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A ^{119m}Sn variable-temperature Mössbauer study of tin(IV) chloride and dibutyltin dichloride when dispersed in a poly(vinyl chloride) matrix

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Variable-temperature Sn-119m Mössbauer studies of tin(IV) chloride ($SnCl_4$) and dibutyltin dichloride (Bu_2SnCl_2) when dispersed in a poly(vinyl chloride) (PVC) matrix have been interpreted using a Debye model. Recoilless fractions have been determined which indicate that at 80 K the Mössbauer technique is nearly three times as sensitive to the presence of $SnCl_4$ compared with Bu_2SnCl_2 within the poly(vinyl chloride) matrix. These observations have been explained in terms of structural changes occurring on dispersion in the polymer matrix which result in the tin atom in tin(IV) chloride becoming six-coordinate whereas that in dibutyltin dichloride reduces its coordination to five. The implications of these results for future applications of Mössbauer spectroscopy to the study of organotin compounds present in polymers are considered.

Keywords: Mössbauer, dibutyltin dichloride, PVC, polymers

INTRODUCTION

As part of a recent study of the degradation of organotin-stabilized poly(vinyl chloride) (PVC) by gamma irradiation,[1,2] certain anomalies were observed in the quantitative determination of the relative proportions of degradation products as determined by chemical derivatization and Mössbauer spectroscopy respectively. In particular, milled PVC containing 1.2% (w/w) dibutyltin bis(iso-octylthioglycollate) [$Bu_2Sn(IOTG)_2$], when exposed to a gamma irradiation dose of 100 kGy, resulted in an observed Mössbauer spectrum which was dominated by one major component, attributed to the presence of tin(IV) chloride. However, analysis of the same sample using a chemical derivatization gas chromatographic method showed only 47% conversion to tin(IV) chloride, and the greater part of the remaining tin was found in the dialkyl state.[2] This suggested that the tin(IV) chloride may be more sensitive to detection by the Mössbauer technique when held in the polymer matrix than other dialkyl- and monoalkyl-tin degradation products, and hence an enhanced Mössbauer resonance absorption area could dominate the spectrum.

The sensitivity of the ^{119}Sn Mössbauer technique to a particular tin species is determined by the recoilless fraction f (Eqn 1):

$$f = \exp\left(-\frac{4\pi\langle x^2\rangle}{\lambda^2}\right) \quad (1)$$

where λ is the wavelength of the Mössbauer gamma ray, and $\langle x^2\rangle$ is the mean square vibrational amplitude of the absorbing atom. The wavelength λ is determined by the Mössbauer transition which is being employed ($E_\gamma = 24$ keV for Sn-119 Mössbauer spectroscopy), while $\langle x^2\rangle$ is determined by the strength and nature of the chemical bonds to the absorbing atom, and the temperature of the absorber.

The relative magnitudes of recoilless fractions can be obtained by applying the simple Debye model of solids to variable-temperature Mössbauer data. In this study the lattice dynamics of two characteristic organotin degradation products have been studied: tin(IV) chloride and dibutyltin dichloride dispersed in PVC at 4% (w/w) respectively, by solvent-casting. The Mössbauer spectra of these samples were recorded over a temperature range of 12–80 K, and the variation of absorption area with temperature interpreted in terms of a Debye model.

THEORY

The absorption line area is related to the Mössbauer thickness t by the expression given in Eqn 2:[3]

$$A(t) \propto \frac{t}{2}\exp\left(-\frac{t}{2}\right)\left[I_0\left(\frac{t}{2}\right)+I_1\left(\frac{t}{2}\right)\right] \qquad [2]$$

where I_0 and I_1 are zero- and first-order Bessel functions, and

$t = \beta n f_a \sigma_0$,

$\beta = \begin{cases} 1 \text{ for a singlet and} \\ \frac{1}{2} \text{ for a quadrupole doublet,} \end{cases}$

$\sigma_0 = 1.403 \times 10^{-18}\,\text{cm}^2$,

n = number of resonant nuclei per cm^2,

f_a = absorber recoilless fraction.

For small values of $t(\ll 5)$ Eqn 2 reduces to Eqn 3;

$$A(t) \propto t(1-0.25t+0.0625t^2+\ldots). \qquad [3]$$

To avoid 'saturation effects' and to enable the approximation to be made that the absorption area is proportional to t^1 (and hence to the number of resonant nuclei), 'thin' Mössbauer absorbers are normally used.

The Debye model

The temperature dependence of the recoilless fraction is given by the Debye model of solids by an expression of the form of Eqn 4.[4]

$$f_a(T) = \exp\left(-\frac{3E_R}{2k_B\theta_D}\right)\cdot\left[1+4\left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x\,dx}{(e^x-1)}\right] \qquad [4]$$

where $E_R = E_\gamma^2/2M_{eff}c^2$, M_{eff} is the effective vibrating mass of the absorbing nucleus, and θ_D is the Debye temperature.

In the high-temperature limit $(T > \theta_D/2)$ this expression simplifies to Eqn 5;

$$f_a(T) = \exp\left[-\frac{6E_R T}{k_B\theta_D^2}\right]. \qquad [5]$$

Hence if the system can be modelled as an ideal monatomic isotropic cubic solid, then the slope of the $\ln f_a(T)$ versus T graph would be given by Eqn 6:

$$\frac{d[\ln f_a(T)]}{dT} = -\frac{6E_R}{k_B\theta_D^2} \qquad [6]$$

and hence for 'thin' Mössbauer absorbers the variation of absorption area with temperature is as follows (Eqn 7):

$$\frac{d(\ln A)}{dT} = -\frac{3E_\gamma^2}{(M_{eff}c^2)k_B\theta_D^2}. \qquad [7]$$

If a plot of $\ln A$ versus temperature yields a straight line, and there is no anharmonicity, then measurement of the gradient results in a determination of the term $M_{eff}\theta_D^2$. In general, it is not possible to evaluate the effective vibrating mass of the absorbing unit, and it has become common practice to assume that it is equal to the relative molecular mass of the compound. Without a fully detailed vibrational analysis of the absorbing system, this approximation is as realistic as can be achieved, and is likely to introduce no worse errors than those inherent in the adoption of the Debye model to describe a non-ideal system. This enables an evaluation of θ_D to be made (most useful on a comparative basis), which will relate to the strength and nature of the binding of the absorbing unit.

EXPERIMENTAL

Sample preparation

Solvent-cast films containing dibutyltin dichloride and tin(IV) chloride, respectively, were prepared by dissolving the polymer and the tin compound in dry dichloromethane, and allowing slow evaporation of the solvent under nitrogen (4% w/w of tin compound to polymer).

Instrumentation

The Mössbauer spectra were recorded using a conventional constant-acceleration Mössbauer spectrometer, with a room-temperature 15 mCi barium [$^{119\text{m}}$Sn]stannate source. The absorber discs were cooled in the temperature range 12–80 K using a closed-cycle Displex system.

Table 1 Sn-119 Mössbauer hyperfine parameters for dibutyltin dichloride (Bu_2SnCl_2) and tin(IV) chloride ($SnCl_4$) as pure compounds and when dispersed in PVC

	Isomer shift δ(mm s^{-1})	Quadrupole splitting Δ(mm s^{-1})	Line width Γ(mm s^{-1})
Bu_2SnCl_2 pure	1.64 (2)	3.47 (2)	0.97 (2)
Bu_2SnCl_2 in PVC (4% w/w solvent-cast)	1.50 (5)	3.02 (5)	0.94 (5)
$SnCl_4$ pure	0.82 (2)	—	1.32 (2)
$SnCl_4$ in PVC (4% w/w solvent-cast)	0.30 (5)	—	1.24 (5)

All spectra were recorded with the absorber at 80 K and using a room-temperature 15 mCi $BaSnO_3$ source.

The cryogenic refrigeration system is based upon a two-stage expander module using gaseous helium as the refrigerant. The sample is mounted on a heat exchanger interface which is mounted independently of the expander module to isolate all vibrations from the sample. The heat exchanger interface is cooled using a static head of helium exchange gas.

The experimental data were computer-fitted with sums of Lorentzian line shapes using non-linear least-squares fitting routines.[5] Care was taken to ensure that there was no evidence of saturation in the spectra. The normal Mössbauer hyperfine parameters were used as fitting variables and their values recorded at 80 K for the four samples studied as presented in Table 1.

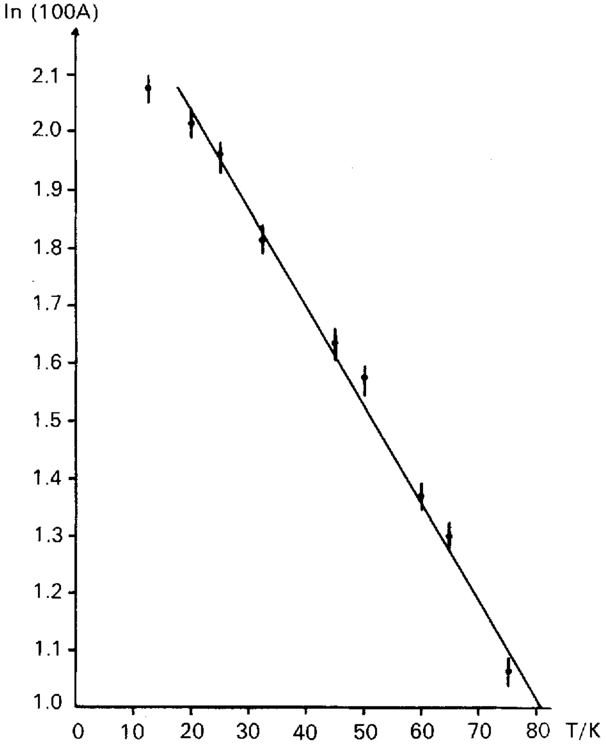

Figure 1 Absorption line areas for pure dibutyltin dichloride over the temperature range 12–75 K.

Table 2 Mössbauer and lattice dynamics parameters for tin(IV) chloride ($SnCl_4$) and dibutyltin dichloride (Bu_2SnCl_2) as the pure compounds and when dispersed in PVC

Compound	M_{eff} (u)	$d\ln A/dT$ (K^{-1})	θ_D (K)	$f(80)$
$SnCl_4$ pure (Ref. 5)	260.5	1.5×10^{-2}	74	0.30
$SnCl_4$ dispersed in PVC	260.5	1.2×10^{-2}	83	0.38
Bu_2SnCl_2 pure	305.2	1.7×10^{-2}	64	0.26
Bu_2SnCl_2 dispersed in PVC	305.2	2.5×10^{-2}	53	0.13

RESULTS AND DISCUSSION

Variable-temperature Mössbauer data have been recorded for pure tin(IV) chloride by Herber and Leahy.[6] Assuming the effective vibrating mass to be the relative molecular mass allows a value for the Debye temperature to be calculated from these data, and hence a value for the recoilless fraction determined at 80 K. No data could be found in the literature for pure dibutyltin dichloride and hence variable-temperature experiments were first performed on a 'thin' Mössbauer absorber of the pure material (t values of less than 0.2 were used throughout). Figure 1 shows the plot of natural logarithm of normalized area for spectra recorded in the temperature range from 12 to 75 K. The linear region of the graph yields the gradient and hence the Debye temperature. Table 2 summarizes the lattice dynamics parameters for the pure compounds. The important feature is the very similar values determined for the recoilless fractions, and hence only slightly enhanced sensitivity of the Mössbauer technique to tin(IV) chloride in the pure state.

Samples containing 4% w/w of tin(IV) chloride and dibutyltin dichloride dispersed in PVC were studied over the same temperature range. (Figure 2 shows the results for dibutyltin dichloride.) The low levels of Sn-119 present in these samples required long run times to ensure adequate statistics. The plots of ln A versus temperature revealed some slight high-temperature curvature, probably arising due to an anharmonic potential associated with the vibrational properties of PVC. Brooks et al.[7] have described a method for incorporating the effect of an anharmonic potential and allowing the Debye temperature to be determined. The uncertainties associated with this type of analysis are large, and indeed the justification for the use of the simple Debye model is doubtful. Nevertheless, the lattice dynamics parameters obtained and summarized in Table 2 yield some very interesting comparative data. For tin(IV) chloride dispersed in PVC this results in an increase in the Debye temperature and a corresponding increase in the recoilless fraction evaluated at 80 K. Conversely the corresponding results for dibutyltin dichloride show a decrease in the Debye temperature and recoilless fraction.

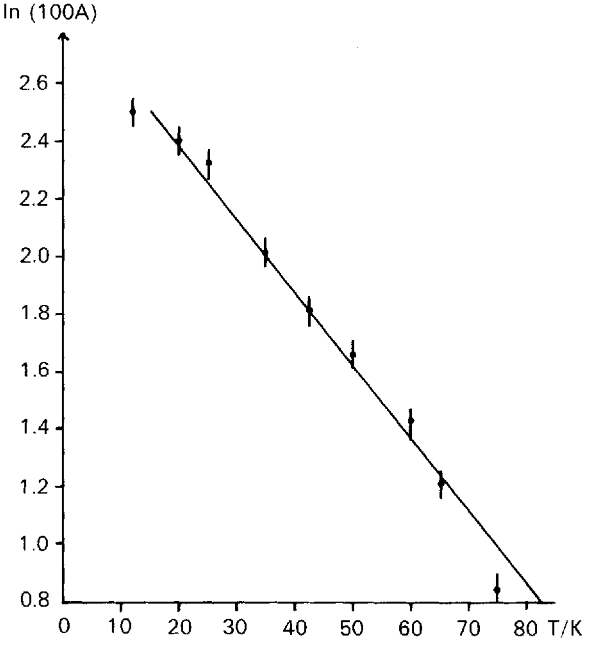

Figure 2 Absorption line areas for 4% (w/w) dibutyltin dichloride in PVC over the temperature range 12–75 K.

As a result of the difficulties encountered earlier with this type of determination, the errors associated with the determined values of the recoilless fractions are large. However, the significant feature of this study is the comparative difference in recoilless fractions when dispersed in PVC and the corresponding change in relative sensitivity indicating that at 80 K the Mössbauer technique appears to be nearly three times as sensitive to the presence of tin(IV) chloride. This observation has a very important analytical consequence and an interesting structural interpretation.

The increase in recoilless fraction of tin(IV) chloride when dispersed in PVC may result from an interaction with either hydrogen chloride liberated from the polymer[8] or with chlorine atoms still attached to the polymer. This could result in the tin(IV) chloride becoming six-coordinate, and it is interesting to note that many six-coordinate complexes of tin(IV) chloride show recoilless fractions close to that observed for tin(IV) chloride dispersed in PVC.[9]

For dibutyltin dichloride, the situation is reversed and an appreciable reduction in the recoilless fraction occurs when dispersed in PVC. A Sn-119 Mössbauer study of the structural properties of dibutyltin dichloride when dispersed in PVC has been carried out by Brooks et al.[10] It was proposed that the change in the magnitude of the quadrupole splitting observed for dibutyltin dichloride dispersed in PVC at 2% (w/w) from that of the pure compound suggested a structural change from six-coordinate in the pure state to five-coordinate when dispersed. Partial quadrupole splitting calculations were carried out for the possible structures that dibutyltin dichloride may adopt when diluted in an inert matrix. The conclusion was that, whereas in the pure state a six-coordinate polymeric structure predominates, for dibutyltin chloride, at low concentrations in the matrix a dimeric five-coordinate structure is adopted. This structural change could also account for reduction in recoilless fraction that would be expected for a five-coordinate dimer.

Thus it is now possible to rationalize the earlier discrepancy between the Mössbauer and chemical analysis results for our irradiated polymers. It is clear that, in future applications of Mössbauer spectroscopy to the study of organotin compounds in polymeric matrices, it will be necessary to gain information on the *in situ* relative recoilless fractions of compounds suspected to be present before any semi-quantitative conclusions can be drawn.

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