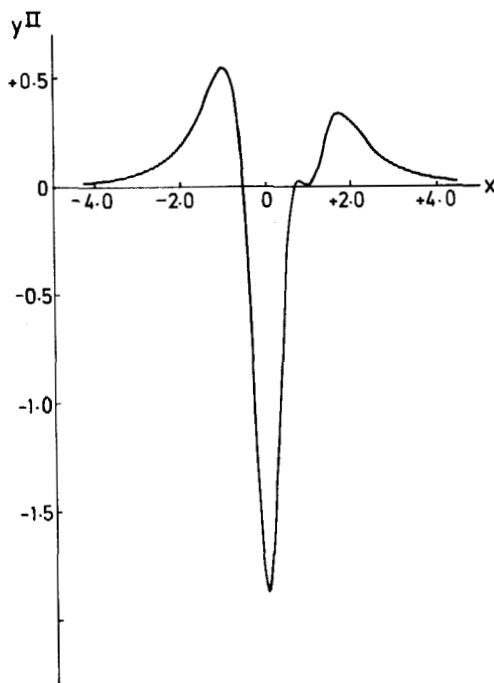


FIG. 3. The second derivative of the composite peak obtained by summing two Lorentzian peaks having an intensity ratio of 4:1, equal half widths, and separated by 50% of this half width.

systems of overlapping peaks. There is a strong discrimination against the broader components, as is evident from elementary considerations, and although this effect is implicit in the results of O'Haver and Green for overlapping systems of Gaussian bands [20] and has been discussed briefly by Cahill [21], a quantitative examination of the problem seems to be lacking. This will now be considered in the context of Lorentzian bands, although the effect is a general one.

In its simplest form the Lorentzian profile is generated by $y = (1 + x^2)^{-1}$. This gives a peak of unit height and half-width 2. The width may be varied by inserting a coefficient a in the term x^2 , to give $y = (1 + ax^2)^{-1}$. The abscissal half-width values x_H occur for an ordinate value of 0.5. Hence $(1 + ax_H^2)^{-1} = 0.5$ and, by rearrangement, $x_H = \pm a^{-\frac{1}{2}}$. The second derivative of $y = (1 + ax^2)^{-1}$ is

$$y'' = -\frac{2a(1 - 3ax^2)}{(1 + ax^2)^3}$$

The maximum value y_m^{II} occurs at $x = 0$; hence $y_m^{\text{II}} = -2a$. Thus the half-width varies as $a^{-\frac{1}{2}}$, and the amplitude of the negative peak in the second derivative is proportional to a . Hence the relative amplitude of this peak for two bands varies inversely as the square of their half-width ratio. For two bands, one three times broader than the other, a not uncommon situation in vibrational spectra, the amplitude of the second derivative peak of the broader component will be one-ninth that of the sharper peak.

The consequences of this fact are compounded by the effect of noise, the third limitation in derivative spectroscopy. For white noise Cahill has shown [21] that the noise in the first derivative is $\sqrt{2}$ greater than that in the original spectrum and the increase is by the factor $\sqrt{6}$ in the second derivative. This is rather smaller than the values given by O'Haver and Green [20] who calculated derivative spectra from synthetic Gaussian peak systems with added random noise and concluded that the signal-to-noise ratio decreased by approximately two for each derivatization. If the noise is of relatively high frequency, its amplitude will be much greater in derivative spectra, for the reasons demonstrated above; however, it should be correspondingly simpler to reduce or eliminate it by smoothing techniques. This decrease in signal-to-noise ratio upon derivatization, coupled with the amplitude discrimination against broader bands, makes their detection difficult. What can be achieved will clearly depend upon the particular circumstances.

In the case of the fourth derivative of the Lorentzian profile (Fig. 4), the major peak, which is positive, has a half-width 20% of that of the Lorentzian profile and the resolution capability is correspondingly greater. It is possible to separate a pair of Lorentzian peaks of equal half-width and height separated by 25% of their half-widths. There are subsidiary peaks at abscissal values of ± 0.6 , and these are stronger than their counterparts in the second derivative, being 40% of the intensity of the main peak. Predictably, this again leads to anomalous situations with overlapping systems. Figure 5 shows the fourth derivative of two Lorentzian peaks, of equal half-width but with an intensity ratio of 1:0.4 and separated by 30% of their half-widths. Only one positive peak is present, although the anomalous pattern of the subsidiary peaks suggests the presence of a second component.

The algebraic expression for y^{IV} is

$$y^{\text{IV}} = \frac{24a^2 (1 - 10ax^2 + 5a^2x^4)}{(1 + ax^2)^5}$$

so at the maximum, $x = 0$, the amplitude is $24a^2$. Hence, remembering that $x_H = \pm a^{-\frac{1}{2}}$, the relative amplitude of the major peak in the fourth

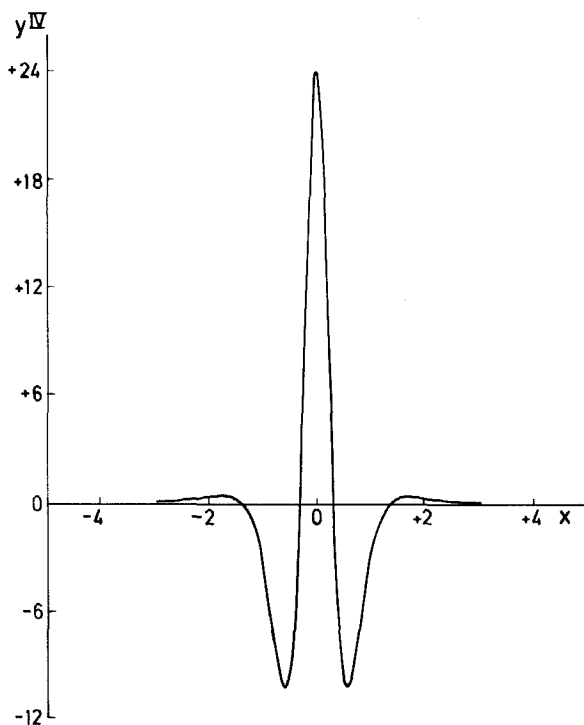


FIG. 4. The fourth derivative of the Lorentzian profile.

derivative for two bands varies inversely as the fourth power of their half-width ratio. For two bands, one twice as broad as the other, the amplitude of the fourth derivative of the broader peak will be one-sixteenth that of the sharper peak. The signal-to-noise ratio also deteriorates further in the case of this higher derivative by a factor of $\sqrt{70}$ in comparison to the original spectrum according to Cahill [21] and by about 16 on the basis of the results of O'Haver and Green [20]. Hence, on both counts, the value of fourth derivatives is open to question. However, they have been examined, together with second derivatives, for peak finding in the C-Cl stretching region of the IR spectrum of PVC.

RESULTS

Second and fourth derivative spectra have been obtained by two methods which will be detailed elsewhere and will be outlined for

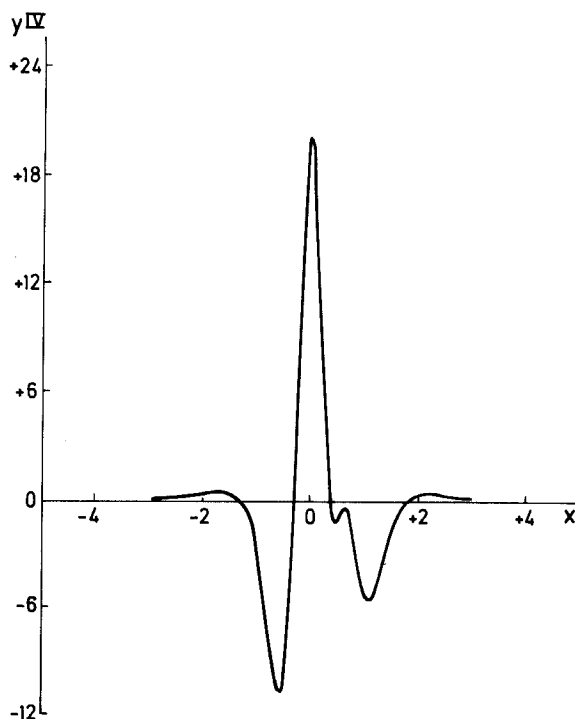


FIG. 5. The fourth derivative of the composite peak obtained by summing two Lorentzian peaks having an intensity ratio 2.5:1, equal half widths, and separated by 30% of this half width.

present purposes. The first is an analogue method using an operational amplifier/differentiation unit based on integrated circuits in conjunction with a Perkin-Elmer 577 IR spectrometer. This has the disadvantage that it is an on-line system and the time constant of the system, which causes a lag with respect to the wavelength drive of the spectrometer, makes it difficult to attach precise wavelength values to the bands in the derivative spectra. Furthermore, an automatic grating change at 600 cm^{-1} causes additional complications in this respect. However, this system has considerable flexibility, particularly with respect to the smoothing out of noise. Some measurements have also been made on a Digilab FTS 15 Fourier transform IR spectrometer, using a Newton-Gregory seventh-order interpolating polynomial in order to obtain the derivatives. Optimum noise smoothing was not always achieved and, on a relative basis, the quality of the fourth-derivative spectra was inferior to that obtained with the analogue system.

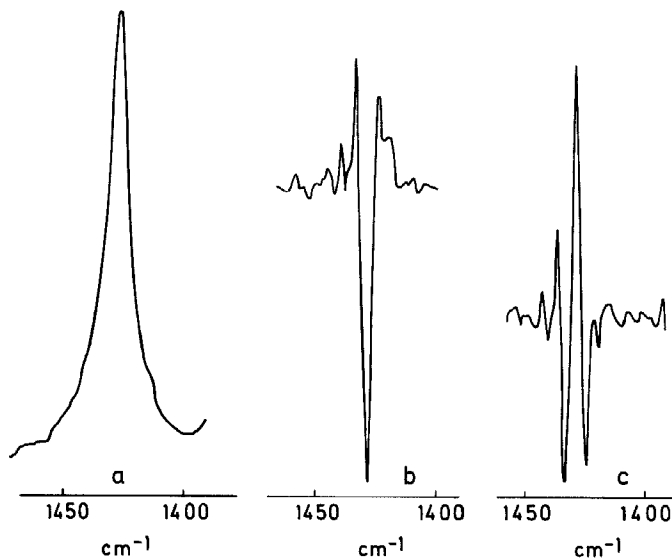


FIG. 6. The IR spectrum of urea clathrate PVC in the CH_2 deformation region (a), together with the second (b) and fourth (c) derivative spectra.

In view of the known complexity of the overlapping band system in the carbon-chlorine stretching region, work was done initially on the simpler overlapping band system from the CH_2 deformation vibration. Even with commercial low order polymers a doublet is clearly visible and, following the work of Germar et al. [22], it has been generally assumed that two overlapping peaks are present. One, at 1428 cm^{-1} , is taken to be characteristic of planar syndiotactic structures and the other, at 1434 cm^{-1} , to be indicative of three structural units, bent syndiotactic and the two most energetically favored isotactic structures. Germar et al. used this as the basis of a method for measuring syndiotacticity, and a number of other workers have subsequently followed their lead.

Second and fourth derivative spectra have been obtained for this overlapping band system for three PVC samples: a urea clathrate polymer, a material polymerized at -30°C , and a commercial mass polymer. Results for the urea clathrate polymer are given in Fig. 6. The initial spectrum shows a single band only, as anticipated, but there is a slight visual indication of asymmetry around 1434 cm^{-1} . The second derivative gives a single peak only, at 1427 cm^{-1} , but its width is greater than anticipated on the basis of the original data, and the presence of a second component may be inferred. This is resolved in the fourth derivative as a peak at 1434 cm^{-1} . In the light

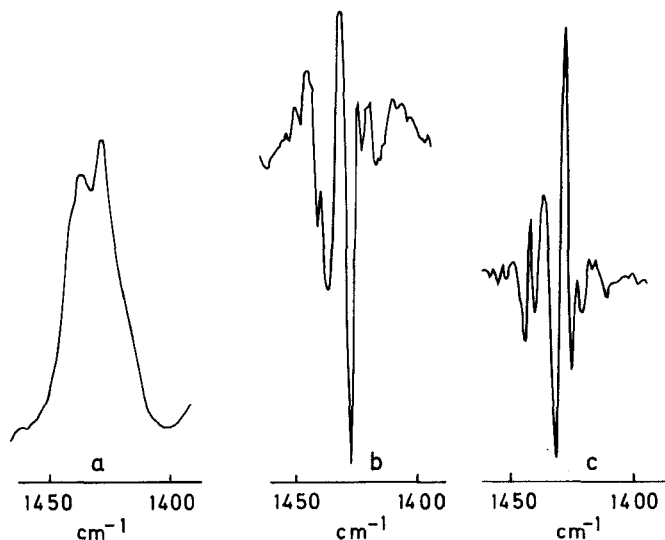


FIG. 7. The infrared spectrum of a commercial mass PVC in the CH_2 deformation region (a), together with the second (b) and fourth (c) derivative spectra.

of the curve fitting results of Baruya et al. [23] and of Robinson et al. [9], this may be assigned to the most energetically favorable bent syndiotactic conformer whose C-Cl stretching mode occurs at about 647 cm^{-1} .

In the case of the commercial mass polymer (Fig. 7), the conventional spectrum shows two clear peaks, at about 1427 and 1434 cm^{-1} , with a suggestion of an inflection at about 1440 cm^{-1} . This is confirmed in the second derivative, which gives negative bands at 1427 , 1434 , and 1438 cm^{-1} , and these appear more clearly resolved in the fourth derivative as positive peaks. By comparison with the peak at 1434 cm^{-1} in the derivative spectra of the urea clathrate polymer, the one in the present instance is detectably broader and it is reasonable to surmise that it consists of two closely overlapping components. One of these will characterize the bent syndiotactic conformer and the other one will almost certainly be specific for one or more bent isotactic conformers. The assignment of the band at 1438 cm^{-1} is less certain. Its intensity, relative to the 1434 cm^{-1} band, is lower in the case of the -30°C polymer, which suggests that it arises from an energetically less favorable conformer but it will be necessary to examine a wider range of samples to establish if it is associated with the isotactic or syndiotactic configuration. The relative complexity of the CH_2 deformation region shows that the simple tacticity determination proposed by Germar et al. [22] is unlikely to prove adequate. This point will be discussed below.

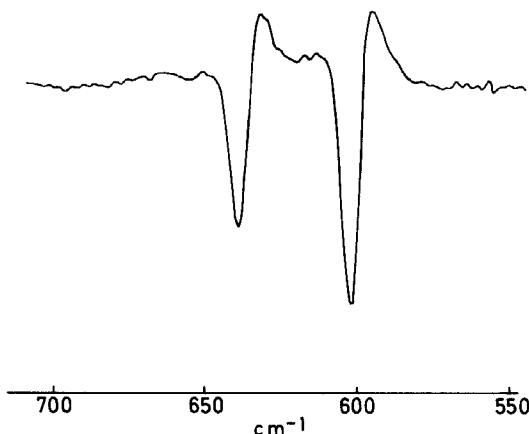


FIG. 8. The second derivative IR spectrum of urea clathrate PVC in the C-Cl stretching region.

The formal curve fitting calculations of Robinson et al. [9] suggest that nine peaks are required to account for the observed spectrum in the carbon-chlorine stretching region. Furthermore, these peaks vary in width by a factor of about three, so that the broader ones will be relatively weak in derivative spectra. Hence the method is likely to prove less specific than in the case of the CH_2 deformation mode. The results for the potentially simplest material, the urea clathrate polymer, are less revealing than might have been anticipated. The second derivative (Fig. 8) shows two clear negative peaks, at 602 and 639 cm^{-1} , corresponding to the two stretching modes of long planar syndiotactic sequences, but no peak in the vicinity of 650 cm^{-1} , although the presence of a third band here is well established by curve fitting [9, 23]. However, the subsidiary positive peak that would have been expected at about 650 cm^{-1} is absent and the 639 cm^{-1} negative peak is asymmetric, so the presence of an additional peak may be inferred. The situation is clearly analogous to that shown in Fig. 3. Furthermore, there is no obvious indication for the peak in the fourth derivative; this failing in the two cases will be discussed further below. The absence of a second subsidiary positive peak, at about 610 cm^{-1} , suggests the presence of a fourth component. This is undoubtedly the band at 614 cm^{-1} , characteristic for short planar syndiotactic sequences, although it is probably not present at as high a concentration as the bent syndiotactic conformer absorbing at 647 cm^{-1} .

The 614 cm^{-1} band shows clearly in the second derivative spectrum of the mass polymer (Fig. 9) and there is also a weak rather broad peak centered at about 650 cm^{-1} . There are additional broad weak peaks at about 678 and 698 cm^{-1} ; the latter could well consist

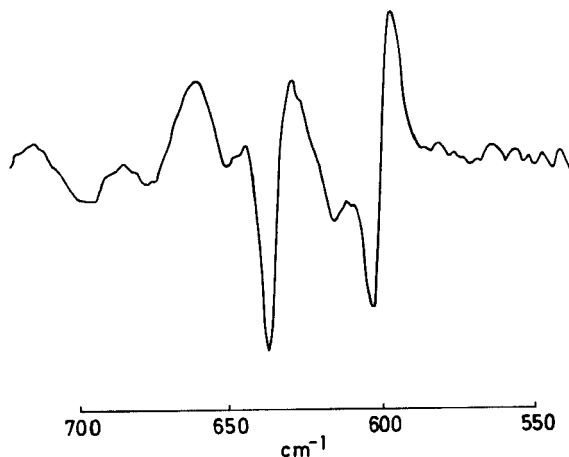


FIG. 9. The second derivative IR spectrum of a commercial mass PVC in the C-Cl stretching region.

of two components. Hence the information from the region between 650 and 700 cm^{-1} , although not conclusive, is in agreement with the results of formal curve fitting [9]. The quality of the corresponding fourth derivative spectra leaves considerable room for improvement, and there are fundamental sensitivity problems because the bands in the interval 650-700 cm^{-1} are broader than their counterparts between 600 and 650 cm^{-1} . Nevertheless, the limited information that may be gleaned from them is in line with that from the second derivative spectra and from the results on the -30°C polymer.

DISCUSSION

The present studies have proved useful in two contexts, one general and one specialized. They have demonstrated the scope and limitations of derivative spectroscopy for peak finding in complex systems of overlapping bands, and they have provided confirmatory evidence that earlier work, using curve fitting methods, aimed at obtaining quantitative conformational information for PVC is proceeding along essentially correct lines.

The value of derivative spectroscopy for resolution enhancement has been amply publicized but the limitations of the method, which are of two types, have received less attention. The first relates to the problem of obtaining an adequate signal-to-noise ratio, and this is dependent on the type and amount of noise present in the original spectral data. As noted above, if the noise is white, its amplitude

approximately doubles for each derivatization operation and, furthermore, it will be difficult to remove completely. If its frequency is high by comparison with that of the peaks being examined, it will produce very large peaks in the derivative spectra but will be removable by filtering without serious loss of resolution of the required data. In practice a considerable amount of high frequency noise is obviously present in IR spectra, as shown by the appearance of the derivative spectra; this has proved to be the case both with spectra run on a conventional dispersive instrument and those obtained from the Digilab FT spectrometer. Work on suitable smoothing routines to minimize the effect of noise without seriously degrading the resolution of the derivative spectra is still in progress. It has been possible to obtain very satisfactory second derivatives, but an improvement in the quality of the fourth derivatives is desirable and should be feasible. When the signal amplitude is comparable with that of the noise, it is clearly not possible to make meaningful deductions. When it is somewhat larger, it is possible to obtain useful information by making replicate runs and regarding the recurrent nonrandom features of these as definitive signals. This method has been used for the present work; it is on this basis that the signals have been identified in the second derivative spectra shown in Figs. 8 and 9.

The fundamental limitations imposed by overlapping peaks of unequal widths and the presence of subsidiary peaks in the derivative spectra emerge clearly from the work on the C-Cl stretching bands. The curve-fitting studies of Robinson et al. [9] indicate that the bands lying in the interval $650\text{--}700\text{ cm}^{-1}$ have half-widths in the range $24\text{--}34\text{ cm}^{-1}$ whereas those between 600 and 650 cm^{-1} have values between 12 and 20 cm^{-1} . For equal absorbances the former will be the more difficult to detect, the more so in the fourth derivatives when the signal-to-noise ratio is likely to be inferior. This combination of factors may well limit the use of fourth derivatives and second derivatives, which, despite their lower resolution, could prove more effective overall.

The second fundamental limitation occurs because of the accidental coincidence, at the appropriate relative intensities, of a subsidiary derivative peak of one component with the main derivative peak of a second component. The absence of a peak indicative of the 647 cm^{-1} band in the second and fourth derivatives provides a good example. The curve-fitting results indicate that this is separated from the 638 cm^{-1} band by about 50% of their mean half-widths. In the urea clathrate polymer the area of the 647 cm^{-1} band is about 60% that of the one at 638 cm^{-1} . Allowing for the fact that it is broader by a factor of about 1.5, its effective intensity in the second derivative is decreased by approximately four. This, coupled with its separation from the 638 cm^{-1} band, gives a situation akin to that shown in Fig. 3.

In the case of the fourth derivative the absence of a peak indicative of the 647 cm^{-1} band may, in part, be the result of accidental coincidences, although the amplitude discrimination factor, about five, will also be significant. Second and fourth derivative spectra

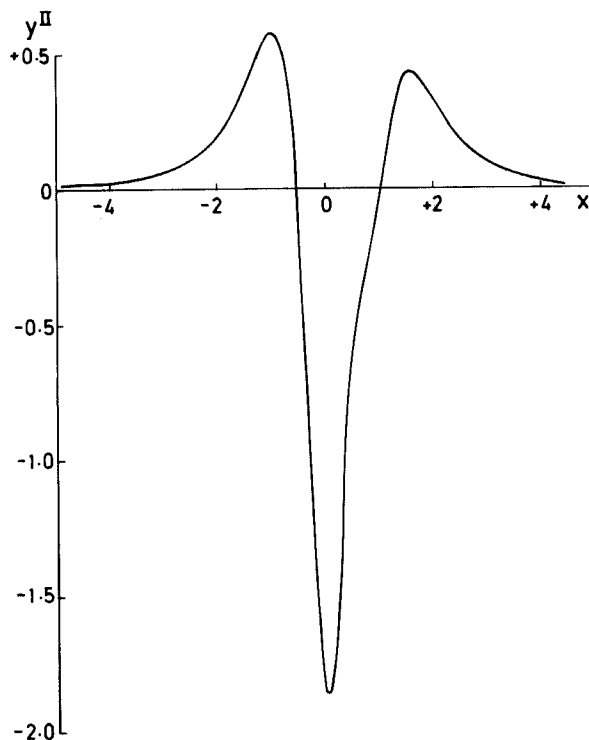


FIG. 10. The second derivative of the composite peak obtained by summing two Lorentzian peaks having an intensity ratio of 3:1, equal half widths, and separated by 40% of this half width.

have been calculated for a number of pairs of overlapping bands, and the case of two Lorentzian peaks of equal width separated by 40% of this value and with an intensity ratio of three, shown in Figs. 10 and 11, is typical. In the case of the second derivative only one negative peak is present, although the presence of a second component may be inferred from the unequal amplitudes of the subsidiary positive peaks and the asymmetry of the negative peak. A second small positive peak appears in the fourth derivative but, in practice, it may not be detectable against the background noise. Here, also, a careful examination of the general form of the derivative spectrum suggests the presence of a second component.

It is evident that interpretational difficulties of this type will be of more frequent occurrence, and more difficult to overcome, with multicomponent overlapping band systems. Caution must therefore be exercised, and when a tentative deduction has been drawn it is desirable to confirm it by calculating the appropriate derivative

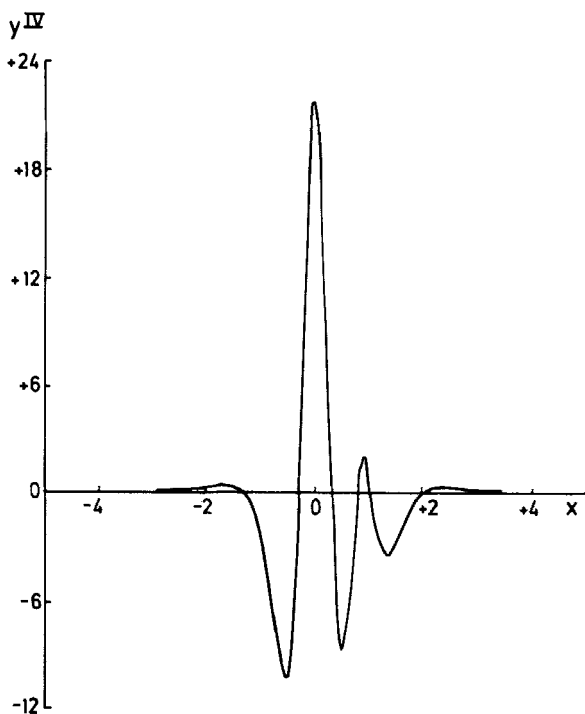


FIG. 11. The fourth derivative of the composite peak obtained by summing two Lorentzian peaks having an intensity ratio of 3:1, equal half widths, and separated by 40% of this half width.

spectrum for a synthetic band system approximating to that inferred from the derivative spectra.

In view of these difficulties it is not surprising that the results on the CH_2 deformation bands are more informative than those on the various C-Cl stretching modes. It has been shown that the overlapping band system around 1430 cm^{-1} is more complex than had been supposed by Germar et al. [22]. This opens the way to a more quantitative method based on curve fitting, which should provide more reliable tacticity values for low temperature polymers than those reported [9, 24].

The less detailed information on the number of components in the overlapping C-Cl band system is very useful because it provides independent confirmation for the essential correctness of the results obtained by curve fitting. When it is possible to constrain the curve-fitting calculations by inserting information about the shapes of the component peaks and their approximate number, the intensity information from the calculations will be more reliable. There still remains

the problem of converting this intensity data into the required concentrations of configurational and conformational isomers, and this is difficult in the absence of absorptivity data for the various bands. Hitherto [9, 11] the naive but simplifying assumption that the various bands have equal absorptivities has been made, but recent intensity measurements on 2-chlorobutane in solution have shown that this is incorrect [25]. Three conformers, $S_{HH'}$, $S_{CH'}$, and $S_{HH'}$, are present and they have values of 19.2, 27.4, and 22.7 mol dm⁻³ m⁻¹, respectively. A more detailed study of the conformers of meso- and dl-2,4-dichloropentane and of isotactic, heterotactic, and syndiotactic 2,4,6-trichloroheptane may provide some additional relevant information. The fact that the information being obtained from curve-fitting calculations is now approaching the stage of quantitative reliability will undoubtedly provide the impetus to obtain an answer to the problem of absorptivity values.

ACKNOWLEDGMENTS

We are grateful to Dr K. Krishnan, of Digilab, Boston, Massachusetts, for providing derivative spectra from a Digilab FTS 15 spectrometer. Permission to publish this paper has been given by The British Petroleum Company Limited.

REFERENCES

- [1] M. E. R. Robinson, D. I. Bower, W. F. Maddams, and H. Pyszora, Makromol. Chem., **179**, 2895 (1978).
- [2] C. J. Carman, Macromolecules, **6**, 725 (1973).
- [3] R. E. Cais and W. L. Brown, Ibid., **13**, 801 (1980).
- [4] G. Natta and P. Corradini, J. Polym. Sci., **20**, 251 (1956).
- [5] J. A. Juijn, "Crystallinity in Atactic Polyvinyl Chloride," Thesis, Gravenhage, Holland, 1972.
- [6] P. E. McMahon and W. C. Tincher, J. Mol. Spectrosc., **15**, 180 (1965).
- [7] D. Doskočilová, J. Štokr, B. Schneider, H. Pivcova, M. Kolinsky, J. Petránek, and D. Lim, J. Polym. Sci., **C16**, 215 (1967).
- [8] S. Krimm, V. L. Folt, J. J. Shipman, and A. R. Berens, Ibid., **B2**, 1009 (1964).
- [9] M. E. R. Robinson, D. I. Bower, and W. F. Maddams, Polymer, **19**, 773 (1978).
- [10] J. L. Koenig and M. K. Antoon, J. Polym. Sci., Polym. Phys. Ed., **15**, 1379 (1977).
- [11] H. U. Pohl and D. O. Hummel, Makromol. Chem., **113**, 190, 203 (1968).
- [12] B. G. M. Vandeginste and L. De Galan, Anal. Chem., **47**, 2124 (1975).

- [13] P. Gans and J. B. Gill, Appl. Spectrosc., 31, 451 (1977).
- [14] W. F. Maddams, Ibid., 34, 245 (1980).
- [15] C. Baker, P. S. Johnson, and W. F. Maddams, Spectrochim. Acta, 34A, 683 (1978).
- [16] C. Baker, W. F. Maddams, J. G. Grasselli, and M. A. S. Hazle, Ibid., 34A, 761 (1978).
- [17] C. Baker, I. P. Cockerill, J. E. Kelsey, and W. F. Maddams, Ibid., 34A, 673 (1978).
- [18] F. Singleton and G. L. Collier, British Patent 760,729 (1953).
- [19] A. E. Martin, Spectrochim. Acta, 14, 97 (1959).
- [20] T. C. O'Haver and G. L. Green, Anal. Chem., 48, 312 (1976).
- [21] J. E. Cahill, Int. Lab., p. 64 (1980).
- [22] H. Germar, K.-H. Hellwege, and U. Johnsen, Makromol. Chem., 60, 106 (1963).
- [23] A. Baruya, A. D. Booth, W. F. Maddams, J. G. Grasselli, and M. A. S. Hazle, J. Polym. Sci., Polym. Lett. Ed., 14, 329 (1976).
- [24] A. Nakajima, H. Hamada, and S. Hayashi, Makromol. Chem., 95, 40 (1966).
- [25] J. E. Goodfield, W. O. George, and W. F. Maddams, Unpublished Results.