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Considerations for Raman Spectroscopic Determination of Polyene Length Distribution in Degraded Poly(vinyl chloride)

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ABSTRACT: Practical complications in the quantitative Raman spectroscopic determination of the polyene sequence length distribution in degraded poly(vinyl chloride) samples were found. If samples are measured directly, i.e. without dissolving them, the distribution of polyenes changes during the Raman experiment if power densities above 20 W/mm^2 are used. Lower power densities or short exposure times (<1 min) must be used to avoid these effects. The direct method turned out to be an appropriate method for the quantitative determination of the polyene length distribution in lightly degraded poly(vinyl chloride) samples (<0.05 % HCl loss). If the samples are dissolved in tetrahydrofuran, the influence of laser power is negligible. However, in that case other problems are encountered; solutions must be stored in a cooled state and in the dark in order to avoid disappearance of the polyenes. Moreover, the solution process results in an altered polyene sequence distribution. The tetrahydrofuran method turned out to be a quick and convenient way to obtain information about the polyene sequence distribution for samples with relatively high degradation levels (>0.05% HCl loss).

Introduction

It is well-known and documented that PVC can degrade thermally, photochemically, and chemically by the elimination of HCl and the formation of all-trans polyenes.[1] It is generally accepted that the degradation proceeds according to an unzipping mechanism. Once after the first HCl molecule is eliminated, adjacent HCl molecules are quickly split off leading to a polyene of a certain length. Therefore, already for very low dehydrochlorination levels (0.01 % HCl loss, relative to the total amount of HCl present in the PVC) the PVC starts to color. At dehydrochlorination levels above 1 % HCl loss the material is brown/black and starts to become brittle. In order to study the degradation process techniques are required to characterize the very low amounts of polyenes formed during the early stages of the degradation (0.0001–1.0% HCl loss). The absorption energy of polyenes depends on the length of the polyenes and therefore UV/vis spectroscopy can be used to characterize the polyene sequence distribution.[2] However, other absorbing species (e.g., antioxidants, plasticizers, stabilizers) can inhibit the detection of the individual absorption bands of the present polyenes. Moreover, distinct absorption maxima can only be distinguished for short polyenes ($n < 8$) and sensitivity for longer polyenes is rather low. The combination of ozonolysis and viscosimetry can be used to determine the average amount of polyenes[2,3] but does not give information about the polyene sequence distribution. Liebman et al.[4] and Gerrard and Maddams[5] reported on the use of resonance Raman spectroscopy for the determination of the polyene sequence distribution. The resonance Raman technique can be used to probe polyenes of a certain length, depending on the excitation wavelength.

The resonance Raman effect occurs if the energy of the incident light approaches that of an electronic transition; the intensity of the resonance Raman bands can be enhanced by up to a factor of 10^6, resulting in a very low detection limit.[6] Less than 0.0001% dehydrochlorination can be detected.[5a] For polyenes, the excitation wavelength for which the optimum resonance effect occurs depends on the length of the polyene as follows:

$$\lambda = 700 - 537.7 \exp[-0.0768n] \quad (1)$$

in which λ is the excitation wavelength (in nanometers) and n is the number of conjugated double bonds in the polyene. This expression was determined using model compounds with known polyene length.[5c] Thus, by using a certain excitation wavelength λ, a certain length of polyenes is probed. In general, the resonance Raman spectrum of degraded PVC shows two intense bands around 1100 and 1500 cm^{-1} originating from the $\nu_1((=C-C=)_n)$ and $\nu_2((-C=C-)_n)$ stretching vibrations, respectively, as well as the bands originating from PVC itself (C—Cl stretching vibrations (around 650 cm^{-1}), C—H bending (1440 cm^{-1}) and stretching (2800 cm^{-1})). The position of the ν_2 band also depends on the length of the polyene (ν_2 in cm^{-1}):[5d]

$$\nu_2 = 1461 + 151.2 \exp[-0.07808n] \quad (2)$$

Normally, the polyene lengths n determined from eqs 1 and 2 are similar. However, the position of the ν_2-band provides a weighted average of the polyene sequence length. This can lead to a mismatch between n determined by eqs 1 and 2. In particular, if a sample contains a high concentration of polyenes with a narrow range of length, e.g. $n = 14$, which would be coincident with 514-nm excitation and a ν_2-band at 1512 cm^{-1}, a preresonance effect will occur for excitation at e.g. 632 nm. The ν_2-band in the Raman spectrum recorded using 632-nm excitation will then also be located at 1512 cm^{-1}.

The resonance Raman technique can be used to study the formation of polyenes in degraded PVC but can also be used to study polyenes in poly(acetylene),[6–8] in degraded poly(vinyl alcohol), in poly(ethylene),[9] and in iodine-doped *cis*-poly(isoprene).[10]

In order to determine the polyene sequence distribution in a quantitative way, two methods can be used: either the resonance Raman spectrum can be measured directly on the degraded PVC sample (direct method) or the sample can be dissolved in tetrahydrofuran (THF, this method will be called the THF method). Since reproducibility of

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Table I
Amount of HCl Loss during Degradation in Braun Apparatus

	degradation			
sample no.	medium	temp (K)	time (min)	% HCl loss
1	N_2	423	45	0.0057
2	N_2	423	90	0.045
3	N_2	423	180	0.210
4	N_2	453	90	0.200
5	air	423	45	0.029
6	air	423	75	0.076
7	air	423	180	0.373
8	air	393	960	na

Raman intensity is rather poor, internal standards must be used. In the direct method the bands originating from PVC itself can be used. The C–H deformation is preferred because it is located between the two polyene bands, thus minimizing the effects of self-absorption of the Raman-scattered light. In the THF method, the intensity of the 915-cm^{1} band originating from THF is used as an internal standard.

At the BP Research Centre, a modified THF method was developed to measure the HCl loss from the resonance Raman spectra. In this method the intensities of the polyene bands from a sample with an unknown dehydrochlorination level are ratioed to the intensity of the 915-cm^{-1} THF band for several excitation wavelengths. These are compared to a large set of data, measured for compounds with a known dehydrochlorination level (evolved HCl measured conductometrically) and covering different methods of degradation and different levels of degradation.

In the study of degradation from industrial PVC samples all three methods have been used (the direct method in refs 5a–d, 6, 11, and 12, the THF method in ref 13, and the modified THF method in refs 14–19). In this paper we report on several practical considerations for the methods mentioned. It has been found that each of these methods does have its drawbacks. For the direct method, only low degradation levels can be measured reliably. At higher levels of degradation, the fluorescence background masks the internal reference bands. We also show that the use of high laser power levels, used to bleach the fluorescence, results in an altered polyene sequence distribution. For the THF methods, it is shown that due to dissolving and subsequent storage, the polyene sequence distribution is affected.

Experimental Section

Materials. Unstabilized PVC (*K* value = 57), delivered as powder, was degraded in an apparatus described by Braun and Thallmaier[20] under either nitrogen or air atmosphere. The amount of HCl formed during the dehydrochlorination was measured conductometrically. Details of the samples are collected in Table I. The degraded samples were stored in air at room temperature.

THF (Baker, pa), stabilized with 10 ppm butylhydroxytoluene in order to scavenge radicals, was used to dissolve PVC samples for the THF method. At the BP Research Centre, THF (BDH Chemicals) was stabilized with 0.1% hydroquinone. Solutions of 30 mg of PVC/mL of THF were prepared by vigorous stirring.

Methods. At DSM Research, UV/vis spectra of PVC samples dissolved in THF were recorded on a Perkin-Elmer Lambda 5 UV/vis spectrometer operating in the transmission mode. A 1-mm quartz cuvette was used.

At DSM Research, Raman spectra were recorded using a Jobin-Yvon U1000 spectrometer (600 grooves/mm) equipped with a diode array detector (resolution 6 cm^{-1}). Excitation wavelengths used were 457.9, 488.0, and 514.5 nm (using an Ar$^+$ laser, Spectra Physics Model 2025), 540 and 580 nm (using a dye laser system, Spectra Physics Model 375B operated with Rhodamine 110 from Exciton), and 632 nm (using a HeNe laser, Spectra Physics Model 124B). All samples were studied in a back-scattering geometry either in a macro setup (100-mm focusing lens, 50-μm spot size, *f*/1 collection optics) or in a micro setup. For the latter setup a Zeiss Axioplan microscope equipped with Neo Fluar objectives (×10, ×20, ×50 and ×100 magnification) was used. An Anaspec 300S laser filter was used to remove the plasma lines from the laser beam. Laser powers were determined at the sample position. Spectra were obtained under ambient conditions unless stated otherwise.

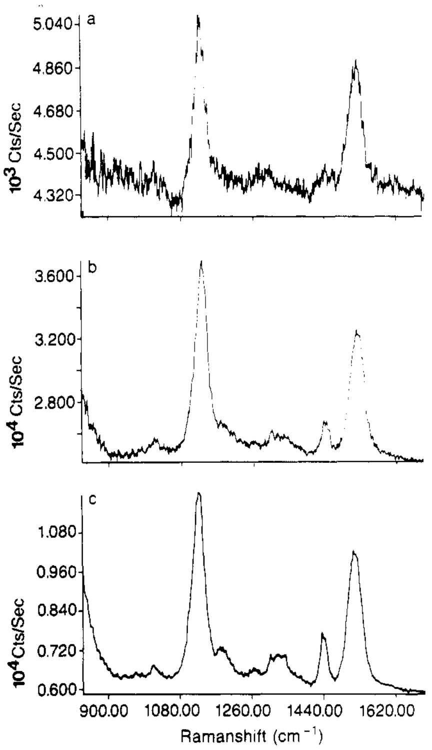

Figure 1. Resonance Raman spectra recorded from sample 8 using the direct method (macro setup, Ar 514-nm line): (a) 1.0-mW laser power; (b) 20-mW laser power, within 1-min exposure of the sample to the laser beam; (c) 20-mW laser power, after 25-min exposure of the sample to the laser beam. The spectra were recorded with identical acquisition parameters.

At the BP Research Centre, Raman spectra were recorded using a Jobin-Yvon HG-2S monochromator equipped with a photomultiplier. Excitation at 457.9, 488.0, and 514.5 nm (Spectra Physics Ar$^+$ laser, Model 2016) and at 632 nm (Spectra Physics HeNe laser, Model 124B) was used. All spectra were obtained using a macro setup, comprising 90° scattering geometry and *f*/1 Cassegrain type collection optics.

Results and Discussion

Direct Method. Figure 1a shows the resonance Raman spectrum (excitation at 514 nm) of sample 8 (PVC degraded in air for 960 min at 393 K) recorded using 1.0-mW laser power in the macro setup. The two polyene bands at 1125 and 1515 cm^{-1} can be clearly discerned from the (fluorescence) background. However, the C–H bending band (near 1440 cm^{-1}) from the PVC itself, which is used as an internal standard, is obscured by the high fluorescence background. As a consequence it is not possible to quantify the concentration of polyenes present. A method often used to circumvent this problem is to use high laser power to bleach the (fluorescence) background. In Figure 1b,c spectra are shown obtained after bleaching 1 and 25 min, respectively, with a laser power of 20 mW. Clearly, due to the bleaching of the (fluorescence) background the signal-to-noise ratio increased with time (compare Figure 1c with Figure 1b). However, the intensity of the polyene bands simultaneously decreased with time: for the

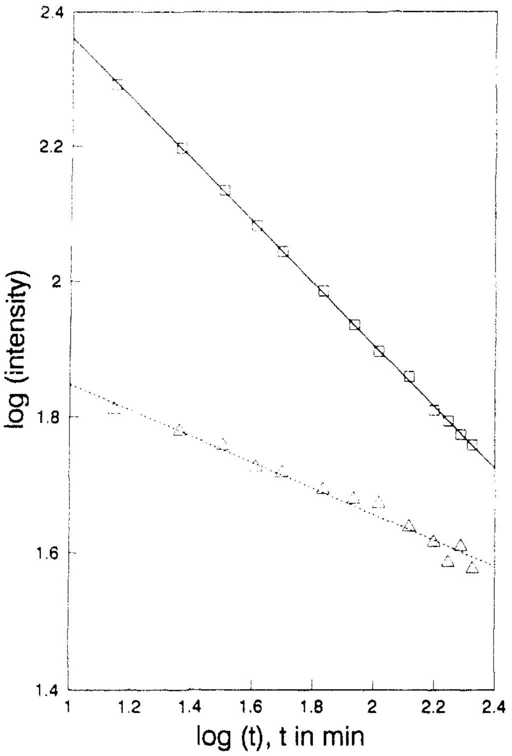

Figure 2. Time dependence of the intensity of the fluorescence background (□) and the ν_2 polyene band (△) measured using sample 8, ×100 objective and 14-mW 514-nm excitation.

1515-cm^{-1} band the intensity after 25 min of 20-mW irradiation was about 40% of the intensity measured after 1 min of increased irradiation.

The decrease of the amount of polyenes due to laser excitation was studied further for sample 8 using the micro setup. Figure 2 depicts the intensity of the (fluorescence) background and the peak intensity of the polyene band near 1515 cm^{-1} plotted as a function of time for 514-nm excitation using the micro setup (14 mW) with a ×100 objective. Over the studied time span (between 10 and 200 min) both the time dependence of the peak intensity of the (fluorescence) background and of the intensity of the polyene bands can be described by

$$\log I = -\alpha(\log t) + c \tag{3}$$

It is apparent that the intensity ratio of the polyene band/background increased with time, which resulted in an improved S/N ratio. However, during the experiment the concentration of polyenes decreased significantly. The decay constant for the polyenes $\alpha_{\mathrm{pol}} = 0.21$, whereas for the fluorescence α_{fluor} was 0.46. On inspection after laser radiation there was no visual sign of irradiation damage. The decay constant α_{pol} increased with increased power density at the sample, i.e. with increasing laser power and tighter focusing. Furthermore, α_{pol} decreased with increasing excitation wavelength, as can be seen from Table II. Figure 3 shows the time dependence of the intensity of the 1515-cm^{-1} polyene band ratioed to the area of the C–Cl stretching band near 650 cm^{-1} (internal standard) for several magnification factors. It should be noted that back-extrapolation of these data results in a coincidence at the intensity axis at about 1 min, which will be discussed in more detail later.

A possible explanation for the observed decay is the photoinitiated reaction of polyenes with oxygen. In an attempt to validate this hypothesis, an experiment was performed in vacuo. The decay constant measured in this way was similar to that measured in air within the experimental error (see Table II). We conclude that the decay is a result of either laser-induced cross-linking or chain scission, since both would result in a shorter conjugation length. In an additional experiment the amount of polyenes determined by excitation at both 457.9 and 514 nm was measured before and after bleaching at 514 nm. Due to the 514-nm bleaching both the number of polyenes measured at 514 nm (about 14 double bonds) and the number of polyenes measured at 457.9 nm (about 10 double bonds) decreased. This experiment shows that bleaching does not lead to single chain scission, for in that case the number of polyenes measured at 457.9 nm would have increased. Because of the very local character of the laser excitation (micrometer scale) and the very low numbers of polyenes, it is impossible to use other analytical methods in order to further elucidate the nature of the shortening of the polyenes.

Table II
Decay Constant α_{pol} for Sample 8, Using Various Sampling Conditions

setup recorded in	magnification	excitation line (nm)	power on sample (mW)	decay constant α_{pol}
macro		514	65	0.10
micro	×10	514	15	0.13
micro	×20	514	15	0.14
micro	×50	514	6	0.18
micro	×50	514	15	0.19
micro	×50	514	30	0.24
micro	×100	514	15	0.21
macro[a]		514	65	0.13
micro	×50	457	15	0.23
micro	×20	457	8	0.13

[a] Sample stored in vacuo during the Raman experiment.

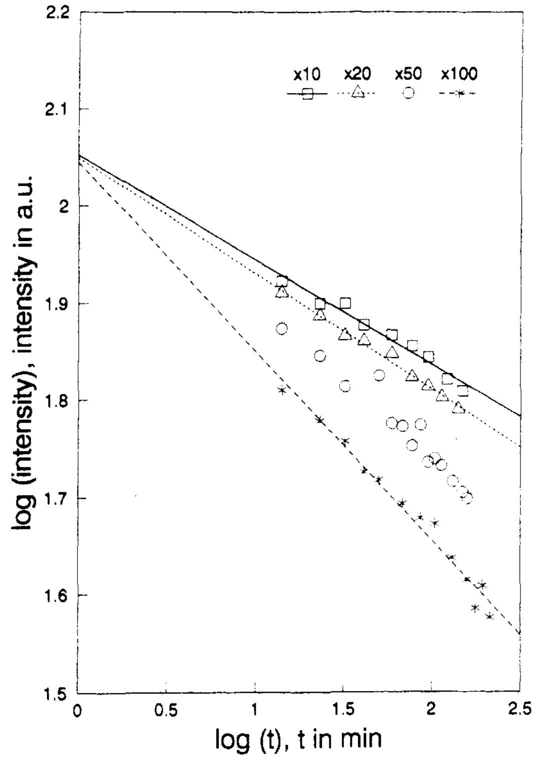

Figure 3. Time dependence of the intensity of the ν_2 polyene band for several magnifications (15-mW 514-nm excitation). The ν_2-band intensities are ratioed to the area of the C–Cl vibration band at 650 cm^{-1}.

A way to circumvent the problems described above is to measure the spectra at low laser power to determine the polyene band intensity and subsequently measure at higher laser power to determine the intensity of a reference band.

Table III
Intensity Ratio I_{pol}/I_{C-H} Determined Using the "Modified Direct Method" (Estimated Experimental Error ±20%)

		sample 1			sample 5		
excitation (nm)	n from eq 1	ν_2-band (cm^{-1})	n from eq 2	int ratio	ν_2-band (cm^{-1})	n from eq 2	int ratio
457	10	1543	8	20	1543	8	11
488	12	1535	9	81	1536	9	28
514	14	1522	12	98	1526	11	45
540	16	1502	17	63	1507	15	14
580	20	1495	19	58			<1
632	27	1491	21	41			<1

This method is called the "modified direct method". For example, the decay constant α_{pol} is less than 0.02 when 0.5-mW 514-nm excitation is used with a ×50 objective, making it possible to record the Raman spectrum of the polyene bands without a significant decrease in intensity during the measurement. The intensity ratio of the polyene and reference band is corrected for the difference in laser power.

The modified direct method has been applied to samples 1 and 5. For the other samples it was not possible to obtain spectra at high laser power with a S/N ratio high enough to distinguish the reference bands from the fluorescence background. The results for samples 1 and 5 are shown in Table III. The high intensity of the polyene band and the coincidence with the C—H deformation reference band at 1440 cm^{-1} make it difficult to determine the intensity ratio accurately. The experimental error in the ratio is estimated to be ±20%. The polyene chain length distributions for both samples show a maximum around 14 C=C—C sequences corresponding to 514-nm excitation. However, for the nitrogen-degraded sample polyenes with more than 27 sequences were observed. For the oxygen-degraded sample the maximum polyene length was estimated to be 16–20.

The results presented in Figure 3 suggest that if high laser powers are used and the intensity of the polyene band is measured within 1 min, the decay of the polyenes is negligible. This was indeed observed. For sample 1, the nitrogen-degraded sample, no difference was found between the polyene band intensity measured at low laser power (<1 mW) and the intensity measured directly, i.e. within 1 min, after exposing the sample to a laser beam with a higher power (20 mW).

In conclusion, it would appear that the direct method can be used quantitatively for low levels of degradation (<0.05% HCl loss). Furthermore, care must be taken to prevent changes in the polyene sequence distribution due to laser-induced bleaching effects. This can be done in two ways. One possibility is measuring at a low laser power (<1 mW) to determine the intensity of the polyene bands and then measuring at high laser power (about 20 mW) to determine the intensity of a PVC reference band. This requires an accurate measurement of the used laser power. The other possibility is recording a spectrum at a high laser power level (about 20 mW) immediately after exposing the sample to the laser beam (within 1 min) to determine the polyene band intensity and then measuring after about 0.5 h to determine the intensity of a PVC reference band.

THF Method. By dissolving the PVC samples in stabilized THF, all signals originating from the degraded PVC will become less intense due to the significantly lower concentration. This method circumvents the problem of the low intensity of the reference band as compared to the fluorescence background and polyene band intensities.

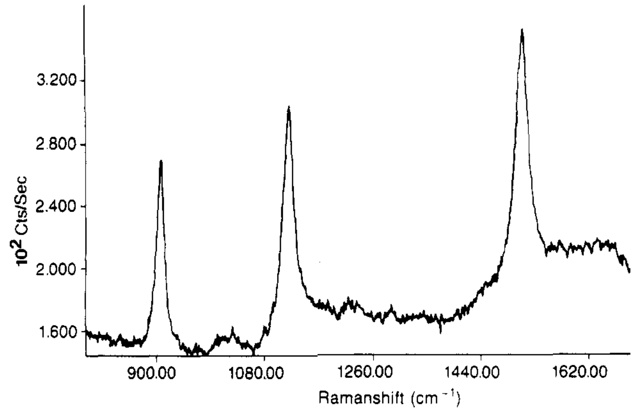

Figure 4. Resonance Raman spectrum obtained from sample 2 (nitrogen degraded) dissolved in THF (28.1 mg/mL), recorded using 3-mW 514-nm excitation in the macro setup.

Table IV
Study of Bleaching Effect for PVC/THF Solutions[a]

sample	laser power (mW)	I_{pol}/I_{C-H}[b]	sample	laser power (mW)	I_{pol}/I_{C-H}[b]
2	2	1.5	4	2	3.0
	50	1.5		25	3.1
	2[c]	1.5			

[a] Experiments were performed on a single solution using various laser powers. No polarization analyzer was used. [b] ν_2-band intensity ratioed to the THF band intensity corrected for instrumental response. [c] Repeat of the initial power after the use of high laser power.

PVC samples 1–7 were dissolved in THF (about 30 mg of PVC/mL of THF). Highly degraded samples had to be shaken vigorously in order to dissolve them completely. The resonance Raman spectrum of PVC sample 2 dissolved in THF is shown in Figure 4. Clearly, both polyene bands at 1128 and 1519 cm^{-1} and the THF solvent band at 915 cm^{-1} are observed. For the purpose of quantification, all intensity ratios were corrected to a PVC concentration of 30 mg/mL. The intensity measured from the THF reference and ν_2-band were corrected for instrumental response and used for calculation of the I_{pol}/I_{THF} ratio.

Several experiments were performed in order to validate the method. First, the influence of laser power was studied. No bleaching effect was observed within the experimental error (α_{pol} < 0.01), using 0.8-mW Ar$^+$ 457-nm excitation in the macro setup. It was also noted that an increase of the laser power up to 50 mW did not cause a detrimental effect on the observed intensity ratios (see Table IV). Next, the influence of the atmosphere under which dissolution takes place was investigated. The difference in the intensity ratios I_{pol}/I_{THF} for samples dissolved under nitrogen or under air was less than 5% (excitation at 457, 488, and 514 nm). Also, no differences were observed between a sample dissolved immediately after degradation and one stored 4 weeks (at room temperature and in daylight) and subsequently dissolved.

Finally, the influence of storage on PVC/THF solutions was studied. Storing the solutions at room temperature in daylight or in the dark caused a dramatic decrease in the ν_2-band intensity (see Table V). However, storage in a freezer (253 K) in the dark did not alter the ν_2-band intensity. UV/vis spectra were recorded to further study the storage effect. In Figure 5 UV/vis spectra are shown recorded from a sample stored in the freezer (a) and from a sample stored in daylight at room temperature (b). From the spectrum of the sample stored in the freezer a significant absorption in the 200–600-nm range is observed, indicating that polyenes with n = 2–22 (see eq 1) are present

Table V
Influence of Storage of a THF Solution of PVC Sample 2 (Excitation at 514 nm (1 mW) in Macro Setup)

	measurement	I_{pol}/I_{THF}[a]
series 1	(a) immediately after dissolving	1.76
	(b) 3 weeks storage at 295 K, daylight	0.06
series 2	(c) immediately after dissolving	1.86
	(d) 3 weeks storage at 253 K, dark	1.89
	(e) (d) with additional storage for 3 weeks at 295 K, dark	0.37

[a] ν_2-band intensity ratioed to the THF band intensity corrected for instrumental response.

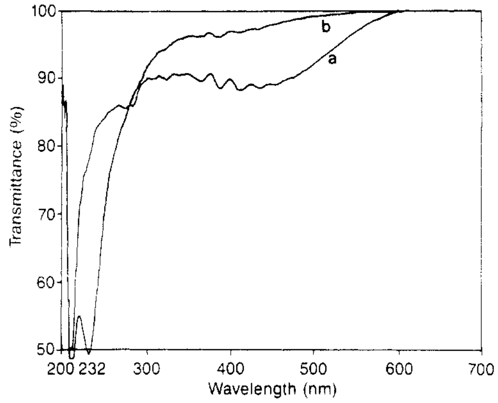

Figure 5. UV/vis spectra from PVC sample 3 dissolved in stabilized THF and either (a) stored in a freezer (253 K, dark) or (b) stored at room temperature in daylight.

in this sample. It is apparent from the spectrum of the sample stored at room temperature in daylight that the absorption above 300 nm is dramatically lower. Furthermore, there is an additional intense absorption band at 230 nm, which corresponds to a polyene sequence length of 2. We conclude from these observations that a significant shortening of polyenes occurs upon storage at room temperature in either light or dark. This can be attributed to either cross-linking or oxidation of unsaturated bonds. THF is known to be unstable under ambient conditions. This can lead to the formation of peroxides which are able to readily oxidize polyenes.

Taking into account these considerations, samples 1–3 and 5–7 were examined using both the Raman apparatus at DSM Research and at the BP Research Centre. In our first attempt to correlate the BP and DSM data, it was found that the I_{pol}/I_{THF} ratio was approximately the same for excitation at 514 nm but differed for excitation at 488 nm (by a factor of about 1.4) and at 457.9 nm (by a factor of 2–3). This is caused by differences in throughput, sensitivity, and polarization effects of the spectrometers used at the BP Research Centre and DSM Research. The polyene bands and the THF solvent band have different depolarization ratios ($\rho_{pol} = 0.35$, $\rho_{THF} = 0.12$); thus, the intensity ratio I_{pol}/I_{THF} is different for scattered light polarized horizontally and vertically. In order to obtain conformity between results from both laboratories, the $^{\perp}I_{\perp}$ spectra were recorded by placing a polarization analyzer between the sample and the entrance slit of the spectrometer. Figure 6 illustrates a good correlation between the data obtained from the two laboratories.

Figure 7 depicts the ν_2-band intensity ratioed to the intensity of the THF reference band for nitrogen- and oxygen-degraded PVC samples. This figure does not, however, provide a fully quantitative analysis of the polyene sequence distribution. One of the main factors that influences the Raman band intensity is the polarizability of a bond (the Raman intensity depends on the square of the polarizability). It is known that the bond polarizability increases with polyene sequence length. As a consequence it is clear that the relative abundance of long polyenes as measured from Figure 7 is an overestimate. However, it is clear from Figure 7 that the number of polyenes increases with increasing level of degradation, whereas the shape of the polyene sequence distribution is the same for all samples. For the nitrogen-degraded samples the number of polyenes with a sequence length of 11–22 is higher than for the oxygen-degraded samples. In Figure 8, the UV/vis spectra recorded from the same PVC/THF solutions are shown. From these absorption spectra the same picture emerges. The oxygen-degraded samples show an intense absorption below 350 nm,

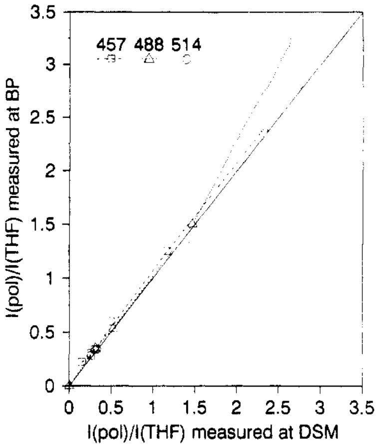

Figure 6. Comparison of data obtained at DSM Research and at the BP Research Centre using the same degraded PVC samples but with different instrumentation. Intensities were, however, corrected for differences in instrumental response.

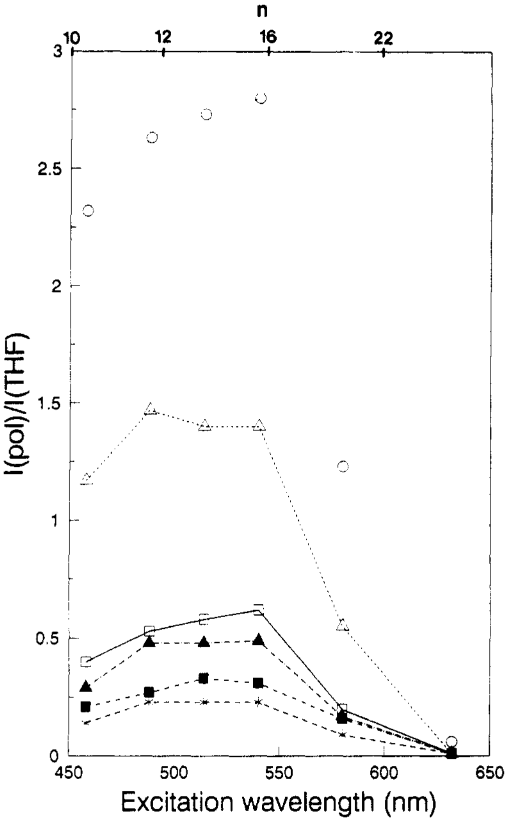

Figure 7. ν_2-band intensity ratioed to the intensity of the THF reference band for nitrogen- and oxygen-degraded PVC samples: (□) sample 1; (△) sample 2; (○) sample 3; (*) sample 5; (■) sample 6; (▲) sample 7. The $^{\perp}I_{\perp}$ spectrum was recorded using the polarization analyzer according to the text. Intensities were corrected for instrumental response.

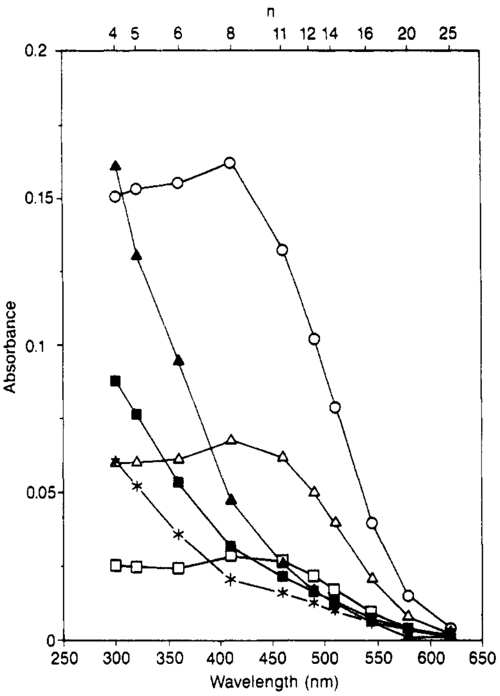

Figure 8. UV/vis absorption spectra from several degraded PVC samples dissolved in THF: (□) sample 1; (△) sample 2; (○) sample 3; (*) sample 5; (■) sample 6; (▲) sample 7. Spectra are corrected for variations in PVC concentrations. The indicated polyene sequence length at the upper x-axis is deduced from eq 1.

indicating that for these samples a large number of short polyenes is present.

The question remains whether the dissolving process influences the polyene sequence distribution. The results obtained from samples 1 and 5, using both the direct method and the THF method, can be compared by reference to Table III and Figure 7. A significant difference is observed between the polyene sequence distribution obtained from the THF method and from the direct method. The sequence distribution from the direct method shows a more distinct maximum and a larger number of long sequences (long-wavelength side) than that obtained from the THF method. This is also observed from the UV/vis data. The UV/vis spectrum obtained from sample 2 dissolved in THF is shown in Figure 9a. The UV/vis reflectance spectrum recorded from the solid PVC sample is shown in Figure 9b. The spectrum of the THF-dissolved PVC shows a weak absorption at long wavelengths (between 500 and 700 nm) as compared to the reflectance spectrum.

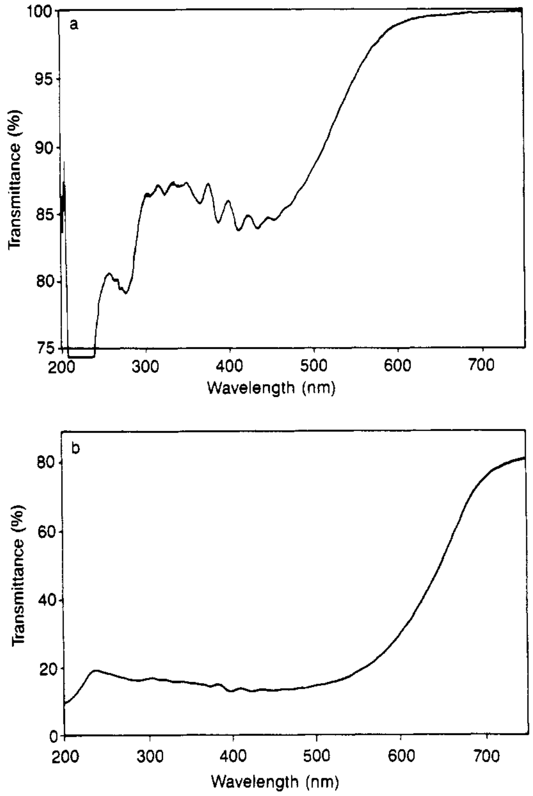

Figure 9. UV/vis spectra obtained from sample 2 measured from a THF solution with a concentration of 28.1 mg of PVC/mL of THF (a) and measured directly from the solid in reflectance (b).

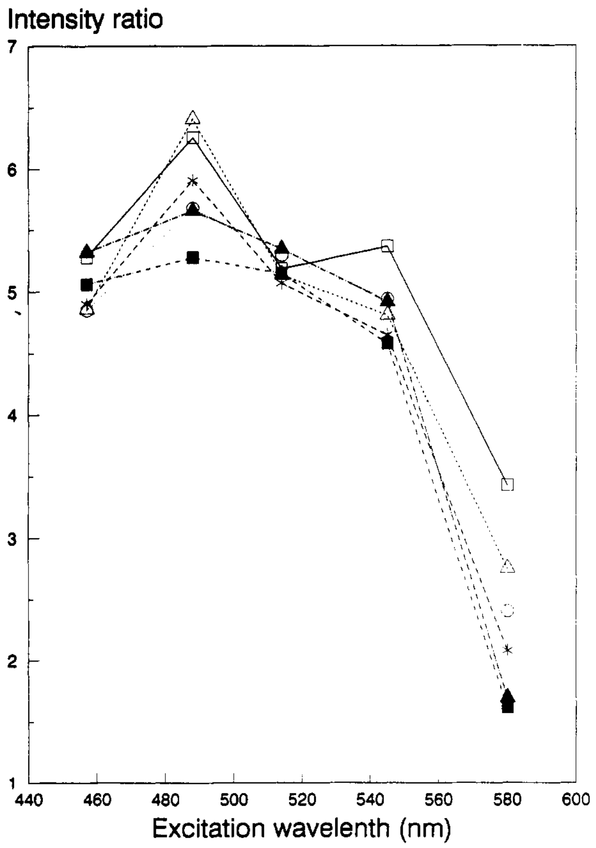

Figure 10. Influence of the PVC concentration on the ν_2-band intensity ratioed to the intensity of the THF reference band (sample 4): (□) 1.34, (△) 3.16, (○) 12.2, (*) 23.5, (■) 53.2, (▲) 94.3 mg of PVC/mL of THF.

Two possible explanations can be given for this observation. First, the polyene sequence distribution might not be the same for the skin and core of the PVC grains. However, it is unlikely that there is a substantial difference in degradation level between skin and core, for the primary PVC grains are very small (diameter about 10 μm). Moreover, the Raman information depth in the case of PVC is estimated to be in the order of several microns. Therefore, the direct method probes a substantial part of a primary grain. The second possible explanation is that the dissolving process introduces a higher mobility of the longer polyenes making several reactions more likely. These include either cross-linking or oxidation, both resulting in a shortening of the polyene length. In turn, this effect explains the reduction in the ν_2-band intensity measured at 632 nm and the increased ν_2-band intensity measured at 457.9 nm. The effect of oxidation of long polyenes is well-known from studies on poly(acetylene).[21] Cross-linking is supported by an experiment in which the concentration of the PVC in THF is varied. Figure 10 depicts the polyene sequence distributions for various PVC concentrations as measured with resonance Raman spectroscopy. At high concentrations the number of long polyenes is lower. This suggests that longer polyenes react with each other via a cross-linking reaction during the dissolution process. This effect is more pronounced for higher PVC concentrations. Most of the considerations mentioned here for the THF method will also apply to the modified THF method.

Conclusions

The direct method is shown to be an appropriate method for the quantitative determination of the polyene length distribution in lightly degraded PVC samples. From the direct method local information is obtained (1–10 μm^2), which permits the possibility of mapping. An overall idea of the degradation level can be obtained by rotating the sample. Care must be taken in order to avoid changes in polyene sequence distribution due to bleaching effects.

The THF method is a very convenient and quick way to obtain information about the average degradation level. The method is not appropriate for low degradation levels. It cannot be used to map degradation in PVC. The method requires fresh, well-stabilized THF, and samples must be stored in a freezer. Due to the dissolving process, the longer polyenes are shortened which is due to either oxidation or cross-linking, resulting in an altered polyene sequence distribution.

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