

Degradation of oriented poly(vinyl chloride) films in the presence of metal chlorides

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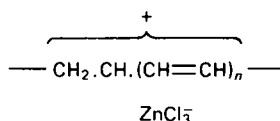
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Films of poly(vinyl chloride) containing added stannous chloride and stretched at 90°C to elongations up to 600% discolour, in shades from purple to grey, when heated at 110°C. The electronic and resonance Raman spectra of such films show characteristic features, which are a function of sample preparation conditions, particularly the time of annealing at 110°C. Resonance Raman spectra show the presence of conjugated polyene sequences, as long as 30 units for the most extensively annealed samples. The electronic spectra are not explicable on this basis, and are probably indicative of a polyene-metal salt complex of the type proposed by Owen and Msayib in the case of poly(vinyl chloride) thermally decomposed in the presence of zinc chloride. Substitution of zinc chloride for stannous chloride with the present degradation conditions gives very similar electronic spectra, though substantially different from those reported by Owen and Msayib. This result is tentatively explained in terms of the very different degradation conditions.

(Keywords: degradation; poly(vinyl chloride); film; Raman spectroscopy; ultra-violet/visible spectroscopy)

INTRODUCTION

Owen and Msayib¹ heated poly(vinyl chloride) (PVC) films containing zinc chloride at four levels over the range 1.6–10.3 wt% at seven temperatures within the interval 65–95°C. At the higher levels of zinc chloride the thermal decomposition proved to be largely catalysed, whereas at the lower levels both catalysed and uncatalysed decompositions occur. All the materials after decomposition displayed a broad electronic absorption band, centred at about 610 nm when degradation occurred in air, and at approximately 660 nm for high zinc levels and vacuum degradation. Owen and Msayib proposed that the species responsible for these electronic absorption bands are of the type:



They suggested two routes for the formation of such species, one direct and the other involving HCl, liberated during the thermal decomposition, which forms the Brönsted acid H^+ ($\text{ZnCl}_2 \cdot \text{Cl}$)⁻.

We have an interest in the thermal degradation of stretched PVC films, as the greater conformational regularity of such films may lead to the formation of longer conjugated polyene sequences. The films used during these studies have been cast from tetrahydrofuran (THF) and this was purified by shaking with stannous

chloride, followed by distillation under nitrogen² to remove traces of hydroperoxides formed by atmospheric oxidation. On one occasion the distillation step was inadvertently omitted, and the films prepared with this particular batch of solvent gave unexpected visual discolorations, ranging from purple to grey, on heating at 110°C following stretching at 90°C. Their visible absorption spectra showed broad bands having a resemblance to those of the general type, described by Owen and Msayib, which may be associated with the presence of stannous chloride. This has prompted a more detailed study, including the use of resonance Raman spectroscopy to explore in more detail the nature of the coloured species, and the ability of other inorganic compounds, most notably zinc chloride and stannous bromide, to promote the formation of coloured species. The first results from this study are now described.

EXPERIMENTAL

The PVC sample used in this study is an I.C.I. suspension-type polymer, prepared at 50°C and taken to 70% conversion. It has an M_n value of 79 400. Films, approximately 0.1 mm in thickness, were cast from 10% w/v solutions in tetrahydrofuran of stannous chloride dihydrate. Strips of film, about 10 cm long and 2 cm wide, cut from the cast film, were stretched in an Instron Tensometer with a high-temperature chamber attachment, at 90°C. Extensions in the range 100–600% were obtained, using the slow draw rate of 50 mm min⁻¹. The stretched films were then annealed under tension at one

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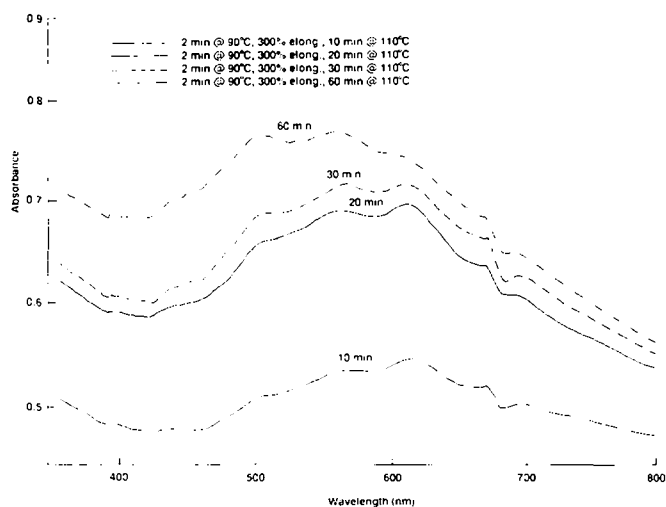


Figure 1 U.v./vis. spectra of PVC films stretched to several extents at 90°C and annealed at 110°C

of several temperatures higher than 90°C, most frequently 110°C, for varying lengths of time.

After cooling to ambient temperature while remaining stretched in the Instron grips, the discoloration that developed in the films during the annealing process was assessed by ultra-violet/visible and in selected cases by resonance Raman spectroscopy. Ultra-violet/visible spectra were obtained from the films using Varian Super Scan and Hitachi model 100/60 u.v./vis. spectrometers. The resonance Raman spectra were measured with an Anaspec model 33 Raman spectrometer, fitted with Spectra-Physics model 164-08 argon-ion and 164-11 krypton-ion lasers. The samples were examined in solution in tetrahydrofuran and the intensities of the ν_2 resonance peak are expressed as a ratio against that of the solvent band at 915 cm^{-1} . The measured frequencies of the ν_2 peaks for various exciting wavelengths were used to calculate average polyene sequence lengths, and hence sequence distributions, using the relationship between ν_2 and n established by Baruya *et al.*³.

RESULTS

Degradation in the presence of stannous chloride

Following the initial serendipitous measurements with tin-contaminated THF, the subsequent procedure has been to add stannous chloride at known levels to the purified solvent. Most of the films examined have been cast from a solution of 0.5% $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in THF.

Figure 1 shows the visible spectra that have been obtained from a series of films, all drawn to 300% elongation, but annealed for differing times at 110°C. These results are typical of what is obtained more generally. Each spectrum exhibits three peaks. At the shorter degradation times the most prominent of these is located at 615 nm, and is accompanied by a second at 565 nm and an inflection at about 505 nm. As the degradation time increases, the 615 nm feature becomes less prominent, whereas the one at 565 nm becomes more clearly resolved and relatively stronger, while the inflection at 505 nm develops into a readily observable peak that is particularly prominent in the 60 min sample. The overall effect is to increase the absorbance at all wavelengths below 600 nm at the expense of that found

at longer wavelengths. The pseudo-discontinuity at about 680 nm has been observed in all spectra on both instruments and appears to be associated with the change of detector in the spectrometer. It is inexplicable, but inconsequential for present purposes.

Figure 2 shows the visible spectra of three samples, drawn to elongations of 200%, 300% and 500% respectively, and all annealed at 110°C for 10 min. They are essentially similar and show the 615 nm peak, together with inflections at 565 and 505 nm. Clearly the major factor determining the details of these spectra is the time of annealing at 110°C rather than the degree of elongation.

The resonance Raman spectral results for the four samples whose visible spectra are shown in Figure 1 are given in Figure 3. These show marked differences in the distribution of the conjugated polyene sequence lengths and integrated intensities, which are an approximate measure of the polyene concentrations. Annealing for 10 min produces a relatively low total concentration, with a maximum in the sequence length distribution for n values of about 11. An increase in the annealing time by factors of 2 and 3 increases the total polyene content appreciably and shifts the maximum of the distribution function to an n value of 15–17. Both trends are markedly

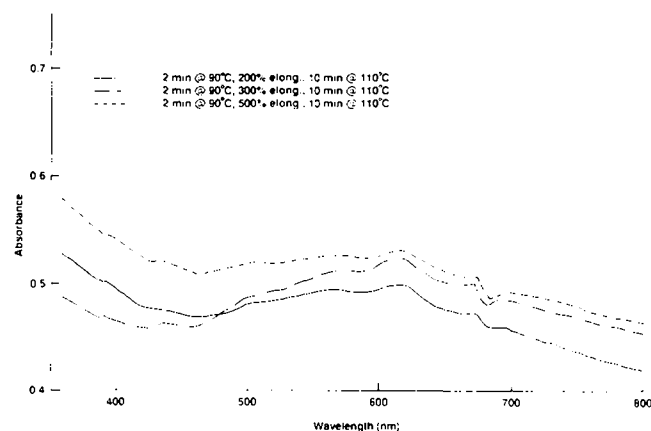


Figure 2 U.v./vis. spectra of PVC films stretched at 90°C and annealed at 110°C for different lengths of time

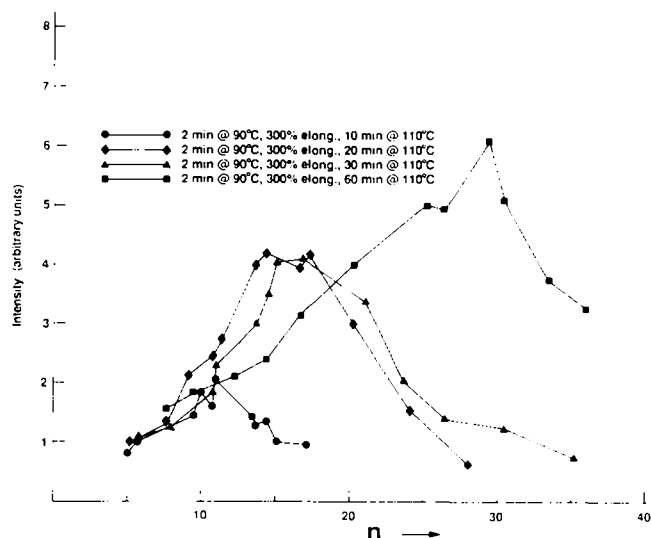


Figure 3 Intensity against n for PVC films stretched to several extents at 90°C and annealed at 110°C (obtained from resonance Raman spectra)

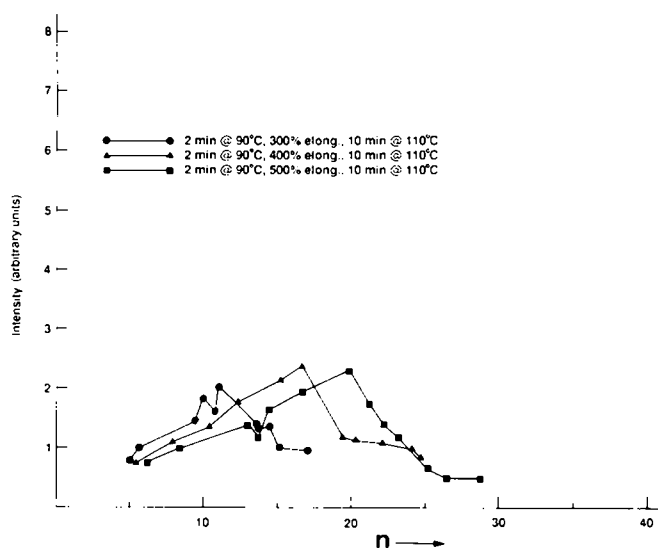


Figure 4 Intensity against n for PVC films stretched at 90°C and annealed at 110°C for different lengths of time (obtained from resonance Raman spectra)

accentuated with the sample annealed for 60 min, particularly in the case of the distribution function. A maximum is observed at an n value of about 30, and the concentration of polyenes with n values up to approximately 15 is, relatively, quite low.

The similarity of the visible spectra shown in *Figure 2* is to a considerable degree paralleled in their resonance Raman spectra, which are shown in *Figure 4*. However, changes are very much less marked than those already noted in the case of *Figure 3*. There is a discernible shift in the maximum of the distribution function to larger n values with increasing degree of elongation and some increase in the overall integrated intensity but, as was the case with the visible spectra, the time of annealing at 110°C appears to be the dominant variable.

Degradation in the presence of zinc chloride

In the light of the results of Owen and Msayib it is clearly of interest to ascertain the behaviour of zinc chloride in the rather different experimental conditions employed for the present study. A limited number of measurements have therefore been made, using visible spectroscopy to characterize the reaction products.

Figure 5 shows the spectra that have been obtained from films cast from 10% of PVC in a 1% solution of $ZnCl_2$ in THF. These films were all drawn to 600% elongation and then annealed for differing times at 110°C. After 10 min the specimen gives three rather poorly defined peaks, at approximately 610, 560 and 500 nm. These are rather more apparent after annealing times of 20 and 40 min with a slight increase in the relative intensity of the peak at 500 nm, which is also more clearly resolved. This trend continues with the 60 min sample, where the 610 nm peak is now no more than an inflection. These peak positions are virtually indistinguishable from those obtained from comparable samples containing stannous chloride and there is the same type of change as a function of annealing time, although less marked.

DISCUSSION

Although the visible spectra shown in *Figures 1* and *2* differ appreciably from those normally obtained from

thermally degraded PVC⁴, an interpretation in terms of a mixture of long conjugated polyenes should be attempted before complexes of the type proposed by Owen and Msayib are considered. Conveniently degraded samples give a broad, structureless maximum at about 450 nm, although Behnisch and Zimmerman⁵ have reported a broad maximum at 550 nm in the case of a commercial PVC powder sample degraded for a long period of time at 73°C. They assign this to a polyene distribution with a maximum at $n = 21$. The increase in the wavelength of the maximum in the visible spectrum with increasing n value is asymptotic⁶ and it is unlikely to reach approximately 600 nm, even in the case of the 300% elongated material annealed for 60 min at 110°C. The more compelling evidence against an interpretation of the observed visible spectra in terms of a mixture of conjugated polyenes comes from the presence of fine structure in these spectra. Although individual polyenes show very well defined vibrational fine structure⁷, the superposition of such spectra when a whole range of sequence lengths is present completely blurs out this detail, as is evident from the various reported results for commercial type samples, and those of Behnisch and Zimmerman⁵. It is simply not possible to account for the spectra shown in *Figures 1* and *2* in terms of a mixture of conjugated polyenes of varying sequence lengths.

At this juncture it is convenient to continue the discussion by tacitly assuming the presence of a complex between the conjugated polyenes and the stannous chloride without being too specific about its precise structure and mode of formation. There seems little doubt that such a complex would absorb at longer wavelengths than the constituent polyenes, and might well account for the observed spectra in general terms. Is such a complex consistent with the observed resonance Raman spectra? Although no results for model compounds of this type are available, it is very probable that ν_2 , the

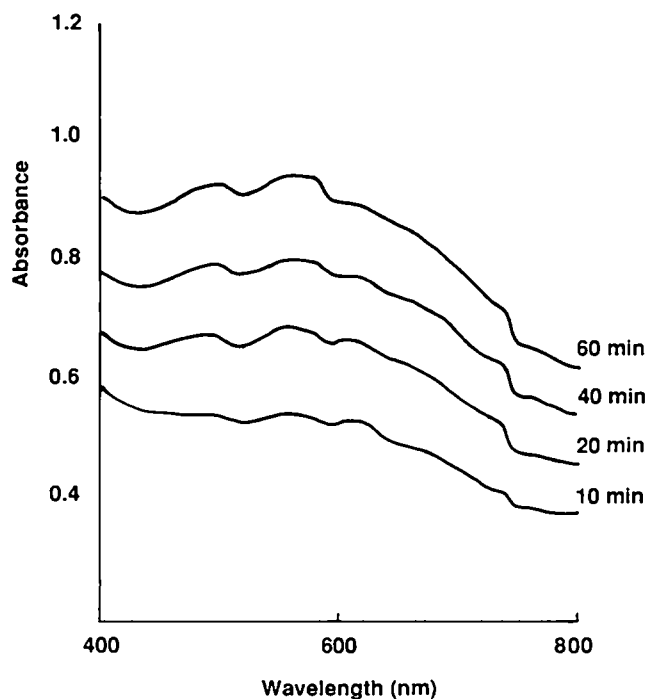


Figure 5 U.v./vis. spectra of films, prepared from PVC/ $ZnCl_2$ /THF solution, stretched to 600% elongation at 90°C and annealed at 110°C for the lengths of time indicated

C=C stretching mode whose frequency is used to characterize the conjugated sequence length, will be little affected by the complexation of a polyene with a metal salt⁸. Hence, the Raman spectra will not give an indication for the presence of a complex, unlike the visible spectrum, but it may be used with some confidence to provide information about the distribution of sequence lengths of complexed polyenes, using the well established relationship³ between ν_2 and n .

The value of this approach is illustrated by considering the four spectra shown in *Figure 1*. As already noted, there is an increase in the absorbance at all wavelengths below 600 nm at the expense of that found at longer wavelengths as a function of increasing annealing time. These spectra provide no evidence for an understanding of this change. The corresponding resonance Raman spectra (*Figure 3*) show an increasing proportion of longer conjugated polyenes with increasing time of annealing, and this is clearly a relevant factor. If the electronic spectrum of a polyene-metal salt complex shows a variation with polyene sequence length one might conclude, on general grounds, that the band maximum would increase in wavelength with increasing polyene sequence length. The reverse appears to be the case from *Figure 1*. However, the changes in the spectrum as a function of annealing time are capable of an alternative interpretation, namely a constant component plus an increasing structureless absorption in the region 500–550 nm. The former is readily interpretable in terms of the polyene-metal salt complex and it is tempting to assign the latter to uncomplexed polyenes, which would give a peak similar to the one observed by Behnisch and Zimmerman⁵. This peak would be most prominent in the case of the material annealed for 60 min, which is known from the Raman measurements to contain by far the highest concentration of long polyenes. If this explanation for the changes observed among the four spectra of *Figure 1* is correct, it follows that not all of the polyenes undergo complexation, either because this process is less favoured in the case of the very long polyene sequences, or because the equilibrium constant for the formation of complexes is not particularly high.

The combined interpretation of the visible and Raman spectra does not therefore provide any conclusive evidence that the former change according to the degree of conjugation of the polyene involved. Furthermore, they provide no indication as to whether the spectra will be a function of the metal salt involved in the complex. The difference between the spectra obtained by Owen and Msayib for zinc chloride complexes and the present results involving stannous chloride should be interpreted with caution, because of the high probability that the two degradation processes involved, which are significantly different, will yield very different polyene distributions. The relevant comparison is between the two sets of results in the present work involving the two salts. These are substantially identical in terms of peak positions and the clear inference is that the nature of the metal salt is not a major factor.

Nevertheless, this must be regarded as a tentative conclusion. The spectra of Owen and Msayib show a peak at about 610 nm with inflections at approximately 560 and 665 nm, and the absorption at wavelengths greater than 600 nm increases relative to that below 600 nm with increased time of heating. Furthermore when the degradation occurs in vacuum, not in air, the peak broadens, moves to 660 nm and loses its fine structure. These differences and changes call for explanations, and they are not forthcoming on the basis of the present experimental evidence. There is the need for a more widely based study, involving the use of a range of degradation conditions and metal salts. Furthermore, the possible effect of water on crystallization, which is present in some cases, cannot be ignored. Such studies require the combined applications of visible and resonance Raman spectroscopy, which, in the limited work to date, have proved to be very useful methods for characterizing the formation of complexes, whatever their nature, and for identifying the degree of conjugation of the polyenes involved. There is also scope for the preparation of the complexes under defined conditions. Owen and Msayib have shown that when a dilute solution of zinc chloride in dichloroethane is added to a dilute solution of chemically degraded PVC in the same solvent, there is a marked change in the visible spectrum. This requires additional study, and the use of low-molecular-weight model polyenes would appear to offer an approach in which the number of possible variables is reduced.

However, preliminary experiments in which an attempt was made to form a charge-transfer complex between β -carotene and hydrogen chloride led to the almost complete disappearance of the two resonance Raman peaks specific for $\nu(\text{C}=\text{C})$ and $\nu(\text{C}\cdot\text{C})$. A chemical reaction occurred and it seems probable that the reactivity of the conjugated polyene sequences in such model compounds is appreciably greater than when they are present in partially degraded poly(vinyl chloride). This may prove the limiting factor in the use of model compounds.

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