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A ^{119m}Sn MÖSSBAUER STUDY OF THE STATE OF ASSOCIATION OF DIBUTYLTIN DICHLORIDE DISPERSED IN PVC

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Summary

Incorporation of dibutyltin dichloride into a PVC matrix results in a decrease in the Quadrupole Splitting parameter from 3.45 mm s^{-1} for the pure compound to 3.09 mm s^{-1} when dispersed in PVC at 1.2% w/w. This reduction has been attributed to the breakdown of an associated six coordinate structure and the progressive formation of dimeric units involving five-coordinate tin. Partial quadrupole splitting calculations support these conclusions.

Introduction

Our recent studies of the thermal [1] and photochemical [2] degradation of organotin stabilised PVC by ^{119m}Sn Mössbauer Spectroscopy resulted in the observation of an apparent change in structure of dibutyltin dichloride (Bu_2SnCl_2) when dispersed at low concentration in a PVC matrix. Here we report a detailed study of the changes in ^{119m}Sn Mössbauer parameters as the Bu_2SnCl_2 is progressively diluted in a PVC matrix by solvent casting.

Experimental

Samples of PVC containing Bu_2SnCl_2 at various concentrations down to 1.2% w/w were prepared by conventional solvent casting. The samples were cooled to 80 K using a continuous flow nitrogen cryostat and helium exchange gas. The Mössbauer spectra were recorded using a constant acceleration Mössbauer Spectrometer with a room temperature 15 mCi ^{119m}Sn barium stannate source. The Mössbauer hyperfine parameters were obtained from computer least-squares fits to the spectra using Lorentzian line shapes.

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Results and discussion

The Mössbauer parameters of Bu_2SnCl_2 dispersed in the PVC matrix are shown in Table 1. A typical spectrum is shown in Figure 1. The isomer shift (δ) and quadrupole splitting (Δ) parameters for Bu_2SnCl_2 at 1.2% w/w are significantly different from those of the pure Bu_2SnCl_2, and it is clear that there is a transition region at approximately 20% w/w of Bu_2SnCl_2 where the parameters change rapidly. This is shown in Fig. 2, where δ and Δ are plotted as a function of concentration. This indicates that a possible structural change is occurring when Bu_2SnCl_2 is dispersed in the PVC.

On the basis of the reported octahedral associated structures of dimethyl- and diethyl-tin dichloride [3] and the similarity in Mössbauer parameters between these compounds and Bu_2SnCl_2 [4], it is suggested that pure Bu_2SnCl_2 also has the associated six-coordinate structure shown in Fig. 3(a). The magnitude of the quadrupole splitting for Bu_2SnCl_2 at 1.2% w/w dispersed in PVC by solvent casting is typical of five-coordinate tin (Fig. 3(b)), suggesting that a change in structure and coordination occurs. To confirm the proposed change in structure from octahedral to a five-coordinate state, partial quadrupole splitting (p.q.s.) calculations have been performed for the possible structures which Bu_2SnCl_2 may adopt when diluted in an inert matrix. The possible structures are shown in Fig. 4.

Using the additive model proposed by Bancroft et al. [5] for the five-coordinate structure shown in Fig. 3(b) gives:

$$\Delta_{calc} = \frac{-7[\text{alkyl}]^{tbe} + 8[\text{Cl}^-]^{tba} + [\text{Cl}^-]^{tbe}}{\sqrt{7}}$$

where:

$[\text{alkyl}]^{tbe}$ (trigonal-bipyramidal-equatorial) $= -1.13$ mm s^{-1}
$[\text{Cl}^-]^{tba}$ (trigonal-bipyramidal-apical) $= 0.00$ mm s^{-1}
$[\text{Cl}^-]^{tbe}$ (trigonal-bipyramidal-equatorial) $= +0.20$ mm s^{-1}
$\Delta_{calc} = 3.06$ mm s^{-1}

TABLE 1

^{119m}Sn MÖSSBAUER PARAMETERS OF Bu_2SnCl_2 DISPERSED IN PVC

Concentration (%)	Isomer shift [a] δ(mm s^{-1}) ±0.02	Quadrupole splitting Δ(mm s^{-1}) ±0.02	Full width at half maximum Γ(mm s^{-1}) ±0.02	Relative % of dimeric unit ±5%
1.2	1.54	3.09	1.00	100
10	1.54	3.09	1.04	100
15	1.55	3.07	1.02	65
20	1.55	3.21	1.05	50
30	1.57	3.25	1.02	49
50	1.60	3.28	1.12	44
75	1.59	3.28	1.12	38
Pure Bu_2SnCl_2	1.62	3.45	1.00	0
Bu_2SnCl_2 in polystyrene at 1.2% w/w	1.53	3.00	1.04	[a]

[a] Measured relative to $BaSnO_3$.

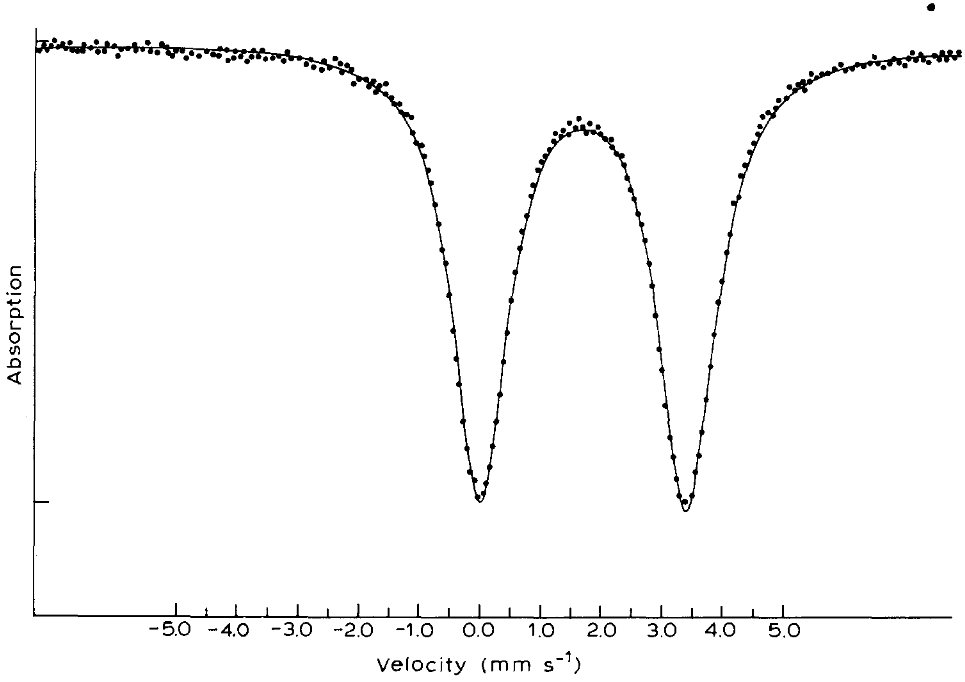


Fig. 1. Bu_2SnCl_2 dilution study.

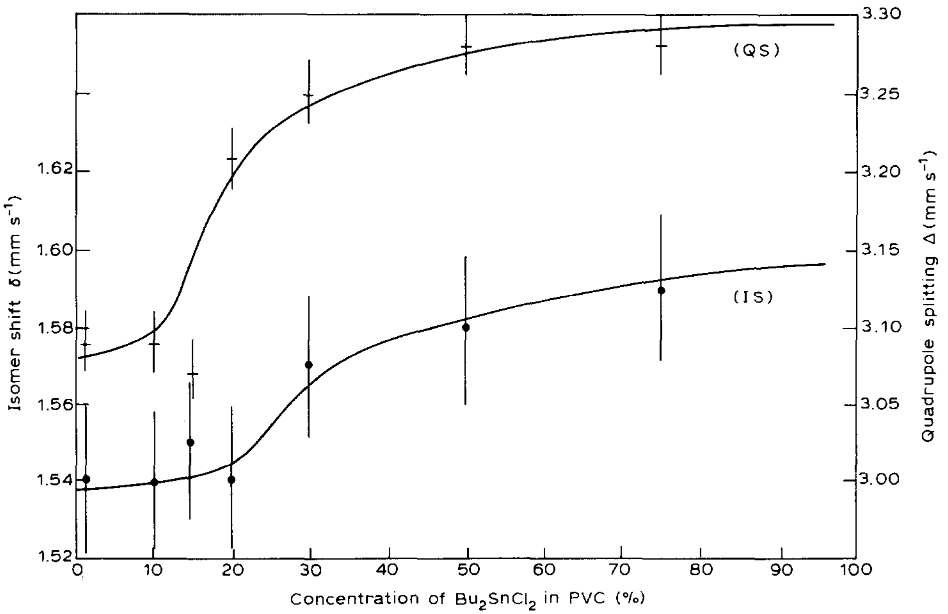
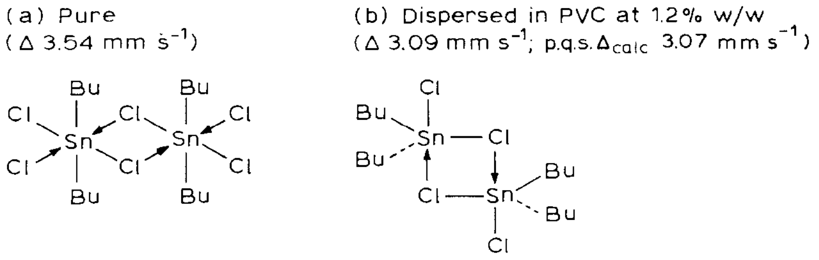


Fig. 2. Plot of isomer shift (δ) and quadrupole splitting (Δ) parameters for Bu_2SnCl_2 as a function of concentration.



(a) Pure (Δ 3.54 mm s^{-1})

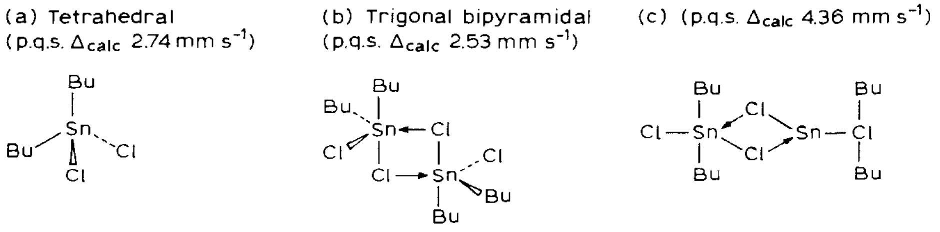
(b) Dispersed in PVC at 1.2% w/w (Δ 3.09 mm s^{-1}; p.q.s. Δ_{calc} 3.07 mm s^{-1})

Fig. 3. Proposed structures for Bu_2SnCl_2.

Similarly, the p.q.s. values can be calculated for the other possible isomers shown in Fig. 4, and these are easily distinguishable.

Our results therefore indicate that at a concentration of 1.2% w/w, the Bu_2SnCl_2 is present as a five-coordinate dimer. On increasing the concentration, six-coordinate tin species are formed, the relative number of which is observed to increase as the concentration increases. This results in an increase in the quadrupole splitting parameter. The values for the quadrupole splitting parameter above a concentration of 20% w/w represent an average of the values arising from both five- and six-coordinate forms of Bu_2SnCl_2 in the PVC. In order to estimate the relative concentration of the dimeric units, at respective Bu_2SnCl_2 concentrations, the data were fitted as two doublets with parameters corresponding to the five- and six-coordinate species. From a determination of the relative absorption line areas, the relative percentage of dimeric unit was estimated. Because of the uncertainty in fitting unresolved quadrupole doublets corresponding to the five- and six-coordinate units, the errors associated with the estimate of dimeric units is large. However, these results do indicate a significant structural change occurring below the 20% concentration level, corresponding to the predominant formation of dimeric units.

To ensure that the change in coordination is not caused by coordination from the chlorine atoms of the polymer, a dispersion of Bu_2SnCl_2 (at 1.2% w/w) in a polystyrene matrix was prepared and the Mössbauer parameters recorded. The results are shown in Table 1 and show that coordination with the chlorine in PVC is not responsible for the change in quadrupole splitting for Bu_2SnCl_2 at low concentrations in PVC. Finally, it is noteworthy that a similar "dilution effect" has been observed in our laboratories for dioctyltin dichloride on dispersion in PVC (at 2% w/w).



(a) Tetrahedral (p.q.s. Δ_{calc} 2.74 mm s^{-1})

(b) Trigonal bipyramidal (p.q.s. Δ_{calc} 2.53 mm s^{-1})

(c) (p.q.s. Δ_{calc} 4.36 mm s^{-1})

Fig. 4. Possible structures for dilute Bu_2SnCl_2 and their calculated quadrupole splitting parameters.

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