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# MÖSSBAUER SPECTROSCOPIC STUDIES ON THE MOLECULAR DYNAMICS OF ORGANOTIN(IV) POLYMERS

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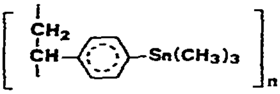
## Summary

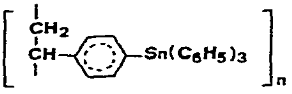
Linear organotin(IV) polymers with tin appended to the polymer chain or inserted into the polymer backbone have been characterized by Mössbauer spectroscopy. The lattice dynamics of three representative examples of these classes, as well as of a cross-linked organotin(IV) polymer, have been investigated by temperature-dependent Mössbauer spectroscopy. It has been shown that parameters associated with polymers having low interchain interactions practically correspond to those of molecular, non-coupled, solids.

## I. Introduction

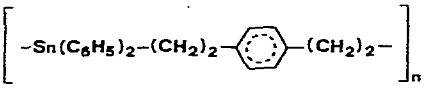
In a previous study we investigated by temperature-dependent $^{119}$Sn Mössbauer spectroscopy the molecular dynamics of solid polymers, obtained by linking organotin(IV) and tin(IV) moieties through a bulky bis-monodentate ligand bridge [1]; that work was considered as exploratory and a preliminary to studies on the interaction of tin with biological systems [1]. In such a context it also seemed worthwhile to establish whether "molecular" polymers exhibit lattice dynamics parameters corresponding to those of monomeric species, as theoretically predicted [2]. Indeed, the slope of the function ln $f_a$ $(T)$ of the cyclic oligomer $(Me_2SnS)_3$ [3], $f_a$ being the Debye-Waller-Mössbauer factor, would fit data typical of molecular compounds. We have consequently carried out lattice dynamics investigations on some long-chain organotin(IV) polymers representative of systems in which a triorganotin(IV) residue is appended to the polymer chain (I and II) [4], or a diorganotin(IV) moiety is inserted into the polymer backbone (III) [5]. The recently obtained cross-linked organotin polymer (IV) [6] was investigated for purposes of comparison.



I



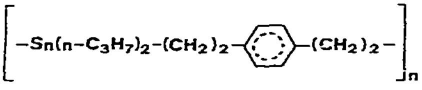
II



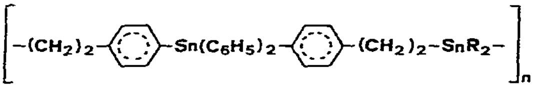
III

$[-Sn(n-C_4H_9)_2-OCH(CCl_3)O-]_n$

IV



V



VI $R=C_6H_5$ and $n-C_3H_7$, alternately

Compounds V and VI [5] were also studied by conventional Mössbauer spectroscopy to permit a more complete characterization of the series. The results obtained are reported and discussed below.

While this work was in progress, a paper appeared on the lattice dynamics of polymers obtained from di-*p*-tolyldi-*p*-styrenyltin(IV) and tetra-*p*-styrenyltin(IV) [7] (very probably multi-dimensional polymers), and these data are also discussed below in connection with our results.

## II. Experimental

Compounds I—VI were prepared by published procedures as follows: I and II, by radical-initiated homopolymerization of triorgano-*p*-styrenyltin [4,8]; III, V and VI, by polyaddition of $R_2SnH_2$ to 1,4-divinylbenzene or to diphenyl-*p*-styrenyltin [5]; IV, by addition of $(Bu_2^n SnO)_n$ to chloral [6].

Infrared spectra were measured with a Perkin-Elmer 457 spectrometer in the 4000—250 $cm^{-1}$ region (Nujol and hexachlorobutadiene mulls between CsI disks) and a Beckman IR 11 instrument in the 500—80 $cm^{-1}$ region (Nujol mulls, polyethylene windows).

The Mössbauer spectra were determined by using a R.T. $Ca\,^{119m}Sn\,O_3$ source, 10 mCi (R.C., Amersham), moving at constant acceleration in triangular or sawtooth waveform; the apparatus and techniques have been previously reported [9,10]. Temperature-dependent transmission spectra were measured with an AERE Harwell instrument (insert MVTIN 200, T controller CTC 200), and with an Elscint (Haifa) instrument (Ricor cryostat and related equipment [10]), $T$ values being constant within ±0.5° with respect to nominal values. Data reduction was effected through a least-squares program which corrects baseline geometric distortions prior to fitting with Lorentzian lineshapes [9,10]. The parameters of the Lorentzian fits, $\epsilon$ (the effect magnitude [11a]) and $\Gamma$ (mm $s^{-1}$, the full width at half height of the peaks [11a]), were em-

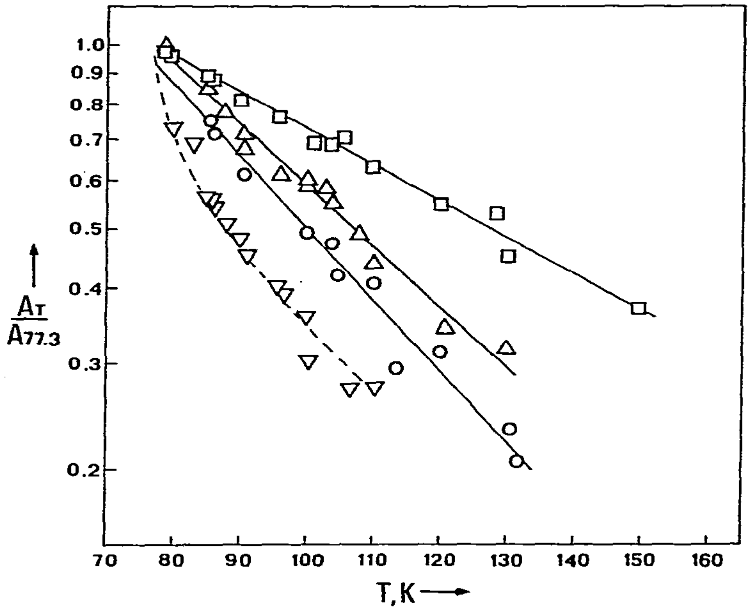


Fig. 1. The temperature-dependence of Lorentzian peak areas, $A$ ($T$), normalized to 77.3 K data points. Full lines are least squares fits.▽: compound I; absorber thicknesses in repeated runs were 0.80, 0.95 and 1.51 mg $^{119}$Sn/cm$^2$. △: II, thickness = 0.54, 0.89, 0.97 and 2.00. ○: III, thickness = 0.93 and 1.00; □: IV, thickness = 0.51, 1.11 and 2.32.

ployed to get areas $A = \pi/2 \times \epsilon \times \Gamma$, mm s$^{-1}$. The experimental functions $A$(T) are reported in Fig. 1.

## III. Characterization of the compounds

The structure assigned to I—III, V and VI were confirmed by infrared and conventional Mössbauer spectroscopy. All the vibrational bands expected to occur on the basis of the proposed [4,5,8] valence bond formulas and literature data [12] were easily identified in the 4000—80 cm$^{-1}$ region. The Mössbauer spectra of compounds I—III, V and VI are all one-line (i.e., quadrupole splitting [11a], $\Delta E$, is zero). The isomer shift [11a] values, $\delta$, are shown in Table 1 for I—III, the respective full widths at half height [11a], $\Gamma$, ranging between 0.8 and 1.0 mm s$^{-1}$. For V and VI we found $\delta$ = 1.35, $\Gamma$ = 1.06, and $\delta$ = 1.27, $\Gamma$ = 1.26, respectively, at liquid $N_2$ temperature. The pattern is fully consistent with the occurrence of tetrahedral-type sites $R_nSnR'_{4-n}$ [11b,13], where the symmetry of charge distribution around tin is nearly cubic. The larger $\Gamma$ value of VI may be due to the fact that, according to the formula, three different tin sites would occur in the repeating unit ($SnAr_4$, $SnAr_2Alk_2$ and $SnAlk_4$), and somewhat different $\delta$ values would be expected for them [13b].

The IR data and Mössbauer parameters of IV have been discussed previously [6].

## IV. Calculation of lattice dynamics functions, and discussion

The treatment of temperature-dependent data and the calculation of related functions were performed as described in detail in our previous paper [1], which

TABLE 1

PARAMETERS FROM TEMPERATURE-DEPENDENT MÖSSBAUER SPECTROSCOPY

| Compound [a] | d ln $A$/d$T$ [b] (deg$^{-1}$ × 10$^2$) | $f_a$ [c] | $\langle x^2 \rangle$ ($T$) [d] ranges (Å$^2$ × 10$^{-2}$) | $\vartheta_D$ [e] (K) | $\bar{\nu}_D$ [e] (cm$^{-1}$) | $M\,\vartheta_D^2$ [f] (a.m.u. deg$^2$ × 10$^{-6}$) | $\delta_{av}$ [g] (mm s$^{-1}$) |
|---|---|---|---|---|---|---|---|
| I | [h] | 0.061 | 1.90(77.3)–3.09(110.0) | 44.6 ± 0.3 | 31.0 ± 0.2 | 0.53 | 1.231 ± 0.005 |
| II | −2.301(0.991) | 0.169 | 1.22(77.3)–2.05(130.0) | 45.2 | 31.4 | 0.93 | 1.252 ± 0.005 |
| III | −2.721(0.988) | 0.122 | 1.44(77.3)–2.45(131.5) | 44.0 | 30.5 | 0.78 | 1.275 ± 0.004 |
| IV | −1.367(0.994) | 0.348 | 0.72(77.3)–1.40(149.5) | 62.7 | 43.6 | 1.56 | 1.304 ± 0.003 [i] |
| $Me_4Sn$ [l] | −2.758 [m] | 0.065 | [n] | 65.7 | 45.7 | 0.77 | 1.22 ± 0.02 |
| | | | | 58.9 [o] | 41.0 | | |
| $Ph_4Sn$ [l] | −1.659(0.994) | 0.325 | [n] | 54.8 | 38.1 | 1.28 | 1.225 ± 0.009 |

[a] See Introduction. [b] "$A$" is the total Lorentzian area under the resonant peaks. Slopes are least-squares values extracted from data points. Correlation coefficients are in parentheses. [c] The Debye-Waller-Mössbauer factor; the value for I is $f_a^{abs}$, others are $f_a^{rel}$ (see text). I—IV at 77.3 K; $R_4Sn$, 80 K. [d] The mean square displacements of the Mössbauer atom at limiting $T$ values, K. investigated. [e] Debye temperature, $\vartheta_D$, and cutoff frequency, $\bar{\nu}_D$, with standard error in case of I (data being derived from $f_a^{abs}$ values); parameters of II—IV are obtained from d ln $A$/d$T$ data (see text). The effective vibrating mass $M$ is taken as the formula weight. [f] Parameter of intermolecular force constant, see text. [g] Isomer shift with respect to R.T. Ca $SnO_3$, averages and standard errors in the $T$ ranges investigated. For I—III, and $R_4Sn$, $\Delta E = 0.00$. [h] The function ln $A$ ($T$) is non-linear (see Fig. 1 and text). [i] $\Delta E = 3.199 \pm 0.006$ mm s$^{-1}$ in the $T$ range explored. Ref. 6: $\delta = 1.31$, $\Delta E = 3.21$, at 77 K. [l] Data are taken from refs. 16, 18, 25, 26, or calculated in this work. [m] Calculated from d $\log_{10} A$/d$T = -1.198 \times 10^{-2}$, ref. 18. [n] See refs. 18 and 25. [o] Calculated from $f_a^{rel} = 0.065$.

reviews the main relevant literature. The Debye approximation has been assumed to hold, so that the absorber recoil-free fraction $f_a$ is expressed as [11a]:

$$f_a = \exp\left[\frac{-3E_\gamma^2 T}{Mc^2 K_B \vartheta_D^2}\right] \tag{1}$$

($E_\gamma$ = energy of the Mössbauer transition; $M$ = effective vibrating mass; $K_B$ = Boltzmann constant; $\vartheta_D$ = Debye temperature). It follows:

$$\frac{\mathrm{d}\ln A}{\mathrm{d}T} = \frac{\mathrm{d}\ln f_a}{\mathrm{d}T} = \frac{-3E_\gamma^2}{Mc^2 K_B \vartheta_D^2} \tag{2}$$

from which relative values of the recoil free fraction, $f_a^{el}$, are obtained, and employed to get estimates of the mean square displacements of the nucleus:

$$f_a = \exp[-K^2\langle x^2\rangle] \tag{3}$$

($K$ = wave vector of $\gamma$ rays). Debye temperature estimates are obtained from eq. 2, and subsequently values of cutoff frequencies are calculated by:

$$\nu_D = (K_B/h)\ \vartheta_D \tag{4}$$

Absolute recoil free fractions, $f_a^{abs}$, are needed when dealing with non-harmonic lattices, where ln $f_a$ ($T$) functions appear to be non-linear. These were calculated as usual [1], from spectra of $\beta$-tin which allow the computation of the source recoil-free fraction $f_s$, provided a previous estimate of the absorber thickness $t_i$, and consequently of the saturation function $L(t_i)$, is made; conversely, $L(t_i)$ for absorbers are obtained from the relationship between experimental absorber peak areas and $f_s$, which allows one to get $t_i$ and, finally, the desired function:

$$f_a^{abs} = \frac{t}{\frac{\pi}{2}\Gamma_{Nat}\sigma_0 N} = \frac{t_1 + t_2}{\frac{\pi}{2}\Gamma_{Nat}\sigma_0 N} \tag{5}$$

in the case of one-line and two-line spectra, respectively ($\Gamma_{Nat}$ = $^{119}$Sn natural linewidth, $\sigma_0$ = $^{119}$Sn resonant absorption cross section, $N$ = number of resonant atoms per cm$^2$). Data $f_a^{abs}(T)$ are finally employed to get related values $\langle x^2\rangle(T)$, $\vartheta_D$ ($T$) and $\nu_D$ ($T$) (see eqs. 1, 3, 4 and text).

The related calculations, including linear regression analysis, were carried out with a suitable computer program. In particular, $L$ ($t_i$) was calculated by assuming a parabolic function:

$$L_{(t_i)} = a\ t_i + b\ t_i^2 \tag{6}$$

i.e., limiting to the $t_i^2$ term the expansion in Lang's Equation [14]. Constants $a$ and $b$ were determined by fitting the quadratic eq. 6 with tabulated $L_{(t_i)}$ and $t_i$ values [14,15]. It was observed that in the $t$ range 0.0—0.6 (the upper value being seldom reached in our $T$-dependent Mössbauer studies), for $a$ = +0.994 and $b$ = —0.206, the error of $t$ is around 0.2% with respect to Lang's value [14]. Moreover, in the $t_i$ range 7.0—9.0, concerned for example with 0.1 mm $\beta$-tin ($t_i$ = 7.8), the error of $L(t_i)$ is 0.5% for $a$ = +0.568 and $b$ = —0.023.

By these procedures lattice dynamics parameters were derived from data of

Fig. 1, and these are reported in Table 1.

It appears from Fig. 1 that the function ln $A(T)$ is non-linear for compound I, at least from 77.3 to 85 K. Possible reason may be: i) anharmonicity in the motion of the Mössbauer atom, as assumed for $(CH_3)_4Sn$, $(C_6H_5CH_2)_4Sn$ and others [16]; ii) the occurrence of a phase transition; iii) area saturation effects [14]. We exclude ii) in view of the constancy of $\delta(T)$ (Table 1), and iii) because of the reasonable agreement of data points for absorbers with different thicknesses, cf. Fig. 1 (area saturation indeed occurs in this case for thicknesses larger than 2.3 mg $^{119}Sn/cm^2$). Motional anharmonicity may then be assumed for I. Its lattice parameters were obtained through calculations of $f_a^{abs}$ functions. For compounds II—IV the functions ln $A(T)$ are linear (Fig. 1). The calculations used the slopes d ln $A/dT$. (The results are expected to coincide with those from $f_a^{abs}$; for example, from the latter functions we found $\vartheta_D = 43.8 \pm 0.2$, $\bar{\nu}_D = 30.4 \pm 0.2$ and $M\vartheta^2 = 0.78$, for III). The effective vibrating mass [17] $M$ (eqs. 1 and 2) was taken as that of the polymer repeating units (Table 1).

The parameters obtained in this way may be directly compared with those in the literature in cases in which M is identical to the formula weight. A further possible choice is M = mass of tin, but this does not alter the interpretation of the present investigation (vide infra).

The lattice parameters in Table 1 are now discussed in the light of the existing systematics for molecular and polymeric ("Debye") solids; in connection with I—III, the data for $Me_4Sn$ and $Ph_4Sn$ are especially important since these molecules are essentially the monomeric counterparts of I—III.

A large temperature dependence of the recoil-free fraction, which generates large (negative) slopes d ln $A/dT$ [3,10,16,18—24], is generally associated with molecular solids; data for II and III match the $Me_4Sn$ value quite well, and are also consistent with the slopes for monomeric di-*p*-tolyldi-*p*-styrenyltin(IV) and tetra-*p*-styrenyltin(IV) [7]. In contrast, the polymers formed from the last two compounds show appreciably lower d ln $A/dT$ values [7], which is in line with the probable existence of polydimensional networks characterized by extensive crosslinking of the chains. The Debye-Walter-Mössbauer factors $f_a$ of I—III are smaller than the value of $Ph_4Sn$; $f_a^{abs}$ for I corresponds to $f_a^{el}$ of $Me_4Sn$. Mean square displacements of Sn, $\langle x^2 \rangle$ $(T)$, are well within the range typical of monomers and unidimensional polymers [25], the data points of I lying on a curve even deeper than for $Me_4Sn$ [25].

Debye temperatures $\vartheta_D$ (and consequently cutoff frequencies $\bar{\nu}_D$) are significantly lower for monomers than for coupled solids [2]: the parameters of I—III, consistently of the same order of magnitude, are definitely smaller in value than those of $R_4Sn$. Lastly, the parameters of intermolecular force constant [26], $M\vartheta_D^2$, of I—III are near to the $Me_4Sn$ value.

The magnitude of the effective vibrating mass, $M$, determines the values of the parameters $\vartheta_D$ and $\bar{\nu}_D$ only. Taking $M$ as the mass of tin, there is a correspondence between $\vartheta_D$ for I and $Me_4Sn$, while the values for II and III are consistently smaller than that for $Ph_4Sn$ (Table 2).

In conclusion, the magnitudes of all lattice dynamics parameters of I—III, whatever model is chosen for the analyses, appear to be typical of molecular solids, quite often corresponding to those of $Me_4Sn$. By contrast, the data for IV are largely indicative of an extended polymer, according to the preceding

TABLE 2

DEBYE TEMPERATURES, $\vartheta_D$, FOR EFFECTIVE VIBRATING MASSES CORRESPONDING TO THE ATOMIC MASS OF TIN

| Compound | I | II | III | IV | $Me_4Sn$ | $Ph_4Sn$ |
|---|---|---|---|---|---|---|
| $\vartheta_D$ (K) | 70.3 [a] | 88.3 [b] | 81.2 [b] | 114.6 [b] | 71.0 [c] | 113.5 [c] |

[a] From $f_a^{abs}$ at 77.3 K, see Table 1 and text. [b] From d ln $A/dT$, see Table 1 and text. [c] From ref. 2, at 70.0 K.

discussion and refs. already cited. In particular, the $\langle x^2 \rangle$ $(T)$ function of IV definitely lies in the bi- and tri-dimensional polymer zone [25], according to our previous proposal [6]. Compounds I—IV are all real polymers in the chemical sense, the mass of III being, for example, around 33.000 a.m.u. [5a]. The difference between solids I—III, and IV, lies in the fact that I—III are characterized by quite low interchain interactions [5a,27], while IV would consist of an extended network in which the polymeric alkoxide chains (catena-$\mu$-[2,2,2-trichloro-1,1-ethanediolato (2-)-*O*,*O'*]-di-n-butyltin(IV)) are cross-linked by three-coordinated oxygen, thereby giving rise to a two-dimensional structure [6]. Thus, in this field aslo, the lattice dynamics parameters give unequivocal indications of the extent of molecular intercoupling, as theoretically expected [2]. Lastle, the results presented here clearly demonstrate the usefulness of Mössbauer lattice dynamics studies for the characterization of organotin(IV) polymers, which in recent years have attracted considerable attention [28,29].

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