Synthesis and properties of organotin epoxy polymers from tri-n-butyltin esters of ω-amino acids

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Structure–property relationships in a series of thermoset organotin polymers have been investigated. The tri-n-butyltin esters of glycine, 4-aminobutanoic, 6-aminohexanoic, and 11-aminoundecanoic acids were synthesized and reacted with diepoxides to prepare prepolymers carrying epoxide end groups. The prepolymers were crosslinked by diethylenetriamine or metaphenylenediamine. Similar epoxy network polymers were prepared directly from the tributyltin ester of 3,5-diaminobenzoic acid which was also synthesized. The strength, moduli, toughness, glass transition and dynamic mechanical response of the polymers were investigated, and correlated with structural changes introduced in the network. The results establish the utility of the adopted synthesis schemes in exercising considerable control over the bulk polymer properties, and consequently, in modifying the controlled release of organotin groups from the crosslinked network.

INTRODUCTION

Triorganotin polymers are being studied now with increasing interest in their potential for controlled release of the toxic organotin groups[1-3]. Organotins are compatible with many polymer types, and many derivatives can be chemically linked to polymer backbones. Their high selectivity combined with high toxicity to fungi, bacteria and fouling organisms and low toxicity to mammals, has made triorganotin compounds ecologically desirable in such applications as fungicides, molluscicides, or antifouling coatings[2]. In addition, they degrade to non-toxic inorganic oxides in the natural environment[4], and do not cause corrosion problems when added to paints as some other biocidal additives such as cuprous oxide do.

Trialkyltin compounds, and in particular trialkyltin derivatives such as bis(tri-n-butyltin) oxide (TBTO) have been studied extensively during the last decade as replacements for salts of copper, arsenic and mercury which, though effective as biocides, suffer from short service lives because of their high leachability from the matrix in which they are contained[5-8]. Extended life times could be achieved through incorporation of increased amounts of these salts in the protective coatings and devices but only at high cost to the environment due to excessive release of the biocide and the nonselectivity of these salts[7].

A significant improvement in service life was achieved with dispersions of TBTO in elastomers, such as natural rubber, polychloroprene and polyisobutylene which were saturated with TBTO and vulcanized[5,9]. However, due to the high cost of the process and lengthy application times, the method is more suitable for protective coating of small boats or sonar domes than for prevention of marine fouling of ships hulls. Therefore, there has been an emphasis on the controlled release of tributyltin (TBT) derivatives through chemical bonding of the biocide to polymer matrices as triorganotin esters and through matrix modification[1,3,10-12].

While initial experiments with polymers of trialkyltin acrylates and methacrylates revealed poor film forming properties[2,13], the copolymerization of the organotin monomers has resulted in better mechanical properties[3,14,15]. Earlier work in our laboratories showed that partial TBT esters of maleic anhydride copolymers can be crosslinked with cycloaliphatic epoxides at elevated temperatures (150°C) to give a controlled release polymer with good adhesion and film forming properties[16]. The mechanical and biocidal properties of the polymer were modified by the degree of esterification, and variations in network structure and crosslink density. Further studies with thermoset organotin polymers have confirmed these early observations and emphasized the need to control the matrix flexibility and hydrophilicity in order to control the release of organotin from these crosslinked systems[17]. It was also established that tributyltin carboxylates exchange the TBT group very rapidly and that the active species likely to be released in an ocean environment is TBT chloride[18].

The present paper is part of our continuing and comprehensive investigation of fundamental interrelationships of synthesis, structure, mechanical behaviour and controlled release properties of organotin polymers[19,20]. This research shows that (1) the TBT moiety can be bound to an epoxy prepolymer utilizing TBT esters of ω-amino acids ($H_2N(CH_2)_nCOOSnBu_3$) where the length of the chain connecting the TBT group to the polymer backbone is controlled by varying the number of $-CH_2-$ units in the amino acid, and that (2) these epoxy prepolymers can be crosslinked with diethylenetriamine (DETA) or meta-phenylenediamine (MPDA) without hydrolysing the TBT ester. The manifestation of changes in the polymer structure in corresponding changes in the tensile, flexural, impact and dynamic mechanical proper-

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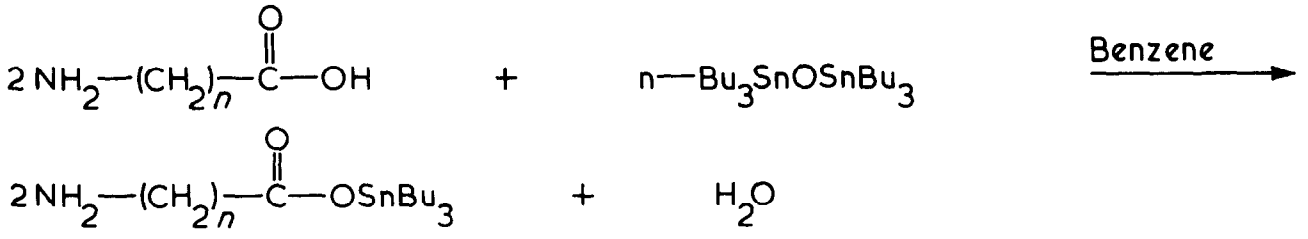
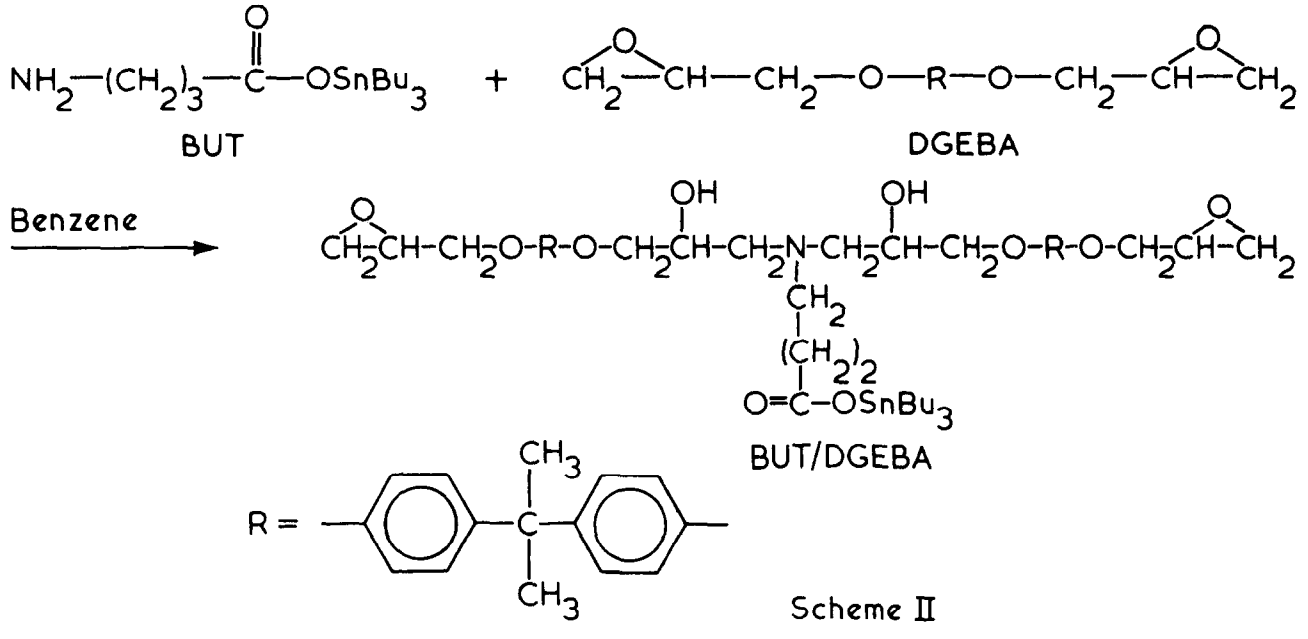


Scheme I



Scheme II

ties of the thermoset polymer was also investigated.

In forming the prepolymer, the TBT esters of ω-amino acids were prepared (Scheme I), reacted with diglycidyl ether of bisphenol A (DGEBA) according to Scheme II, and finally crosslinked with MPDA (Scheme III) or, similarly, with DETA. During this research, a new concept of attaching the organotin directly onto a polyfunctional curing agent was also developed and tested. The synthesis was proved feasible and these results are included in this paper.

EXPERIMENTAL

All chemicals, unless otherwise mentioned, were reagent grade. The petroleum ether used had a boiling range of 35–66 C. Tin was analysed by gravimetric determination of SnO_2[21]. Epoxy equivalents were determined by Durketaki's method[22] utilizing the $AgNO_3$ procedure. Infrared spectra were obtained using a Perkin–Elmer 621 grating infrared spectrophotometer and thermomechanical spectra from a Rheovibron model DDV II C at 35Hz with temperature varied from -150°C to 30° above T_g. Melting points were measured using a capillary in an oil bath or a Fisher apparatus and are uncorrected.

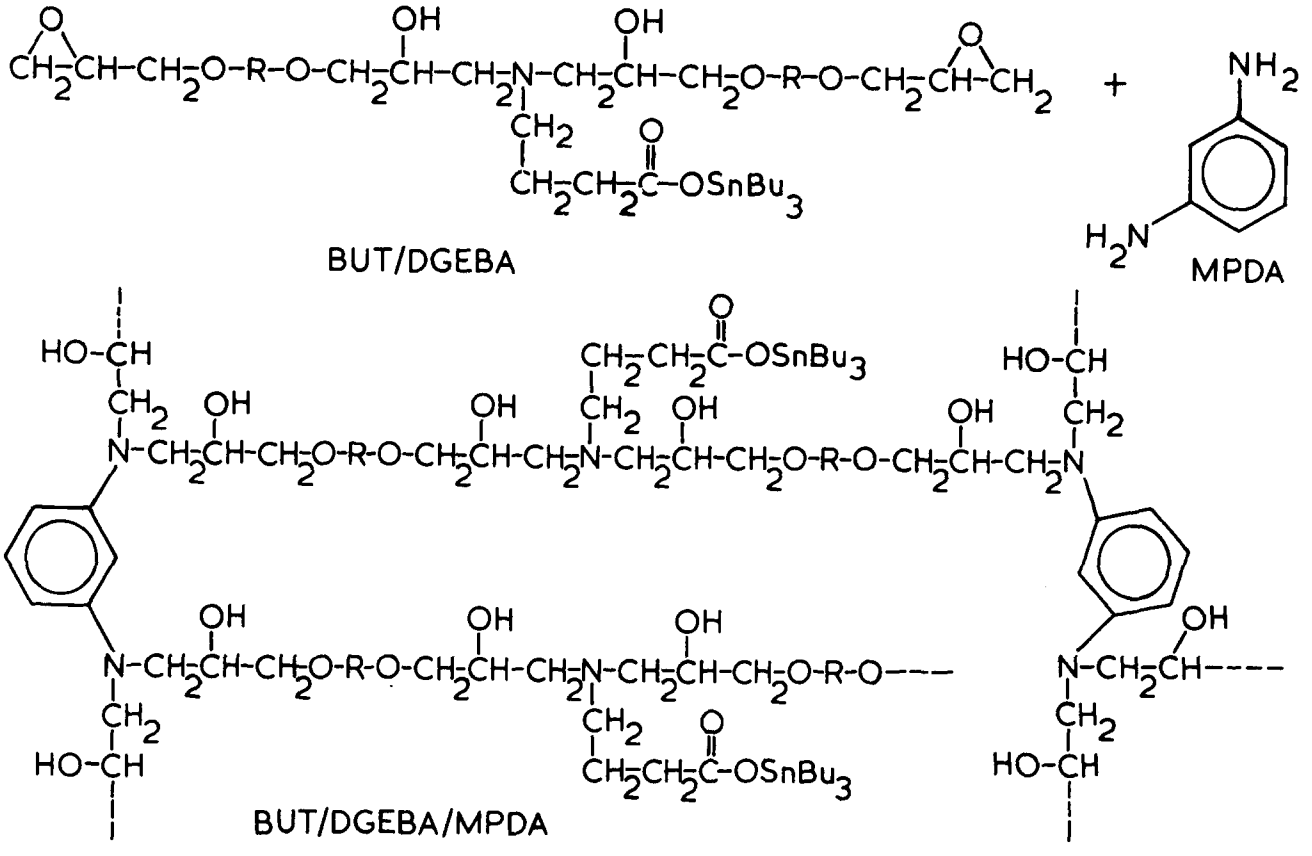
The specific preparations of TBT 4-aminobutanoate, its prepolymer, and the thermoset polymer are outlined below. All other amino carboxylates, prepolymers and test specimens were prepared in the same manner except as noted for TBT glycinate. The prepolymer was prepared using DGEBA (diglycidyl ether of bisphenol A, EPON 828, Shell Chemical Company).

Preparation of TBT 4-aminobutanoate

A two-necked, 500 ml round-bottomed flask was fitted with a magnetic stirrer, reflux condenser, Dean–Stark trap, and a dropping funnel. 2.06 g (0.02 mol) of 4-aminobutanoic acid and 200 ml of benzene were placed in the flask, and brought to reflux under nitrogen. After refluxing briefly, 6.0 g (0.01 mol) of freshly vacuum distilled TBTO was added from the dropping funnel over 5–10 min. Refluxing was continued until water ceased to be evolved. (In most cases, all the amino acid was dissolved at this point). Following partial removal of solvent by distillation, the solution was filtered if necessary, and placed in a rotary evaporator to remove the remaining solvent. The flask was sealed with a septum and the resulting material was washed several times with dry cold petroleum ether. Recrystallization from petroleum ether gave 6 g of white crystalline material with a melting point of 66–68°C. Dimethylformamide (5%) was used to catalyse the preparation of the TBT ester of glycine[23].

Preparation of epoxide prepolymer

30.9 g (0.30 equivalent) of 4-aminobutanoic acid and 89.3 g (0.30 equivalent) of TBTO were combined in 700 ml benzene and refluxed as above. Upon completion of the reaction, 200–300 ml of solvent was distilled from the flask and 471 g of EPON 828 was added. The residual solvent was then removed by rotary evaporator and in a vacuum oven (50°C overnight). Epoxide determination was done by Durketaki's procedure[22] of adding excess HBr in acetic acid, followed by titration with 0.1 N silver nitrate. The epoxide equivalent was 344 g/equivalent.



Scheme III

Preparation of castings for mechanical testing

450 g (1.30 equivalents) of the epoxy oligomer was warmed slightly (50–60°C) and combined with 26.9 g (1.30 equivalents) of freshly distilled DETA, poured into a steel mould and allowed to cure at room temperature. Castings measured 25 × 25 × 0.64 cm. Specimens for mechanical testing were cut and machined in accordance with ASTM D 638–71 for tensile (sample size was 12.7 cm with a 5 cm gauge length), ASTM D 790–71 for flexural (0.64 × 1.27 × 12.7 cm, single point load on a 10.16 cm span), and ASTM D 256–73 for impact testing (standard notched).

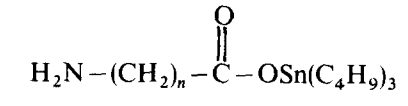
Preparation of castings for Rheovibron testing

Several grams of the mixture used to form the 25 × 25 cm castings were placed between two polished steel plates treated with release agent. Spacers (0.40 mm) were used to maintain uniform thickness. The polymer was cured in a press at 60 psi for the same time and temperature as the castings for other mechanical tests. Sample specimens 80 × 5 mm were cut and used for dynamic mechanical tests in the Rheovibron.

RESULTS AND DISCUSSION

TBT amino carboxylates

As noted in the synthesis scheme, the TBT moiety was joined to an epoxy matrix via ω-amino acids, the main variable structural parameter being the length of the chain between the ω-amino group and the tin carboxylate:



$n = 1,3,5,10$

ω-amino carboxylic ester

TBT esters of glycine ($n = 1$), 4-aminobutanoic ($n = 3$), 6-aminohexanoic ($n = 5$), and 11-aminoundecanoic ($n = 10$) acids were synthesized by Scheme I. Analytical samples of all esters were prepared to obtain the data summarized in *Table 1*. In cases where the compounds had been previously prepared in other laboratories (TBT glycinate and TBT aspartate) the melting point and i.r. spectrum were in good agreement.

TBT esters of amino acids have been used as protective groups for peptide synthesis. Frankel *et al.*[24] and Ho and Zuckerman[23] have characterized many compounds of this type. These esters are prepared by azeotropic removal of water and are purified by sublimation[23], vacuum distillation, or recrystallization from petroleum ether. Care must be exercised during purification to exclude water since the ester bond is labile and can be cleaved easily by a strong nucleophile or electrophile[24]. In addition, the esters decompose immediately when in contact with ethanol, benzyl alcohol, *m*-cresol, or benzoic acid, and react with acetic acid to give trialkyltin acetate. This sensitivity may be due to the coordination of the amino group[24]. The TBT esters are, however, stable to amines under anhydrous conditions.

Table 1 Analytical data on TBT esters of amino acids

TBT esters	Carbonyl i.r. band, (cm^{-1})	Elemental analysis				MP (°C)
		C	H	N	Sn	
Glycinate	1625	46.01 (46.16)*	8.72 (8.59)	3.89 (3.85)	32.22 (32.61)	129–131
4-amino butanoate	1610	49.22 (49.01)	8.89 (8.99)	3.76 (3.57)	28.72 (30.99)	66–68
6-amino hexanoate	1602	51.47 (51.45)	9.50 (9.35)	3.39 (3.33)	28.25 (28.27)	46–47
11-amino undecanoate	1612	56.15 (56.34)	10.21 (10.07)	2.86 (2.86)	24.22 (24.21)	<20
Aspartate (Amino-succinate)	1660	47.08 (47.29)	8.59 (8.36)	2.09 (1.59)	34.49 (33.38)	90–92
3,5-diamino benzoate	1600	50.45 (51.71)	7.94 (7.77)	7.64 (7.90)	26.30 (26.93)	43–46

* Numbers in parentheses are calculated

Table 2 Epoxy equivalents and pendant chain concentrations

Polymer	Epoxy equivalent of oligomer (g/eq)	Moles of pendant chains per gram of polymer
GLY/DGEBA/DETA	365	5.1×10^{-4}
BUT/DGEBA/DETA	344	4.9×10^{-4}
HEX/DGEBA/DETA	345	5.0×10^{-4}
UND/DGEBA/DETA	370	5.0×10^{-4}
GLY/DGEBA/MPDA	364	5.0×10^{-4}
BUT/DGEBA/MPDA	312	4.8×10^{-4}
HEX/DGEBA/MPDA	345	5.0×10^{-4}
UND/DGEBA/MPDA	370	5.0×10^{-4}

The abbreviations used in referring to the tin esters are GLY (TBT glycinate), BUT (TBT 4-aminobutanoate), HEX (TBT 6-aminohexanoate), UND (TBT 11-aminoundecanoate), ASP (TBT aminosuccinate, i.e., TBT aspartate) and DABA (TBT 3,5-diaminobenzoate).

With the exception of the TBT ester of glycine (which was prepared in 30–50% yields utilizing a dimethylformamide catalyst), the yields of all TBT ester preparations were quantitative. The esters used for the preparations of samples for testing were therefore not isolated prior to the reaction with DGEBA, which formed the prepolymer. The ester of glycine was isolated in order to separate it from the catalyst and by-products.

Prepolymers

In the preparation of the different prepolymers from the tin esters of amino acids and DGEBA, the amount of DGEBA used was adjusted to give approximately the same concentration of pendant groups per gram of the final cured polymer as calculated using the equation shown below. The results are listed in *Table 2*.

$$\frac{\text{Wt. Sn ester}}{MW\ \text{Sn ester}\,(\text{Wt. Sn ester} + \text{Wt. DGEBA})} \times \frac{\text{Wt. prepolymer}}{\text{Wt. prepolymer} + \text{Wt. curing agent}} = \frac{\text{Moles pendant}}{\text{Gram cured polymer}}$$

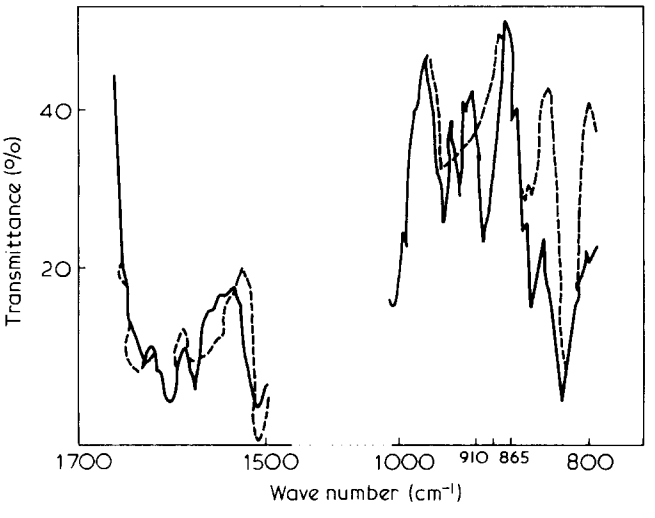


Figure 1 I.r. spectra of DGEBA–TBT 11-aminoundecanoate mixture after various curing times at 80°C: (——) 0 and (— — —) 23 h

The basic reaction and the resulting schematic structure of the prepolymer are shown in Scheme II. Scheme II does not take into account the presence of oligomers which exist in DGEBA (equivalent weight 190) or the slight homopolymerization which occurs during the preparation of the prepolymer. The experimentally determined epoxide equivalents of the prepolymers ranged from 312–370 g/equivalent (*Table 2*).

Epoxide curing reaction

Two experiments were carried out to show that the TBT group remained chemically bound to the network during polymerization Stoichiometric amounts of TBT 11-aminoundecanoate and DGEBA were mixed, and the C=O and  i.r. absorption peaks were monitored. The results (*Figure 1*) show that the carbonyl absorption was maintained while the epoxide absorptions at 910 and 860 cm^{-1} disappeared[25]. In a second experiment, the cured polymer was ground (−10, +40 mesh) and solvent extracted for 10 days with benzene. The tin content was analysed before and after extraction, and the results are tabulated (*Table 3*).

Table 3 Solvent extraction of crosslinked organotin polymers using dry benzene

Polymer	Initial %Sn	Final %Sn
GLY/DGEBA/DETA	5.97	3.58
BUT/DGEBA/DETA	5.37	4.24
HEX/DGEBA/DETA	5.65	4.02
GLY/DGEBA/MPDA	5.84	3.77
BUT/DGEBA/MPDA	5.40	4.82
HEX/DGEBA/MPDA	5.59	4.02
UND/DGEBA/MPDA	5.84	5.14

Table 4 Tensile moduli and strength of TBT-modified epoxy polymers

Polymer	Modulus MPa (psi)	Strength MPa (psi)
GLY/DGEBA/MPDA	3240 ± 220 (470 000 ± 32 000)	73.8 ± 8.0 (10 700 ± 1200)
BUT/DGEBA/MPDA	3800 ± 170 (551 000 ± 24 000)	86.9 ± 2.2 (12 600 ± 330)
HEX/DGEBA/MPDA	3050 ± 350 (443 000 ± 51 000)	60.9 ± 4.7 (8840 ± 680)
UND/DGEBA/MPDA	2830 ± 350 (410 000 ± 51 000)	57.7 ± 5.1 (8360 ± 740)
GLY/DGEBA/DETA	3270 ± 190 (475 000 ± 28 000)	28.3 ± 18 (4100 ± 2600)
BUT/DGEBA/DETA	3850 ± 71 (559 000 ± 10 000)	61.4 ± 3.35 (8900 ± 480)
HEX/DGEBA/DETA	2940 ± 320 (427 000 ± 47 000)	60.6 ± 2.9 (8780 ± 420)

From the weight fraction of extractables and the decrease in tin content, it can be calculated that the extract contains approximately 40% tin. Since this is the tin content of TBTO, it is surmised that only TBTO is extracted and that little unbound TBT ester or short chain segments were lost during extraction.

The loss of tin could arise in two ways: Infrared analysis of the oligomer showed a slight amount of organic ester formation as the material aged, indicating that some hydrolysis of the TBT ester occurred prior to complete curing. It is also possible that the large surface area of the ground polymer exposed a considerable amount of the polymer to atmospheric moisture prior to extraction which resulted in hydrolysis at the surface. The important consideration, however, is that TBT esters are not readily lost under anhydrous conditions.

Polymer properties

The prepolymers were crosslinked with either MPDA or DETA to give a clear casting as shown in Scheme III. The results of mechanical tests are tabulated in *Tables 4–8*.

The strength and modulus, both tensile (*Table 4*) and flexural (*Table 5*), showed the expected trends of increasing flexibility as the pendant chain was lengthened. This was particularly true for chains with $n=3$, 5, and 10. The DETA-cured system had lower modulus and strength than MPDA-cured samples. The samples containing the TBT ester of glycine, particularly when cured with DETA, did not have comparable strength, perhaps due to poor test specimens rather than to the polymer itself. This is indicated by the larger standard deviations for this system. It should be noted in comparison that the strength, modulus and toughness values for the polymer modified with TBT aspartate, which causes backbone modification similar to TBT glycinate, are significantly higher (*Table 8*).

Load-deflection curves as seen in *Figure 2* illustrate the trend for TBT-modified prepolymer cured with MPDA–A steady decrease in both modulus and strength was observed with increasing pendant length. The shapes of the curves also indicate a change in mode of failure; while A and B suffer brittle failure, C and D exhibit a yield point. This transition in the mode of failure and associated improvement in toughness as shown by the increased area under the curves (*Figure 2*), are further substantiated by higher impact strength (*Table 6*).

A similar family of load-deflection curves drawn for the DETA-cured polymers shows lower moduli and strength values. This difference is shown in the comparison of HEX/DGEBA/DETA (A) and HEX/DGEBA/MPDA (B) in *Figure 3*. This typical comparison between aromatic and short aliphatic chains could be extended to include aliphatic diamines such as 1,6-hexanediamine or 1,12-diaminododecane which would allow greater segmental mobility of the matrix and therefore better diffusion of mobile organotin species through the matrix.

However, higher crosslink densities can be achieved through TBT esters of diaminocarboxylic acids H_2N–CH_2–R–CH(NH_2)–COOH (ref 26) or 3,5-diaminobenzoic acid. By combining the polyfunctional amine curing agent and the TBT ester function in the same molecule, these compounds avoid the prepolymer step necessary

Table 5 Flexural modulus and strength of TBT-modified epoxy polymers

Polymer	Modulus MPa (psi)	Strength MPa (psi)
GLY/DGEBA/MPDA	3270 ± 120 (475 000 ± 17 000)	125 ± 4.6 (18 100 ± 660)
BUT/DGEBA/MPDA	3210 ± 71 (466 000 ± 10 000)	128 ± 2.5 (18 500 ± 360)
HEX/DGEBA/MPDA	2970 ± 50 (431 000 ± 7300)	108 ± 1.3 (15 600 ± 190)
UND/DGEBA/MPDA	2550 ± 70 (370 000 ± 10 000)	90.3 ± 1.4 (13 000 ± 200)
GLY/DGEBA/DETA	2470 ± 123 (358 000 ± 18 000)	86.2 ± 0.5 (12 500 ± 70)
BUT/DGEBA/DETA	3300 ± 85 (472 000 ± 12 000	107 ± 5.3 (15 500 ± 800)
HEX/DGEBA/DETA	2700 ± 61 (391 000 ± 8800)	87.7 ± 0.7 (12 700 ± 100)

Table 6 Impact strength of TBT-modified epoxy polymers

Polymer	Impact strength J/m
GLY/DGEBA/DETA	9.2 ± 0.6
BUT/DGEBA/DETA	21 ± 2
HEX/DGEBA/DETA	22 ± 2
GLY/DGEBA/MPDA	14 ± 5
BUT/DGEBA/MPDA	20 ± 2
HEX/DGEBA/MPDA	23 ± 2
UND/DGEBA/MPDA	25 ± 1

Table 7 Tensile, flexural, impact, and T_g data for DGEBA-cured with MPDA or TBT 3,5-diaminobenzoate

Curing agent	Tensile strength MPa (psi)	Flexural		IZOD Impact strength (J/m²)	T_g (°C)
		strength MPa (psi)	modulus MPa (psi)		
MPDA	82.9 ± 7.5 (12 000 ± 1100)	123 ± 3.4 (17 800 ± 500)	3090 ± 93 (449 000 ± 13 000)	10.7 ± 0.7	174
TBT ester	63.9 ± 4.8 (9270 ± 690)	106.2 ± 3.2 (15 400 ± 500)	2700 ± 250 (392 000 ± 36 000)	9.1 ± 0.4	148

Table 8 Tensile, flexural, impact properties and T_g for DGEBA modified with TBT aminosuccinate

Curing agent	Tensile MPa (psi)		Flexural MPa (psi)		Impact strength (J/m²)	T_g (°C)
	Modulus	Strength	Modulus	Strength		
DETA	3420 ± 639 (496 000 ± 93 000)	67.1 ± 4.3 (9730 ± 630)	3230 ± 71 (468 000 ± 10 000)	105 ± 17 (15 200 ± 2400)	17.5 ± 1.0	114
MPDA	3464 ± 320 (502 000 ± 47 000)	61.2 ± 2.0 (8880 ± 280)	3130 ± 65 (454 000 ± 9400)	110 ± 22 (16 000 ± 3200)	20.2 ± 0.8	127

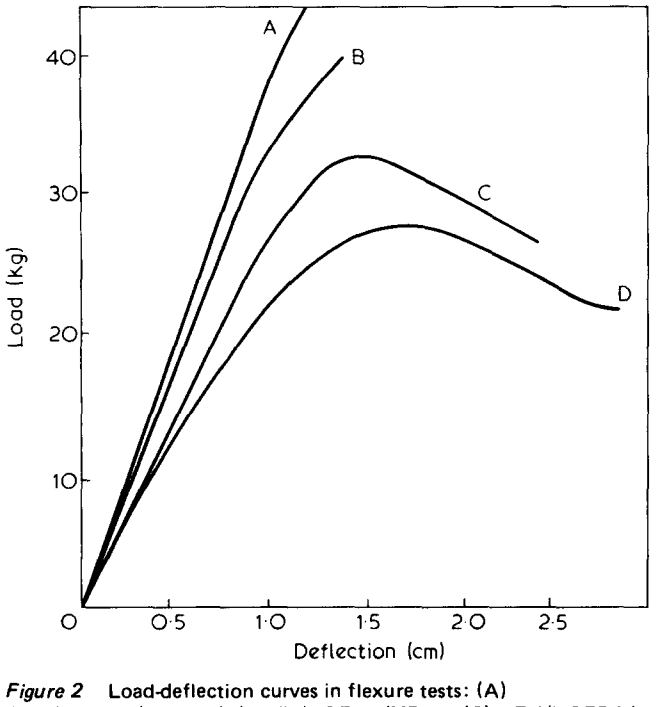


Figure 2 Load-deflection curves in flexure tests: (A) GLY/DGEBA/MPDA, (B) BUT/DGEBA/MPDA, (C) HEX/DGEBA/MPDA and (D) UND/DGEBA/MPDA

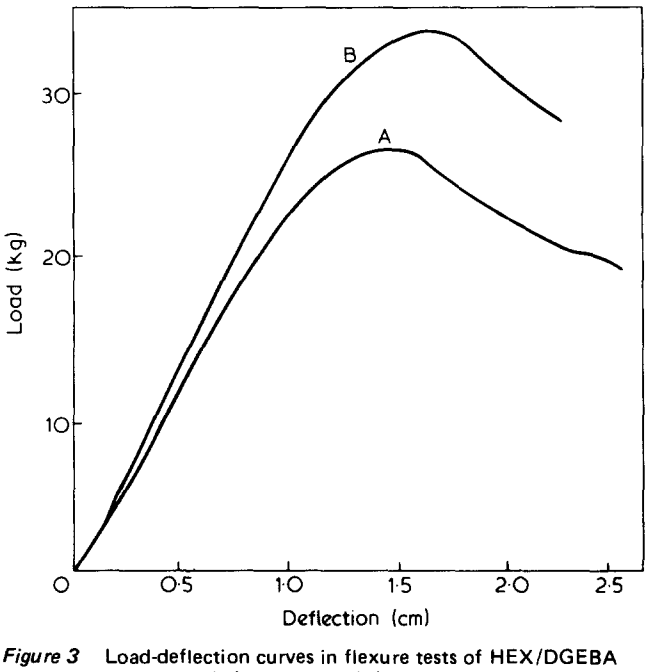
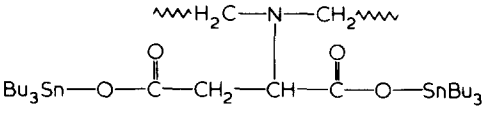


Figure 3 Load-deflection curves in flexure tests of HEX/DGEBA prepolymers cured by (A) DETA and (B) MPDA

with the ω-amino acids, and yet permit the choice of room temperature or high temperature cure.

TBT esters of compounds such as 3,5-diaminobenzoic acid have been prepared to introduce TBT functionality into the curing agent. This compound is unique in that the polymer properties can be compared with MPDA-cured polymers to determine changes caused solely by inclusion of TBT carboxylates, since only changes in matrix structure and crosslink density would occur. The results of mechanical and dynamic mechanical tests (*Table 7*) show only minor changes in tensile and flexural strength, modulus, impact strength, and glass transition temperature with 10% tin in the fully cured polymer. Such comparable bulk properties are advantageous in considering this organotin epoxy polymer as a matrix resin for composites[19]. The tin content is approximately twice that obtained with ω-amino acids.

Higher organotin loading was also achieved through the use of difunctional acids. The modulus and strength values for TBT aspartate (*Table 8*), bear reasonable comparison to the values in *Tables 4*, *5*, and *6*, with the number of pendants in this case being 4.6×10^{-4} mol g^{-1}. The presence of two TBT ester groups close to each other and to the backbone of the polymer will probably increase chain stiffness rather than act as a plasticizer:



These polymer modifications permit a wide range of structural variations in the network polymer, not only

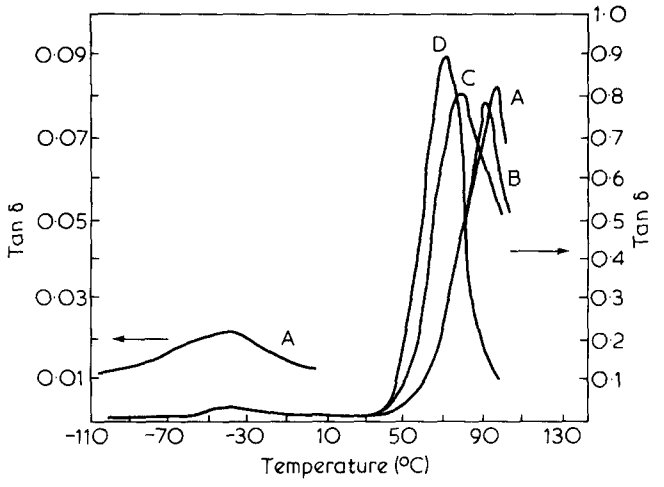


Figure 4 Loss tangents (35 Hz) for DETA-cured triorganotin epoxy polymers: (A) GLY/DGEBA/DETA, (B) BUT/DGEBA/DETA, (C) HEX/DGEBA/DETA and (D) UND/DGEBA/DETA. Only one curve (A) is shown expanded to illustrate weak β-transition which had peaks at (A) −52°C, (B) −45°C, (C) −50°C, (D) −41°C

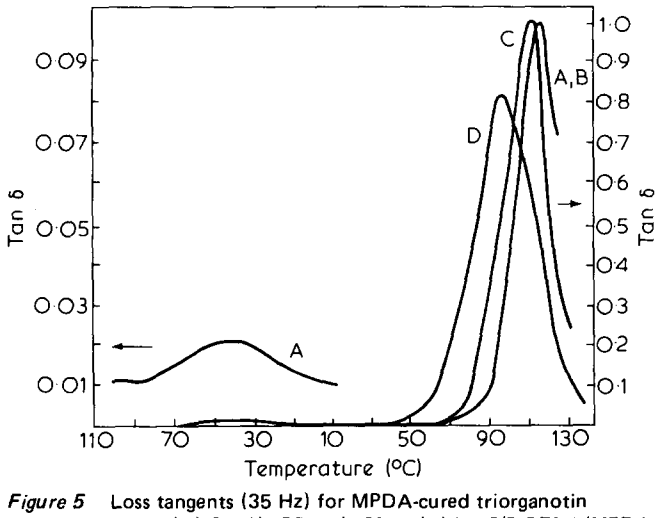


Figure 5 Loss tangents (35 Hz) for MPDA-cured triorganotin epoxy polymers: (A) GLY/DGEBA/MPDA, (B) BUT/DGEBA/MPDA, (C) HEX/DGEBA/MPDA and (D) UND/DGEBA/MPDA. Only one curve (A) is shown expanded to illustrate weak β-transition which has peaks at (A) −53°C, (B) −50°C, (C) −53°C and (D) −54°C

through changes in crosslinking agent, but also through the manipulation of compounds similar to TBT aspartates and other room temperature curing agents containing acid functions.

Glass transition temperature

Glass transition values were obtained from thermechanical spectra using a Rheovibron (*Figures 4* and *5*). The results (*Tables 9* and *10*) correlate quite well with indications obtained from the flexural and tensile tests. The α-transition associated with T_g did not change appreciably in the series until TBT 6-aminohexanoate. Although the T_g of the DETA-cured polymers varied from 92 to 68°C as compared with 114 to 93°C for MPDA cured systems, the trends were similar. It is apparent that there was substantial change in the segmental mobility as the pendant chain length was varied. It is instructive to compare these results for pendant TBT esters with those obtained for pendant chains of comparable length without the TBT carboxylate end groups. To make such a comparison a series of normal amines were chemically bound in a DGEBA matrix in the same concentrations as the TBT carboxylate pendants. Normal decyl-, n-amyl-, and n-propylamine prepolymers were cured with MPDA. The results are shown in *Table 11*. It is seen that even n-propylamine (T_g = 147°C) caused significant decrease in the T_g of DGEBA/MPDA which, under the same conditions, had a T_g of 174°C without the presence of the pendant chain from n-propylamine. It is interesting to note, however, from a comparison with *Tables 9* and *10*, that the decrease in T_g is much greater for the TBT-modified polymers.

The α-transition is rather broad indicating the unfreezing of a broad spectrum of segmental mobilities. However, it should also be noted that the T_g damping peak did not shift but remained a single peak through repeated runs with the same sample. No broadening indicative of off-stoichiometric reactants or incomplete cure could be observed.

Secondary transitions

In addition to the major damping peak at the glass transition (*Figures 4* and *5*), a secondary transition in the glassy state was observed at approximately −50°C. This transition was quite weak in comparison to the glass transition peak. However, by plotting the data on an expanded scale, the shapes and maxima were easily observed. First observed by Kaelble[27] and later reported in a wide range of systems[28,29], this damping peak has been defined as the β-relaxation[30–32]. It has been shown not to be affected greatly by the curing agent even though the intensity of the loss peak can be increased by curing agents which introduce mobile groups[32]. The present

Table 9 Glass transition temperatures for TBT-modified epoxy polymers cured with MPDA

Polymer	T_g (°C)
GLY/DGEBA/MPDA	114
BUT/DGEBA/MPDA	114
HEX/DGEBA/MPDA	110
UND/DGEBA/MPDA	93

Table 10 Glass transition temperatures for TBT modified epoxy polymers cured with DETA

Polymer	T_g (°C)
GLY/DGEBA/DETA	92
BUT/DGEBA/DETA	90
HEX/DGEBA/DETA	80
UND/DGEBA/DETA	68

Table 11 Glass transition of epoxy polymers modified with primary amines

Amine	Curing agent	T_g (°C)
$NH_2C_3H_7$	MPDA	147
$NH_2C_5H_{11}$	MPDA	146
$NH_2C_{10}H_{21}$	MPDA	135

results show the same features with the transition remaining close to $-50°C$ in all the systems studied here. The intensities also remained constant. It had been suggested that the β-relaxation arose from the glyceryl units generated from the polyglycidyl units[27-29]. However, from an examination of Hirschfelder models of derived structures, Cuddihy and Moacanin[31] find this group to be immobile and prefer to attribute the peak to the diethylether of bisphenol A. The maximum value of the loss tangent in this region has also been explained in terms of contributions to the β-relaxation from relaxations of both glyceryl and diphenylpropane units in DGEBA[30]. The observed increase in intensity of the β-transition when mobile groups are introduced by curing agents is probably caused by coupling between mobile groups of DGEBA and those introduced by curing agents[32]. In the present study, the intensities did not change with different lengths of pendant groups introduced by the ω-amino acids. Therefore coupling between these groups and the mobile DGEBA is not indicated.

In addition to the β-relaxations associated with DGEBA at $-50°C$, other transitions might be expected to arise from the motion of the pendant chains, particularly at $n \geqslant 5$. These transitions could not be confirmed using the Rheovibron. Dynamic mechanical measurements which are more sensitive in this range should be more enlightening.

CONCLUSIONS

It is seen that TBT groups can be bound in prepolymers by using TBT esters of ω-amino acids to partially cure diepoxide monomers. Similarly, other trialkyltin groups such as tripropyl can be introduced into the prepolymer by the same synthesis. Since the biocidal activity of trialkyltin compounds varies for different alkyl substituents[3], a broad spectrum of activity should be attainable in the cured polymers by incorporation of more than one type of trialkyltin group.

The formation of prepolymers according to the procedure adopted here allows precise control of the pendant TBT chains and epoxide equivalents. Crosslinking of the prepolymers can be achieved either at room temperature or elevated temperature by the appropriate choice of curing agents, DETA, MPDA, etc. When desired, the crosslinked epoxy polymer can be formed directly from the TBT esters of polyfunctional aminoacids, such as TBT 3,5-diaminobenzoate. The network rigidity is altered not only by the type of curing agent chosen but also by the pendant TBT chains.

Since the effects of side chain, TBT moiety and crosslinker are manifested in property variations, the desired flexibility and toughness can be imparted to the network by manipulating the structural features introduced in the successive synthetic steps. Tailoring polymers to specific applications is, therefore, made possible. In particular, the desired control over release of mobile triorganotin species from the polymer network should be attainable in biocidal applications by changing the bulk properties of the matrix.

The desirable levels of strength and toughness observed in these organotin epoxy polymers suggest their use as matrix resins for reinforced composites. The detailed evaluation and confirmation of this conclusion are presented elsewhere[19,33].

REFERENCES

1 Castelli, V. J. and Yeager, W. L. in 'Controlled Release Polymeric Formulations', (Eds. D. R. Paul and F. W. Harris). American Chemical Society, Washington DC 1976, p 239
2 Phillip, A. T. *Prog. Org. Coat.* 1973, **2**, 159
3 Subramanian, R. V. and Garg, B. K. *Polym-Plast. Technol. Eng.* 1978, **11**(1), 81
4 Sheldon, A. W. *J. Paint Technol.* 1975, **47**, 54
5 Cardarelli, N. F. 'Controlled Release Pesticide Formulations', CRC Press, Cleveland, Ohio, 1976
6 Vizgirda, R. J. *Paint and Varnish Production*, Dec. 25, 1972
7 Thayer, J. S. *J. Organometal. Chem.* 1974, **76**, 265
8 Neumann, W. P. 'The Organic Chemistry of Tin', Wiley-Interscience, New York, 1970
9 Wuerzer, D. R., Senderling, R. L. and Cardarelli, N. F. *Rubber World* 1967, **157**, 1977
10 Migdal, S., Gertner, D. and Zilkha, A. *Isr. J. Chem.* 1967, **5**, 163
11 Dyckman, E. J., Montemarano, J. A., Andersen, D. M. and Miller, A. M. 'Nonpolluting Antifouling Organometallic Polymers', Report No. 3581, Nov. 1972
12 Subramanian, R. V. and Garg, B. K. 'Proc. Internatl. Controlled Release Pesticide Symposium (Ed. R. L. Goulding) Oregon State University, Corvallis, Oregon, Aug. 22-24, 1977, p iv-154
13 Montermoso, J. C., Andrews, T. M. and Marinelli, L. P. *J. Polym. Sci.* 1958, **32**, 523
14 Dyckman, E. J. Montemarano, J. A. and Fischer, E. C. *Nav. Eng. J.* 1973, **85**(6), 33; Ibid. 1974, **86**(2), 59
15 Garg, B. K., Corredor, J. and Subramanian, R. V. *J. Macromol. Sci.-Chem.* 1977, **A11**, 1567
16 Subramanian, R. V. and Anand, M. in 'Chemistry and Properties of Crosslinked Polymers', (Ed. S. S. Labana) Academic Press, NY, 1977, p 1
17 Subramanian, R. V., Garg, B. K. and Corredor, J. in 'Organometallic Polymers', (Eds. C. E. Carraher, J. E. Sheats and C. U. Pittman), Academic Press, NY, 1978, p 181
18 Somaskeharan, K. N. and Subramanian, R. V. in 'Modification of Polymers', (Eds. C. E. Carraher and N. Tsuda), American Chemical Society, Washington, DC, 1980, p 165
19 Williams, R. S., *PhD Thesis*, Washington State University (1980)
20 Somasekharan, K. N. and Subramanian, R. V. in 'Controlled Release of Bioactive Materials', (Ed. R. W. Baker), Academic Press, NY, 1980
21 Gilman, H. and Rosengerg, D. *J. Am. Chem. Soc.* 1953, **75**, 3592
22 Durketaki, A. J. *Anal. Chem.* 1958, **30**, 2024
23 Ho, B. Y. K. and Zuckerman, J. J. *Inorg. Chem.* 1973, **12**(7), 1552
24 Frankel, M., Gertner, D., Wagner, D. and Zilkha, A. *J. Org. Chem.* 1965, **30**, 1596
25 Lee, H. and Neville, K. 'Handbook of Epoxy Resins', McGraw Hill, Inc., NY, 1967
26 Greenstein, J. and Winitz, M. 'Chemistry of the Amino Acids', Vol 3, J. Wiley, New York, 1961, p 2463
27 Kaelble, D. H. *SPE J.* 1959, **15**, 1071
28 May, C. A. and Weir, F. E. *Polym. Eng. Sci.*, (*SPE Trans.*) 1962, **2**, 207
29 Van-Hoorn, H. *J. Appl. Polym. Sci.* 1968, **12**, 871
30 Williams, J. G. *J. Appl. Polym. Sci.* 1979, **23**, 3433
31 Cuddihy, E. F. and Moacanin, J. in 'Epoxy Resins', Adv. Chem. Ser. 92. American Chemical Society, Washington, DC, 1970, Ch 9
32 Cuddihy, E. F. and Moacanin, J. *J. Polym. Sci., A-2* 1970, **8**, 1627
33 Subramanian, R. V. and Williams. R. S. *J. Appl. Polym. Sci.*, in press