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A ^{119}Sn MÖSSBAUER STUDY OF THE THERMAL DEGRADATION OF ORGANOTIN STABILISERS IN PVC

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Summary

^{119m}Sn Mössbauer studies of the thermal degradation of PVC containing the stabilisers dibutyltinbis(isooctylthioglycollate) (1.2% by weight of the polymer), dioctyltinbis(isooctylthioglycollate) (4% by weight of the polymer) and dibutyltinbis(isooctylmaleate) (2% by weight of the polymer) indicate that in each case the stabiliser is converted into the dialkylmonochlorotin ester $R_2SnCl(X)$ ($X = SCH_2CO_2C_8H_{17}$ or $O_2C.CH = CHCO_2C_8H_{17}$), and not into the dialkyltin dichloride, R_2SnCl_2, as recently suggested by other workers. Comparison of the Mössbauer data for organotin-stabilised PVC samples prepared by both hot-milling and room temperature solvent casting processes indicates that there is little degradation of the polymer (and stabiliser) during the initial hot-milling process.

Introduction

Recently, we reported ^{119}Sn Mössbauer studies of the thermal degradation of samples of PVC containing the organotin stabiliser, dibutyltinbis(*iso*octylthioglycollate) ($Bu_2Sn(IOTG)_2$), present at 4% w/w of the polymer [1]. Our results indicated the formation of dibutyl(monochloro)tin (*iso*octylthioglycollate) after degradation of the polymer at 185° C for 1 hour. Harrison *et al* [2] have recently reported their findings in a similar study of PVC samples containing 1 - 2% of the above organotin stabiliser, and concluded that partial exchange of IOTG for chlorine occurred during the milling stage but following thermal degradation, the stabiliser was completely converted into dibutyltin dichloride.

Using a new 15 mCi ^{119}Sn ($BaSnO_3$) source, we have repeated our original experiments at the commercially-used level of 1.2% w/w of the $Bu_2Sn(IOTG)_2$ stabiliser in the polymer, and now report a detailed study of the progressive changes in the stabiliser during thermal degradation of the polymer. Also reported are related studies on other organotin stabilisers.

Experimental

Samples of PVC containing dibutyltinbis(*iso*octylthioglycollate) (1.2% by weight of the polymer) were prepared by conventional hot-milling techniques and then subjected to thermal degradation at 185°C for varying periods of time. The samples were then cooled to 80 K using a continuous flow cryostat with helium exchange gas and then analysed on a constant acceleration Mössbauer spectrometer, with a room temperature 15 mCi ^{119}Sn barium stannate source. The parameters were obtained from least-squares fits to the spectra using Lorentzian line shapes.

Dibutyl(monochloro)tin(*iso*octylthioglycollate) was prepared as described by Hutton *et al* [3], and incorporated into a PVC sample by the hot-milling process, also at a level of 1.2% by weight of the polymer.

In a similar manner, samples of PVC containing dioctyltinbis(*iso*octylthioglycollate) (4% by weight of the polymer) and dibutyltinbis(*iso*octylmaleate) (2% by weight of the polymer) respectively, were prepared.

The related dialkyltin(chloro) esters were prepared by the general procedures described by Hutton *et al* [3] and incorporated into PVC samples by the hot-milling process.

Analytical data for the previously unknown monochloro esters:

Monochloro(dioctyl)tin(isooctylthioglycollate) (a viscous oil which decomposed on attempted distillation)
(Found : C, 52.95; H, 8.9; Cl, 5.6; S, 5.5; Sn, 20.7; $C_{26}H_{53}ClO_2SSn$ requires C, 53.5; H, 9.1; Cl, 6.1; S, 5.5; Sn, 20.4%)
Dibutyl(monochloro)tin(isooctylmaleate) (a viscous oil which decomposed on attempted distillation)
(Found : C, 48.75; H, 7.55; Cl, 6.95: Sn, 24.6; $C_{20}H_{37}ClO_4Sn$ requires C, 48.5; H, 7.5; Cl, 7.2; Sn, 24.0%)

Solvent-cast samples were prepared by allowing a thin film of a solution of PVC and the appropriate stabiliser in an organic solvent (CH_2Cl_2 for thioglycollate stabilisers and THF for the maleate stabiliser) to evaporate at room temperature.

Results and Discussion

The Mössbauer parameters of samples of PVC stabilised by $Bu_2Sn(IOTG)_2$, together with those of the pure stabiliser and dibutyltin dichloride are given in Table 1. A typical spectrum obtained for the thermally aged samples is shown

TABLE 1

^{119m}Sn Mössbauer Parameters of Dibutyltinbis(*iso*octylthioglycollate)

Sample	*Isomer Shift mm/sec	Quadrupole Splitting mm/sec	Full Width at Half Height mm/sec
$Bu_2Sn(IOTG)_2$ (Pure)	1.39	2.20	0.88
Bu_2SnCl_2 (Pure)	1.64	3.47	0.97
$Bu_2SnCl(IOTG)$ (Pure)	1.44	2.88	1.14
$Bu_2SnCl(IOTG)$ in PVC	1.43	2.85	0.95
$Bu_2Sn(IOTG)_2$ in PVC at 1.2% (freshly milled)	1.45	2.29	1.07
$Bu_2Sn(IOTG)_2$ in PVC at 4.0% (solvent cast)	1.48	2.32	0.90
$Bu_2Sn(IOTG)_2$ in PVC at 1.2% Thermally aged for 85 mins	1.47	2.86	1.08

in Figure 1. The computer fit is the sum of two components corresponding to the unaged stabiliser and the monochlorotin ester.

Comparison of the data for the freshly-milled sample with that for the pure stabiliser indicates a small change, which is probably due to a small degree of degradation during the initial hot-milling process, as concluded by Harrison *et al* [2]. However, the similarity of the data clearly indicates that there is no significant structural change in the stabiliser which might have arisen as a result of co-ordination between the chlorine atoms of the polymer and the tin atoms of the stabiliser, as has been suggested by other workers, (Frye *et al* [4]).

After prolonged thermal degradation at 185°C, when the sample had become completely blackened, the Mössbauer

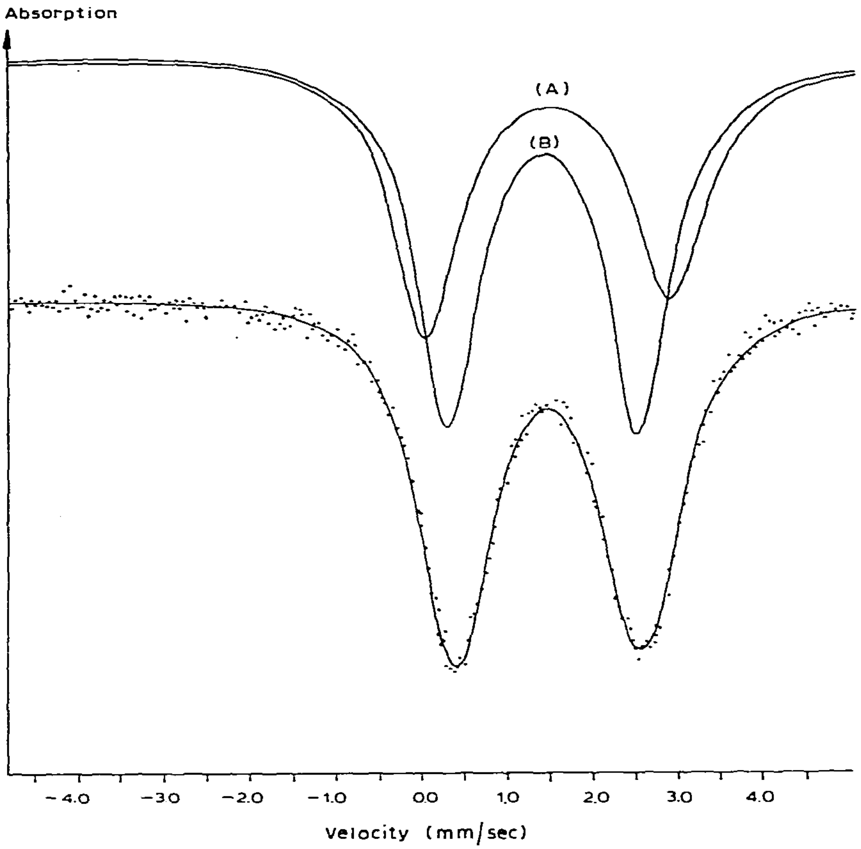


Fig. 1. Mössbauer spectra of thermally degraded PVC-containing $Bu_2Sn(IOTG)_2$ stabiliser at 1.2% after heating at 185°C for 30 min. The two components of the computer fit are shown corresponding to (A) $Bu_2SnCl(IOTG)$ and (B) $Bu_2Sn(IOTG)_2$.

parameters compare exactly with those of the sample of the monochlorotin ester dispersed in the polymer.

Further studies of progressive aging for short periods in the range 5 – 85 minutes indicate a gradual increase in the apparent quadrupole splitting from that of the pure stabiliser to that of the monochloro ester (Table 2). This trend is shown in Figure 2. It is apparent that during the course of thermal degradation, the presence of both the monochloro ester and unchanged stabiliser would

TABLE 2

^{119m}Sn Mössbauer Parameters of thermally aged Dibutyltinbis(*iso*octylthioglycollate)

Sample	*Isomer Shift mm/sec	Apparent Quadrupole Splitting mm/sec	Full Width at Half Height mm/sec
$Bu_2Sn(IOTG)_2$ in PVC at 1.2% Thermally aged for:			
5 mins	1.48	2.38	1.13
10 mins	1.45	2.42	1.14
15 mins	1.46	2.41	1.11
30 mins	1.47	2.56	1.27
50 mins	1.48	2.90	1.00
70 mins	1.47	2.84	0.99
85 mins	1.47	2.86	1.08

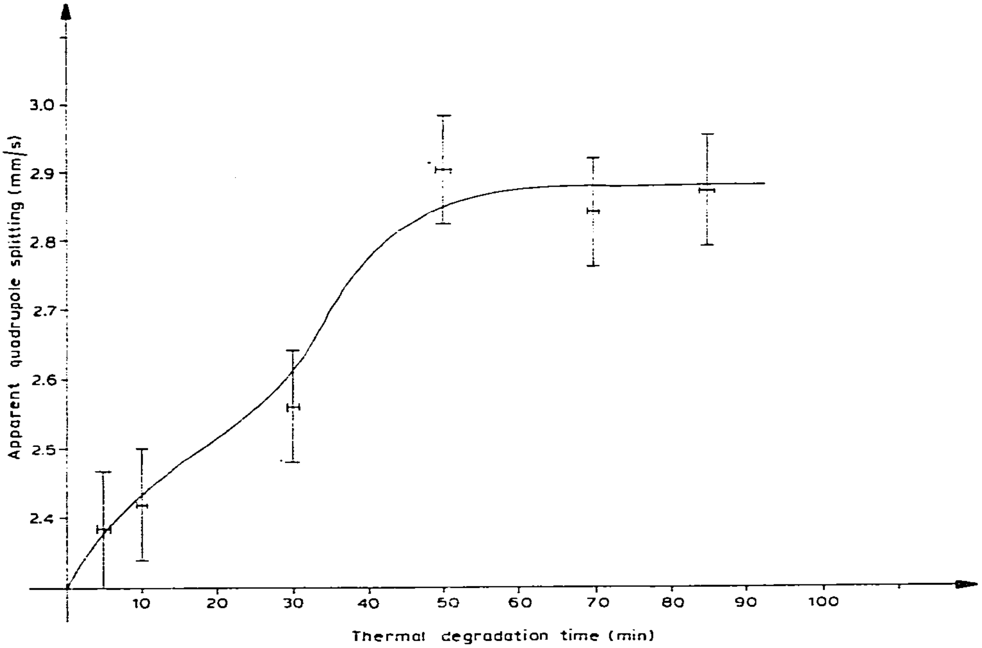


Fig. 2. Apparent quadrupole splitting as a function of thermal degradation time.

result in unresolved Mössbauer quadrupole doublets. However, a gradual increase in the apparent quadrupole splitting and a broadening of the line-width would be expected for such a mixture, and our data is consistent with this.

The trend shown in Figure 2 indicates the gradual change in 'apparent quadrupole splitting parameter' corresponding to the change to the monochloro ester as degradation occurs. There is no indication that further degradation occurs at 185°C to form Bu_2SnCl_2. We have computer fitted the data at 10, 30 and 50 mins using two doublets with parameters corresponding to the unchanged stabiliser and the monochlorotin ester and a significant reduction in the χ^2 term was obtained. The line width parameters were also comparable to those expected for the absorber thickness used. From the relative areas of the two contributions, the percentage of Bu_2SnCl(IOTG) was calculated and this is shown in Figure 3. From these results, it is not clear how rapidly the conversion to Bu_2SnCl(IOTG) occurs as the technique is

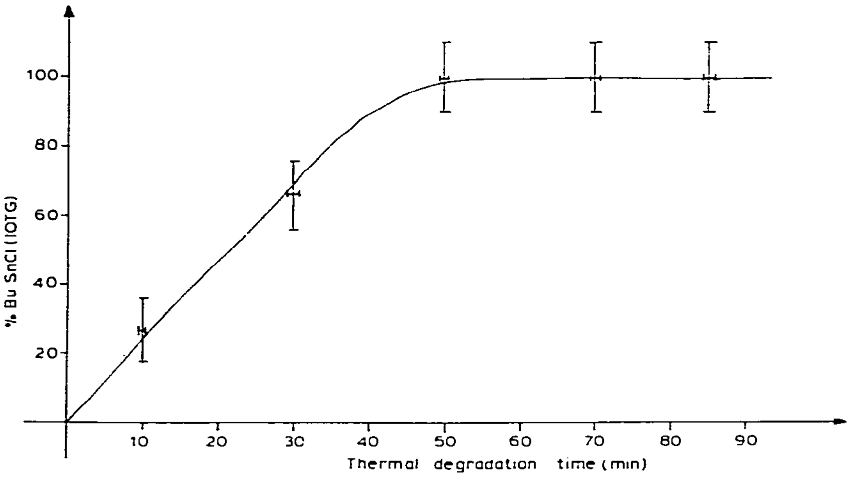


Fig. 3. Percentage of Bu_2SnCl(IOTG) as a function of thermal degradation time.

relatively insensitive to small contributions in unresolved mixed quadrupole spectra. However, complete conversion to $Bu_2SnCl(IOTG)$ has taken place after 50 mins heating, and this corresponds to the rapid darkening observed in the PVC as degradation occurs. The optical density of thermally degraded PVC samples was measured using a radiological densitometer. Figure 4 shows the change in optical density (arbitrary units) as a function of heating time, and a rapid increase is seen after 50 minutes when the stabiliser has been completely converted to $Bu_2SnCl(IOTG)$.

From these results, it is quite clear that the final product is the monochlorotin ester, and not dibutyltin dichloride as concluded by Harrison et al [2]. The discrepancy between our results and those of Harrison et al may arise due to the

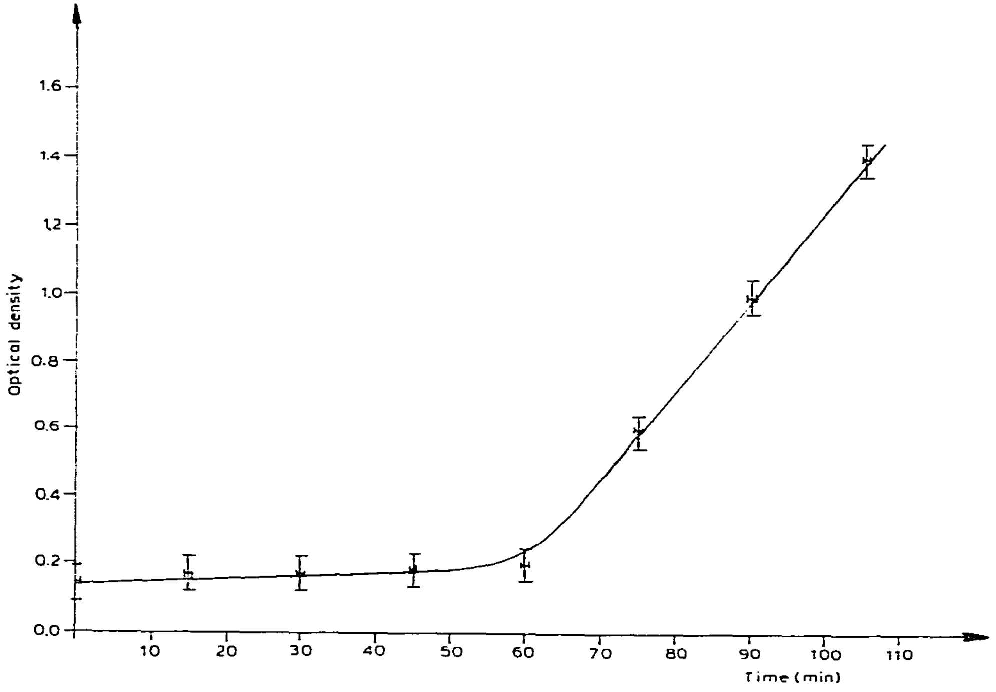


Fig. 4. Optical density of PVC as a function of thermal degradation time.

low value of the quadrupole splitting parameter of dibutyltin dichloride quoted by those workers [5] and also possibly larger experimental errors resulting from long run times due to the weakness of their source and low levels of tin in the absorber.

We have also carried out similar studies of the degradation of PVC stabilised with dioctyltinbis(*iso*octylthioglycollate) ($Oct_2Sn(IOTG)_2$)(Table 3) and dibutyltinbis(*iso*octylmaleate) ($Bu_2Sn(IOM)_2$) (Table 4) respectively.

TABLE 3

^{119m}Sn Mössbauer Parameters of Dioctyltinbis(*iso*octylthioglycollate)

Sample	*Isomer Shift mm/sec	Quadrupole Splitting mm/sec	Full Width at Half Height mm/sec
$Oct_2Sn(IOTG)_2$ (Pure)	1.49	2.36	0.96
Oct_2SnCl_2 (Pure)	1.75	3.73	1.03
$Oct_2SnCl(IOTG)$ (Pure)	1.47	2.94	1.03
$Oct_2SnCl(IOTG)$ in PVC at 1.2%	1.46	2.97	1.02
$Oct_2Sn(IOTG)_2$ in PVC at 4% (freshly milled)	1.50	2.27	0.97
$Oct_2Sn(IOTG)_2$ in PVC at 4% Thermally aged for 60 mins	1.46	2.62	1.03

In the case of the $Oct_2Sn(IOTG)_2$ stabiliser, the data in Table 3 shows quite clearly that on thermal degradation, the stabiliser is, as for the dibutyltin analogue, converted into the monochlorotin ester.

Similarly, the maleate stabiliser, $Bu_2Sn(IOM)_2$ is also seen to be converted into the monochlorotin ester. In the case

TABLE 4

^{119m}Sn Mössbauer Parameters of Dibutyltinbis(*iso*octylmaleate)

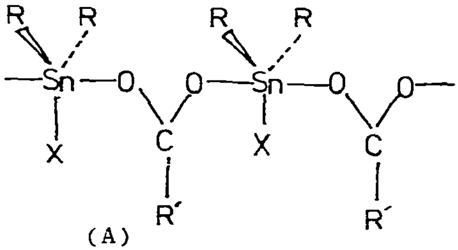
Sample	*Isomer Shift mm/sec	Quadrupole Splitting mm/sec	Full Width at Half Height mm/sec
$Bu_2Sn(IOM)_2$ (Pure)	1.44	3.62	1.04
$Bu_2Sn(IOM)_2$ in PVC at 2% (freshly milled)	1.42	3.36	0.94
$Bu_2Sn(IOM)_2$ in PVC at 2% (solvent cast)	1.36	3.34	0.98
$Bu_2SnCl(IOM)$ (Pure)	1.49	3.54	1.02
$Bu_2SnCl(IOM)$in PVC at 2%	1.40	3.16	0.97
$Bu_2Sn(IOM)_2$ in PVC at 2% Thermally aged for 60 mins	1.39	3.18	0.98

* All isomer shifts measured at 80 K relative to $BaSnO_3$

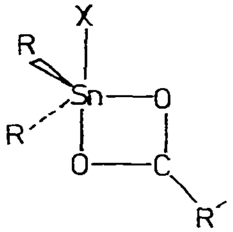
All parameters accurate to ± 0.02 mm s^{-1}

of this stabiliser, it is of interest that distinct differences in the quadrupole splitting are observed for the stabiliser in the pure state and when incorporated by hot-milling *or* by solvent-casting into the polymer. From the magnitude of the quadrupole splitting in the pure state, it would appear that the tin atom is probably six-co-ordinate with a *trans*-octahedral structure. The observed reduction in ΔE_{QS} on incorporation into the polymer may indicate a disruption of intra or intermolecular co-ordination by ester carbonyl groups or possible co-ordination by chlorine atoms of the polymer.

It is also noteworthy that for dibutyl(monochloro)tin*iso*octylmaleate, there is a significant difference in the magnitude of the quadrupole splitting between the pure compound (Δ = 3.54 mm s^{-1}) and that of the compound dispersed in the PVC matrix (Δ = 3.16 mm s^{-1}), indicating that the structure has changed. Honnick and Zuckerman [6] have recently discussed the structures of the diorganotin-halide carboxylates and suggested that the origin of certain changes in infrared spectroscopic properties, in passing from the pure compound to a solution in an inert solvent, might be a change from a polymeric pentaco-ordinated structure (A) to a monomeric pentaco-ordinated structure (B).



(A)



(B)

The change in quadrupole splitting between the pure dibutyl(monochloro)tin(isooctylmaleate) and the compound dispersed in the PVC matrix at the 2% level might be explained by a similar structural change.

In conclusion, it is also of interest that comparison of the Mössbauer parameters for hot-milled and solvent-cast samples containing respectively the $Bu_2Sn(IOTG)_2$ and $Bu_2Sn(IOM)_2$ stabilisers, indicates that the extent of thermal degradation of the stabiliser during the hot-milling process is very small.

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