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Polyene formation in poly(vinyl chloride) stabilised with pre-heated metal stearates

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Summary

PVC stabilised with mixtures of pre-heated metal stearates are degraded thermally for specific periods of time, in order to determine their influence on the production of polyenes by uv spectroscopy. Additionally the PVC samples are treated with $NaBH_4$ to reduce the carbonylic groups produced during the thermo-oxidative process. Important differences in the polyene formation trends are observed, between the reduced and non-reduced samples, indicating that the carbonyl groups attached to polyenes shift the absorbance maxima and alter considerably the quantification of the double bond conjugations.

Introduction

During the thermal degradation of PVC, some processes such as crystallisation, isomerization, crosslinking and aromatization take place (1). The last two addition reactions involve polyene sequences and determine the end products obtained during the process.

The evaluation of double bond formation is a common parameter used to follow the discoloration of PVC, and is often considered as an indicator of degradation. However, it is known that during processing conditions, where air is present, oxidation of the double bonds compete with polyene formation. The same has been found for PVC photooxidation competing with photodiscolouration (2).

Considering the presence of allylic chlorine as a defect in PVC, the formation of double bond sequences is the first step during dehydrochlorination and such process can be initiated by any of the mechanisms proposed in the literature (3). For some authors (4-6) the most plausible mechanism for the growth of polyenes, is the ion-pair process.

In previous reports (7), we have shown that the degradation mechanism of stabilised PVC is altered, when metal stearates (stabilisers) are treated thermally before incorporation into

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the polymer. Experimental results indicate the formation of a stable complex between the soaps after heating.

We have also reported on the formation of polyenes when such pre-heated compounds (at 180°C) were used to stabilise the PVC (8). The evaluations consisted in monitoring the formation of short and long polyenes with degradation time, by means of uv spectroscopy, and measuring the relative intensity in the light absorbance at different wavelengths. Finally, fluorescence spectroscopy also gave information about the type of polyenic species when reducing the carbonylic groups, formed during oxidation, by treating the samples with $NaBH_4$ (9).

In this paper, we have monitored the formation of polyenes and the effect of pre-heated metal stearates, by means of uv spectroscopy, after the reduction of the carbonylic groups with $NaBH_4$. This implies that such groups interfere with the absorption of the polyenes, resulting in a more real spectrum, which represents closely the formation of such conjugations.

Experimental

The materials, PVC, $CaSt_2$ and $ZnSt_2$ were kindly provided by Akcros Chemicals, Manchester. The samples were the same as previously described (8), where the PVC was doped with 3 phr of the metal soaps which had been treated and untreated thermally. Such samples were degraded for specific periods of time: 5, 10, 15 and 20 min. to be able to follow the formation of chromophoric species throughout the degradation time.

Each sample (50 mg) were placed into glass tubes for extraction with spectroscopic grade peroxide free THF during 60 h, at room temperature, under continuous magnetic stirring. The air in the tubes were properly evacuated with nitrogen to keep an inert atmosphere during the extraction time.

These samples were subsequently filtered (some had crosslinked material) to have clear solutions for uv analysis. The instrument used was a Philips PU8720 uv-visible spectrophotometer, in the 200-600 nm range and in the absorbance mode.

After uv evaluations, solutions were returned to their respective tubes to add them with 100 mg of $NaBH_4$, for reduction of carbonylic groups. The tubes were flushed with nitrogen to maintain an inert atmosphere, and left for 24 h under continuous magnetic stirring. Spectra were taken again for the samples after filtration.

Results and discussion

We reported previously on the formation of polyenes with degradation time for PVC samples that had been stabilised with pre-heated metal soaps (8). The observed trends appeared to correlate and have some explanation related to the findings with other techniques, however, the reduction of carbonylic groups changed those trends considerably, and provided a clearer explanation of real polyene formation.

The same two absorbance values at 273 and 360 nm, corresponding to polyenes of 3 and 5-7 double bond conjugations (10,11), were used to intercompare the samples, and is shown as P_3 and P_{5-7} (where P is a polyene of certain conjugation length). Absorbance is indicative of the respective concentration of each type of polyene. P_T is the sum of P_3 and P_{5-7}, and is indicative of the total amount of polyenes and the P_3/P_{5-7} ratio, which is indirectly related to the polyene distribution.

An important feature observed in general for the results, after the reduction treatment, is that the final values of absorbance (20 min. degradation) are higher and that the initial value (no degradation) are lower than the respective non-reduced samples. This indicates that before any degradation, there are some inherent carbonylic compounds which increase the absorption, and are effectively reduced by treatment with $NaBH_4$. The degraded samples on the other hand, form carbonylic compounds during the thermooxidative treatment, which effectively shifts the absorptions of their corresponding polyenes to higher wavelengths, giving lower absorbance values. After their reduction there is an increase in the absorptions at the specific measured wavelengths.

Figures 1 and 2 show the results obtained with the control sample, with no pre-heating, where the differences before and after reduction of carbonyls are not very important. The increase of the values, especially at 20 min. degradation, with the reduction confirms what has previously been mentioned and is an example of the effect of carbonylic groups on the evaluation of polyene formation. The results after reduction appears to be the real polyene formation, and show a sort of induction time very similar to the ones obtained by means of HCl evolution(12).

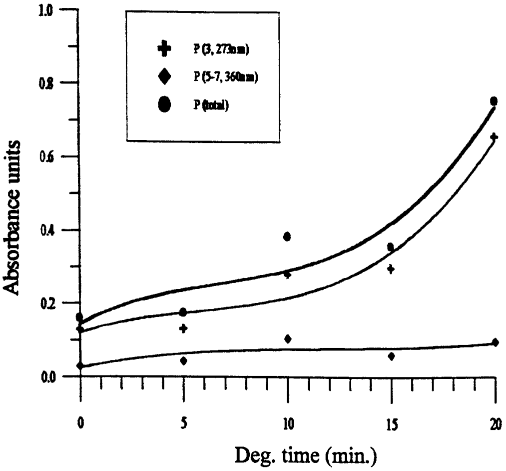

Fig. 1 Total polyenes formed in PVC stabilised with $CaSt_2$ and $ZnSt_2$ and degraded up to 20 min.

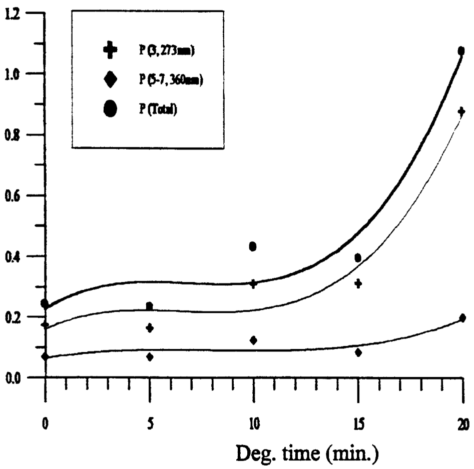

Fig. 2 Total polyenes formed in PVC stabilised with $CaSt_2$ and $ZnSt_2$ and degraded up to 20 min., after reduction of carbonyls.

The addition of the pre-heated mixture of metal soaps generated a relatively low amount of polyenes in the PVC (Figure 3), although when the sample was reduced (Figure 4), a greater difference was observed. The low absorbance values at zero degradation suggests that the pre-heating of the compounds generates carbonylic compounds that were reduced with the $NaBH_4$ treatment. On the other hand, the high amount of polyenes after 20 min. degradation indicates that the dehydrochlorination mechanism is stopped at the formation of carbonylic groups, rather than continuing to form aromatic compounds by secondary reactions, or at least it is delayed at this step. The fact that the short polyenes are less in concentration, compared to the longer polyenes (than in the reduced control sample) confirms that there is no consumption of the long polyenes in cyclisation reactions.

The case of individual pre-heating of $ZnSt_2$ reduced the formation of polyenes as well, which is the difference between the reduced and non-reduced samples in the initial and final data (Figs. 5 and 6). The trends of formation of polyenes are more clearly shown in the reduced sample, upon elimination of "noise" induced by the carbonylic groups.

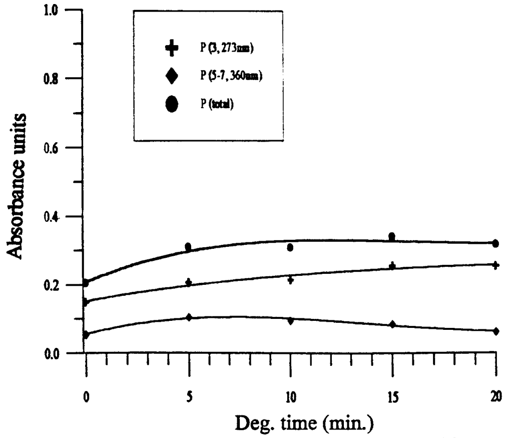

Fig. 3 Total polyenes formed in PVC stabilised with $CaSt_2$ - $ZnSt_2$ (pre-heated at 180°C) and degraded up to 20 min.

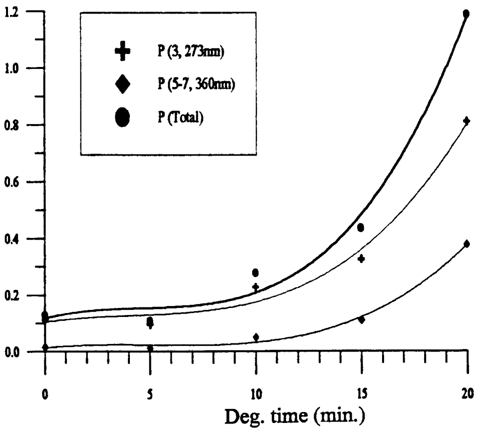

Fig. 4 Total polyenes formed in PVC stabilised with $CaSt_2$ - $ZnSt_2$ (pre-heated at 180°C) and degraded up to 20 min., after reduction of carbonyls.

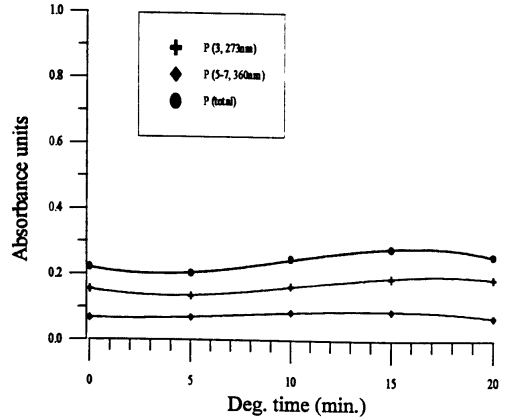

Fig. 5 Total polyenes formed in PVC stabilised with $CaSt_2$ and $ZnSt_2$ (pre-heated at 180°C) and degraded up to 20 min.

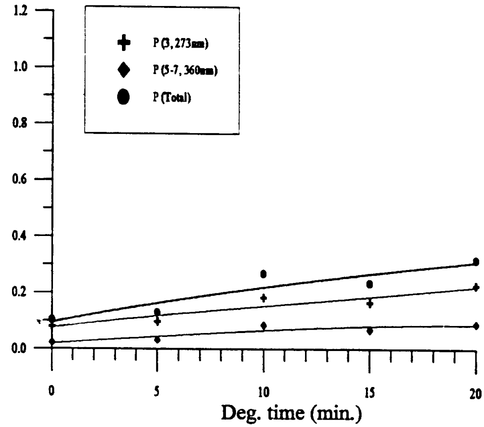

Fig. 6 Total polyenes formed in PVC stabilised with $CaSt_2$ and $ZnSt_2$ (pre-heated at 180°C) and degraded up to 20 min., after reduction of carbonyls.

It is very clear that the formation is low and that the sample is still at the induction time stage, even after 20 min. degradation time, since for this sample the formation of black polyaromatic structures is very low as indicated by the visible reflectance evaluations (8). Hence, the result indicates that the formation of polyenes up to 20 min. degradation time, is very low with this pre-heated soap.

The formation of polyenes with the pre-heated $CaSt_2$ (Fig. 7) was not very well resolved. It was mentioned in our previous paper (8), that the samples degrade very rapidly and the black compounds are formed in the early stages that it did not allow the existence of polyenes in the samples, since they were consumed very fast. However, Figure 8 shows the same sample after the reduction treatment and the increase after the 20 min. degradation period, for both short and long polyenes. This result suggests that pre-heating of this soap allows the formation of carbonylic groups, which are then effectively eliminated with the $NaBH_4$. One interesting point observed is that the formation of polyenes follows a steady trend throughout the degradation time, even at 15 and 20 minutes of degradation where the samples are completely black. The previous result seems to indicate that the blackness of the sample does not mean complete degradation, and that there are still a substantial number of molecules available to form double bonds. However, this only applies to the part of the sample that has been extracted with the THF.

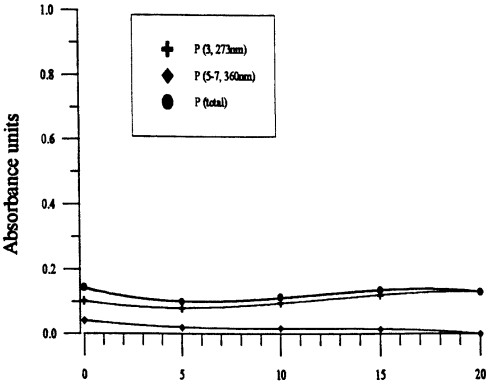

Fig. 7 Total polyenes formed in PVC stabilised with $CaSt_2$ (pre-heated at 180°C) and $ZnSt_2$ and degraded up to 20 min.

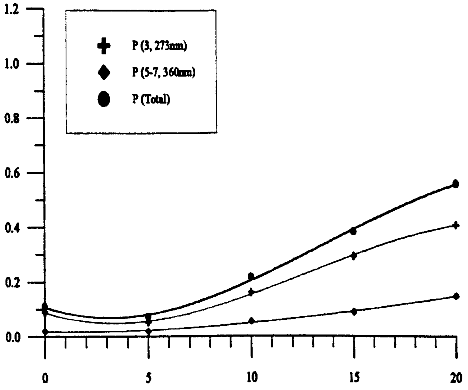

Fig. 8 Total polyenes formed in PVC stabilised with $CaSt_2$ (pre-heated at 180°C) and $ZnSt_2$ and degraded up to 20 min., after reduction of carbonyls.

The short/long polyenes ratio of the reduced samples provides another view of the results, as shown in Figures 9 and 10. The reduction treatment has an important effect on the ratio values of almost all the samples. The control sample (PCZ) shows a lower tendency to increase the ratio value with the degradation time; this is due to the greater amount of long polyenes at longer times, after the reduction. With the pre-heated mixture of soaps (PC-Z(180)), the initial enhancement of the ratio is basically due to the lower production of long polyenes; an effect very well covered by the carbonylic groups, as seen in the non-reduced sample (Fig. 3). The sample with $ZnSt_2$ pre-heated alone (PCZ(180)), shows no important difference in the ratio value, after the reduction, apparently due to the lower production of both, polyenes and carbonylic groups. Finally, for the sample with pre-heated $CaSt_2$ (PC(180)Z), the difference in the ratio, after the $NaBH_4$ treatment, is due to the appearance of the polyenes with the reduction, especially the long polyenes, which were well covered by the carbonyls. In general, the short/long polyenes ratio is kept between values of 2 and 4, when no carbonylic groups are interfering; suggesting that for most of the samples there is a steady production of both, short and long polyenes during the course of the degradation. The exception being the sample with the mixture of soaps pre-heated.

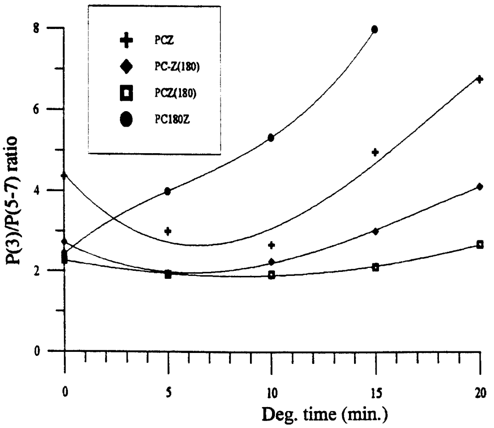

Fig. 9 Short/long polyene ratios found in PVC stabilised with pre-heated $CaSt_2$ and $ZnSt_2$ and degraded up to 20 min.

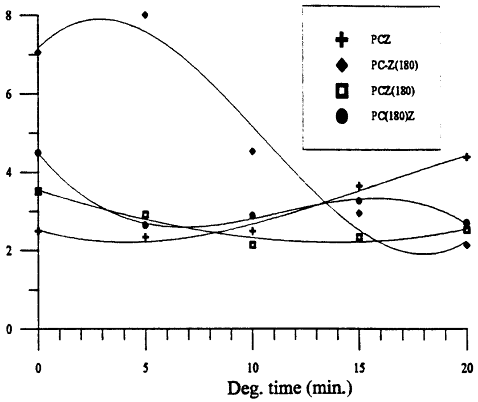

Fig. 10 Short/long polyene ratios found in PVC stabilised with pre-heated $CaSt_2$ and $ZnSt_2$ and degraded up to 20 min., after reduction of carbonyls.

Conclusion

The formation of double bond conjugations during the degradation of PVC happens in the first stage when the dehydrochlorination has commenced. As such, the evaluation of polyenes has been a popular method to evaluate the extent of the polymer degradation. Furthermore, uv spectroscopy is the preferred method for such a purpose.

The results suggest that it is not convenient to evaluate polyene formation by simply measuring absorbance values in the uv spectrophotometer and calculating their concentration with the help of molar extinction coefficients obtained from model compounds.

The formation of carbonylic groups is well known to be part of the side-products during the thermo-oxidation of PVC, and their production seems to be dependent on the way the degradation experiments are undertaken. Such groups, apparently attached to the polyenes, appear to shift the absorption maxima of the specific conjugations, and hence alter their quantification.

During the normal stabilisation of PVC with 3 phr of calcium and zinc stearates (1:2 ratio), the production of carbonylic groups are not very important, since the evolution of polyenes are very similar before and after reduction with $NaBH_4$. On the other hand, when such a mixture of soaps is pre-heated before addition to the polymer, the carbonylic groups have an enormous influence in the polyene trends. The addition of $CaSt_2$ and pre-heated $ZnSt_2$ to the PVC, reduces the production of polyenes and carbonylic groups, there being not much difference between reduced and non-reduced graphs. Finally, the pre-heating of $CaSt_2$ alone induces the production of carbonyls at longer degradation times, which once reduced, indicate that even when the material is completely black (as seen previously (8)) there are still short and long polyenes in formation.

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