Applied Organometallic Chemistry (1987) 1 393–401
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0268-2605/87/01502393/$03.50

The fate of tributyltin toxicants in neoprene-based elastomeric antifouling coatings: ^{119m}Sn Mössbauer, ^{119}Sn NMR and chemical studies

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Received 28 June 1987 Accepted 24 July 1987

The fate of a series of tributyltin toxicants on incorporation into cured neoprene elastomers has been studied by ^{119m}Sn Mössbauer and ^{119}Sn NMR spectroscopic techniques, together with supporting chemical derivatization techniques. It is shown that all of the toxicants undergo chemical change during the curing process, being converted into tributyltin chloride, together with (in some cases) tributyltin stearate and a small amount of dibutyltin distearate. Possible interactions between the organotin agents and other components of the elastomer, e.g. carbon black filler, and cure accelerators such as tetramethylthiuram disulphide, have also been investigated.

Keywords: Tributyltin elastomers, curing process, chemical changes, ^{119m}Sn Mössbauer spectra, ^{119}Sn NMR spectra, carbon black, neoprene

INTRODUCTION

The need to protect ocean-going vessels, sonar buoys and other underwater installations from the effects of marine fouling has led to the development and widespread use of elastomeric coatings incorporating triorganotin toxicants. Typical of these are the neoprene-based coatings of the 'NOFOUL'® variety, originally incorporating both bis(tributyltin)oxide (TBTO) and sulphide (TBTS), which were developed in 1964 by the B.F. Goodrich Company. More recent formulations omit the use of TBTS since it is more expensive than TBTO and offers no additional antifouling activity.[1,2] There have been few studies of the fate of organotin toxicants on incorporation into elastomeric matrices, which in addition to the potentially reactive elastomer commonly contain many other reactive components, e.g. stearic acid, sulphur compounds and organic herbicides, with which the organotin toxicant could combine under the fabrication conditions (150°C, under pressure). It is important to establish the fate of the organotin toxicant as this may have a bearing on the biocidal activity and release rate of the toxicant, and also on its fate in the environment. In an early publication, it was suggested that, on incorporation of TBTO into a neoprene matrix, the organotin compound is involved in the curing process, and undergoes conversion to tributyltin chloride and tributyltin carboxylates. These are then released slowly from the elastomer via a diffusion–dissolution mechanism and provide the antifouling properties.[3] In a recent preliminary communication,[4] we reported brief details of our application of ^{119m}Sn Mössbauer and ^{119}Sn NMR spectroscopy to a study of the fate of a range of tributyltin toxicants on incorporation into neoprene. We showed that, irrespective of the nature of the tributyltin compound used in the original formulation, the major organotin component of the elastomer was tributyltin chloride. Following the appearance of this work, Blunden *et al.*[5] published a similar but more detailed study of the behaviour of TBTO in both neoprene and natural rubber systems. We now present a full account of our work in this area on neoprene elastomers which complements that presented by Blunden *et al.*

EXPERIMENTAL

Various tributyltin toxicants (Table 1) were in-

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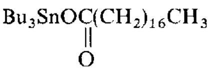
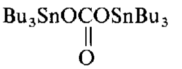
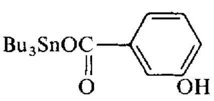
Table 1 Organotin biocides dispersed in neoprene elastomeric matrix at 2.6% w/w and subjected to curing at 150°C

Biocide	Abbreviation	Formula
bis(tributyltin) oxide	TBTO	$Bu_3SnOSnBu_3$
Tributyltin stearate	TBTSt	 $Bu_3SnO\underset{\underset{O}{\Vert}}{C}(CH_2)_{16}CH_3$
Tributyltin carbonate	TBTCO	 $Bu_3SnO\underset{\underset{O}{\Vert}}{C}OSnBu_3$
Tributyltin phosphate	TBTPO	$(Bu_3SnO)_3PO$
Tributyltin *m*-hydroxybenzoate	TBTPh(OH)	
Tributyltin chloride	TBTCl	Bu_3SnCl
Tributyltin fluoride	TBTF	Bu_3SnF

corporated into a neoprene-based antifouling rubber composition at *ca* 2.6% w/w, respectively, and the materials cured at 150°C under standard conditions. The resulting rubber sheets were examined initially by ^{119m}Sn Mössbauer spectroscopy, enabling investigation of the environment of the tin atom to be studied *in situ* without further chemical treatment. The Mössbauer spectra were recorded using a constant-acceleration spectrometer with a room-temperature, 15 mCi barium stannate source. Samples of elastomer, and appropriate reference compounds, were held in perspex discs and cooled to 80 K using a continuous-flow liquid-nitrogen cryostat with helium exchange gas. The Mössbauer parameters for the various samples are presented in Tables 2, 4 and 6; the quoted experimental errors of $\pm 0.02\ mm\ s^{-1}$ (for pure compounds) and $\pm 0.05\ mm\ s^{-1}$ (for the elastomers) in the measured values of isomer shift (δ), quadrupole splitting (ΔE_Q) and full width at half-height (Γ) take into account errors associated with non-linearities, calibration, zero-velocity determination and computer-fitting.

^{119}Sn NMR spectra were recorded for deuteriochloroform solutions using Bruker WP80SY and WH400 FT–NMR spectrometers under nuclear Overhauser suppressed conditions. Chemical shifts ($\delta^{119}Sn$) presented in Tables 3 and 5 are relative to tetramethyltin (Me_4Sn) and are accurate to ±0.1 ppm.

Pure samples of tetra-*n*-propyltin (Pr_4Sn), tri-*n*-butyl-*n*-propyltin (Bu_3SnPr), di-*n*-butyldi-*n*-propyltin (Bu_2SnPr_2) and *n*-butyltri-*n*-propyltin ($BuSnPr_3$) were prepared by a conventional Grignard procedure as described previously.[6] Purity was checked chromatographically and by ^{119}Sn NMR spectroscopy, whereby it was confirmed that the Grignard reaction conditions and subsequent isolation steps did not induce Sn–C bond cleavage.

Samples of the elastomers were subjected to Soxhlet extraction in dichloromethane for two days. After evaporation, an aliquot of the resultant oily residue was redissolved in deuteriochloroform for ^{119}Sn NMR analysis; the remainder was derivatized by treatment with *n*-propylmagnesium chloride, and the resulting mixture of stannanes subjected to gas-chromatographic analysis. The chromatographic conditions were as follows:

Instrument:	Pye Unicam Series 104
Detector:	Flame ionization
Column length:	10 ft (glass)
Packing:	10% SE-30 on 80–120-mesh Celite
Column temperature:	200°C (isothermal)
Detector temperature:	250°C
Carrier gas:	Nitrogen at $40\ cm^3\ min^{-1}$
Hydrogen flow rate:	$40\ cm^3\ min^{-1}$
Air pressure:	15 p.s.i. (72.4 bPa)

RESULTS AND DISCUSSION

Table 2 lists the Mössbauer parameters obtained from each elastomer sample and the corresponding pure organotin compounds. It is clear from the results in Table 2 that all seven tributyltins have suffered extensive structural modification upon incorporation into the coating matrix. The similarity of results for the elastomer samples further suggests that each organotin has been converted to the same species during the compounding/curing processes. The final Mössbauer parameters are identical, within experimental error, with those of a sample of tributyltin chloride (TBTCl) dispersed in the same elastomeric matrix. It is significant that the spectrum of the latter compound in the elastomer is also different from that of the pure material. On the basis of studies of the temperature dependence of the Mössbauer spectra of both the pure material and the related elastomer, we believe

Table 2 ^{119m}Sn Mössbauer data for tributyltin compounds in antifouling elastomers at 80 K

Toxicant	δ^a (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})
(i) In elastomers ($\sim$2.6% w/w):			
TBTO	1.40	2.82	1.09
TBTCl	1.41	2.78	1.05
TBTCO	1.43	2.84	0.97
TBTSt	1.44	2.82	0.99
TBTPO	1.39	2.82	1.08
TBTPh(OH)	1.39	2.72	0.99
TBTF	1.40	2.83	1.04
(ii) Pure materials:			
TBTO	1.25	1.53	1.11
TBTCl	1.52	3.42	1.06
TBTCO^b	1.38	2.70	1.08
	1.43	3.79	0.88
TBTSt	1.45	3.65	0.95
TBTPO^c	1.31	2.40	1.04
	1.33	3.53	1.04
TBTPh(OH)	1.43	3.18	1.12
TBTF	1.40	3.82	1.05

Errors: ±0.02 mm s^{-1} for pure compounds, ±0.05 mm s^{-1} for the elastomer samples.

[a] Isomer shifts were measured relative to BaSnO$_3$. [b] Data fitted as two unresolved doublets consistent with the presence of both four- and five-coordinate tin sites in this molecule.[7] [c] Data fitted as two unresolved doublets in accordance with the findings of Blunden *et al.*[8]

Table 3 ^{119}Sn NMR spectroscopic data for tributyltins extracted from marine antifouling rubbers

Toxicant	$\delta(^{119}$Sn) in elastomer (ppm)	$\delta(^{119}$Sn) pure compound (ppm) (as 10% w/v solutions in CDCl$_3$)
TBTO	−165.2 97.7 154.7	98.8
TBTCl	−164.2 98.1 155.4	155.7
TBTCO^a	−164.6 98.4 154.9	104.9
TBTSt	−164.6 97.1 154.6	102.7
TBTPO^a	154.9	100.6
TBTPh(OH)	154.9	119.2
TBTF^b	−164.2 97.9 155.2	—

Errors: ±0.1 ppm.

[a] Two resonances are observed in toluene solution, corresponding to the four- and five-coordinate sites of associated structures,[7,8] which appear to break down in chloroform. [b] This polymeric material was insufficiently soluble in any common organic solvent to yield a useful NMR spectrum.

that this difference is, in part, the consequence of the breakdown in the elastomer of intermolecular interactions present in the pure material at 80 K which give rise to a pseudopolymeric five-coordinate tin site.[9]

In order to confirm the presence of TBTCl in the elastomers, the cured materials were Soxhlet-extracted with dichloromethane. After evaporation of the extracts, the residues were dissolved in deuteriochloroform, and the ^{119}Sn NMR spectra recorded. In each case, a prominent signal was observed at $\delta = 155$ ppm identical with that for TBTCl. However, for all but two of the samples [TBTPO and TBTPh(OH)], signals were also observed at $\delta \simeq 98$ and -164 ppm (Table 3). Thus it is clear that species other than TBTCl are also present in the cured materials.

Blunden *et al.*,[5] on the basis of their similar study of a neoprene elastomer originally prepared from TBTO, have concluded that the signals in the above regions arise from the presence of tributyltin stearate and dibutyltin distearate, respectively, formed in the reactions of butyltin moieties with stearic acid, and we concur with this view. As Blunden *et al.*[5] have pointed out, a consequence of the similarity in Mössbauer parameters for TBTCl, TBTSt and dibutyltin distearate is that it is extremely difficult to identify the presence of the individual components of the mixture by Mössbauer spectroscopy alone. In our studies, it is of interest that the stearate derivatives are not formed on incorporation of tributyltin phosphate and tributyltin *m*-hydroxybenzoate into neoprene, these compounds appearing to be converted cleanly into the chloride. In all samples, the proportion of dibutyltin distearate is very small (*ca* 5–6%) as judged by the intensity of the signal at $\delta = -164$ ppm, and this has been confirmed in subsequent chemical derivatization studies in which the residue from the extract of the respective tile was treated with an excess of propylmagnesium chloride, and the resulting stannanes analysed by gas chromatography. It is noteworthy that under the elastomer curing conditions, tributyltin fluoride (in the pure state an insoluble and unreactive substance as a result of its polymeric nature) is also transformed to the related chloride and stearate, indicating the extremely aggressive environment prevailing in the elastomer during curing.

A major constituent of such elastomeric materials is carbon black, which is added as a reinforcing pigment and contributes substantially to the mass (*ca* 32% w/w). It is produced by the partial combustion of oil and coal tar and consists of aggregated spheres (mean particle size 60 nm) of partly graphitic elemental carbon. The other major constituents are oxygen and hydrogen, which are present as chemically bound functional groups (phenolic, ketonic and carboxylic) on the surfaces of individual particles.[10]

The surface activity that results from these functional groups is known to affect cure and degradation rates of polymer systems,[10,11] and other factors, such as particle size, strongly influence the release rates of organotins from elastomer matrices.[12] In view of this apparent reactivity, the following experiment was undertaken in order to assess the influence of carbon black on the Mössbauer parameters of several bioactive tri-*n*-butyltin derivatives. The organotins were added at 10% w/w to the carbon black, which was suspended in carbon tetrachloride. The materials were then reflux heated under nitrogen for about 30 min, after which the solvent was removed by evaporation under reduced pressure. Mössbauer spectra were recorded for each sample at 80 K and in some cases the broad experimental line widths and distorted line shapes justified modelling the data as a composite of unresolved quadrupole doublets.

In this procedure, a fitting matrix was constructed which made it possible to model several theoretical quadrupole doublets (Lorentzian line functions) to one data-set. The fitting matrix required a set of starting parameters (in number of channels) for each proposed doublet in terms of: isomer shift; half-splitting; and full width at half-maximum. Each doublet was then fitted independently by varying the starting parameters to achieve the minimum overall χ^2 value.

The result of this fitting process was to produce a composite of theoretical lines which represented an improvement in the quality of computer-fit for the complex data obtained in the organotin–carbon black Mössbauer experiments. In particular, the effect of modelling one, two and three unresolved quadrupole doublets to the raw TBTO–carbon black data can be appreciated from Fig. 1(a)–(c) in which a reduction of χ^2 is observed as more lines are accommodated. Data which have been processed in this way for the remaining systems yield the Mössbauer parameters which are bracketed together in Table 4. The individual experimental line widths, Γ_1, for the low-velocity line and Γ_2 for the high-velocity line, are given in order to illustrate the appreciable line-shape asymmetry in particular cases. Where multiple quadrupole doublets have been fitted to unresolved spectra, the line widths of pairs of lines have been constrained to be equal as is evident from the data in Table 4.

The results in Table 4 clearly indicate that dispersion into carbon black has a marked effect on the Mössbauer parameters of most of the organotins studied. The notable exceptions are TBTCl and TBTF. It is thought that these effects arise from the initial adsorption of the organotin onto the carbon black particles followed by chemical reactions with the surface-active groups which have been identified (these also include quinone and free-radical species).[11] Reactions involving TBTO, TBTCO and TBTS appear to have resulted in the formation of two or more distinct compounds, or the formation of single compounds in which there exist different tin site geometries.

The possibility of intercalation, in which an organotin moiety is accommodated between the two-dimensional crystalline planes of graphitic carbon, was also considered as an additional interaction mechanism to the surface processes. The photochemically induced intercalation of stannic chloride[13] and trimethyltin chloride[14] has been demonstrated using X-ray diffractometry to monitor the change in interplanar spacing that occurs between the graphite layers.

Unfortunately, experiments with the carbon black incorporated into the elastomers showed this material to be largely amorphous in structure and, therefore, unlikely to produce any meaningful data by X-ray techniques. The diffractogram, obtained over the range $2\theta = 4$–$122°$ and using copper K_α radiation ($\lambda_{\text{mean}} = 1.5418$ Å), was characterized by a broad distribution of reflections centred at $2\theta = 24.5°$. A similar experiment using synthetically produced graphite (BDH Chemicals Ltd) produced a series of narrow-line reflections, the most intense of which ($2\theta = 26.2°$) was associated with an inter-

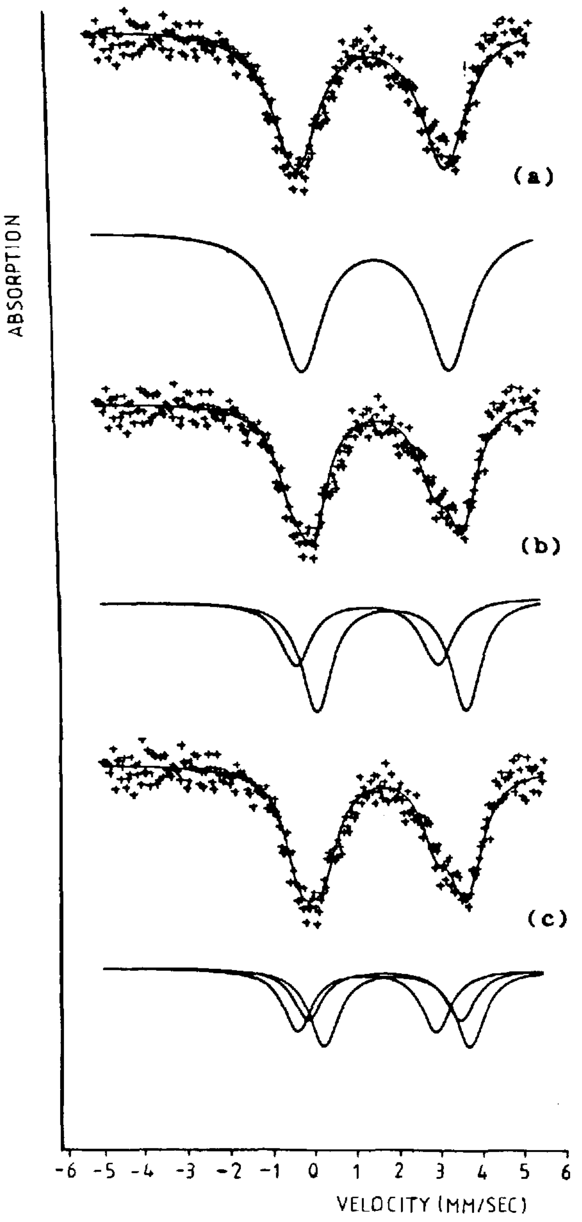
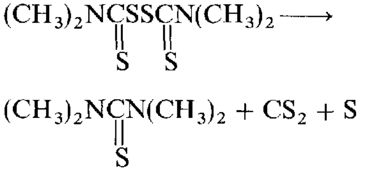


Figure 1 ^{119m}Sn Mössbauer spectra obtained for TBTO dispersed in carbon black: (a) one doublet; (b) two unresolved doublets; (c) three unresolved doublets.

layer spacing of 3.40 Å. Simple dispersion of TBTO and TBTCl at 10% w/w into synthetic graphite did not result in any modification of the reflection line energies or their relative intensities. Thus, intercalation into graphite under the conditions prevailing in these experiments was therefore ruled out as a competing process to the physical and chemisorptive processes already mentioned.

Also present in the mixture subjected to the curing process are organic sulphur compounds which function as accelerators during the curing stage. Typical of these is tetramethylthiuram disulphide, $(CH_3)_2NC(S)SSC(S)N(CH_3)_2$ (TMTD). It is clearly a possibility that the organotin biocides may react with this substance and thereby reduce the rate at which the elastomer is cured. It is known that the addition of TBTO to such elastomer systems results in a substantial reduction in the rate of cure, which may be a consequence either of a reduction in the rate of formation of Lewis acid catalysts such as zinc chloride (from zinc oxide present as a curative agent) or of a reaction with TMTD. In order to determine whether TBTO and TMTD could react together under the polymer curing conditions, both these materials were heated together in equimolar amounts at 150°C for 30 min. The resulting product consisted of a brown, non-viscous liquid and a brown solid. These phases (both offensively smelling) were separated and analysed by infrared, ^{119}Sn NMR and Mössbauer spectroscopy.

It was apparent from the fully decoupled ^{119}Sn NMR spectra that there are at least five non-equivalent tin sites distributed between the solid and liquid reaction products (Table 5). The absence of the characteristic asymmetric Sn—O—Sn stretching band at $\approx 770\ cm^{-1}$ in the infrared spectra suggested that all of the TBTO had been consumed in the reaction with TMTD. The presence of an infrared band at $360\ cm^{-1}$ in the liquid product is typical of the asymmetric Sn—S—Sn stretching mode, for which the normal range is 360–$386\ cm^{-1}$. The corresponding ^{119}Sn NMR spectrum shows a signal at $+83.7$ ppm which suggests that bis(tributyltin) sulphide (TBTS) is present in the liquid phase. The formation of this compound can be explained by examining some of the products formed in the thermal degradation of TMTD. Bateman *et al.*[15] suggest that the decomposition of TMTD under typical curing conditions proceeds according to the reaction [1]:



$$(CH_3)_2N\underset{\underset{S}{\|}}{C}SS\underset{\underset{S}{\|}}{C}N(CH_3)_2 \longrightarrow$$

$$(CH_3)_2N\underset{\underset{S}{\|}}{C}N(CH_3)_2 + CS_2 + S \qquad [1]$$

Table 4 ^{119m}Sn Mössbauer data for organotin compounds dispersed in carbon black (data are modelled as unresolved quadrupole doublets and values in parentheses represent pure compounds)

Organotin	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	χ^2
TBTO[a]	1.61 (1.25)	3.52 (1.53)	1.28 (1.12)	1.30 (1.06)	1111
TBTO[b]	1.24	3.40	0.89	0.89	949
	1.82	3.57	0.86	0.86	
TBTO[c]	1.20	3.32	0.82	0.82	936
	1.62	3.63	0.82	0.82	
	1.92	3.50	0.82	0.82	
TBTCO[a]	1.27	3.14	1.00	1.10	1180
TBTCO[b]	1.34 (1.43)	3.57 (3.79)	0.76 (0.88)	0.76 (0.88)	1069
	1.20 (1.39)	2.68 (2.70)	0.81 (0.98)	0.81 (0.98)	
TBTS[a,d]	1.49 (1.40)	3.50 (1.62)	1.04 (1.06)	1.28 (1.06)	1166
TBTS[b]	0.98	2.96	1.06	1.06	1054
	1.52	3.53	0.98	0.98	
TBTS[c]	0.98	2.96	1.06	1.06	1029
	1.46	3.97	0.84	0.84	
	1.48	3.34	0.76	0.76	
TBTF	1.28 (1.29)	3.83 (3.80)	0.94 (1.08)	0.94 (1.08)	—
TBTCl	1.49 (1.52)	3.34 (3.42)	0.99 (1.02)	0.98 (1.10)	—
TBTSt	1.19 (1.45)	2.37 (3.65)	0.90 (0.94)	0.88 (0.96)	—

Error: ± 0.05 mm s^{-1}.

[a] Data fitted as a single quadrupole doublet. [b] Data fitted as two unresolved quadrupole doublets. [c] Data fitted as three unresolved quadrupole doublets. [d] TBTS, Bis(tributyltin sulphide).

Table 5 ^{119}Sn NMR data for products obtained from the TBTO–TMTD reaction, and data for reference substances

Phase	δ^{119}Sn (ppm) (CDCl$_3$ solution, 10% w/v)
Liquid	83.7
	26.2
	−340.1
Solid	139.3
	−229.5
TBTS	84.0
Bu$_3$SnSC(S)N(CH$_3$)$_2$	27.3

Since TBTO is known to react readily with carbon disulphide[16] and with thioureas[17] to product TBTS, the presence of this compound, as indicated in both the infrared and ^{119}Sn NMR spectra, is not unexpected.

The intense ^{119}Sn NMR resonance at +26.2 ppm in the liquid TBTO–TMTD product was attributed to the presence of tributyltin dimethyldithiocarbamate, Bu$_3$SnSC(S)N(CH$_3$)$_2$, and this was confirmed by preparing an authentic sample of this compound according to the method of Srivastava and Rastogi.[18]

The yellow oil obtained by mixing together equimolar quantities of tributyltin chloride and sodium dimethyldithiocarbamate dihydrate in ethanol gave rise to a single resonance in the fully decoupled ^{119}Sn NMR spectrum at +27.3 ppm which is consistent with a four-coordinate geometry about the tin atom.[19] The Mössbauer parameters of this compound were $\delta = 1.43$ mm s^{-1} and $\Delta E_Q = 2.24$ mm s^{-1}, both in good agreement within experimental error with those quoted by Hill and Smith,[20] $\delta = 1.36$ mm s^{-1} and $\Delta E_Q = 2.23$ mm s^{-1}.

As yet, it has not been possible to identify the compounds responsible for the signal at 139.3 ppm and also for the high field resonances at −340.1 ppm and −229.5 ppm in the liquid and solid phases, respectively. However, such

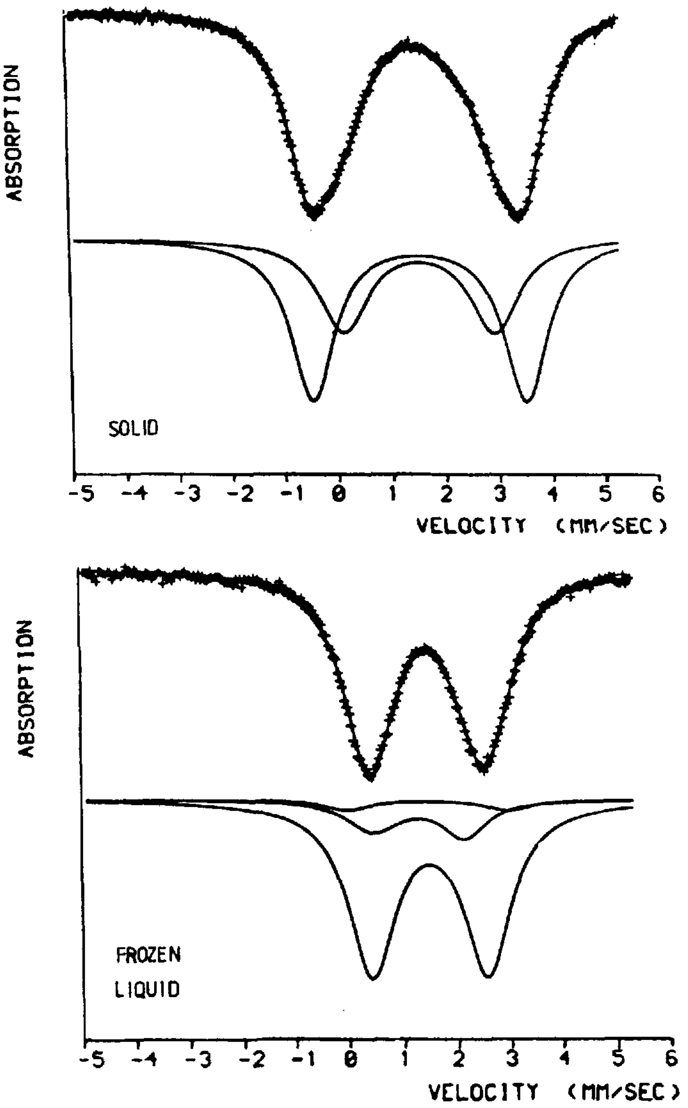


Figure 2 ^{119m}Sn Mössbauer spectra obtained from the solid and frozen liquid residues from the TBTO–TMTD reaction.

large upfield shifts are typical of those observed for dialkyltin bis(dialkyldithiocarbamate) species[21] in which the tin atom is probably hexacoordinate.[22] Since debutylation under the polymer curing conditions was evident in the chromatographic studies reported above, the possible formation of dibutyltin bis(dimethyldithiocarbamate) cannot be ruled out.

The Mössbauer data for the solid and frozen liquid products were best computer-fitted as two and three unresolved quadrupole doublets respectively (Fig. 2). The fitted parameters are given in Table 6.

According to the ρ-values given in Table 6, the solid residue contains tin atoms in both four- and five- (or six-)coordinate geometries.[23] The isomer shift and quadrupole splitting are typical of those exhibited by dialkyltin bis(dithiocarbamate) complexes in which the tin atom exists in a *trans* octahedral geometry. Reference to some of the data presented by Fitzsimmons[22] for analogous dibutyltin compounds supports the proposed

Table 6 ^{119m}Sn Mössbauer parameters obtained from the solid and frozen liquid products of the TBTO–TMTD reaction, and data for reference substances

Absorber	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})	ρ^a	Relative area
Solid residue	1.65	3.86	0.96	2.34	61
	1.66	2.72	1.09	1.64	39
Frozen liquid residue	1.61	2.08	1.02	1.29	79
	1.43	1.63	1.06	1.13	16
	1.59	2.92	0.99	1.84	5
$(Bu_3Sn)_2S$	1.40	1.62	1.06	1.15	
$Bu_3SnSC(S)NMe_2$^{b}	1.36	2.23		1.64	
$Bu_2Sn[SC(S)NPh_2]_2$^{c}	1.72	3.21		1.86	
$Bu_2Sn[SC(S)N(CH_2Ph)_2]_2$^{c}	1.69	3.38		2.00	
$Bu_2Sn[SC(S)N(CH_2)_4]_2$^{c}	1.53	3.06		2.00	

Errors: ±0.02 mm s^1 on δ, ΔE_Q and Γ; ±0.005 on ρ; ±5% on relative area.
$^a\rho = \Delta E_Q/\delta$ (Ref. 23). ^{b}Ref. 20. ^{c}Ref. 22.

formation of dibutyltin bis(dimethyldithiocarbamate).

The ρ-values calculated for the liquid residue components are indicative of four-coordinate moieties and are consistent with the proposed formation of tributyltin dimethyldithiocarbamate [$Bu_3SnSC(S)N(CH_3)_2$] and TBTS. The ρ-value for the third tin component, however, is at variance with the structural implications of the high-field ^{119}Sn NMR resonance at −340.1 ppm which is more typical of a five- or six-coordinate geometry.[21]

CONCLUSION

It is clear that the fate of organotin biocides of the type R_3SnX in a typical neoprene coating is subject to a variety of influences and this study has demonstrated that the reactive medium provided by a typical antifouling coating formulation leads to extensive chemical and structural modifications of the incorporated organotin biocides.

We have also carried out a similar study of the fate of a series of triphenyltin biocides on incorporation into neoprene. A preliminary account of this work has been published,[24] and the full paper is now in preparation. The significant finding in the latter is that triphenyltin biocides undergo much more drastic degradation compared with the related tributyltin systems on incorporation into neoprene elastomers, with the formation of predominantly monophenyltin species, together with smaller amounts of diphenyltin and inorganic tin(IV) species.

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