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The origin of bandshapes and intensities of polyene resonance Raman bands from degraded polyurethane foam-backed poly(vinyl chloride) sheet at different excitation wavelengths

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A new method has been developed that uses model u.v./visible absorption spectra to determine the relative resonance enhancement factors and the ranges of polyene lengths that contribute to a particular resonance Raman spectrum from a thermally degraded poly(urethane) foam-backed poly(vinyl chloride) sheet. Resonance Raman spectra were recorded using Microline Focus instrumentation with 514.5, 488.0, 457.0 and 632.8 nm excitation. The individual polyene ν_2 resonance Raman bands contributing to the observed ν_2 resonance Raman band have been determined and polyene concentration profiles have been calculated. Interpretation of the data shows that polyene propagation is the dominant mechanism in the degradation. Detailed modelling of the 514.5 nm excitation data, over the full range of degradation times, indicates an inverse relationship between concentration and polyene length. This new result suggests that there is no maximum length to which a polyene propagates in this system.

(Keywords: poly(vinyl chloride); degradation; Raman spectroscopy)

INTRODUCTION

Poly(vinyl chloride) (PVC) is known to degrade thermally just above its glass transition temperature by dehydrochlorination[1]. In this reaction, sequential loss of HCl from the polymer chain results in the formation of conjugated polyenes. The mechanism of the dehydrochlorination reaction is complex. Initiation occurs at labile centres in the PVC chain such as tertiary chlorine and allylic chlorine sites. An 'unzipping' reaction begins, in which HCl is lost from successive units along the PVC chain. The reaction is thought to be catalysed by the released HCl. Successive HCl loss results in the formation of conjugated polyenes in the PVC chain and, even at very low concentrations, these are responsible for the strong colour changes observed in the degraded PVC. It has also been shown that the presence of amine catalysts present in a poly(urethane) (PU) foam backing accelerates the rate of thermal degradation of PVC sheet and often results in the formation of longer conjugation length polyenes in the polymer[2,3].

Raman spectroscopy has been used extensively in the study of polyenes formed during PVC thermal degradation[3,4]. Polyenes formed during dehydrochlorination of the PVC exhibit strong u.v./visible absorption bands, which allow the resonance Raman condition to be met. This phenomenon occurs when the wavelength of the Raman excitation is within the envelope of an electronic transition of the scattering species. Considerable enhancement of the associated Raman signals results and spectral intensity enhancement factors of up to 10^6 have been reported[4]. The resonance effect allows extremely low concentrations of polyenes to be detected in the Raman spectrum of degraded PVC. Detection of polyenes at the 0.001% dehydrochlorination level in degraded PVC has been reported using Raman spectroscopy[5].

There exists a well defined relationship[6] between the u.v./visible absorption maximum ($\lambda_{\max}$) and the conjugation length (n) of a polyene:

$$\lambda_{\max} = 700 - 537.7\exp(-0.0768n) \qquad (1)$$

The consequences of this relationship are significant in that by use of the appropriate Raman excitation wavelength (λ_{ex}), it is possible to 'select' from which polyene conjugation length the resonance Raman spectrum is obtained. Furthermore, intensity data from the resonance Raman spectra recorded from a sample using different excitation wavelengths (excitation profiles) have been used to calculate the relative concentration profile of all those polyene lengths present[4]. This sensitivity and

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'selectivity' of the resonance Raman technique makes it invaluable in the analysis of PVC degradation.

Application of the relationship between λ_{ex}, the Raman excitation frequency, and n, the conjugation length (equation (1)), is more complex than implied above. As the relationship is exponential, the red shift in the absorption maximum decreases rapidly with increasing conjugation length. Considerable overlap of absorption spectra of the individual length polyenes occurs at $n > 8$. At a particular Raman excitation wavelength, a maximum resonance enhancement may be observed for a particular value of n and an intense Raman band will be observed. However, contributions to the Raman band will also be observed from preresonance Raman enhancement in polyenes $n \pm 1$, $n \pm 2$ and possibly $n \pm 3$.

Preresonance Raman enhancement occurs when the excitation wavelength falls within the high or low wavelength wings of the electronic absorption band. If the intensity of a Raman band observed over a range of excitation wavelengths of a species is plotted as a function of wavelength, the shape of the plot obtained matches the shape of the electronic absorption profile associated with that species. Thus the extent of resonance Raman enhancement is directly related to the magnitude of optical absorption of a species. Prediction of resonance Raman enhancement factors is possible when the absorption spectrum is available. In degraded PVC, overlap between individual absorption spectra of the polyenes renders accurate predictions of the contributions which each polyene length makes to the observed resonance Raman spectrum at a given wavelength a complex problem. The observed ν_2 polyene band in the Raman spectrum at any given excitation wavelength is a composite, the result of overlap of the individual Raman spectra of the contributing polyene lengths.

Baruya *et al.*[7], using model compounds, derived a relationship between the Raman shift of the ν_2 band and polyene length, n:

$$\nu_2 = 1461 + 151\exp(-0.07808n) \qquad (2)$$

The ν_2 bands from individual polyene lengths have different Raman shifts. Consequently, overlap in the polyene Raman bands results not only in an overall increase in intensity, but also in an increase in width of the observed ν_2 band from degraded PVC.

For detailed PVC degradation analysis using the resonance Raman technique, a determination of which polyene lengths contribute to the observed Raman spectrum at different excitation frequencies is required. The resonance enhancement factors for the contributing polyene lengths will be dependent on the absorption of each polyene length at the excitation wavelength used.

No method has yet been reported which allows *ab initio* calculation of which range of polyenes contribute to the resonance Raman spectrum from degraded PVC, or to what extent each of those polyenes are undergoing resonance enhancement at the particular excitation wavelength used. Excitation profiles have been used as a method for determining the relative concentrations of polyenes in a sample[4]. The data derived are often used in support of various theories on the nature of polyene formation. For example, many studies suggest that there is a limiting factor on the conjugation length to which a polyene may propagate since a maximum is observed in the excitation profile. The use of excitation profiles to derive information on polyene concentration is not valid if the distribution of polyene lengths giving rise to the resonance Raman spectra is significant, and if the resonance enhancement factors of the contributing polyenes are of a similar magnitude.

In this paper we present data from the resonance Raman spectra for a series of degraded PVC samples recorded at four different excitation frequencies. A new method has been developed which uses model u.v./visible absorption spectra to determine those ranges of polyenes which contribute to a particular resonance Raman spectrum and to estimate the relative resonance enhancement factors for the individual lengths at a particular excitation frequency. This approach has been used successfully here to interpret the polyene Raman data recorded from PVC degraded samples.

The method has been extended to allow the theoretical, contributing individual polyene ν_2 resonance Raman bands to be fitted to the observed ν_2 resonance Raman band where the range of contributing polyenes is known. A model for an individual polyene ν_2 band is developed and discussed. The relative weightings of the contributing Raman ν_2 model bands to observed bands are found by curve fitting. Coupling the weightings of individual polyene ν_2 bands to estimates of the resonance enhancement factors of the contributing polyenes, leads to calculation of a concentration profile for that range of polyenes. The development of this new analysis and the preliminary results from its application are presented here. The results obtained so far have important implications for the mechanism of the dehydrochlorination reaction.

EXPERIMENTAL

The PVC formulation studied is used commercially in the form of a polyurethane (PU) foam-backed sheet (approx. 1000 μm thick). The sheet, provided by BP Research (UK), comprised PVC resin (100 parts), dioctyl phthalate plasticizer (60 parts), calcium stearate (0.5 parts) and lead phthalate (3 parts). Samples of PU foam-backed PVC sheet were degraded in an oven at 120°C and removed at regular intervals up to 36 h.

Resonance Raman spectra were recorded from the samples of PVC sheet using microline focus spectrometry (MiFS) instrumentation. The instrument details and the advantages and applications of the MiFS technique to PVC degradation analysis are described elsewhere[3,8-10]. Four different wavelengths were used to excite the Raman spectra: the 514 nm (19 435 $\mathrm{cm^{-1}}$), 488 nm (20 492 $\mathrm{cm^{-1}}$) and 457 nm (21 881 $\mathrm{cm^{-1}}$) lines from a Spectra Physics argon ion laser (model 164-07) and the 632.8 nm (15 802 $\mathrm{cm^{-1}}$) line from a He/Ne laser.

RESULTS

Figures 1a and *b* illustrate the typical resonance Raman spectra recorded from the degraded samples. The 1600 $\mathrm{cm^{-1}}$ spectral peak (originating from the plasticizer, dioctyl phthalate) is used as a standard to normalize intensity data from the samples. This method results in repeat data variations from a single sample of < 5% and also allows the direct comparison of spectra from a series of samples. Furthermore, since the plasticizer peak shows no resonance Raman enhancement, this method may

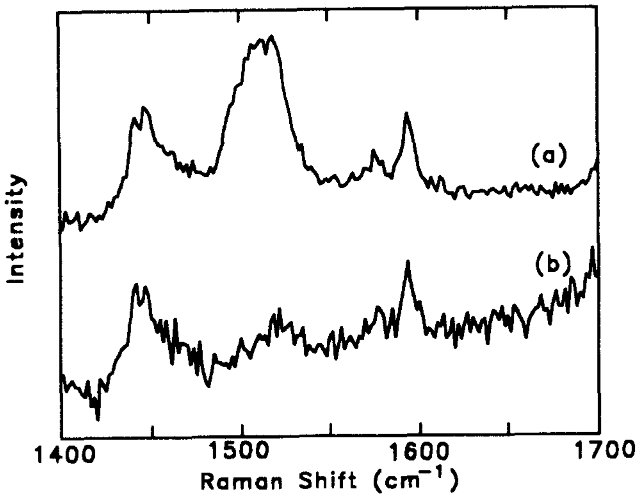

Figure 1 Typical resonance Raman spectra (in range 1400–1700 cm^{-1}: λ_{ex} = 514.5 nm) recorded from degraded PVC. (a) PVC/PU interface of sample degraded for 10 h at 120°C. (b) PVC/PU interface of sample before degradation

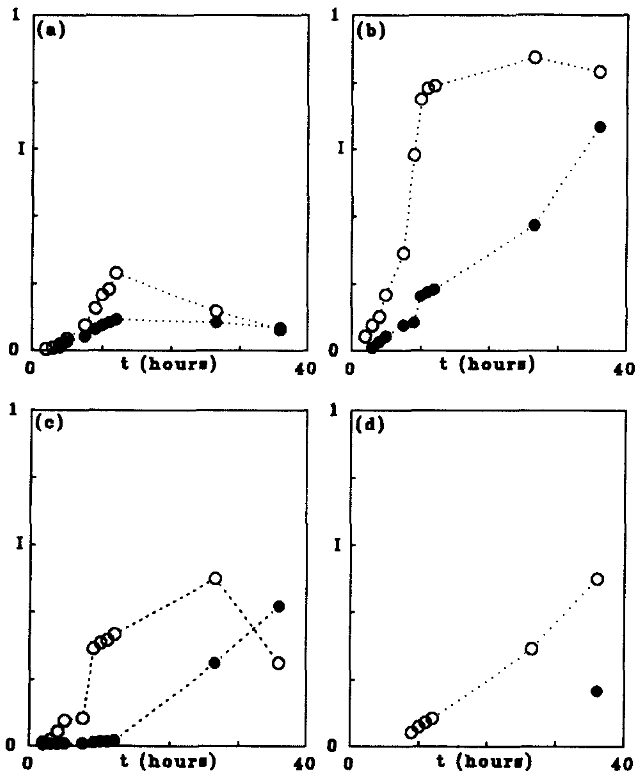

Figure 2 Normalized polyene ν_2 intensities (I) as function of contact interface (O, PVC/PU interface; ●, PVC/non-PU interface) and excitation wavelength. (a) λ_{ex} = 457 nm, (b) λ_{ex} = 488 nm, (c) λ_{ex} = 514.5 nm, (d) λ_{ex} = 633 nm

also be used to allow direct comparison of spectral data from different excitation frequencies.

The normalized polyene ν_2 intensities recorded at the PVC/PU and PVC/non-PU interfaces as a function of degradation time are shown at the four Raman excitation frequencies in *Figures 2a–d*.

An excitation profile, derived from the normalized ν_2 intensity data recorded at the PU/PVC interface of the sample degraded for 36 h at 120°C, may be seen in *Figure 3*.

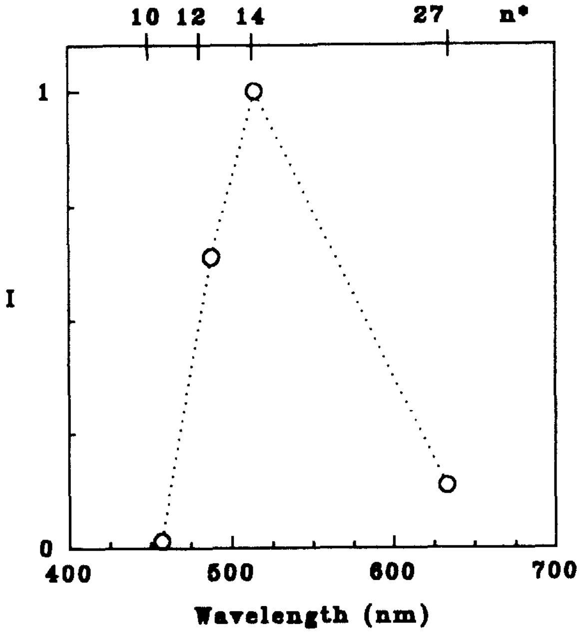

Figure 3 Excitation profile of polyene ν_2 intensity (I) recorded from PVC/PU interface of sample degraded for 36 h at 120°C. *Values of conjugations lengths calculated from equation (1)

Model polyene absorption and resonance Raman spectra

The extent of resonance Raman enhancement for a single-length polyene will be dependent on the shape of the u.v./visible absorption profile and the wavelengths of the Raman excitation (λ_{ex}) relative to the absorption maximum (λ_{max}) of that polyene. The u.v./visible absorption spectra of isolated, individual length polyenes recorded under the same conditions are required for such a calculation. The u.v./visible absorption spectra of degraded PVC are not suitable for this purpose due to the extensive overlap that occurs between the individual absorption profiles of the different length polyenes present (see equation (1)). The pigment *trans* β-carotene (which contains a polyene segment with $n = 9$) has been used extensively as a polyene model[7,11]. Studies on other $[\alpha,\omega]$ carotenoids such as capstanthin (in a crude ethanolic extract from paprika, $n = 9$) and lutein (in a crude ethanolic extract from spinach, $n = 9$) have shown that the presence of different alkyl end groups has no appreciable affect on the characteristics of observed absorption and resonance Raman spectra of the molecules[12,13]. Thus it is the polyene segment of the molecule that determines the dominant features of the observed resonance Raman and absorption spectra. Characteristic Raman and absorption spectra of model polyene compounds may therefore be used to predict the spectral features of the individual length polyenes found in degraded PVC.

New polyene models have also recently appeared. Chance and colleagues synthesized a series of tri-butyl capped polyenes with $n = 0$–12, and the absorption and resonance Raman spectra have been presented[14]. However, no indication was given of the excitation wavelength that was used to obtain the Raman spectra.

Figure 4 shows the normalized u.v./visible absorption spectrum of *trans* β-carotene. Absorption spectra of other polyenes have been found to be similar in shape[15], differing only in absorption maxima according to equation (1) and extinction coefficient. The *trans* β-carotene

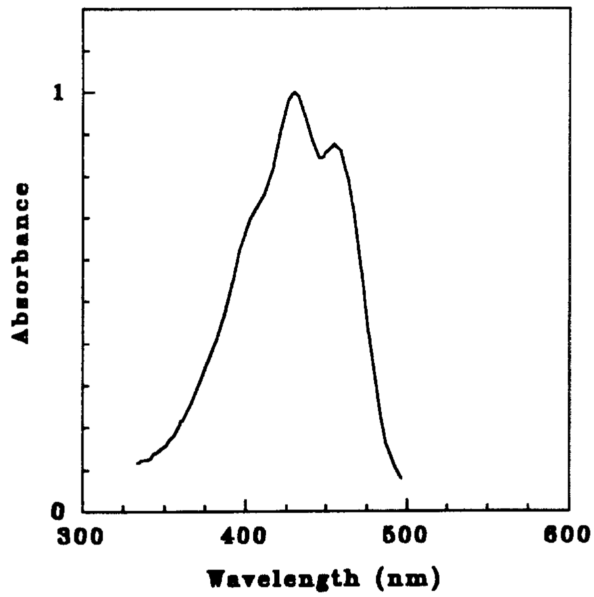

Figure 4 Normalized absorption spectrum of β-carotene (1% solution in THF)

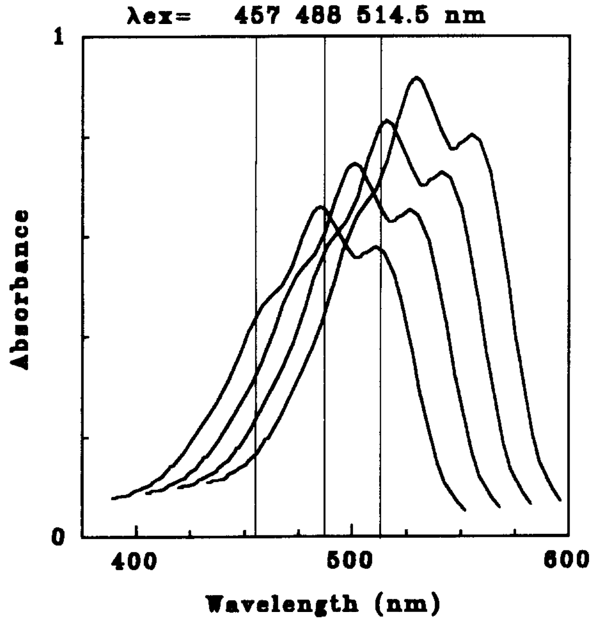

Figure 5 Calculated absorption profiles of equimolar amounts of polyenes with conjugation lengths in the range $n = 13$–16. Also indicated are the range of excitation frequencies used in this study

Table 1 Calculated resonance Raman enhancement factors (for the four excitation frequencies used in this study) for the polyenes with conjugation lengths in the range $n = 8$–20

λ_{ex} (nm)	457	488	514.5	633
n				
8	0.42	–		–
9	0.87	0.15	–	–
10	1	0.72	0.07	–
11	0.81	0.85	0.22	–
12	0.70	1	0.46	–
13	0.46	0.81	0.88	–
14	0.20	0.70	1	–
15	0.18	0.46	0.81	–
16	0.14	0.35	0.70	–
17	0.11	0.25	0.54	–
18	–	0.17	0.40	–
19	–	0.11	0.20	0.15
20	–	–	0.16	0.21

absorption profile has been used here as a model for the range of polyene lengths $n = 9$–15. Rimai *et al.*[15] measured extinction coefficients for a number of different length polyenes, the data collected over the range $n = 4$–12 are linear with n, as described by equation (3)

$$\epsilon_{max} = 30\,000n - 39\,000 \tag{3}$$

The absorption spectrum for a polyene of length n is arrived at by positioning the model spectrum (*Figure 4*) on the wavelength scale with its absorption maximum set by equation (1), and scaled to the correct maximum absorption using equation (3). *Figure 5* illustrates the absorption spectra of a number of different length polyenes calculated in this manner.

The models in *Figure 5* may be used to determine which individual absorption spectra coincide with a particular wavelength used to excite the Raman spectrum. This allows the range of individual polyenes that contribute to the observed resonance Raman spectrum to be determined, along with the individual absorption values at the excitation wavelength. A linear relationship between sample absorbance and resonance Raman enhancement for these systems, with the particular instrumentation used here, was verified by an independent experiment in which resonance Raman intensities and sample absorbance at specific wavelengths for β-carotene were correlated. The absorption values for particular length polyenes at the desired excitation wavelength provide a measure of the appropriate resonance Raman enhancement factors. This procedure has been completed for the polyene range $n = 8$–20 over the four excitation frequencies used in this study and the results are collected in *Table 1*. Note that at this stage, the values in *Table 1* relate to equimolar amounts of polyene. However, the data show some interesting detail. The range of polyene lengths which contribute to the resonance Raman spectrum is greater with increasing λ_{ex}. This accounts for the observation of increasing ν_2 bandwidth at longer excitation wavelengths. Equation (1) predicts that at 457, 488 and 514.5 nm the highest resonance enhancement is observed in polyene lengths 10, 12 and 14 respectively. However, *Table 1* shows that significant contributions also arise from polyenes shorter and longer than those predicted, these contributions are significant and the effects should be incorporated into the overall interpretation. It is also noticeable that at a particular excitation wavelength, the calculated resonance enhancement factors are higher for polyene lengths longer than the maximum value predicted by equation (1) than for those that are shorter than that value. This phenomenon accounts for the asymmetry observed in the ν_2 resonance Raman bands in degraded PVC.

Polyene concentration profiles

The intensity of the ν_2 Raman band for a single length polyene such as β-carotene at a given excitation wavelength (λ_{ex}) may be described by[16]

$$I_{\nu 2} = kI_o C_n(\nu_o - \nu_i)^4 \xi_n \tag{4}$$

where I_o is the incident intensity, C_n is the concentration of the polyene, ν_o the incident frequency, ν_i the scattered light frequency, ξ_n represents the resonance enhancement factor for that length polyene at the excitation wavelength and *k* is a constant. Two assumptions are now made in the application of this formula to the prediction of the composite ν_2 bands from the polyene system in degraded PVC. First, the frequency scattering term is incorporated into the constant since the difference in the Raman intensities due to $(\nu_0 - \nu_i)^4$ is negligible for increasing length polyenes when recorded at the same excitation frequency. The second and most important assumption made was that the polarizability of the polyene molecule does not change appreciably as the conjugation length increases, and is thus considered as a constant. This assumption will be discussed in detail later. With these assumptions, equation (4), when applied to the intensity of the composite ν_2 bands from the polyene system in degraded PVC, becomes:

$$I_{\nu 2} = \Sigma k C_n \xi_n \qquad (5)$$

The ν_2 intensity observed at any excitation frequency will be proportional to the sum of the concentrations of polyenes present, multiplied by their respective resonance enhancement factors at that wavelength. Equation (5) represents a new method of interpreting these data, taking full account of the contributions from preresonant polyene lengths. A similar approach has been applied to a study of conjugation lengths in polyacetylenes[17], but we are unaware of any successful interpretation of conjugation lengths at very low dilutions in a non-conjugated polymer matrix, such as the system being studied here.

The shape of the experimental ν_2 bands from degraded PVC was rationalized by curve fitting. An iterative technique fits the appropriate set of polyene ν_2 bands to an experimental band. The fitting coefficients of the polyene models are related to the product of concentration and resonance enhancement factor of each polyene model fitted. Manipulation of these fitting coefficients (using the data from *Table 1*) allows calculation of the relative concentration profile of those polyenes in the sample that contribute to the spectrum.

The method adopted to produce model polyene spectra uses the resonance Raman spectrum recorded at 514.5 nm from β-carotene using the MiFS instrument in single point mode. The spectrum may be seen in *Figure 6*. A similar procedure to that used to produce the model absorption spectrum was used to produce a model polyene ν_2 resonance Raman band. The data in *Figure 6* were normalized and then plotted across the Raman shift scale for the range of polyenes $n = 8$–20, with the band shifts appropriately set according to equation (2).

Consider, for example, the resonance Raman spectrum recorded from degraded PVC samples using 514.5 nm excitation. *Table 1* suggests that the polyene lengths with the strongest contributions to the resonance Raman spectrum at that excitation frequency have $n = 13$–16. *Figures 7a* and *b* demonstrate the results of curve fitting the model ν_2 bands for polyenes $n = 13$–16 on a spectrum recorded from the PVC/PU interface of the sample degraded for 7 h at 120°C. The figure shows the initial model polyene ν_2 band overlaid on the experimental ν_2 band prior to fitting (*Figure 7a*). The result of the curve fitting may be seen along with the experimental band in *Figure 7b*.

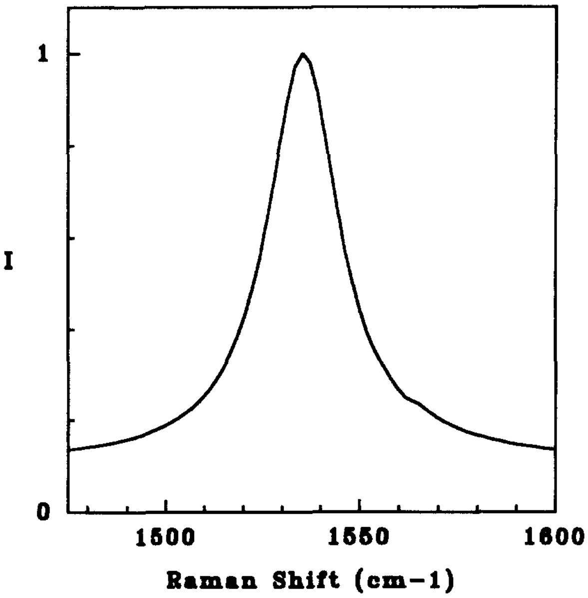

Figure 6 The resonance Raman spectrum of β-carotene (range 1450–1600 cm^{-1}: $\lambda_{ex} = 514.5$ nm)

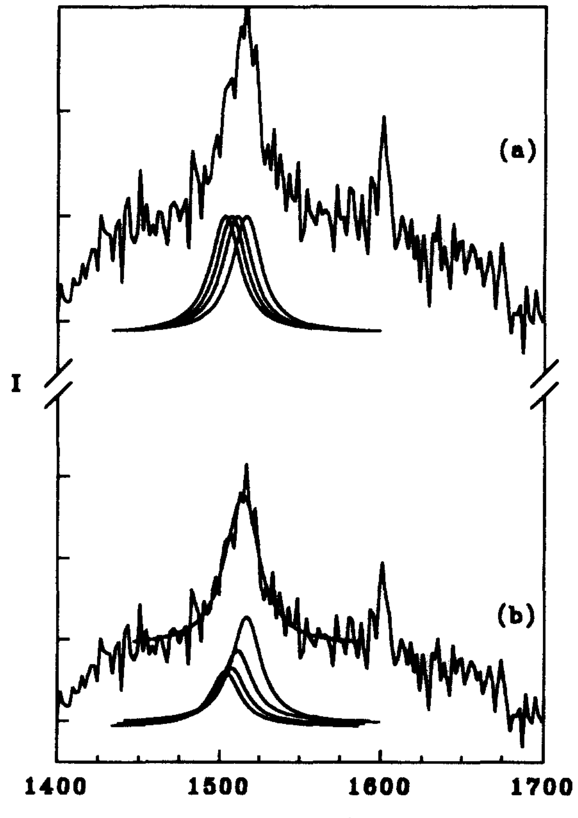

Figure 7 Results of curve-fitting model polyene ν_2 bands to the resonance Raman spectrum recorded from the PVC/PU interface of a sample degraded for 7 h at 120°C. (a) The original spectrum and the model polyene bands to be used in the fit. (b) The resulting curve fit and weighted model bands of which it is comprised

Since the model ν_2 band is initially normalized to unity, the set of weighting coefficients used to fit the individual polyene ν_2 bands to the experimental band represent the relative intensities of the individual polyene bands present. The relative set of resonance Raman enhancement factors for these polyene lengths have been estimated for this excitation wavelength and thus equation (5) may be used to calculate the relative concentration profile of those polyenes which are contributing to the experimental ν_2 band. This procedure was carried out for the ν_2 bands recorded from the PVC/PU interface of samples degraded for 7, 11 and 26.5 h; the calculated concentration profiles obtained from these samples are presented in *Figure 8*.

DISCUSSION

It has been shown that the resonance Raman spectra of degraded PVC recorded using different excitation wavelengths are determined by different ranges of polyene lengths. A polyene will also exhibit differing extents of resonance Raman enhancement at the different excitation wavelengths. Thus a simple interpretation of the trends in Raman intensity observed with degradation time recorded using these different wavelengths is not appropriate. Analysis of the characteristics of the u.v./visible absorption spectra of model polyenes has shown that the resonance Raman spectra recorded from degraded PVC samples need to be interpreted in terms of the sum of concentrations of polyenes contributing to the band at that excitation wavelength, weighted by the appropriate resonance enhancement factors. The normalized ν_2 intensity data recorded from the samples in this investigation (*Figures 2a–d*) have been interpreted successfully in this manner.

For example, the data recorded using 457 nm excitation are dominated by polyenes of length 9, 10 and 11 (*Table 1*). The increase in the normalized ν_2 intensity at the PVC/PU interface observed over the first 10 h of degradation (*Figure 2a*) may be simply attributed to an increase in concentration of those length polyenes. The normalized intensities observed at degradation times greater than 10 h show a marked decrease, a fact which may be explained by the kinetics of polyene formation and the nature of the resonance effect. The initial rate of formation of those length polyenes contributing to the resonance Raman spectrum at this wavelength is exemplified by the fast initial increase in polyene intensity. At longer degradation times, the propagation of polyenes to longer conjugation lengths becomes the dominant process. These longer polyenes are not in resonance at this wavelength and thus the ν_2 intensity observed reaches a plateau as a steady state is reached and then decreases as the concentrations of those polyenes in resonance at this frequency decreases. It has also been suggested that reactions such as oxidation and crosslinkage will also affect the kinetics of the propagation process[18]. The data recorded using 457 nm excitation from the PVC/non-PU interface of the samples (*Figure 2a*) show similar variations with degradation time, suggesting that the same kinetics apply. It is noticeable that the intensities observed at the PVC/non-PU interface never reach those found at the PVC/PU interface, illustrating the additional catalysis of the dehydrochlorination which occurs due to the amine residues present in the poly(urethane) diffusing to the PVC.

The trends in the data recorded from the PVC/PU interface observed using the other excitation wavelengths have been interpreted in a similar manner. The main differences between these data is in the magnitude of the normalized intensities observed. This may be attributed to changes in the resonance enhancement factors, distributions and concentrations of those polyenes contributing to the resonance Raman spectra. For example, the polyene range contributing to the spectra recorded using 488 nm (*Table 1*) encompasses those which are also observed at 457 nm, but the relative magnitude of the resonance enhancement factors is higher. Thus the trends in the normalized polyene intensity (*Figure 2b*) with degradation time at either contact interface are similar to those observed using 457 nm, but of a greater magnitude.

The range of polyenes in resonance when using 514 nm excitation may be seen in *Table 1*. The average length of the polyenes in resonance at 514 nm is greater than polyene lengths in resonance at 488 or 457 nm. However, the normalized intensity observed using 514 nm (*Figure 2c*) are much lower, indicating that the concentration of polyenes in resonance at 541 nm is lower than those in resonance at 488 nm. A decrease in the normalized intensity is also observed using 514 nm excitation; however, it occurs much later into the degradation experiment than was seen at 488 or 457 nm. This is consistent with a continual polyene propagation along the degrading PVC chain.

Table 1 indicates that the polyene lengths in resonance when using 633 nm excitation all have $n > 20$. No attempt was made to estimate the resonance enhancement figures for these lengths. The trends in the normalized intensity with degradation time observed at 633 nm (*Figure 2d*) may only be interpreted tentatively. Polyenes of these lengths are not detected until late into the degradation experiment, resonance Raman spectra first being observed after 9 h and 36 h at the PVC/PU and PVC/non-PU interfaces, respectively. At the degradation times used in these experiments, no plateau in the data was observed. The trends in the normalized intensity data with degradation time at the PVC/non-PU interface observed using the different excitation wavelengths also illustrate that polyene propagation is the dominant process, but the levels of degradation found are much lower than those at the PVC/PU interface.

The curve-fitting technique developed as a method of calculating the relative weightings of individual polyene ν_2 bands to the ν_2 band in the resonance Raman spectrum of degraded PVC has produced some interesting results. Good curve fits have been obtained between the experimental and composite model bands (*Figure 7b*) for all the spectra recorded using 514.5 nm excitation. The polyene concentration profiles (*Figure 8*) calculated using this new method show (a) that the concentration of a single polyene increases with degradation time and (b) that in all the spectra investigated so far, a decrease in polyene concentration with increasing conjugation length is found. Comparison of the data in the excitation profile (*Figure 3*) and the polyene concentration profiles (*Figure 8*) leads to the conclusion that maxima in the excitation profiles do not correspond to concentration maxima for particular length polyenes as had been assumed previously[4]. Although the trends in the results are clear, the uncertainty associated with the individual data points may be quite large as a number of assumptions have been made. For example, the resonance enhancement factors have been calculated from the electronic absorption spectra of the carotenoids without taking into account the overlapping contributions due to the various vibrations in the vibrational sideband region. Also, since these studies are largely restricted to the surface layers of the

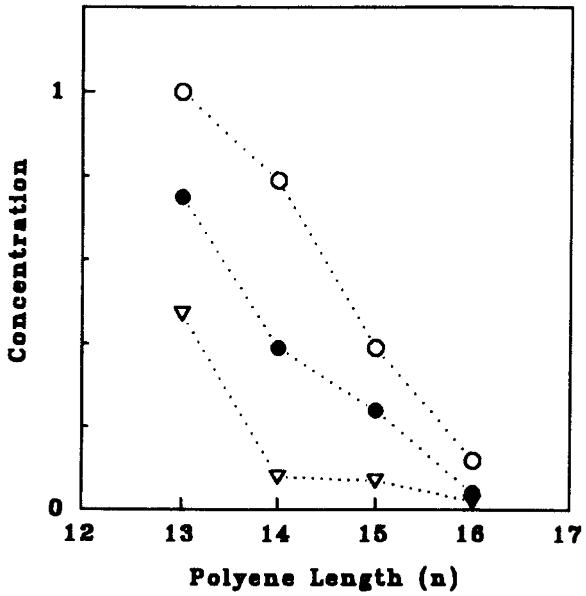

Figure 8 Polyene concentrations calculated from the resonance Raman spectra from the PVC/PU interfaces of three samples, degraded for 7 (▽), 11 (●), and 26.5 (○) h, respectively

sample we assume that the absorption of the incident and scattered light due to polyene chromophores is negligible.

CONCLUSIONS

A simple interpretation of the Raman ν_2 intensity observed in a degraded PVC sample using relationships between excitation wavelength and polyene length (equation (1)) is not valid. Overlap of the absorption spectra of the differing length polyenes found in a degraded PVC sample results in the observation of broad, asymmetric Raman ν_2 bands and the corresponding excitation profiles are not accurate descriptions of single length polyene concentrations present. The distribution of polyene lengths exhibiting resonance Raman enhancement has been shown to change with the excitation wavelength. The extent of resonance Raman enhancement for a single length polyene also changes with excitation wavelength, making any attempts at a quantitative analysis difficult. Model polyene absorption spectra have been generated and used to estimate the extent of resonance Raman enhancement which a single length polyene exhibits at the wavelengths used in our studies. Interpretation of the data shows that polyene propagation is the dominant mechanism in the degradation.

The detailed modelling of the data obtained using 514.5 nm excitation over the full range of degradation times indicates an inverse relationship between concentration and polyene length. This new result suggests that there is no maximum length to which a polyene propagates. No account has been taken here of the change in polarizability of a polyene as *n* increases. Castaglioni *et al.*[19] have presented MO calculations with calculated Raman ν_2 intensities for different length polyenes suggesting that the Raman intensity increases with polyene length, but no details of the calculations are given. Such data would only exaggerate the trends in the results obtained in this study and would not change the overall shape of the data.

The possibility of including the changes in polarizability of increasing length polyenes into our analysis will form the basis of future work. In addition, curve fitting of the data recorded at other wavelengths will be investigated.

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