χ value obtained for the PC–PCL blend system must be considered to be an upper limit to the true value of χ.

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Resonance Raman Spectrum of Degraded Poly(vinyl chloride). 3. Background Studies

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ABSTRACT: Two factors central to the use of resonance Raman spectroscopy for the characterization of the conjugated polyene sequences present in degraded poly(vinyl chloride) are examined. They are the determination of the conjugated sequence length, *n*, from the measured value of ν_2, the C=C stretching mode, and the specificity of the method for a particular sequence length. By combining ν_2 data for low molecular weight conjugated polyenes with the value for *trans*-polyacetylene a more precise relationship between ν_2 and *n* has been established. The specificity of the technique has been examined experimentally and by the calculation of ν_2 profiles. With the former, ν_2 was measured at frequent intervals between 420 and 625 nm, using a tunable dye laser. The ν_2 profile calculations are based on a universal excitation curve for conjugated polyenes, derived from published results on β-carotene. The results show that the specificity decreases for increasing *n* and there is a displacement of the peak position by an amount dependent on both *n* and the relative concentrations of the polyenes of other sequence lengths that are excited.

Resonance Raman spectroscopy has proved to be a simple, convenient, and sensitive technique for the characterization of the conjugated polyene sequences formed during the degradation of poly(vinyl chloride).[1,2] It has two important advantages, sensitivity and specificity. The former is a consequence of the high intensity of the resonance Raman bands, and conjugated polyenes with nine or more double bonds may be detected down to the level of 0.00001%. The specificity is a consequence of the fact that ν_2, the C=C stretching frequency, varies with the conjugated sequence length, and it is possible to induce resonance in a particular sequence length by choosing the excitation wavelength so that it falls within the visible absorption bands of the sequence in question. The method has been used to examine commercial[1] and more syndiotactic[3] polymers degraded thermally and both types of polymer after γ-irradiation.[4]

Hitherto, the characterization of a particular conjugated polyene sequence length, *n*, from the measured value of ν_2 has been based on an essentially empirical relationship between ν_2 and *n*,[1] obtained from published results for simple conjugated polyenes.[5-7] This gives a linear relation between ν_2 and log *n*. In order to interpret the ν_2 values for the longer sequences present in degraded PVC it is necessary to extrapolate beyond the range covered by the data for the model polyenes. The correctness of such an extrapolation is questionable because, in the limiting case of an infinitely long polyene, $\nu_2 \rightarrow 0$, a clearly erroneous result. There is therefore the need for a more exact equation relating ν_2 and *n*.

Although ultraviolet/visible spectroscopy provides a sensitive method for the characterization of shorter conjugated polyenes, it becomes increasingly less specific as the sequence length increases. This is because the red shift of the characteristic bands becomes progressively smaller per unit increase in the sequence length, and when a range of lengths is present, as is the case with degraded PVC, extensive overlap occurs and the characteristic structure either is very blurred or is totally lost. This limits the use of the method to *n* values up to about ten.[8,9] In that the resonance Raman process has its origin in the electronic excitation that leads to the ultraviolet/visible absorption bands it is reasonable to surmise that it will be subject to a similar type to limitation, although it is clear from the work to date that it will only occur for significantly greater *n* values. Nevertheless, there is the need for a systematic examination of the prolem.

The purpose of the present work has been to examine these two factors in sufficient depth to assess their implications and, hence, to place the characterization of

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Table I
Conjugated Polyene Sequence Lengths, *n*, for Various Values of ν_2, Using the Present and Previous Methods

	calculated *n*	
ν_2, cm^{-1}	present method	previous method
1510	14.8	13.8
1506	16.1	14.8
1502	17.6	15.9
1498	19.3	17.0
1495	20.8	17.8
1493	21.8	18.4
1491	23.0	19.0
1489	24.3	19.7
1487	25.7	20.4
1485	27.6	21.1

degraded PVC by resonance Raman spectroscopy on a firmer basis. The quantitative aspects of such measurements are also considered briefly.

Experimental Section

The sample examined was prepared from a commercial polymer made by a mass polymerization process. It was thermally degraded to a level of 0.5%, as assessed by the hydrogen chloride evolved, using the procedure described previously.[1] The Raman spectra were measured in solution in tetrahydrofuran with a Spex Ramalog 4 spectrometer at intervals of 5 nm of the exciting wavelength over most of the range 425–625 nm. The exciting wavelengths were obtained from a Coherent Radiation Ltd. tunable dye laser, pumped by a CR12 argon ion laser with stilbene 3, sodium fluorescein, and rhodamine 6G as dyes.

Results and Discussion

1. Estimation of Conjugated Polyene Sequence Lengths. Hitherto, the measured values of ν_2 have been used to obtain values for conjugated polyene sequence lengths by utilizing the linear relation between ν_2 and log *n*, based on the spectra of simple model polyenes.[5-7] This relation was set up on five data points only, with $n = 11$ the longest sequence. Hence, extrapolation to *n* values of approximately 20, such as are encountered in degraded PVC samples, is open to question. More fundamentally, an extended extrapolation is inadmissible because as *n* becomes very large, ν_2 tends to zero and this is clearly erroneous.

There is the need for an additional calibration point and this can be obtained from the measurements of Shirakawa and Ikeda[10] on *trans*-polyacetylene. This contains very long conjugated polyene units and, using the exciting wavelength 633 nm, they obtained a ν_2 value of 1474 cm^{-1}. This obviously corresponds to an *n* value much in excess of those of the calibration points used previously and of the values encountered with degraded PVC samples. Hence, it is convenient to adopt 1474 cm^{-1} as the value for $n \rightarrow \infty$ and to base a more precise relation between ν_2 and *n* on it. When it is combined with the previously used data points, the set can be fitted by asymptotic regression with the equation $\nu_2 = 1474 + 141.67e^{-0.0925n}$.

n values for various values of ν_2 have been calculated from this equation and are given in Table I, together with those calculated by the method used previously. As anticipated, the difference between the two sets of values increases with decreasing ν_2 and increasing *n* and becomes quite appreciable in the case of the longer sequences known to be present in degraded PVC. For example, the krypton laser line at 568 nm excites resonance at 1498 cm^{-1}; this was formerly interpreted as indicative of an *n* value of 17 but it is now shown to be 19.3. With still longer conjugated sequences, such as are present in degraded poly(vinyl bromide) on the evidence of visible absorption spectra,[11] the use of the new relation between ν_2 and *n* is mandatory. It may be noted, in passing, that the nonintegral *n* values encountered in Table I prove to be meaningful in the light of the specificity studies detailed below.

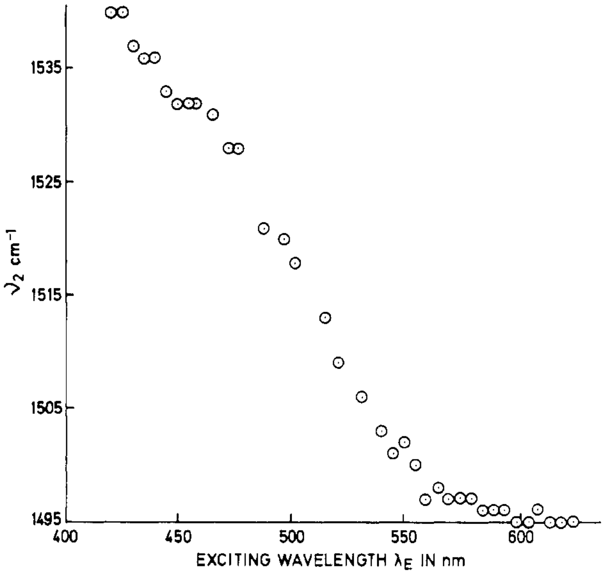

Figure 1. Values of ν_2, obtained from a PVC sample degraded to the 0.5% level, as a function of the exciting wavelength.

2. Specificity of ν_2 Measurements. In the determination of *n* from a measured ν_2 value it has been tacitly assumed that the method is wholly specific and that resonance is excited only in conjugated polyene sequences of length *n*. However, if there is a contribution from longer and shorter sequences, the measured band will represent a weighted mean and an error in *n* is to be expected. Furthermore, if the measured intensity of ν_2 is used to estimate the concentration of sequences of length *n*, the value obtained will be incorrect. Hence, it is necessary to examine the specificity of the method. This has been done in two ways, by experimental measurements and by the calculation of ν_2 profiles.

a. Experimental Results. If the laser radiation of a particular wavelength excites resonance in one conjugated sequence length only, there should be discrete steps in the measured ν_2 values as the exciting wavelength, λ_E, is changed. However, if the ν_2 vs. λ_E plot shows no discontinuities, the specificity must be inadequate to distinguish between *n* and $n + 1$. The results of ν_2 measurements, made at 5-nm intervals over most of the λ_E range 425–625 nm, are shown in Figure 1. The only evidence for a discontinuity is at exciting wavelengths around 450–460 nm and a corresponding ν_2 value of about 1532 cm^{-1}. This suggests that a degree of resolution between $n = 9$ and $n = 10$ is being achieved.

The failure to obtain resolution for larger *n* values can be understood in terms of a simple qualitative model. If resonance is being excited in two sequences of length *n* and $n + 1$, each will give a ν_2 band at the appropriate frequency and the observed profile will be their sum. In the case of Lorentzian profiles, and Raman bands are a good approximation to this shape,[12] resolution into separate components is not obtained in the case of two superimposed peaks of equal intensity and half-width if their separation is less than about 60% of their half-widths. Using the half-width value of 18 cm^{-1} obtained from the ν_2 profile of the model polyene β-carotene and the known change in ν_2 for an incremental change in *n*, one can easily show that complete resolution will occur between $n = 6$ and $n = 7$, but not for longer sequences. With $n = 9$ and $n = 10$ the profile will have a rather flat top because of incipient resolution, and this gives a degree of discontinuity in the ν_2 vs. λ_E plot.

When the observed ν_2 profile consists of two or more component peaks, their relative contributions will alter as the wavelength is changed from a value which excites resonance most strongly in one component to the appropriate values for the second and subsequent components. The result is a gradual change in the frequency at the profile maximum, in line with the experimental findings. However, in order to understand the process in a more detailed way and to assess its implications for the interpretation of experimental measurements it is necessary to calculate ν_2 profiles quantitatively. The method used and the results obtained will now be discussed.

b. Calculation of ν_2 Profiles. When resonance enhancement occurs in a Raman spectrum, the intensity varies with the precise wavelength of the exciting radiation, reaching a maximum at the particular value where the resonance process occurs most markedly and decreasing at longer and shorter wavelengths. The plot of the resonance Raman intensity as a function of exciting wavelengths is known as the excitation profile and it provides the means for calculating ν_2 profiles. If the exciting wavelength is, for convenience, chosen to coincide with the maximum in the excitation profile for a conjugated sequence of length n and if the way in which the wavelength of this maximum shifts in changing the sequence length to $n - 1$, $n + 1$, and other values is known, then it is possible to calculate the intensities of the ν_2 peaks for these other sequences. The ν_2 profile is then obtained by summing the various individual ν_2 peaks at the wavenumber positions appropriate to their lengths, making the assumption that they are Lorentzian in shape.

It is therefore necessary to determine the excitation profiles for the various conjugated polyene sequences. The method used is based on the experimental excitation profile of β-carotene, given by Inagaki et al.[13] It is also necessary to ascertain how this changes with respect to wavelength as n changes and this can be deduced from the close correspondence between the visible absorption spectrum and the excitation profile. The results of Inagaki et al. show a coincidence of the two maxima in the excitation profile with those of the 0–0 and 1–0 vibrational bands in the absorption spectrum. Jaffe and Orchin[14] have summarized the published ultraviolet/visible spectral data on conjugated polyenes and have discussed the various relationships between λ and n that have been proposed. The difficulty is that they are based on results for a limited range of n values and in order to cover the conjugated sequence lengths encountered in degraded PVC it is necessary to extrapolate, leading to the problem already encountered in the case of the ν_2 and n relationship. Although the visible absorption spectrum of *trans*-polyacetylene[10] is rather diffuse and does not show the vibrational fine structure so characteristic for the simple conjugated polyenes, it is possible to assign a value of 700 nm for $n \rightarrow \infty$ with reasonable confidence. When this is combined with the results for the simple conjugated polyenes, the data set can be fitted by asymptotic regression with the equation $\lambda_{0\text{-}0} = 700 - 537.7e^{-0.0768n}$. The $\lambda_{0\text{-}0}$ value at the maximum of the excitation profile for any sequence length may be calculated from this equation.

The experimental excitation profile for β-carotene[13] is not in a convenient form for the present calculations. It has therefore been transposed by expressing the abscissal values as differences, measured in cm^{-1}, from the value $\nu_{0\text{-}0}$ at the maximum intensity. The ordinate values are expressed as ratios against this maximum intensity. This then gives the universal excitation profile for conjugated polyenes shown in Figure 2. It is clear from the general form of this curve that for an exciting wavelength which gives resonance with sequences of n units, there will be relatively little contribution from $n - 1$ and shorter sequences because the relative intensity falls sharply with increasingly negative values of $\nu - \nu_{0\text{-}0}$. However, the decrease in intensity is much slower for positive values so that a contribution from $n + 1$ and longer sequences is to be expected.

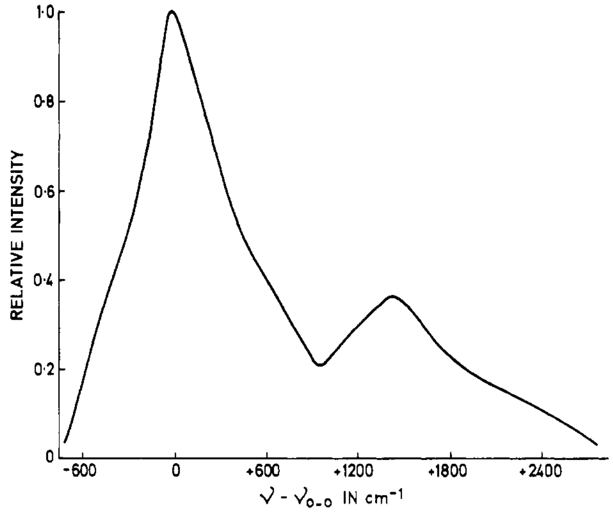

Figure 2. Universal excitation profile for conjugated polyenes, based on published measurements for β-carotene.

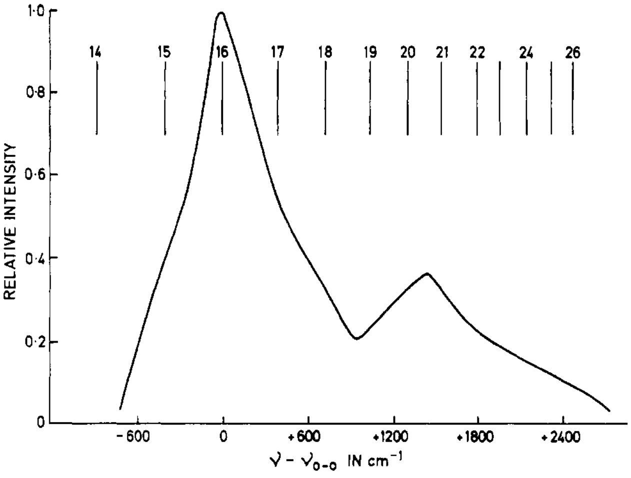

Figure 3. Excitation profile for a polyene containing 16 conjugated double bonds, showing the various sequence lengths which are excited by radiation of wavelength 543 nm, corresponding to $\nu_{0\text{-}0} = 18\,420$ cm^{-1}.

Furthermore, the number of longer sequences involved will increase as n increases because the incremental shift in $\nu_{0\text{-}0}$ decreases with increasing n whereas the width of the excitation profile is constant. The case of $n = 16$ is shown in Figure 3; there are contributions from $n = 15$ and $n = 17$–25. With $n = 9$ only $n = 10$ and $n = 11$ are also excited but with $n = 20$ the other sequences involved are 18, 19, and 21–43, so that the selectivity is very poor. One other assumption has been made in the calculations; it is that ν_2 peaks with less than 10% of the intensity of the major peak may be ignored. This simplifies the calculations and neglect of these minor peaks only affects the overall profile in the wings, well removed from the peak position.

Table II
Details of the Calculation of the ν_2 Profile for $n = 16$ Using Equal Concentrations of the Various Contributing Conjugated Polyene Sequences

n	ν, cm^{-1}	$\nu_0 - \nu$, cm^{-1}	a	ν_2, cm^{-1}	$\Delta\nu_2$, cm^{-1}	b
16	18423 (ν_0)	0	1.000	1506.3	0	0
15	18825	−402	0.395	1509.3	−3.3	−0.367
17	18028	+395	0.540	1503.5	+2.8	+0.311
18	17696	+727	0.322	1501.0	+5.3	+0.589
19	17382	+1041	0.232	1498.7	+7.6	+0.844
20	17117	+1306	0.327	1496.6	+9.7	+1.078
21	16875	+1548	0.323	1494.6	+11.7	+1.300
22	16647	+1776	0.231	1492.7	+13.6	+1.511
23	16458	+1965	0.187	1491.0	+15.3	+1.700
24	16271	+2152	0.153	1489.5	+16.8	+1.867
25	16103	+2320	0.120	1488.0	+18.3	+2.033

The calculation routine may be illustrated by reference to a specific example, that of a degraded polymer containing equal concentrations of the various polyene sequences that are excited; the wavelength is chosen to coincide with the maximum of the excitation profile for $n = 16$. The calculated value of its position, denoted by ν_0, is 18423 cm^{-1} and the corresponding value for ν_2 is 1506.3 cm^{-1}. Values of the position for the maximum, ν, for conjugated sequences longer and shorter than 16 are then calculated, and $\nu_0 - \nu$ values obtained. These are used to read off relative intensity values, denoted by a, from the universal excitation profile and, in those cases where they exceed the minimum limit of 0.1, the corresponding ν_2 values are calculated. These are used to obtain $\Delta\nu_2$ values, the difference from ν_2 for $n = 16$.

In order to sum the ν_2 profiles for the various n values, they are fitted by the Lorentzian profile $y = a/[1 + (x - b)^2]$. This gives a peak of height a, semi-half-width one unit of x, and positioned at b on the x axis. The a values have already been obtained and the b values are calculated by setting the semi-half-width at 9 cm^{-1}, the value for β-carotene, and taking the ratio $\Delta\nu_2/9$. The various values so obtained are set out in Table II. The ν_2 profiles are summed by a computer program that will accommodate up to 50 peaks; the result is displayed graphically.

A representative range of calculations of this type has been made. In the first set of five, for n = 9, 12, 16, 18, and 20, respectively, the concentrations of the various sequences contributing to the observed profile were all made equal. This is by no means an improbable practical situation, particularly for n values at the lower end of the range. It has also been tacitly assumed that the resonance intensity per unit concentration of conjugated polyene is independent of n over a moderate range; this point will be discussed below.

In the second set of calculations different relative concentrations of the various polyenes have been used in order to cover a range of practical situations. In particular, the buildup of longer conjugated polyenes to a maximum at $n = 20$, followed by a decrease for larger n values as the result of cross-linking,[3,4] has been simulated by doubling the concentration of each polyene successively one unit longer than the shortest one for which resonance occurs, up to $n = 20$, followed by a halving for each successive unit beyond this length. The conditions used for the 14 calculations are set out in Table III.

Three typical profiles are given in Figure 4. They are for runs 1, 4, and 5 of Table III and show the effect of increasing the value of n. The abscissal values have been left in units of x, as the displacement from the correct value $x = 0$ is more readily discernible than in units of ν_2 in cm^{-1}.

Table III
Details of the Parameters Used for the Calculation of Various ν_2 Profiles

run no.	n value of nominal component	n values and relative concentrations of other components
1	9	10 and 11, both 1.0
2	12	13–17, all 1.0
3	16	15 and 17–25, all 1.0
4	18	17 and 19–32, all 1.0
5	20	18, 19, and 21–43, all 1.0
6	9	10 (2) and 11 (4)
7	9	10 (0.5) and 11 (0.25)
8	12	13 (2), 14 (4), 15 (8), 16 (16), 17 (32), 18 (64)
9	12	13 (0.5), 14 (0.25), 15 (0.125)
10	16	15 (0.5), 17 (2), 18 (4), 19 (8), 20 (16), 21 (8), 22 (4), 23 (2), 24 (1), 25 (0.5)
11	18	17 (0.5), 19 (2), 20 (4), 21 (2), 22 (1), 23 (0.5), 24 (0.25)
12	20	18 (0.25), 19 (0.5), 21 (0.5), 22 (0.25), 23 (0.125)
13	18	16 (4), 17 (2), 19 (0.5), 20 (0.25), 21 (0.125)
14	20	18 (4), 19 (2), 21 (0.5), 22 (0.25), 23 (0.125)

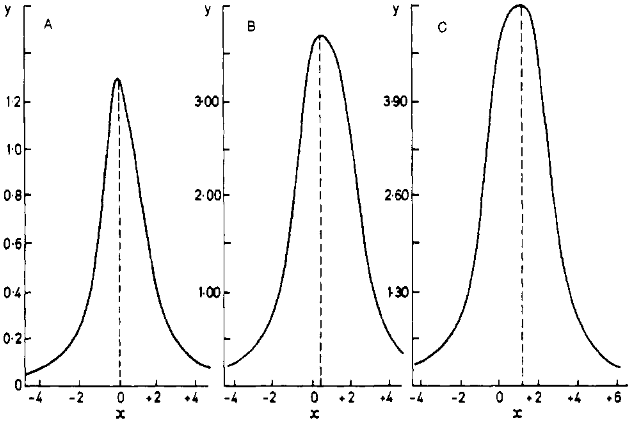

Figure 4. Calculated ν_2 profiles for (A) $n = 9$, (B) $n = 18$, and (C) $n = 20$, using an equal concentration of all sequence lengths lying within the excitation profiles.

Three features are readily apparent from a comparison of the profiles for n = 9, 18, and 20; they are the steadily increasing displacement of $x_{\max}$, the increasing half-widths, and the increasing asymmetry of the profile.

The three effects are as anticipated, on the basis of the qualitative discussion above, but it is now possible to quantify them. For this purpose the displacements of $x_{\max}$ have been calculated as errors in ν_2, the negative sign indicating a shift to a lower value, and as the corresponding errors in the n values deduced from the ν_2 measurements, with a positive sign indicating that the measured value is too great by the amount indicated. Band asymmetries have been expressed as the semi-half-widths $j-$ and $j+$, for the high- and low-frequency sides of the maximum, corresponding to n values smaller than and greater than the nominal figure. It is also useful to consider the overall half-width, the sum of $j-$ and $j+$. The ordinate values, which are a measure of the concentrations of the polyenes, may be expressed in two ways; directly as $y_{\max}$ and as $\sum a$, the sum of the a values of the various polyenes contributing to the overall profile. These various parameters, for the 14 calculations, are collected in Table IV and their implications will now be considered in more detail.

Runs 1–5, in which n is increased from 9, through 12,

Table IV
Results of the Calculations on Various ν_2 Profiles

run no.	error in ν_2, cm^{-1}	error in n	$j-$, cm^{-1}	$j+$, cm^{-1}	half-width, cm^{-1}	$y_{\max}$	Σa
1	−1.2	+0.2	9.7	12.4	22.1	1.29	1.48
2	−2.7	+0.7	10.6	14.8	25.4	1.80	2.28
3	−3.4	+1.0	11.7	16.8	28.5	2.83	3.92
4	−5.0	+3.3	13.0	18.5	31.5	3.67	5.49
5	−10.8	+6.9	20.3	15.8	36.1	5.13	7.89
6	−5.6	+1.0	14.0	15.0	29.0	1.95	2.56
7	−0.5	+0.1	10.2	11.4	21.6	1.12	1.18
8	−13.9	+4.1	15.0	11.8	26.8	10.61	13.08
9	−0.6	+0.2	10.8	11.5	22.3	1.27	1.36
10	−9.2	+3.7	12.8	11.6	24.4	12.89	14.76
11	−3.3	+1.4	11.2	11.8	23.0	4.73	5.22
12	−0.4	+0.2	10.8	10.7	21.5	1.79	1.87
13	+0.8	−0.3	10.8	11.8	22.6	2.39	2.53
14	+1.2	−0.6	11.0	11.2	22.2	2.66	2.88

16, and 18, to 20, with the concentrations of all the contributing polyenes equal, form a coherent set. The error in the measured n increases steadily; in the case of $n = 9$ it is negligible for practical purposes but it becomes significant for $n = 16$ and unacceptably large for $n = 20$. This is the most significant consequence of the rapid loss of specificity with increasing n. It will not be apparent, as such, from the observed ν_2 values but there are two other experimentally observable parameters which do provide a clear indication of this loss of specificity and so point to the need for caution in the interpretation of the measured ν_2 values. They are the band half-width and asymmetry. The former increases steadily with increasing n, and for $n = 20$ it is more than twice the value, 18 cm^{-1}, of that for the simple profile that would be obtained with 100% specificity. There is a corresponding increase in the $j-$ and $j+$ values but although $j+$ is greater than $j-$ for $n = 9$, 12, 16, and 18, the reverse is true for $n = 20$. This seemingly unexpected result is a consequence of the subsidiary maximum in the excitation profile which acts as a secondary weighting factor for the relative contributions of the component peaks in the ν_2 profile in a way which depends on the value of n.

The $y_{\max}$ values are always greater than the true value, 1.0, but are always less than the sum of the values for the contributing peaks, $\sum a$. The divergence between $y_{\max}$ and $\sum a$ increases with increasing n. When the former is expressed as a percentage of the latter, it amounts to 87% for $n = 9$, 79% for $n = 12$, 72% for $n = 16$, 67% for $n = 18$, and 65% for $n = 20$. $y_{\max}$ provides an acceptable measure of the total concentration of polyenes contributing to a particular ν_2 profile when n is at the lower end of the range but not for those at the opposite extreme. However, if $y_{\max}$ is taken as a measure of the concentration of the polyene nominally corresponding to a particular excitation wavelength, serious errors will occur in four of the five cases examined.

A comparison of the results for runs 1 and 6 and for runs 2 and 8, in which the concentration of polyenes longer than the nominal value increases by a factor of 2 for each increment in n for the second member of each pair, shows that for these latter the errors in n are increased considerably. With run 6 the half-width is appreciably greater than with run 1, but the difference is marginal in the case of runs 2 and 8, and the half-width is smaller for run 8 than for run 6. This is a consequence of the fact that the incremental change in ν_2 for a change in n becomes increasingly smaller as n becomes larger. Hence, inferences should only be drawn from measured half-widths of ν_2 profiles when they are considered in conjunction with the nominal n value involved.

Table V
Asymmetry of Experimental ν_2 Profiles

λ_E, nm	ν_2, cm^{-1}	$j-$, cm^{-1}	$j+$, cm^{-1}	half-width, cm^{-1}
501.7	1518	16.1	16.1	32.2
520.8	1509	15.8	16.1	31.9
540	1503	15.6	16.1	31.7
550	1501	17.5	16.9	34.4
560	1499	17.5	16.4	33.9
570	1498	17.2	15.8	33.0
580	1497	17.2	14.4	31.6
590	1496	16.7	14.4	31.1
600	1495.5	16.7	13.9	30.6
610	1495	17.8	13.9	31.7
620	1495	17.8	13.3	31.1

This is confirmed by the results for other profiles, particularly for run 10, where the nominal component is $n = 16$ but $n = 20$ is present at 16 times the concentration and $n = 24$ at the same concentration as $n = 16$, simulating a buildup to a maximum at $n = 20$ followed by a rapid drop for longer polyenes, as the result of cross-linking. In this case the half-width, 24.4 cm^{-1}, is not grossly in excess of the true value but the error in n is very considerable. In those cases where the polyenes other than the nominal component are present at lower concentrations, as in runs 7, 9, and 12, the observed profile does not differ greatly from that for perfect selectivity and the errors in n are trivial. Runs 13 and 14, in which the concentrations of polyenes shorter than the principal component are the largest, give small negative errors. The half-widths and asymmetries do not deviate greatly from ideality and it will not be easy to recognize situations of this type in practice.

c. Measured ν_2 Profiles. During the course of the measurements made to obtain the data used in Figure 1, ν_2 profiles were recorded at each of the exciting wavelengths. These profiles relate to one sample only and hence to a single distribution of conjugated polyene sequence lengths. Nevertheless, the variation of this profile, particularly its asymmetry, with exciting wavelength and hence with n proves of interest for comparison with the above calculations. Results for these profiles, expressed as $j-$, $j+$, and half-width values, are given in Table V. They show that the half-width is substantially independent of the exciting wavelength and so of n but that the asymmetry increases with increasing n. It becomes more pronounced on the high-frequency side, corresponding to n values smaller than the nominal one.

Although the half-width is substantially independent of n, the values are appreciably greater than the majority of

Table VI
Results of the Calculations on Various ν_2 Profiles Based on a Semi-Half-Width of 12 cm^{-1} for the Individual Components

run no.	$j-$, cm^{-1}	$j+$, cm^{-1}	half-width, cm^{-1}
1A	12.6	15.0	27.6
2A	13.9	16.3	30.2
3A	14.2	17.6	31.8
4A	16.6	18.7	35.3
13A	12.8	12.9	25.7
14A	12.5	13.1	25.6

those given in Table IV and it is very unlikely that this is the result of an abnormal distribution of polyene sequence lengths in the sample used for the measurements. The most probable explanation lies in the choice of the value of 9 cm^{-1}, taken from the measurements on β-carotene, for the semi-half-width of the individual ν_2 profiles. It is not possible to infer an exact value from the experimental profiles but the figure of 12 cm^{-1} was selected for a limited number of additional calculations. The results of these, which are for runs 1, 2, 3, 4, 13, and 14 of Table IV, are given in Table VI. The results parallel those for a 9-cm^{-1} semi-half-width, with proportionately larger values for the half-widths of the composite ν_2 profiles. However, they are still somewhat smaller than the measured values and the correct value is probably about 14 cm^{-1}.

The asymmetry of the calculated profiles again differs from the experimental results. In particular, the marked asymmetry on the high-frequency side of the experimental profiles, indicative of much higher concentrations of polyenes with smaller n values than the nominal ones, has not been found in the calculated profiles. The significance of this difference will be discussed below.

3. Discussion. Before the results of the ν_2 profile calculations are discussed in more detail it is apposite to consider possible limitations inherent in the assumptions on which the method is based. Two equations have been derived relating, respectively, ν_2 and n and λ_{0-0} and n. It has also been assumed that the maximum of the excitation profile coincides with λ_{0-0}.

The validity of the relation between ν_2 and n is dependent to an appreciable degree on the value of ν_2 for a very long conjugated polyene, derived from the published measurements on *trans*-polyacetylene. This is also true for λ_{0-0} and it follows that if a value of 700 nm is assumed for the latter, the corresponding ν_2 value should be measured at an exciting wavelength of 700 nm. The figure 1474 cm^{-1} used in the present work was obtained with an exciting wavelength of 633 nm[10] and it will therefore be somewhat too high. However, because of the asymptotic nature of the relation between ν_2 and n it is unlikely to be in error by more than a few wavenumbers. The n values deduced from the measured ν_2 values will be slightly too large and this will offset the systematic error that occurs in most cases (Table IV) as the result of the influence of polyenes longer than the one nominally being measured.

The visible absorption spectrum of *trans*-polyacetylene does not show the vibrational fine structure so characteristic for simple conjugated polyenes and λ_{0-0} is correspondingly more difficult to locate. Nevertheless, the adopted value of 700 nm is unlikely to be seriously in error. The measurements of Inagaki et al.[13] on the absorption spectrum and the excitation profile of β-carotene show that the maxima coincide and it is reasonable to assume that this will be so for conjugated polyenes in general. It is also reasonable, in the absence of evidence to the contrary, to assume that the excitation profile for β-carotene is generally applicable for conjugated polyenes and that the universal excitation profile shown in Figure 2 is valid.

Some doubt attaches to the precise form of this profile for negative values of $\nu - \nu_{0-0}$ because Inagaki et al. give only two experimental points in this region and the precise position of the line drawn through them is therefore rather subjective. If the relative intensity falls off more slowly than shown in Figure 2, the contribution of shorter sequences to the calculated ν_2 profile will be underestimated. This may account for the measured ν_2 profiles being more asymmetric in the direction of lower n values than those calculated. Furthermore, the difference between the observed and calculated profiles will increase with increasing n.

In Figure 1 the value of ν_2 becomes asymptotic with exciting wavelength for values in excess of 600 nm, corresponding to n values greater than about 20. This is because longer polyenes are substantially absent, as the result of cross-linking.[3,4] As the exciting wavelength is increased behyond 600 nm, an increasing proportion of polyenes shorter than the nominal n value, and hence with negative values of $\nu - \nu_{0-0}$, are excited and, in this case also, a knowledge of the precise form of the excitation profile is necessary if the calculated ν_2 profiles are to be realistic. Clearly, there is the need for a more detailed measurement of the excitation profile of β-carotene, using a tunable dye laser.

The discrepancy between the semi-half-width of 9 cm^{-1} for ν_2 for β-carotene and the probable value of about 14 cm^{-1} for the conjugated polyenes present in degraded PVC merits comment. The work of Marks et al.[8] provides one possible explanation. They suggested that, for a given n value, there are four types of conjugated polyenes present. They are those in which the sequence begins at the end of a chain, begins and terminates in the middle of a chain, begins at a branch point along the chain, and starts and ends at chain branch points. All four types are alkyl-substituted conjugated polyenes and there will be bathochromic shifts of their absorption spectra. Marks et al., using Woodward's rules,[15,16] assigned shifts of 5, 10, 15, and 20 nm to the four types, by comparison with the unsubstituted polyene. They assumed, further, that these shifts would be applicable to all n values. This, however, is unreasonable in view of the asymptotic increase of λ_{0-0} with n.

With this diversity of unsaturation type for a particular conjugated polyene sequence length it is clearly difficult to find a wholly suitable model compound for the measurement of a reference excitation profile. However, β-carotene, a substituted conjugated nonaene, should be as relevant as octadecanonaene. The excitation profiles of these two materials may well not differ in overall form but merely in the wavelengths of the peaks, those of the β-carotene showing a small bathochromic shift. Nevertheless, it is clearly desirable to examine the straight-chain conjugated polyene in addition to making more precise measurements on β-carotene, to supplement the work of Inagaki et al.[13]

Daniels and Rees,[9] while accepting the basic premise of Marks et al. on the occurrence of substituted polyene sequences, adopted a more practical approach. They computer fitted experimental ultraviolet/visible absorption spectra of degraded PVC samples and found, for a given n, that they required three peaks in order to match the observed spectrum. The best fit, a purely empirical one, was obtained by giving one peak a hypsochromic shift, by giving the second a bathochromic shift, and by placing the third at the position of the unsubstituted polyene. They did not attempt to assign the two additional peaks in terms of the structures proposed by Marks et al. In view of these results it is not surprising that a ν_2 semi-half-width greater than that of β-carotene is required in the present work. At the present stage of development of the work it is probably best to determine the optimum value empirically, although there is the hope that, at a later date, a more detailed interpretation in terms of specific structures will be possible.

With the reservations about the precise shape of the excitation profile and the semi-half-width of ν_2 it is reasonable to conclude that the present calculations give a good indication of the degree of specificity of the resonance Raman technique for practical purposes. They show that it decreases with increasing n value and that the consequential error in the measured n value is very dependent on the distribution of sequence lengths. Unfortunately, it is not possible to assess the error from the asymmetry of the measured profile, as a comparison of the results for runs 4 and 5 demonstrates. It should be possible, in principle, to deduce correct ν_2 values for a particular exciting wavelength by combining the equations relating λ_{0-0} and n and ν_2 and n. In practice, the uncertainties in both equations make this approach of very questionable value. The examination of a range of degraded samples, with different distributions of sequence lengths shows, as expected, that the ν_2 values cover a small range for a particular excitation wavelength.[17] It may be possible to infer a probable ν_2, for a given n, from an evaluation of a range of such results.

However, the best approach to the problem should be a detailed study of the shapes of experimental ν_2 profiles. The calculated profiles reported in the present work have been obtained by summing ν_2 profiles and the reverse process with measured profiles is possible, by curve fitting. Despite the potential pitfalls of curve fitting,[18-20] it should prove possible to resolve the individual components of ν_2 profiles for those n values, up to about 16, for which the number of component peaks is not too large. This approach is being examined.

Curve fitting should give the number of component peaks, their ν_2 values and hence the corresponding n values, and their intensities. This opens the way to a more quantitative approach than has been posible hitherto, when only relative concentrations of the different sequence lengths have been forthcoming.[1,3,4] It will be necessary to obtain calibration data and this should be possible via the corresponding electronic absorption spectrum. Tonks and Page[21] have given a very simple relation between absorption and resonance Raman intensities, using expressions derived by Hizhnyakov and Tehver,[22] and although Hassing and Mortensen[23] have subsequently suggested that it is strictly applicable only at zero temperature, it ought to provide the basis for a quantitative approach. Further, it is known that the molar absorptivity in the electronic spectrum is proportional to the number of conjugated polyene units present.[24,25] Hence, from data on β-carotene or other suitable model polyenes it will be possible to derive absorptivity values for longer polyenes and then to relate these to the resonance Raman intensities. It is therefore reasonable to anticipate significant progress in the quantitative application of resonance Raman spectroscopy to the study of degraded poly(vinyl chloride).

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