Effect of Organotin Stabiliser on the Thermal Stabilisation of PVC: Part II—Structure Changes in PVC and the Mechanism of Stabilisation

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ABSTRACT

The stabilisation of poly(vinyl chloride) (PVC) by dibutyltin dilaurate (DBTDL) has been studied. Results show that the products of oxidative degradation of PVC are negligible in the presence of DBTDL, which corresponds to a secondary antioxidant effect. There is no correlation between polymer stability and residual tin-content.

The influence of DBTDL on the change in molecular weight of PVC has been determined by GPC. The molecular weight of unstabilised PVC decreases slowly early in the degradation, and then increases, which is in contrast to stabilised PVC in which the molecular weight remains unchanged early in the degradation. The molecular weight distribution increases later. On the basis of the experiments, it is suggested that the mechanism of stabilisation is a free radical process. It is proposed that the allyllic chlorine atoms in PVC are substituted by the carboxylate groups of DBTDL in a radical process. A kinetic equation for the stabilisation of PVC has been deduced.

INTRODUCTION

The process of stabilisation of PVC involves a series of complex reactions which result in products which influence the course of the degradation of the

polymer. In our previous study[1] of the stabilisation of PVC by dibutyltin dilaurate (DBTDL), we found that the organotin stabiliser effectively reduces the average polyene length, increases the induction period and decreases the rate of thermo-dehydrochlorination of PVC. The relationship between the allylic chlorine content and polyene sequence distribution was also revealed.

This present work is devoted to a more detailed IR and GPC study of the stabilisation of PVC by DBTDL and a radical mechanism of stabilisation is presented.

EXPERIMENTAL

Sample preparation and degradation were carried out as previously described.[1] Films for IR spectral measurements (thickness $< 50\,\mu$m) were prepared by evaporation of THF solutions of degraded samples, and dried at 50°C in vacuum for at least 12 h. The IR spectra were recorded on an FT-IR5DXC instrument. GPC, with THF as solvent, was carried out using a Waters-150C instrument. The resulting polymers were purified by precipitation by methanol and exhaustive extraction with hot methanol prior to submission to Atomic Emission Spectrometry.

RESULTS AND DISCUSSION

Atomic Emission Spectrometry study of the organotin stabiliser

The PVC sample stabilised with DBTDL, which was degraded at 160°C in air for 30 min, was used to measure atomic emission spectra and the results demonstrate the presence of the characteristic line of tin. The sample was then dissolved in THF, precipitated three times by methanol and dried, in order that the 'unreacted' stabiliser be removed from the mixture. Measurement of atomic emission spectra was then repeated. The results show that the characteristic line of tin disappears so it can be concluded that the tin atom was not chemically bound to the polymer during heating at 160°C and was removed from the mixture by precipitation.

Ayrey *et al.*[2] studied the influence of the butyl group on the stability of PVC, and concluded that the effect was very small. Combining this with our results, it can be concluded that the tin atom and the butyl group make no contribution to the stability of PVC in this system.
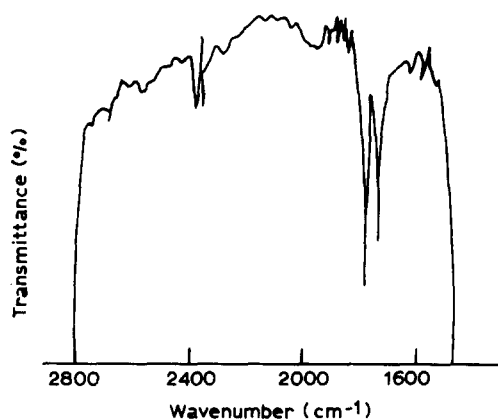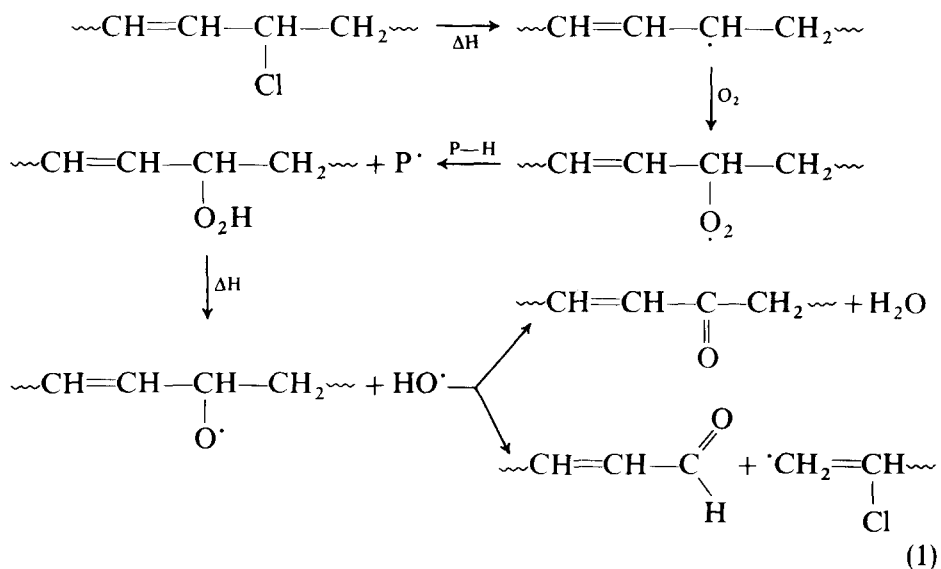
Fig. 1. IR spectrum of thermally degraded PVC in air.

Study of infrared spectra

IR spectral study of unstabilised PVC

Changes in the IR spectrum occur when PVC is thermally degraded in air. Absorption appears in the region of 1700–1800 cm^{-1} (Fig. 1) due to the formation of the carboxyl group.[3] The absorption at 1730 cm^{-1}, illustrated in Fig. 2, shows that the carboxyl group increases with time of degradation. This can be explained in terms of the following reaction:

$$\sim\!CH\!=\!CH\!-\!\underset{\underset{Cl}{|}}{CH}\!-\!CH_2\!\sim \quad \xrightarrow{\Delta H} \quad \sim\!CH\!=\!CH\!-\!\overset{\cdot}{CH}\!-\!CH_2\!\sim$$

$$\Big\downarrow O_2$$

$$\sim\!CH\!=\!CH\!-\!\underset{\underset{O_2H}{|}}{CH}\!-\!CH_2\!\sim + P^{\cdot} \quad \xleftarrow{P-H} \quad \sim\!CH\!=\!CH\!-\!\underset{\underset{\overset{\cdot}{O_2}}{|}}{CH}\!-\!CH_2\!\sim$$

$$\Big\downarrow \Delta H$$

$$\sim\!CH\!=\!CH\!-\!\underset{\underset{O^{\cdot}}{|}}{CH}\!-\!CH_2\!\sim + HO^{\cdot}$$

$$\nearrow \quad \sim\!CH\!=\!CH\!-\!\underset{\underset{O}{\|}}{C}\!-\!CH_2\!\sim + H_2O$$

$$\searrow \quad \sim\!CH\!=\!CH\!-\!\overset{O}{\overset{\diagup}{C}}\diagdown_{H} + {}^{\cdot}CH_2\!=\!\underset{\underset{Cl}{|}}{CH}\!\sim$$

(1)

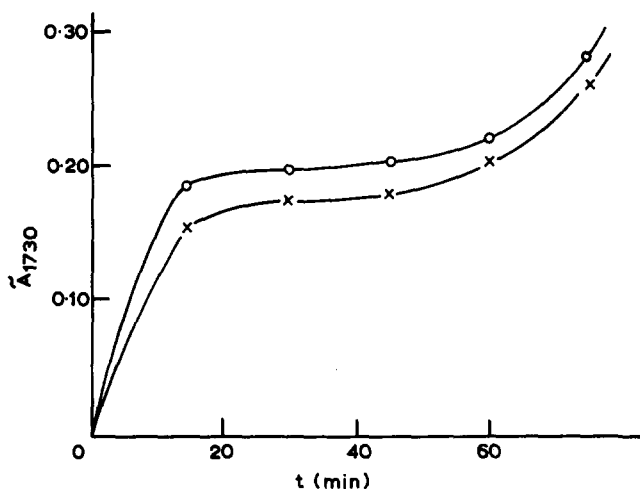The participation of oxygen thus accelerates the thermal degradation of PVC.

Fig. 2. IR absorption of PVC at 1730 cm^{-1} after degradation at 150°C (○) and 140°C
(×) in air.

Effect of stabiliser on the IR spectrum of PVC
The IR spectrum of DBTDL shows absorption bands at 1730 cm^{-1} and
1600 cm^{-1}, both of which can be associated with the carboxyl group. The
absorption band at 1600 cm^{-1} does not exist in unstabilised PVC and may
thus be used to study the action of DBTDL.

The IR absorbance of PVC stabilised with DBTDL, degraded at 150°C
and before and after precipitation, is shown in Fig. 3. It can be seen that the
absorption band at 1600 cm^{-1} decreases slightly after separation of the
polymer, but does not disappear completely. This indicates that the PVC has
been esterified to a small extent. The absorption band at 1730 cm^{-1} does not
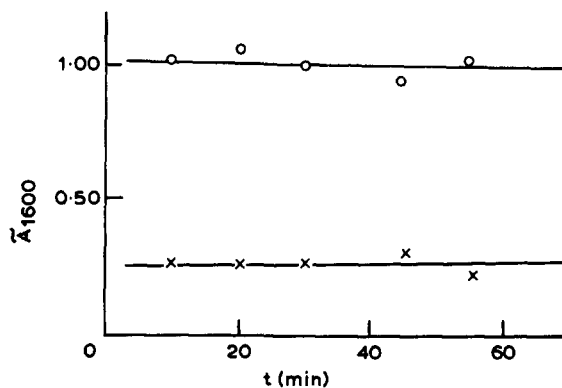change during degradation (Fig. 4), which demonstrates that oxidative

Fig. 3. IR absorption at 1600 cm^{-1} of PVC stabilised with DBTDL (3%) at 150°C in air
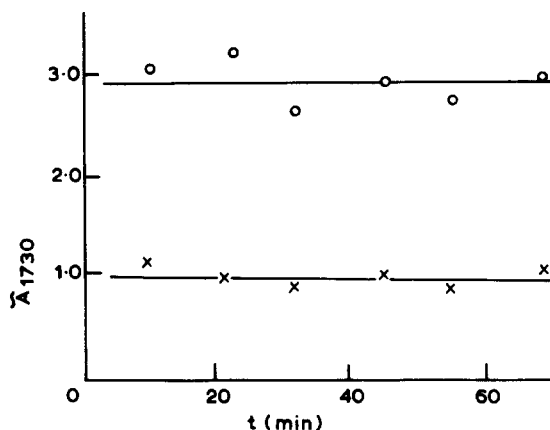before (○) and after (×) separation.

Fig. 4. IR absorption at $1730\,cm^{-1}$ of PVC stabilised with DBTDL (3%) at 150°C in air before (○) and after (×) separation.

degradation of PVC is negligible in the presence of DBTDL, which corresponds to a secondary antioxidant effect since, if oxidation did take place, the absorption at $1730\,cm^{-1}$ would increase due to the formation of oxidation products (carbonyl compounds) (Fig. 1). This agrees with the observations of Rabimoritch *et al.*[4]

Changes in the molecular weight of PVC

As well as giving off HCl and forming conjugated polyene sequences, PVC undergoes a change in molecular weight during thermal degradation which may be followed in detail by the use of GPC.

According to our experiments, the number-average molecular weight $(\overline{M}_n)$ of unstabilised PVC decreases slowly in the early stages of thermo-oxidation, but after a certain point it begins to increase again (Fig. 5). This is because in the early stages of thermo-oxidation, radical chain scission predominates (eqn (1)) while crosslinking takes over in the later stages.

The molecular weight changes in PVC in presence of DBTDL are shown in Fig. 6. Under our experimental conditions there was no gel formation. From Fig. 6, we see that both the number-average and weight-average molecular weights of PVC remain unchanged in the early stages of degradation; later, $\overline{M}_n$ and $\overline{M}_w$ change in different ways, leading to a broadening of molecular weight distribution (MWD). This result is much different from that obtained for unstabilised PVC and demonstrates that the DBTDL plays an important role in the thermo-oxidation of PVC. This can be explained as follows: at low conversion the stabiliser efficiently prevents the oxidative scission and crosslinking of PVC chains by interfering with the thermo-oxidation process and keeping the molecular weight constant.
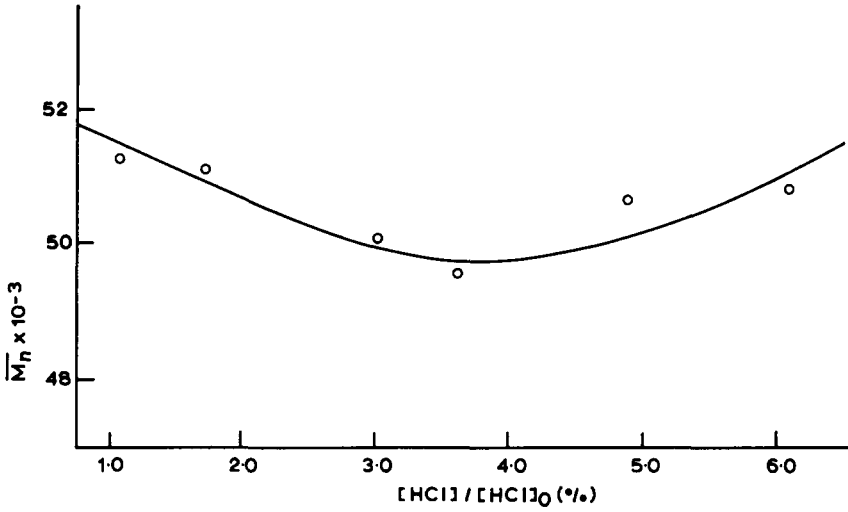
Fig. 5. Change in number-average molecular weight $(\overline{M_n})$ of unstabilised PVC degraded at 180°C in air in the dark.
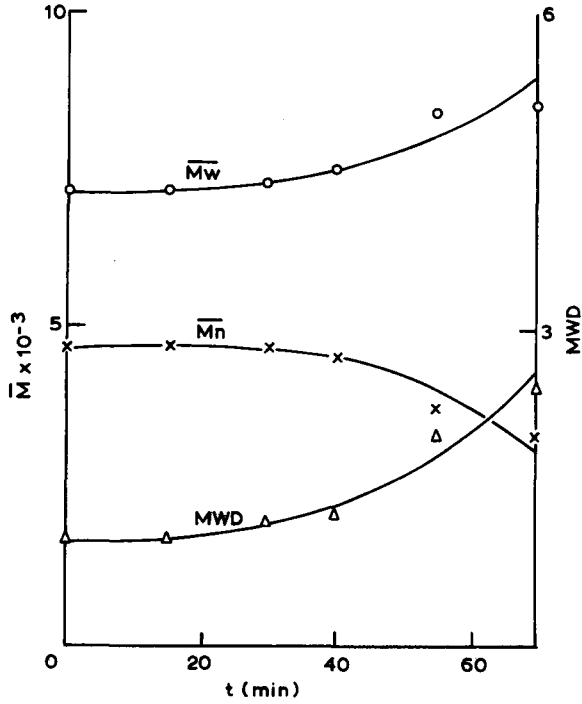

Fig. 6. Changes in $\overline{M_w}$, $\overline{M_n}$ and MWD of PVC stabilised with DBTDL (1%) during degradation at 170°C in air in the dark.

In the later stages of degradation, there is not enough stabiliser left unconsumed to prevent oxygen from participating and scission and crosslinking of macro-radicals taking place.

The PVC with lower molecular weight, which has a larger amount of structural defects, may be subjected to attack by oxygen, bringing about chain scission. However, the PVC with higher molecular weight is inclined to termination of macro-radicals. Under the influence of oxygen, the probability of chain scission is greater than of crosslinking, causing $\overline{M}_n$ to decrease and $\overline{M}_w$ to increase.

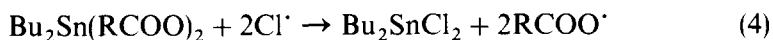## Mechanism and kinetics of stabilisation of PVC

Various mechanisms of stabilisation have been based on the various hypotheses of the possible mechanisms of thermal dehydrochlorination of PVC. In this paper, on the basis of the work described above, a radical mechanism of stabilisation is presented and the kinetics deduced.

In our previous study,[1] it was suggested that the thermal dehydrochlorination (TDHC) process in PVC is initiated at allylic chlorine in the original PVC chain. The main propagation steps may be represented as follows:

$$P^*_{n-1} \xrightarrow{k^*_1} P^{\cdot}_{n-1} + Cl^{\cdot} \tag{2}$$

$$P^{\cdot}_{n-1} + Cl^{\cdot} \xrightarrow{k_2} P_n \tag{3}$$

Where P^*_{n-1} is active polyene allylic chlorine and P_n are the stable polyene sequence.

The chlorine atom which dissociates from the allylic structure attacks the same PVC molecule, taking a hydrogen atom to form HCl, and yields a new macro-radical which can decompose to give another chlorine atom. Thus, if it is trapped, the chlorine atom would lose its activity for propagating dehydrochlorination and meanwhile, if a more thermally stable group combined with the macromolecule, it would be less susceptible to thermal decomposition than the structure from which it was derived. In this way, the stimulus for the loss of chlorine atoms as shown in eqn (2) would be eliminated. The behaviour of organotin stabiliser in this manner is illustrated by eqns (4) and (5):

$$Bu_2Sn(RCOO)_2 + 2Cl^{\cdot} \rightarrow Bu_2SnCl_2 + 2RCOO^{\cdot} \tag{4}$$

$$P^{\cdot}_{n-1} + RCOO^{\cdot} \rightarrow R_{n-1}COOR \tag{5}$$

Hence, the free-radical chain dehydrochlorination would be inhibited.

From this mechanism, the kinetic equation can be deduced as in eqn (6),

$$\frac{dHCl}{dt} = k_1^* \left(1 + \frac{K}{(S)}\right) H_0 \tag{6}$$

where H_0 is the concentration of allylic chlorine in the original PVC, (S) is the content of stabiliser and K is a constant.

From the plot of $dHCl/dt$ vs $1/(S)$, a value of k_1^* of 2.74×10^{-8}/min and K of 2·27 can be calculated.

CONCLUSION

The value of k^* for stabilised PVC is much reduced compared with that of unstabilised PVC, which indicates that the activation energy of thermal dehydrochlorination is raised by the organotin stabiliser and the stability of the PVC is improved.

REFERENCES

1. Xu Ruijian, Zhou Dafei & Zhao Deren, *Poly. Deg. and Stab.*, **27** (1990) 203.
2. Ayrey, G., Poller, R. C. & Siddiqui, I. H., *J. Poly. Sci.*, *Pt A-1*, **10** (1972) 725.
3. Behnich, J., Zimmerann, H. & Auders, H., *Poly. Deg. and Stab.*, **15** (1986) 335.
4. Rabimoritch, Elvira B., Dorsch, J. L., Summer, J. W. & Quisenberry, J. G., *J. Vinyl. Tech.*, **2** (1986) 73.