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SHORT PAPER

The degradation of triphenyltin biocides in neoprene-based elastomeric marine antifouling coatings: ^{119m}Sn Mössbauer and chemical speciation studies

David W Allen,*† John S Brooks‡ and Stephen Bailey‡

Departments of †Chemistry and ‡Applied Physics, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, UK

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The fate of a series of triphenyltin biocides on incorporation into neoprene elastomers has been studied by ^{119m}Sn Mössbauer spectroscopy, together with supporting chemical derivatization techniques. It is shown that triphenyltin compounds undergo drastic degradation on incorporation into neoprene, suffering cleavage of phenyl–tin bonds to give a mixture of products in which all stages of dephenylation are present, including stannic chloride. This degradation occurs not only in elastomers cured at 150°C, but also in room temperature solvent-cast samples.

Keywords: Triphenyltin, neoprene, elastomer, Mössbauer, degradation

INTRODUCTION

In a recent paper,[1] we have reported a study of the fate of various tributyltin toxicants on incorporation into cured neoprene marine antifouling elastomers of the 'Noufoul' variety, originally developed in 1964 by the B.F. Goodrich Company. By the use of ^{119m}Sn Mössbauer and ^{119}Sn NMR spectroscopic techniques, we showed that the tributyltin toxicants underwent 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, were also investigated. We now report a similar investigation of the fate of a range of triphenyltin toxicants, known to be active biocides,[2] on incorporation into neoprene elastomers. A preliminary account of this work has already been published.[3]

EXPERIMENTAL

Various triphenyltin toxicants, bis(triphenyltin) oxide (TPTO), triphenyltin acetate (TPTAc), triphenyltin chloride (TPTCl), and triphenyltin fluoride (TPTF), were incorporated into a neoprene-based antifouling rubber composition, each at *ca* 2.5% w/w, 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 as described in our earlier paper.[1]

Pure samples of tetra-*n*-propyltin (Pr_4Sn), phenyl-tri-n-propyltin ($PhSnPr_3$), diphenyldi-n-propyltin (Ph_2SnPr_2), and triphenyl-n-propyltin (Ph_3SnPr) were prepared by a conventional Grignard procedure from tin(IV) chloride or the appropriate phenyltin chloride and an excess of n-propylmagnesium chloride in ether. Purity was checked by GC under the conditions listed below (Table 1). Samples of the elastomers (4–5g) originally containing triphenyltin toxicants were chopped into small pieces and added to a solution of n-propylmagnesium chloride in diethyl ether. The

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*Author to whom correspondence should be addressed.

Table 1 Gas chromatography conditions

Instrument: Perkin–Elmer 8310B gas chromatograph
Detector: Flame ionization (FID), with H_2 at 16 psi (110 kPa) and air at 20 psi (138 kPa)
Column dimensions: 1.82 m × 0.003 m, stainless steel
Packing: 3% OV-1 on Chromosorb WHP 80/100 mesh
Carrier gas: N_2 at 35 cm^3 min^{-1}
Injector temperature: 350°C
Detector temperature: 350°C
Temperature programming conditions:

	Stage		
	(1)	(2)	(3)
Oven temperature (°C)	200	230	300
Isothermal time (min)	1.2	1.2	1.0
Ramp rate (°C min^{-1})	20	20	—

mixture was then heated under reflux in a nitrogen atmosphere for about 3 h, after which the excess Grignard reagent was hydrolysed with dilute sulphuric acid. The ether layer was separated, dried over anhydrous sodium sulphate and reduced in volume prior to GC analysis. Details of conditions for the GC analysis are given in Table 1.

This procedure was also carried out on the authentic triphenyltin compounds, Ph_3SnX (X = Cl, Ac or $OSnPh_3$), and also on Ph_nSnCl_{n-4} (n = 1 or 2), in order to demonstrate that no dephenylation was induced by the above analytical method.

A range of phenyltin compounds (Ph_3SnF, Ph_3SnCl, Ph_2SnCl_2, $PhSnCl_3$, Ph_3SnF, $Ph_3SnOSnPh_3$) and $SnCl_4$ were also dispersed in neoprene at *ca* 2.5% by weight by evaporation of a dichloromethane solution of neoprene and the respective tin compound. The ^{119m}Sn Mössbauer spectrum of each film was recorded, and the film then subjected to the above chemical derivatization procedure prior to GC analysis of the resulting n-propylstannanes.

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

Toxicant	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})	Relative area ± 5%
Pure compounds[a]				
TPTAc	1.30	3.35	1.01	100
TPTCl	1.33	2.56	0.97	100
TPTF	1.29	3.69	0.94	100
TPTO	1.13	1.42	0.99	100
In elastomers[b]				
TPTAc	0.09	0.00	1.42	76
	0.85	2.48	0.98	24
TPTCl	0.08	0.00	1.50	71
	0.83	2.44	1.04	29
TPTF	0.08	0.00	1.48	81
	0.77	2.38	0.92	19
TPTO	0.08	0.00	1.50	71
	0.83	2.42	1.04	29

[a] Error = ±0.02 mm s^{-1}. [b] Two-component fit, error = ±0.05 mm s^{-1} for each component

RESULTS AND DISCUSSION

The Mössbauer data (Table 2) for the pure triphenyltin compounds studied were found to be identical with literature values,[4] each spectrum appearing as a symmetrical quadrupole-split doublet. In contrast, the spectrum of each elastomer sample is markedly different from that of the appropriate pure substance, and the spectra of all of the elastomer samples are identical. Illustrative spectra of pure bis(triphenyltin) oxide (TPTO) and an elastomer incorporating this substance are presented in Fig. 1. Each elastomer spectrum is

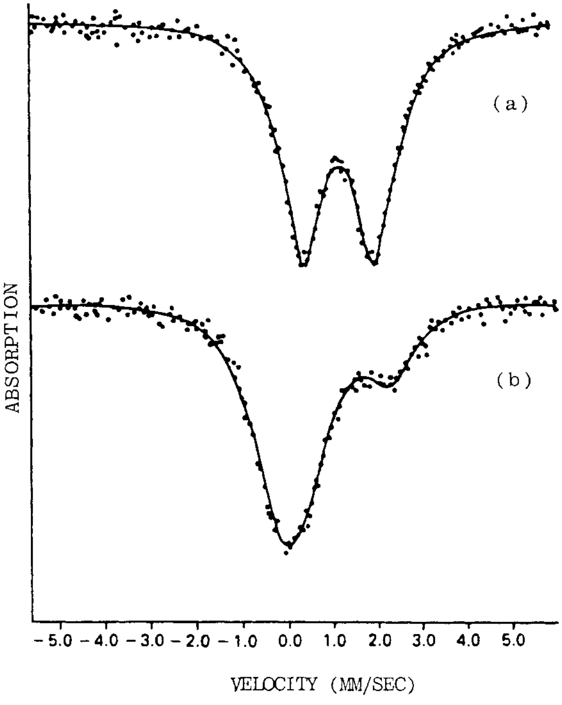

Figure 1 ^{119m}Sn Mössbauer spectra of (a) pure $(Ph_3Sn)_2O$ and (b) $(Ph_3Sn)_2O$ (2.6% w/w) in a cured elastomer.

dominated by an intense broad absorption at *ca* zero velocity, with a smaller, positive velocity contribution at *ca* 2.25 mm s^{-1}, and clearly is a complex unresolved composite representing the superimposed spectra of a number of degradation products. The isomer shifts and quadrupole splittings listed in Table 2 for the elastomer samples are those arising from a simple two-component fit to the observed data.

The drastic changes in the Mössbauer spectra indicate that a substantial proportion of the starting material has been converted into an unresolved range of degradation products, most probably various chlorotin(IV) species arising from the progressive dephenylation of the triphenyltin substrate, followed by possible complexation with hydrogen chloride in the polymer matrix.

In view of the uncertainty about the precise nature of the tin species present, and the above implication of severe degradation of the toxicant during the compounding/curing processes, ancillary techniques have been applied to the problem of identification. Prolonged Soxhlet extraction of the elastomers with dichloromethane gave extracts in which the presence of tin compounds was not detectable by Fourier transform (FT) ^{119}Sn NMR spectroscopy, indicating their possible binding to the polymer matrix. Accordingly, two elastomer samples derived from triphenyltin chloride and bis(triphenyltin) oxide were heated under reflux with an excess of n-propylmagnesium chloride in an attempt to convert all chlorotin species into tetraorganotins which would then be amenable to extraction and subsequent GC analysis. This technique has previously been used for tin speciation in studies of the fate of tributyltin toxicants in neoprene,[1] and also in the study of the degradation of organotin stabilizers in γ-irradiated PVC.[5]

The final extracts from these reactions revealed the presence of phenyltripropyltin (as the major component) with smaller amounts of tetrapropyltin and still smaller amounts of the diphenyl and triphenyltin derivatives. This result supports the above suggestion of drastic degradation of the triphenyltin compounds in a series of protodestannylation steps resulting, ultimately, in the formation of stannic chloride (probably as an adduct with hydrogen chloride). All stages of dephenylation are apparent on the chromatograms, clearly indicating the extensive degradation that has taken place. This is in marked contrast with the behaviour of the related tributyltin toxicants in which the tributyltin moiety survives the compounding/curing processes to a great extent, only traces of dibutyltin compounds being detectable by ^{119}Sn NMR spectroscopy and by application of the above Grignard alkylation procedure to the elastomers containing these materials.[1]

In order to investigate the effect of varying conditions on the nature of the reaction between triphenyltin compounds and neoprene, we have studied the effects of dispersing such compounds in the base polymer at room temperature. A solvent-casting technique was used in which a solution of neoprene and the respective triphenyltin compound [triphenyltin fluoride, triphenyltin chloride, and bis(triphenyltin) oxide] in dichloromethane was allowed to evaporate to form a

Table 3 ^{119m}Sn Mössbauer data from solvent-cast neoprene films containing triphenyltin compounds at 2.5% by wt[a]

Organotin	δ (± 0.05 mm s^{-1})	ΔE_Q (± 0.05 mm s^{-1})	Γ (± 0.5 mm s^{-1})	Relative area ± 5%
Ph_3SnF[b]	0.76 (1.29)	1.86 (3.69)	1.01	32
	1.30	3.58	0.94	68
$(Ph_3Sn)_2O$[c]	0.48 (1.13)	2.16 (1.42)	1.04	30
	0.86	2.28	0.88	29
	1.35	2.62	0.98	41
Ph_3SnCl[c]	0.59 (1.33)	1.90 (2.56)	0.88	34
	0.87	2.10	0.88	30
	1.42	2.52	0.82	36
Ph_2SnCl_2[b]	0.34 (1.37)	0.00 (2.86)	1.26	47
	0.84	1.86	1.02	53
$PhSnCl_3$	0.37 (1.10)	0.00 (1.75)	1.28	100
$SnCl_4$	0.43 (0.82)	0.00 (0.00)	1.28	100

[a] Parameters for the pure compounds are given in parentheses. [b] Data fitted as two unresolved doublets. [c] Data fitted as three unresolved doublets.

thin film of the polymer. These polymer films were investigated by Mössbauer spectroscopy, and then subjected to tin speciation by the Grignard procedure described above. For comparison, similar polymer films were prepared using diphenyltin dichloride, phenyltin trichloride and stannic chloride.

The Mössbauer spectra (Table 3, Fig. 2) of the triphenyltin compounds in the neoprene films indicate that significant chemical change has occurred, even under the mild conditions of the solvent-casting process. Of the three triphenyltin systems studied, the fluoride appears to be least affected, although there is evidence of a second component in the spectrum which probably corresponds to a diphenyltin dihalide. The spectra of the samples derived from bis(triphenyltin) oxide and triphenyltin chloride indicate that these compounds have suffered the same fate on dispersion in neoprene. The spectrum obtained from diphenyltin dichloride in neoprene can be superimposed upon the inner doublet evident in the spectra of the above compounds, and provides indirect evidence for the presence of diphenyltin dichloride as a degradation product. However, it is clear from the spectrum of diphenyltin dichloride dispersed in neoprene that this compound also suffers degradation.

Incorporation of phenyltin trichloride and stannic chloride, respectively, into neoprene, was accompanied by a marked colour change in the polymer from amber–yellow to red–brown, indicating an increase in the degree of conjugation in the polymer. In addition, it was noted that of all the organotin–neoprene systems that were studied, only the films derived from phenyltin trichloride and stannic chloride were insoluble in dichloromethane, implying the formation of extensive cross-linkages. The Mössbauer spectra of the latter films were also identical, exhibiting a broad singlet with an isomer shift of *ca* 0.4 mm s^{-1}.

In order to provide more insight into the various tin compounds present within each solvent-cast polymer film, the respective films were treated with an excess of n-propylmagnesium bromide, and the resulting stannanes analysed by GC as described above for the cured elastomer samples. Each of the triphenyltin compounds studied under these conditions was found to undergo progressive dephenylation to give a mixture of diphenyl-, and monophenyl-tin compounds, together with stannic chloride, the relative amounts varying from one compound to another. In the case of bis(triphenyltin) oxide, the principal product is the monophenyltin halide, whereas for triphenyltin chloride, the

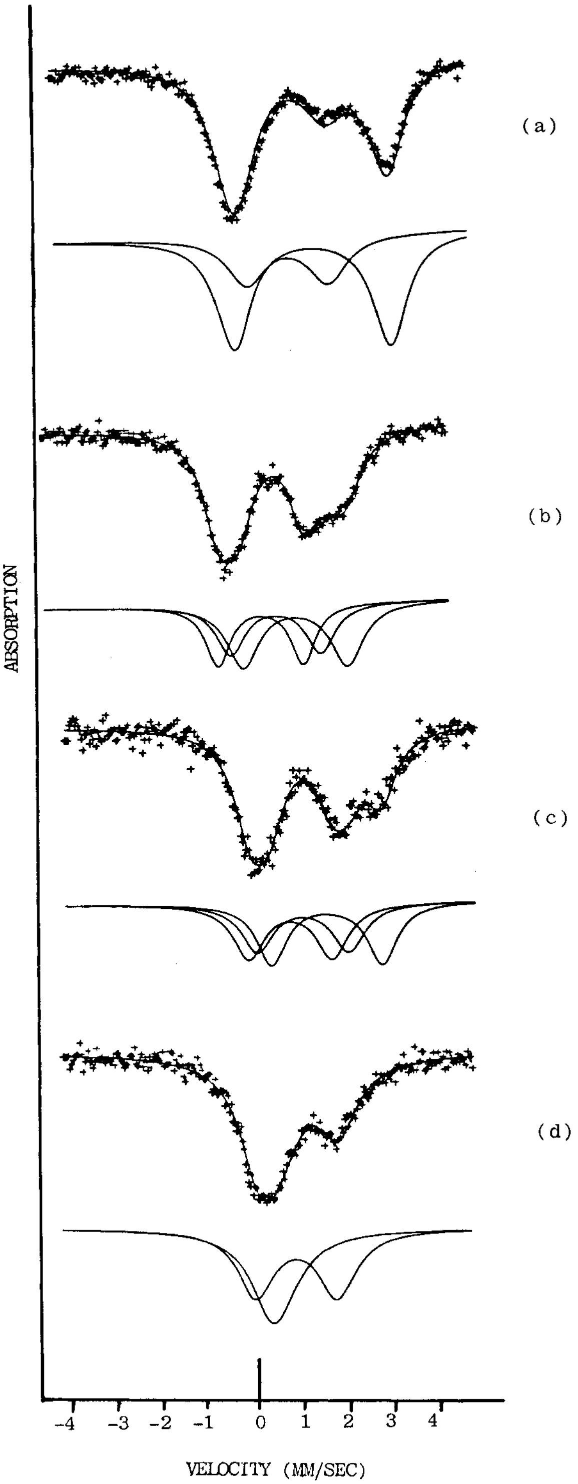

Figure 2 ^{119m}Sn Mössbauer spectra obtained from solvent-cast neoprene films containing (a) Ph_3SnF, (b) $(Ph_3Sn)_2O$, (c) Ph_3SnCl, and (d) Ph_2SnCl_2.

predominant degradation product is stannic chloride. All stages of dearylation were present in the sample derived from triphenyltin fluoride. Similarly, diphenyltin dichloride and monophenyltin trichloride also suffered dephenylation, to give stannic chloride as the principal product.

In view of the rather drastic nature of the degradation process undergone by triphenyltin toxicants which results, ultimately, in the formation of inorganic tin(IV) compounds, there would seem to be little point in promoting the use of triphenyltin-based toxicants in neoprene elastomeric coatings. The related tributyltin compounds would appear to be the better choice based on the above studies.

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