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Novel Polymers Containing Carbon-anchored Organotin Groups*

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Three polymers containing Bu_2SnX (X = OAc or Cl) groups linked to the polymer through a C–Sn bond have been prepared by hydrostannation (via Bu_2Sn HCl) of the following $CH{=}CH_2$-containing polymers: (1) a polybutadiene containing approx. 70% of 1,2 $CH{=}CH_2$ units; (2) poly(allyl methacrylate); (3) poly(tetraethylene glycol monoallyl ether methacrylate). The first and third were tested for activity against a number of marine organisms and found to be inactive. Presumably this observed biological inactivity arises from the fact that $R_3Sn(H_2O)_n^+$ ions are not released into the aqueous medium.

Keywords: Butyltin, polymer, antifouling

1 INTRODUCTION

Polymer-bound organotin derivatives have been of interest in the preparation of aquatic antifouling paints. In these the polymer-immobilized triorganotin group usually is covalently bound to the polymer via a hydrolytically unstable Sn—O_2C bond.[1–4] This results in a slow release of an $R_3Sn(H_2O)_n^+$ cation. The operative assumption of this approach is that the toxic organotin cation must be ingested by the organism for the coating on the ship hull to show antifouling effects. Such organotin antifouling paints are highly effective, but the toxic $R_3Sn(H_2O)_n^+$ cations that are released have detrimental effects on aquatic life in general. The recognition that organotin components of such antifouling paints are undesirable pollutants of the aquatic environment (see, for example, Refs 5, 6) led the United States Congress to pass a law that severely restricted the use of such organotin antifouling paints,[7] and some states have set stricter guidelines (e.g. Ref. 8). As a result, alternative approaches to the serious problem of ship hull fouling have been sought.

Although the prevailing opinion was that it was the free $R_3Sn(H_2O)_n^+$ species in solution which killed the marine organisms whose attachment to the ship hull resulted in fouling, the possibility of firmly anchoring an organotin group to a polymeric component of an antifouling paint appears not to have been examined. In such an approach, firmly anchored $-SnR_2(H_2O)_n^+$ cations might present a hostile surface to the offending marine organisms that might repel them. The two approaches are illustrated in Fig. 1.

While organic polymers functionalized with organotin groups via an Sn–O bond are quite common,[1–4,9–11] organic polymers functionalized with an organotin group via an Sn–C bond are rare. Neumann and his coworkers[12–14] and others[15,16] have shown that such polymers, in the form of crosslinked gels, are useful reagents in organic synthesis. However, what was required for the present application was a soluble, Sn–C linked, organotin polymer that also contained adhesive functions. Such polymers apparently had not been prepared, and their synthesis and properties are the subject of the present paper.

2 RESULTS AND DISCUSSION

2.1 Synthesis and structure of the organotin polymers

Hydrostannation of C=C bonds is an important reaction in organotin chemistry,[17] and the hydrostannation of a polymer containing C=C bonds, either pendant or in the main chain, would be a simple approach to the desired organotin-substituted polymers. In the first system investigated, the polymer chosen was a comercially available polybutadiene with high (70%) 1,2 content (i.e., with 70% pendant vinyl groups). Since the objective was the formation of pendant $-SnR_2X$ substituents, hydrostannation with n-Bu_2SnHCl, a useful and easily prepared

* Dedicated to the memory of Professor Wilhelm P. Neumann, a pioneer of modern organotin chemistry.

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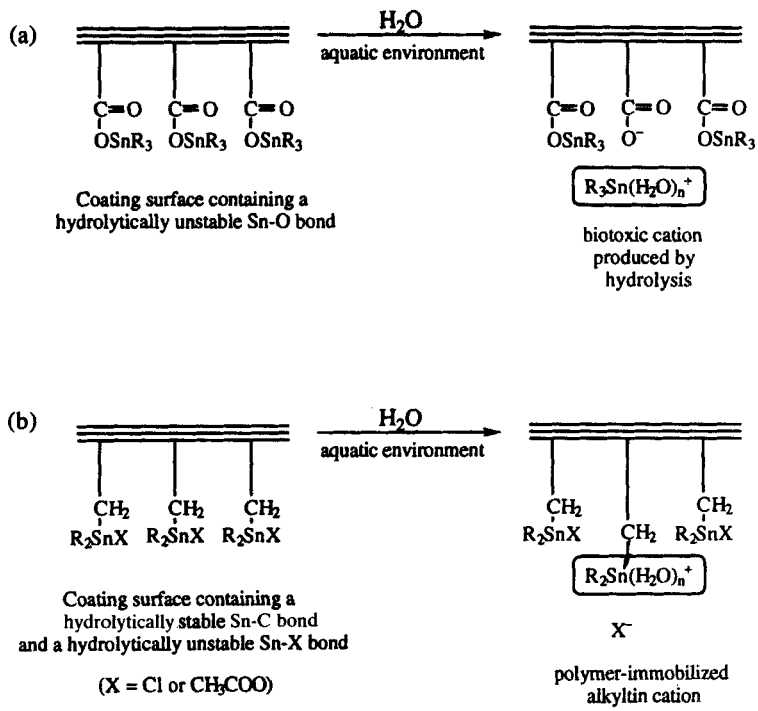


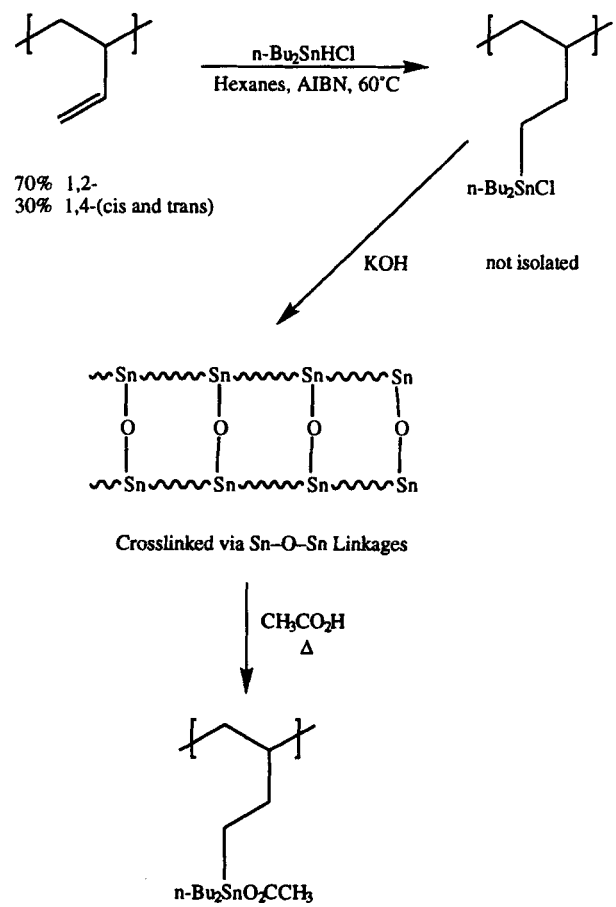
Figure 1 (a) Current technology used for aquatic organotin antifouling coatings. (b) Alternative C—Sn bound organotin coatings.

reagent,[18-20] was carried out; this reagent had been used by Neumann[12-14] and by Ueno *et al.*[16] to produce insoluble, polymer-bonded organotin chlorides. In our work, n-Bu_2SnHCl, prepared by the method of Sawyer and Kuivila,[18] was added to a hexane solution of the high 1,2-polybutadiene. Azobisisobutyronitrile (AIBN) was added to catalyze the Sn—H addition reaction, which was carried out at 60 °C. The $Sn(n\text{-}Bu)_2Cl$-substituted polymer was not isolated; rather it was converted to the polymeric stannoxane (an insoluble gel). The latter was subsequently treated with glacial acetic acid to give the soluble $Sn(n\text{-}Bu)_2OAc$-substituted polybutadiene as a soluble, opaque semisolid (the opacity was possibly a result of some crystallinity, since repeated precipitations did not remove it). In the experiments using different amounts of the n-Bu_2SuHCl reagent, it was found that as the degree of hydrostannation increases (as measured by ^1H NMR spectroscopy and elemental analysis; see Section 3), the purified polymer becomes more opaque and more solid-like and also more soluble in methanol. The preparation of this polymer, **P1**, is summarized in Scheme 1. ^1H NMR spectroscopy showed that the polymer produced under a variety of conditions was hydrostannated to an extent of 20–25% (on average), and this was confirmed by elemental analysis. Even with an excess of the hydrostannating agent, it was difficult to increase the average degree of hydrostannation above 25%. Since monomeric olefins can be hydrostannated in essentially quantitative yield using the chlorotin hydride reagents, the reason for these rather low degrees of hydrostannation of the polymer probably arise from the lower accessibility of the C=C bonds (a steric constraint) in the polymer, when compared with monomeric olefins. The selectivity of the reagent under these conditions is rather low, in that it would appear that both the vinyl and internal vinylene bonds are attacked by the reagent. For example, ^1H NMR spectroscopy showed that at an average degree of hydrostannation of 22%, the polymer contained *ca* 65% 1,2- and 35% 1,4-unreacted polybutadiene units (1,2-/1,4- = 1.9). For comparison, 100% selectivity would imply 70 − 22 = 48% unreacted 1,2-units and 30 − 0 = 30% unreacted 1,4-units (1,2-/1,4- = 1.6). Elemental analysis confirmed these degrees of hydrostannation, as discussed in the Section 3. Gel-permeation chromatography (GPC) analysis

of this polymer showed that the average size (average hydrodynamic volume) of this polymer was smaller than that of the starting high 1,2-polybutadiene, as the GPC distribution was significantly shifted toward longer elution times (smaller-sized molecules).

The infrared spectrum (neat, thin film) of this polymer showed strong absorbances at 1570 and 1450 cm^{-1} that are characteristic of the C(O)O stretches of trialkyltin acetates. The IR spectrum of *n*-$Pr_3SnOCOCH_3$ (KBr) showed COO stretches at 1564 and 1412 cm^{-1}. Additional information on the IR spectra of some tin acetates is given in Refs 21 and 22.

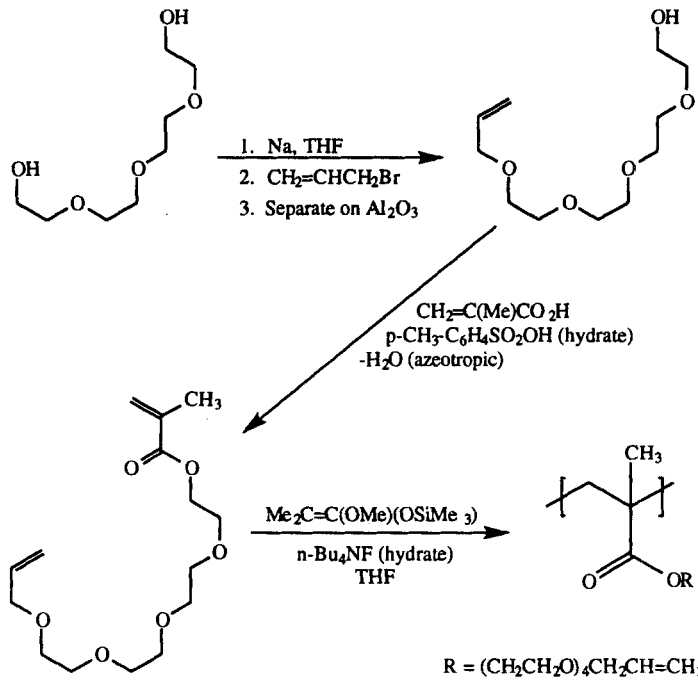
In addition to polymer **P1**, A poly(tin-substituted allyl methacrylate) was prepared using the group transfer polymerization procedure (Eqn [1]).[23] Note that radical-initiated polymerization of allyl methacrylate gives cyclopolymers that gel at high conversion[24-26] and that anionic polymerization usually is only partially successful with such unsaturated methacrylates.[27,28] Hydrostannation of poly(allyl methacrylate) with n-Bu_2SnHCl using AIBN as catalyst at 60 °C in benzene gave, upon precipitation with petroleum ether (b.p. 30–60 °C), the tin-containing polymer, **P2**. The latter, a somewhat tacky white solid, was hydrostannated in



Scheme 1 Preparation of the tin-containing high 1,2-polybutadiene, **P1**. A schematic structure is shown. The actual microstructure is

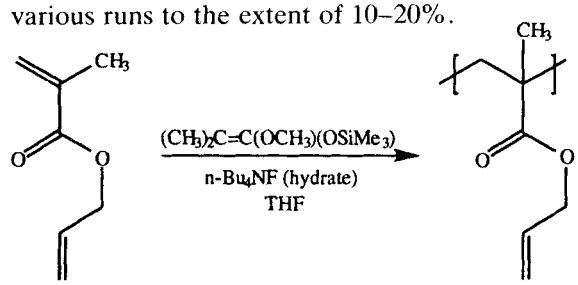
$$(1,2\text{-})_a(1,4\text{-})_b(1,2\text{-Sn})_c(1,4\text{-Sn})_d,$$

where *a* and *b* are numbers of unreacted polybutadiene units and *c* and *d* are the numbers of the hydrostannated 1,2- and 1,4-polybutadiene units, respectively.



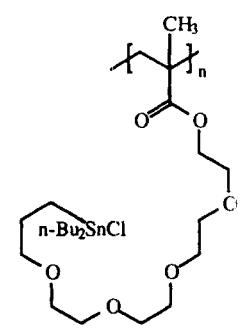
Scheme 2 Preparation of linear 1,2-poly(tetraethylene glycol monoallyl ether methacrylate); $R = (CH_2CH_2O)_4CH_2CH{=}CH_2$.

various runs to the extent of 10–20%.



Equation [1] Hydrostannation of poly(allyl methacrylate) yields **P2**.

In view of the results of the biocidal testing of polymer **P1**, it was decided that a possibly more useful version of **P2** would be one in which the organotin substituent is tethered to the polymer chain via a hydrophilic chain. Also, with less congestion of the C=C terminal side groups near the polymer chain, a higher degree of hydrostannation might be expected. Accordingly, linear 1,2-poly(tetrathylene glycol monoallyl ether methacrylate) was prepared, as shown in Scheme 2. The polymer was isolated as a slightly yellow, viscous oil of low molecular weight (~3100 vs monodisperse polystyrene). Hydrostannation of this polymer was effected with $n\text{-}Bu_2SnHCl$ in benzene at 60 °C in the presence of AIBN initiator. Precipitation with petroleum ether (b.p. 30–60 °C) gave the organotin polymer **P3**, a slightly yellow, viscous material which partially solidified (with some opacity) on standing. Hydrostannation with a slight excess of $n\text{-}Bu_2SuHCl$ resulted in reaction of about 70% of the pendant C=C bonds (by analysis). This markedly higher degree of hydrostannation of **P3**, compared with **P1** and **P2**, is probably a result of the more accessible C=C bonds in **P3**, arising from their greater distance from the polymer chain and, also, from the lower molecular weight of **P3**.



P3

The structures of these organotin polymers were of some interest and the ^{119}Sn NMR spectra

were very useful in providing information on their structures. The ^{119}Sn NMR chemical shift of an organotin compound bearing at least one electronegative substituent is known to be very sensitive to changes in the coordination state of the organotin compound.[9,29–31] Such changes in coordination state may arise from the addition of a neutral coordinating ligand, such as DMSO, HMPT or triphenylphosphine oxide,[32] or by a self-association process if the tin compound itself contains a Lewis basic site. Such self-association may produce polymeric and/or oligomeric materials[33–35] (an intermolecular process), as is the case with some trialkyltin alkoxides, carboxylates and fluorides, or intramolecular chelate complexes.[36–38] Self-associated polymers and oligomers exhibit concentration- and temperature-dependent ^{119}Sn NMR spectra in non-coordinating solvents, due to varying degrees of association with varying concentration and temperature.[29] Presumably, the ^{119}Sn NMR chemical shifts of the chelate complexes should exhibit little concentration or temperature dependence (no ^{119}Sn NMR data appear to have been reported for such systems). Whatever the method of the change in coordination at tin, it is well documented[31] that a change in coordination from four to five and then to six leads to a decrease of *ca* 100–150 ppm (more shielded) in the ^{119}Sn NMR chemical shift per step. The magnitude of the chemical shift change depends upon the position of equilibrium,[29] but with good donor ligands (DMSO, HMPT, etc.), the equilibrium tends to greatly favor adduct formation and, in many cases, such adducts can be isolated.[32] Bellama and Manders[39] observed such coordination effects when they studied the ^{119}Sn NMR spectra of poly(tri-n-butyltin methacrylate/methyl methacrylate) copolymers in various solvents.

The ^{119}Sn{^{1}H} NMR spectrum of **P1** in benzene-d_6, hydrostannated to a degree of *ca* 20–25%, is shown in Fig. 2, along with the structural interpretation. The general features of the spectrum are two groups of resonances, one centered *ca* 120 ppm and the other centered *ca* −140 ppm (a chemical shift difference of *ca* 260 ppm). The ^{119}Sn{^{1}H} resonances exhibited little or no concentration dependence in the range 20–40 polymer wt%. For comparison, a monomeric tin compound, tri-n-propyltin acetate, exhibited a single ^{119}Sn{^{1}H} resonance at 91.3 ppm in benzene-d_6, with litle or no concentration dependence in the range of 10–20 wt%. Clearly, the ^{119}Sn{^{1}H} NMR resonances exhibibited by **P1** are consistent with the presence in the polymer of completely unsaturated tin (four-coordinate tin, centered *ca* 120 ppm) and completely saturated tin (six-coordinate tin, *ca* −140 ppm). That this is an intra-chain association and not an inter-chain association process was clearly shown by a lack of a concentration dependence of the ^{119}Sn{^{1}H}

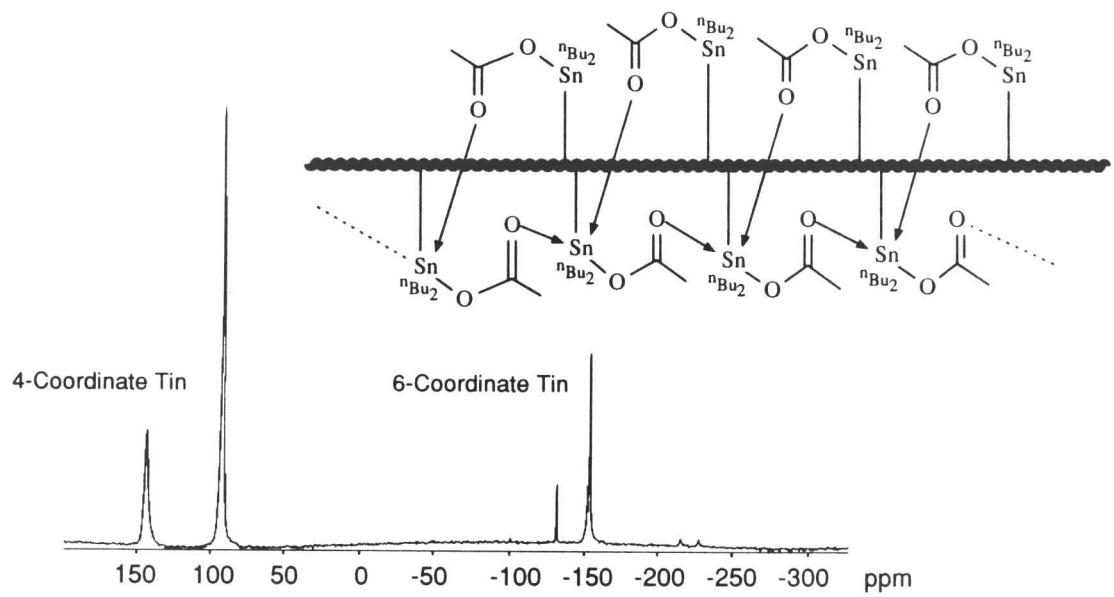


Figure 2 ^{119}Sn{^{1}H} NMR spectrum of **P1** in benzene-d_6, hydrostannated to an extent of 20–25%.

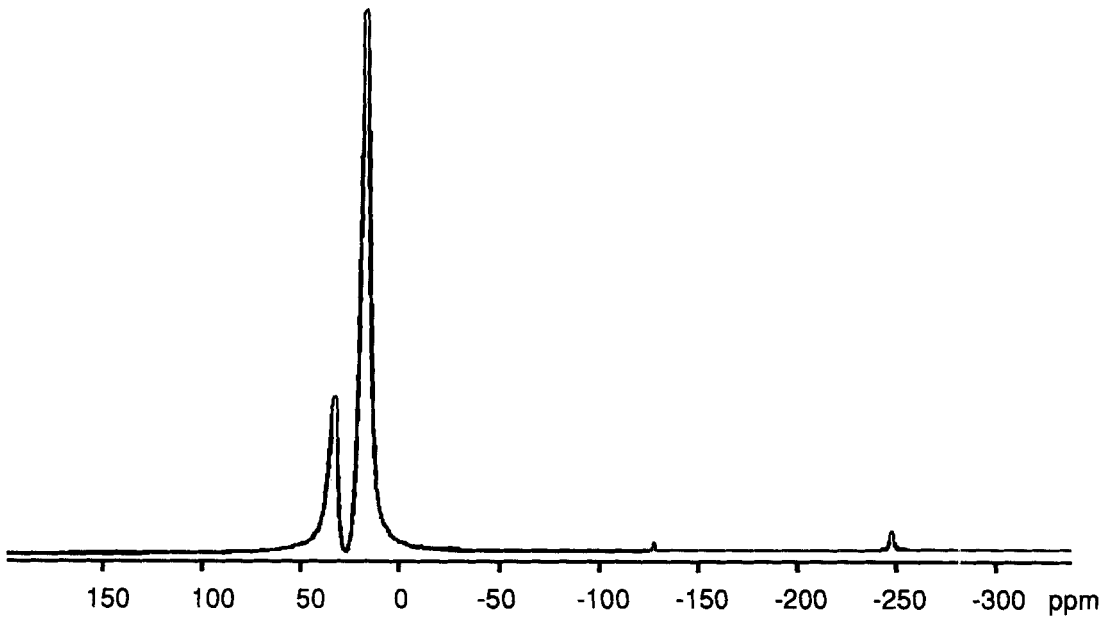


Figure 3 $^{119}Sn\{^1H\}$ NMR spectrum of **P1** in benzene-d_6 + 5 equiv. of DMSO.

NMR resonances; this intra-chain self-association presumably arises from a very favorable neighboring group effect. Note that there would appear to be a total absence of five-coordinate tin, as evidenced by the fact that no resonances in the range 65 to −65 ppm were observed in the $^{119}Sn\{^1H\}$ NMR spectrum of this polymer. Peak multiplicity is attributed to the fact that the polybutadiene was hydrostannated at both the 1,2- and 1,4-double bonds. Since polybutadienes[40] are known to exist as helices in the solid state, it is possible that this highly self-associated polymer, **P1**, adopts a helix structure in non-coordinating solvents. The addition of *ca* five equivalents of DMSO (based on the molar percentage of tin present in the polymer) to a solution of **P1** in benzene-d_6 caused the resonances centred around 120 ppm and −140 ppm to vanish with the appearance of two new resonances, centered at *ca* 15 ppm. For comparison, the addition of DMSO to a solution of the monomeric tri-n-propyltin acetate in benzene-d_6 caused the resonance at 91.3 ppm to vanish with the appearance of a new, single resonance at 16.8 ppm. The $^{119}Sn\{^1H\}$ NMR spectrum of **P1**, with DMSO, is shown in Fig. 3. These results are consistent with the idea that the addition of DMSO destroys the intra-chain, self-associated nature of **P1** in benzene-d_6 by the formation of a five-coordinate DMSO adduct. The fact that the $^{119}Sn\{1H\}$ NMR peak multiplicity of polymer **P1** after the addition of DMSO remained two seems to confirm the assignment of the origin of this peak multiplicity to 1,2- and 1,4-hydrostannated double bonds, as described above.

The $^{119}Sn\{^1H\}$ NMR spectrum of **P3** in benzene-d_6, hydrostannated to an extent of *ca* 70–90%, exhibited a single resonance at 66.1 ppm (Fig. 4). The $^{119}Sn\{^1H\}$ NMR resonance of this polymer exhibited little or no concentration dependence in the range of *ca* 15–25 polymer wt %. For comparison, we found that the $^{119}Sn\{^1H\}$ NMR spectrum of the monomeric tri-n-butyltin chloride in benzene-d_6 consisted of a single resonance at 148.3 ppm, with little or no concentration dependence. These results are consistent with the formation of an intramolecular chelate complex via coordination of one of the ether linkages on the polymer, as the ^{119}Sn chemical shift of this polymer is consistent with the tin atoms being five-coordinate. That this is an intra-chain association, as opposed to an inter-chain process, is consistent with a lack of any detectable chemical shift dependence on concentration. Ethers are normally not considered to be exceptional coordinating ligands for compounds of the R_3SnX type, but evidently the process is facilitated by a very favorable neighboring group effect (the donor is unable to diffuse away from the tin center). The addition of *ca* 5 equivalents of

DMSO (based on the molar percentage of tin present in the polymer) to a solution of **P3** in benzene-d_6 caused only about a 15 ppm change in the chemical shift of the $^{119}Sn\{^1H\}$ NMR resonance. For comparison, however, we found that addition of DMSO to a solution of tri-n-butyltin chloride in benzene-d_6 caused a much more marked change in the chemical shift of this compound, from 141.8 to 41.0 ppm (*ca* 100 ppm difference). This result is consistent with the idea that polymer **P3** in benzene-d_6 is already a five-coordinate chelate complex, so that addition of DMSO indeed destroys the chelate complex to form a 1:1 adduct of each tin atom, but the net coordination state of tin is not changed (i.e., remains five), and, thus, there is a relatively small associated change in chemical shift.

2.2 Preparation of coatings

In order to test the possible antifouling properties of the organotin polymers that we had prepared, coatings of these polymers on glass or plastic rods were required. Such coatings were prepared on sanded glass or G10 epoxy (glass/resin composite) rods by dipping (or painting) such rods, using benzene solutions of the polymers that contained a minimum amount of AIBN (enough to produce crosslinking; see Section 3). Rods were dipped about five to ten times (or painted several times), and were air-dried between dips (coats). The resulting tacky rods were irradiated with UV light (254 nm) in the air for a minimum time (until the rods were no longer tacky and the coating was insoluble in all solvents), usually 12–24 h. Rods prepared by the dipping method generally contained *ca* 5–10 mg material and the painted rods *ca* 25 mg material. In both cases, the material appeared to cover the surface of the rods homogeneously and, in each case the coatings of several rods were removed with a razor and analyzed for tin content.

2.3 Testing of the organotin polymer coatings

The antifouling properties of each rod were tested by the Duke University Marine Laboratory.[41] The testing period was four weeks; the aquatic antifouling characteristics were noted each week and compared with control rods and the common antifoulant AF 121. Standard statistical analysis (Kruskal–Wallis chi-square approximations) was applied to the resulting data. The organisms against which the antifouling characteristics were measured were aborescent bryozoa, barnacles, tube worms, bivalves, tunicates, amphipods, colonial hydroids and encrusting bryozoa. For exper-

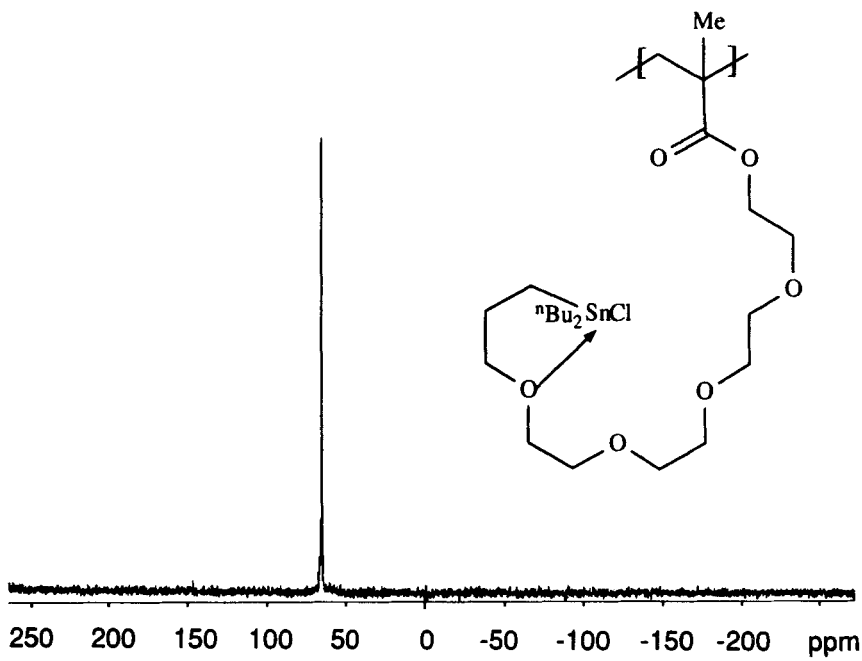


Figure 4 $^{119}Sn\{^1H\}$ NMR spectrum of **P3** in benzene-d_6, hydrostannated to an extent of 70–90%.

imental details, see Section 3.4. None of the coatings prepared appeared to inhibit growth of any of these organisms effectively. It would appear that the 'hostile surface' hypothesis is not correct and that $R_3Sn(H_2O)_n^+$ ions do need to be released into the aqueous environment of the ship's hull in order for antifouling action to take place.

A reviewer has suggested another explanation for the observed lack of antifouling activity, namely that it is the Bu_3SnX systems which have demonstrated high activity, while our polymers involve Bu_2RSnX systems. The R-for-Bu substitution could be responsible for the observed inactivity. This suggestion is testable [via poly(Bu_2RSn methyacrylate/methyl methacrylate) formulations], but such experiments are beyond the scope of our present interests.

3 EXPERIMENTAL SECTION

3.1 General comments

All NMR spectra were recorded using a Bruker WM 250, Varian XL 300 or Varian XR 500 NMR spectrometer at room temperature. ^1H NMR chemical shifts are reported relative to the solvent (residual, DMSO-d_6 at 2.49 ppm and benzene-d_6 at 7.15 ppm, respectively) or internal tetramethylsilane (0.00 ppm). $^{13}C\{^1H\}$ NMR chemical shifts are reported relative to the solvent (DMSO-d_6 at 39.5 ppm) and $^{119}Sn\{^1H\}$ NMR chemical shifts are reported relative to a 20 wt % solution of tetramethyltin in benzene-d_6 (external, 0.00 ppm). The spectra of the tin-containing compounds (monomers and polymers) were measured on the Varian XR 500, due to the much improved signal-to-noise ratio that can be realized, relative to the XL 300 instrument. Precise conditions and references are cited where appropriate below. ^1H NMR spectra were recorded at 25–50 mg compound/g solvent and ^{119}Sn and ^{13}C spectra 100–500 mg compound/g solvent. Typical line broadening used for the ^{119}Sn and ^{13}C spectra at 100–500 mg compound/g solvent. Typical line broadening used for the $^{119}Sn\{^1H\}$ NMR spectra of the polymers was 10–40 Hz, and for the tin-containing monomeric species, 5–10 Hz. Typical line broadening used for the $^{13}C\{^1H\}$ NMR spectra of the polymers was 5–10 Hz and 1–2 Hz for the monomeric species.

Mass spectra were recorded using a Finnigan–Mat system 8200 mass spectrometer with a direct insertion probe in the EI mode. All spectra were recorded under low resolution in the positive-ion mode by ramping the probe temperature from 25 to *ca* 250 °C.

Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Galbraith Laboratories or Robertson Microanalytical Laboratories.

Where necessary, syntheses were performed under an argon atmosphere. Polymerizations and hydrostannation reactions were performed in standard Schlenk-ware under an argon atmosphere. The benzene was freshly distilled from sodium and the hexanes were fresly distilled from $LiAlH_4$. THF was freshly distilled from sodium/benzophenone. All other common solvents and reagents (methanol, light petroleum ether, glacial acetic acid and potassium hydroxide) were of suitable quality and were used as received.

Since the organotin-containing polymers possessing a Sn–Cl bond are water-sensitive, due caution was exercised to avoid exposure of such polymers to water, as deliberate addition of water to some of these polymers over time produced insoluble, crosslinked materials (presumably, through distannoxane linkages). In contrast, **P1**, the tin-containing polymer possessing a tin–acetate bond, is significantly less moisture-sensitive and, in fact, could be taken through an aqueous work-up without evidence of hydrolysis. Hydrolysis was observed, however, during the preparation of the coatings derived from such polymers containing a tin–acetate bond, so it may be that irradiation with UV aids in the hydrolysis.

The n-Bu_4NF (hydrate), dimethyl ketene methyl trimethylsilyl acetal [$Me_2C{=}C(OMe)(OSiMe_3)$], aluminum oxide (Al_2O_3), tetraethylene glycol, allyl bromide, methacrylic acid and n-Bu_2SnCl_2 were purchased from Aldrich and used as delivered, except for degassing as necessary. Allyl methacrylate was purchased from Fluka, high 1,2-polybutadiene from Polysciences, Inc., and 2,2′-azobisisobutyronitrile (AIBN) was purchased from Kodak. The G10 epoxy rod (a glass/resin composite) was purchased from Cadillac Plastic and Chemical Co., Malden, MA, USA. Rods were machined to the appropriate lengths (11 cm × 7 mm) by milling on a standard, circular, water-cooled glass saw. Standard, stock glass rods were cut by scoring and breaking to the appropriate length (also 11 cm × 7 mm). All rods were sanded, washed and dried, prior to coating.

Molecular weight measurements were carried out on a Waters 150C GPC instrument, using a Waters Ultrastyragel linear column [eluting solvent, 10:1 (v/v) mixture of chloroform–dimethyl sulfoxide], or a Waters Ultrastyragel 10^3 column (eluting solvent, toluene). Measurements were carried out at room temperature, at a 1.0 ml min^{-1} flow rate. All molecular weights are reported relative to polystyrene or polybutadiene. Monodisperse samples of polystyrene (polydispersity ≤ 1.05) and polybutadiene (polydispersity ≤ 1.20) were purchased from Polysciences, Inc.

Di-n-butyltin dihydride was prepared by the method of Van der Kerk and coworkers,[42] using di-n-butyltin dichloride and lithium aluminum hydride in ether. The n-Bu_2SnH_2 was stored in a high-vacuum flask (5 °C), containing a Teflon stopcock. In many cases, the yields of the tin-containing polymers have not been optimized. For our study, we were more concerned with preparing polymeric materials that were free from monomeric trialkyltin derivative impurities, since these materials may presumably interfere with the test results on the resulting coatings (yielding false-positive results).

3.2 Preparation of the —CH=CH_2 unsaturated polymers

3.2.1 High 1,2-polybutadiene

High 1,2-polybutadiene was purchased from Polysciences, Inc., and had a nominal 1,2- content of 85% and a nominal molecular weight of 3000. ^{1}H NMR spectroscopy of the viscous liquid polymer was used to determine the proportions of 1,2- and 1,4-polybutadiene, which can be found by integration of the vinyl resonances using the following equation:

$$I(4.8\text{–}5.3\ \text{ppm})/I(5.3\text{–}6.1\ \text{ppm}) = 2x/(x+2y)$$

where $I(\delta)$ is the integral for the appropriate resonance(s), x is the mole fraction of 1,2- and y is the mole fraction of 1,4-polybutadiene ($x+y=1$). The following assignments pertain (benzene-d_6): δ 4.8–5.3(1,2-, —CH=C$\underline{H}_2$); 5.3–6.1 (1,2-, —C$\underline{H}$=CH_2; 1,4- *cis* and *trans*, —C$\underline{H}$=C$\underline{H}$—). For assignments, see Refs 43 and 44. Similar equations can be derived for the aliphatic protons and vinyl:aliphatic ratio, but using the vinyl protons alone would appear to be more accurate for relatively low-molecular-weight polymers because of the unknown nature of the end groups and because of possible branching and cyclization.

The purchased high 1,2-polybutadiene was thus shown to contain *ca* 70% 1,2- and 30% 1,4- (*cis* and *trans*) units [i.e. $(1,2)_{0.70}(1,4)_{0.30}$]. GPC analysis of this polymer, relative to monodisperse polybutadiene standards ($D \leq 1.20$) , showed a trimodal distribution of molecular weights, with $M_n = 2780$ (average degree of polymerization *ca* 51) and $M_w = 5370$.

^{1}H NMR (benzene-d_6 + TMS): δ 0.6–1.9 (broad single resonance, C$\underline{H}_2$, 1,2-); 1.9–2.7 (broad single resonance, C$\underline{H}$, 1.2-; C$\underline{H}_2$, 1.4-*cis* and -*trans*); 4.8–5.3 (broad single resonance, —CH=C$\underline{H}_2$, 1,2-); 5.3–6.1 (broad multiple resonances, —C$\underline{H}$=CH_2, 1,2-; —C$\underline{H}$=C$\underline{H}$-, 1,4-*cis* and -*trans*).

3.2.2 Linear 1,2-poly(allyl methacrylate)

A dry 250 ml three-necked round bottomed flask, equipped with a magnetic stir bar and a 50 ml pressure-equalizing addition funnel was charged with 100 mg of n-Bu_4NF (hydrate) (dry box). The allyl methacrylate was passed through a short column of alumina (Aldrich, activated neutral, Brockmann I, *ca* 150-mesh, 155 $m^2 g^{-1}$) to remove any water and inhibitor and was collected in a dry Schlenk flask that was maintained under argon. To the flask containing the n-Bu_4F catalyst was added 100 ml of freshly distilled, degassed THF via a cannula, and to the addition funnel was added 45 ml (42.2 g, 0.33 mol) of the allyl methacrylate. To the THF/catalyst solution was added, all at once, 2.0 ml (1.7 g, 9.84 mmol) of Me_2C=C(OMe)($OSiMe_3$) via a syringe. While the entire system was maintained under an argon atmosphere, the allyl methacrylate was added dropwise at room temperature with stirring, resulting in a slightly exothermic reaction. The allyl methacrylate was added at such a rate as to maintain the temperature at *ca* 35 °C. Addition was complete after 30 min and the reaction mixture was noticeably more viscous and remained warm. Stirring was continued for an additional 1 h and then 10 ml of methanol was added to quench polymerization. The viscous polymer solution was stirred for an additional 30 min and then poured into a 2 l flask containing 1500 ml of light petroleum ether (b.p. 30–60 °C). The polymer was precipitated from solution and was allowed to settle. The solvent was decanted from the swollen polymer and the latter was redissolved in 100 ml of THF and reprecipitated by the addition of 1500 ml of light petroleum ether. The solvent was

decanted from the polymer and then the polymer was washed with two 100 ml portions of light petroleum ether. Finally, since the polymer was very tacky at this point, the polymer was redissolved in 100 ml THF, transferred to a 250 ml Schlenk flask, and the solvent was removed under reduced pressure. The residue was dried under vacuum at room temperature for 24 h. the ^{1}H NMR spectrum showed the presence of THF, so the polymer was ground using a mortar and pestle, and then further dried under vacuum at room temperature, yielding 27.6 g (65%) of a white, glassy solid. GPC analysis of this polymer, relative to monodisperse polystyrene ($D \leq 1.05$), showed $M_n = 8200$ and $M_w = 24\,400$ (peak maximum molecular weight = 17 500). The IR (KBr) spectrum of the polymer showed a very strong C=O absorbance at 1733 cm^{-1}.

^{1}H NMR (benzene-d$_6$): δ 1.2–1.7 (broad multiple resonances, C$\underline{H}_3$, 3H); 1.8–2.6 (broad multiple resonances, C$\underline{H}_2$, 2H); 4.2–4.7 (broad multiple resonances, O—C$\underline{H}_2$CH=CH$_2$, 2H); 4.8–5.4 (broad multiple resonances, O—CH$_2$CH=C$\underline{H}_2$, 2H); 5.6–6.1 ppm (broad multiple resonances, O—CH$_2$C$\underline{H}$=CH$_2$, 1H).

^{13}C{^{1}H} (benzene-d$_6$): δ 17.7, 19.5 (broad s, $\underline{C}$H$_3$); 45.5, 45.7, 46.2 (broad s, $\underline{C}$H$_2$); 53.0, 54.8, 55.1 (broad s, $\underline{C}$); 65.6 (broad, s, O—$\underline{C}$H$_2$CH=CH$_2$); 118.4, 118.5, 118.6 (broad s); 132.2, 132.5, 132.7 (broad s); 176.2, 176.4, 176.9, 177.3 ppm (broad s, $\underline{C}$=O).

3.2.3 Linear 1,2-poly(tetraethylene glycol monoallyl ether methacrylate

A dry 250 ml Schlenk flask, equipped with a magnetic stir bar, was charged with 50 mg of n-Bu$_4$NF (hydrate). With the flask maintained under argon, 30 ml of dry, freshly distilled THF was added via a syringe and then 0.50 ml of Me$_2$C=C(OMe)(OSiMe$_3$) (0.43 g, 2.5 mmol) via a syringe. To this solution was added 8.8 g (0.029 mol) of tetraethylene glycol monoallyl methacrylate, all at once via a syringe. No exothermic reaction was noted after 45 min, so stirring was continued overnight (such reactions are prone to induction periods of varying lengths[45]). An aliquot of the solution was taken and its ^{1}H NMR spectrum showed that no polymer had been produced. An additional 1.0 ml of the acetal was added and an immediate exothermic reaction ensued, but the solution rapidly cooled back to room temperature. An additional 100 mg of n-Bu$_4$NF in THF was added, and an additional 0.5 ml of the acetal. No exothermic reaction ensued, so the reaction mixture was heated at 50 °C for 24 h. An aliquot was taken and its ^{1}H NMR spectrum showed that polymer had been produced. Methanol (10 mL) was added to quench the polymerization. The entire contents of the flask were poured into a 500 ml one-necked round bottomed flask containing 250 ml of light petroleum ether (b.p. 30–60 °C) and the polymer oiled out of solution. The solvent was decanted away from the polymer and the polymer was washed several times with light petroleum ether and dried at room temperature under vacuum, yielding 5.5 g (63%) of a slightly yellow/orange, viscous liquid polymer. The reason for the difficulty in polymerization of this monomer is not fully understood. GPC analysis of this polymer showed a high symmetrical distribution of molecular weights with a peak maximum molecular weight of *ca* 3100, relative to monodisperse polystyrene.

^{1}H NMR (DMSO-d$_6$+TMS): δ 0.5–1.2 (broad multiple resonances, C$\underline{H}_3$, 3H); 1.2–2.0 (broad multiple resonances, C$\underline{H}_2$, 2H); 3.4–3.7 (broad multiple resonances, —COOCH$_2$C$\underline{H}_2$OC$\underline{H}_2$C$\underline{H}_2$O C$\underline{H}_2$C$\underline{H}_2$OC$\underline{H}_2$C$\underline{H}_2$OCH$_2$CH=CH$_2$, 14H); 3.9–4.2 (broad multiple resonances, —COOC$\underline{H}_2$-CH$_2$O—and —OC$\underline{H}_2$CH=CH$_2$, 4H); 5.0–5.3 (m, —OCH$_2$CH=C$\underline{H}_2$, 2H); 5.8–6.0 (m, —OCH$_2$C$\underline{H}$=CH$_2$, 1H).

3.2.4 Tetraethylene glycol monoallyl ether

A dry 250 ml Schlenk flask, equipped with a magnetic stir bar, was charged with 125 ml of freshly distilled THF and 8.6 g (0.37 g-atom) of sodium metal that had been freshly cut into small pieces. The flask was cooled to *ca* 0 °C and then 63.9 ml (71.8 g, 0.37 mol) of degassed tetraethylene glycol (Aldrich, 99%), was added over 1 h, during which time the surface of the sodium became shiny, and if stirring was stopped, turned blue. After addition, stirring was continued for 1 h under argon at 0 °C, at which time about three-quarters of the sodium metal was reacted and the solution was quite viscous. This mixture was allowed to warm to room temperature, stirred overnight under argon, and then heated at 50 °C for 4 h until all the sodium was reacted. The resulting clear, very viscous solution was transferred to a pressure-equalizing addition funnel that was connected to a 500 ml three-necked round-bottomed flask, euipped with a magnetic stir bar. To the 500 ml flask was added 100 ml of freshly distilled THF and 58 ml (81.1 g, 0.67 mol) of allyl bromide. The THF/allyl bromide solution

was heated to 60 °C and the alkoxide solution was then added dropwise over 2 h. After about 1 h, copious amounts of salts were present. The reaction mixture was allowed to cool to room temperature and was then treated with 250 ml of distilled water and 200 ml of ether. The organic and aqueous layers were separated and then the water layer was extracted with two 150 ml portions of ether. The ether layers were combined and concentrated at room temperature at reduced pressure. Final traces of solvent were removed under reduced pressure at 40 °C, leaving a slightly yellow, viscous liquid. Its ^{1}H NMR spectrum showed that, in addition to tetraethylene glycol monoallyl ether, the diallyl ether was also present. GLC confirmed the presence of two compounds. This mixture of compounds was dissolved in a 50:50 (v/v) mixture of ether/light petroleum ether (b.p. 30–60 °C) and poured onto a column containing alumina (Aldrich, activated, neutral, Brockmann I, *ca* 150-mesh, 155 $m^2 g^{-1}$). Elution with a large amount of the ether/light petroleum ether solvent mixture selectively removed the diallylated product, and the monoallylated product was subsequently eluted with methanol. Removal of methanol left 12.5 g (15%) of a clear, viscous oil whose ^{1}H NMR spectrum showed it to be tetraethylene glycol monoallyl ether.

^{1}H NMR (DMSO-d_6): δ 3.30–3.64 (multiple resonances, $HOC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OCH_2C\underline{H}_2OCH_2CH{=}C\underline{H}_2$, 16H); 3.93 (d, J_{HH} = 5.3 Hz, $-OC\underline{H}_2CH{=}CH_2$, 2H); 4.22 (broad, s, $H\underline{O}-$, 1H); 5.04–5.30 (m, $-OCH_2CH{=}C\underline{H}_2$, 2H); 5.76–5.98 ppm (m, $-OCH_2C\underline{H}{=}CH_2$, 1H).

^{13}C{^{1}H} NMR (DMSO-d_6); δ 60.2 (s); 69.0 (s); 69.7 (s); 69.8 (s); 71.0 (s); 72.3 (s); 116.2 (s, $\underline{C}H{=}\underline{C}H_2$); 135.2 ppm (s, $\underline{C}H{=}\underline{C}H_2$).

3.2.5 Tetraethylene glycol monoallyl ether methacrylate

This ester, a yellowish, viscous oil, was prepared using a standard procedure, the reaction of the alcohol with methacrylic acid in refluxing benzene.

Analysis: Calcd. for $C_{15}H_{26}O_6$: C, 59.58; H, 8.67%. Found: C, 59.91; H, 8.84%.

EI MS (*m/z*, rel. intensity): 303.2 (0.49); 302.2 (0.97, [M^+]); 274.2 (0.99); 261.3 (0.56); 244.2 (3.07); 231.2 (1.27); 216.2 (2.07); 200.1 (8.00); 172.1 (3.75); 157.1 (6.30); 145.1 (3.60); 133.1 (17.02); 113.1 (100.00); 85.0 (37.27); 73.1 (71.38); 69.1 (65.20); 59.2 (18.29); 45.1 (28.65); 43.1 (13.68); 41.1 (47.13).

^{1}H NMR (DMSO-d_6): δ 1.87 (s, $C\underline{H}_3$, 3H); 3.42–3.58 (multiple resonances, $-OC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OC\underline{H}_2C\underline{H}_2OCH_2CH{=}C\underline{H}_2$, 12H); 3.64 (t, J_{HH} = 5.0 Hz, $-COOCH_2C\underline{H}_2O-$, 2H); 3.93 (d, J_{HH} = 5.3 Hz, $-OC\underline{H}_2CH{=}CH_2$, 2H); 4.19 (t, J_{HH} = 4.6 Hz, $-COOC\underline{H}_2CH_2O-$, 2H); (5.05–5.30 (m, $-OCH_2CH{=}C\underline{H}_2$, 2H); 5.68 (m, $C\underline{H}_2{=}$, 1H); 5.78–5.94 (m, $-OCH_2C\underline{H}{=}CH_2$, 1H); 6.02 ppm (m, $CH_2{=}$, 1H).

^{13}C{^{1}H} NMR (DMSO-d_6): δ 17.9 (s, $\underline{C}H_3$); 63.7 (s); 68.2 (s); 69.0 (s); 69.7 (s); 69.8 (s); 71.0 (s); 116.2 (s, $-\underline{C}H{=}\underline{C}H_2$); 125.7 (s, $H_2\underline{C}{=}\underline{C}(CH_3)$); 135.2 (s, $-\underline{C}H{=}\underline{C}H_2$); 135.8 ppm (s, $H_2\underline{C}{=}\underline{C}(CH_3)$).

3.3 Hydrostannation of the —CH=CH$_2$ unsaturated polymers

3.3.1 Hydrostannation of high 1,2-polybutadiene; preparation of the corresponding tin acetate polymer P1

A 100 ml wide-mouthed bottle was charged with 8.1 g (0.15 mol unit) of the liquid, high 1,2-polybutadiene polymer and fitted with a septum. To the polybutadiene was added 15 ml of freshly distilled, degassed hexanes via a cannula, and the polybutadiene was dissolved with mild warming and vigorous shaking. This polybutadiene solution was degassed by bubbling argon through it for 15 min and was then transferred to a 250 ml Schlenk flask, equipped with a magnetic stir bar and containing 100 mg of AIBN.

The di-n-butylchlorotin hydride reagent, n-Bu_2SnHCl, was prepared as follows. Di-n-butyltin dichloride (16.7 g, 0.055 mol) was added to a 100 ml Schlenk flask containing a magnetic stir bar. Subsequently, 12.9 g (0.055 mol) of di-n-butyltin dihydride was added. The resulting liquid/solid mixture rapidly became homogeneous. The mixture was stirred for 5 min, resulting in a slightly yellow chlorotin hydride reagent (theoretically, *ca* 0.11 mol).

The n-Bu_2SnHCl was transferred to the polybutadiene solution and the reaction mixture was heated with stirring at 60 °C. Heating under argon was continued for 24 h, after which time the solution was noticeably more viscous and some grey metallic-looking material had precipitated (*ca* 300 mg). The contents of the flask were fil-

tered through Celite and to this clarified solution was added, with stirring, 14.0 g (0.25 mol) of KOH dissolved in 100 ml distilled water. An exothermic reaction ensued, and after *ca* 15 min stirring was no longer possible as an insoluble, gel-like material resulted. Presumably, this material was highly croslinked through bis-tin-oxide linkages. The gel-like material was broken up and the mixture was shaken from time to time, over a period of 1 h. Filtration through filter paper (the material clogs a glass frit) was followed by thorough washing with distilled water. This slightly yellow material was transferred to a 500 ml flask and 60 ml of glacial acetic acid (62.9 g, 1.0 mol) was added at room temperature. A nearly homogeneous, viscous solution resulted. The latter was stirred for 1 h and from time to time was heated with a heat gun to *ca* 60–70 °C. After this time, the contents of the flask were poured into a 1 l separatory funnel and to this was added 500 ml of ether and 100 ml of distilled water. The organic and aqueous layers were separated and the ether layer was washed with 100 ml of distilled water. Most of the ether was removed and to the clear, homogeneous solution which remained was added 750 ml of methanol. Some polymer precipitated immediately. The resulting cloudy solution was allowed to stand overnight. The solvent was decanted from the polymer and then the polymer was dried under vacuum for 48 h at room temperature, giving 11.0 g (*ca* 30% yield, based on weight of starting materials) of a slightly opaque semi-solid (more solid-like than the polybutadiene prepolymer). The opacity in the polymer could not be removed from it, even after multiple precipitations from ether by the addition of methanol. Further, as the degree of hydrostannation increased, the opacity became more apparent; it is therfore possible that the opacity is caused by crystallinity in the polymer. The IR spectrum (neat, thin film) of this polymer exhibited two strong absorptions at 1570 and 1450 cm^{-1} that are characteristic of the C(O)O stretches of trialkyltin acetates. Absent from the IR specrum of this material were O—H absorbances due to the presence of water, methanol or Sn—OH.

The polymer consists of the following repeat units:
$(1,2\text{-PBD})_a(1,4\text{-PBD})_b(1,2\text{-PBDSn})_c(1,4\text{-PBDSn})_d$, where 1,2- and 1,4-PBD are the unreacted 1,2- and 1,4-PBD repeat units, respectively, and 1,2- and 1,4-PBDSn are the repeat units containing 1,2- and 1,4-tin acetate, respectively. The following exact relations can be derived for the vinyl resonances (V) and the aliphatic resonances (A) for this functionalized polymer:

$$V = 3a + 2b$$

$$A = 3a + 4b + 28c + 28d$$

where a, b, c and d are the numbers of units, as defined above. Since $a \cong b$, we can approximate $V = 2.5B$, where B is the approximate, average number of unreacted butadiene units (both 1,2- and 1,4-). Also we may write

$$A = 3.5B + 28H$$

where H is the number of tin-containing repeat units ($B + H \cong 1$), or the approximate, average degree of hydrostannation. Therefore, the degree of hydrostannation may be estimated using the following relation, where $I(V)$ and $I(A)$ are the integrals of the vinyl and aliphatic resonances, respectively:

$$\frac{I(V)}{I(A)} = \frac{2.5B}{3.5B + 28H}$$

Using ^{1}H NMR spectroscopy and the equation derived for the average degree of hydrostannation with Sn—H, as described above, polymers prepared by this method were hydrostannated to an extent of 20–25%. Also, using ^{1}H NMR and the equation derived for the proportions of 1,2- and 1,4-polybutadiene repeat units in the polymer (Section 3.2.1), one concludes that hydrostannation is not exceedingly selective in that considerable amounts of both 1,2- and 1,4-polybutadiene units are hydrostannated. The ^{119}Sn{^{1}H} NMR spectrum of **P1** showed little or no concentration dependence in the range of 20–40 polymer wt % solution in benzene-d_6. GPC analysis of this polymer ($CHCl_3$/DMSO, 10:1, v/v) showed that the hydrodynamic volume of the tin acetate polymer, **P1**, was smaller than that of the starting polybutadiene, as the polymer eluted considerably later than the starting polybutadiene under identical GPC conditions.

Analysis: Calcd for 25% hydrostannation: C, 61.31; H, 9.10; Sn, 23.30%. Calcd for 20% hydrostannation: C, 63.95; H, 9.30; Sn, 21.06%. Found: C, 63.82; H, 9.30; Sn, 20.92%.

^{1}H NMR (benzene-d_6): δ 0.5–2.7 (broad multiple resonances, aliphatic); 4.8–6.2 ppm (broad multiple resonances, unsaturated).

$^{119}Sn\{^1H\}$ NMR (benzene-d_6): δ −152.4, −131.0 (s, six-coordinate tin); 93.7, 144.1 ppm (s, four-coordinate tin). Note that multiplicity is believed to arise from the fact that both 1,2- and 1,4- C=C were hydrostannated (Fig. 2).

$^{119}Sn\{^1H\}$ NMR (benzene-d_6 + 5 equiv. DMSO): δ 6.2, 24.0 ppm (s, five-coordinate DMSO adduct). Note that multiplicity is believed to arrive from the fact that both 1,2- and 1,4- C=C were hydrostannated (Fig. 3). Note also that the $^{119}Sn\{^1H\}$ NMR chemical shifts of the polymer **P1** + DMSO can vary by ±5 ppm, depending upon the degree of hydrostannation and the exact amount of DMSO that was added.

3.3.2 Hydrostannation of linear 1,2-poly(tetraethylene glycol monoallyl ether methacrylate)

A dry 100 mL Schlenk flask, equipped with magnetic stir bar, was charged with 3.0 g (9.92 mmol unit) of linear 1,2-poly(tetraethylene glycol monoallyl ether methacrylate) and 100 mg of AIBN. This mixture was degassed via three 10 min pump-down cycles, backfilling with argon each time. Degassed benzene (100 ml) was added and the solution was stirred for 5 min to dissolve the polymer and the catalyst. To this solution was added 4.0 g (0.0148 mol) of the liquid chlorotin hydride reagent via a syringe. The homogeneous reaction mixture was heated at 60 °C under argon. Within 15 min, the solution began to turn slightly gray and within 30 min, a gray, metallic solid had precipitated from solution. Heating was continued for 16 h and then the reaction mixture was allowed to cool to room temperature. To the resulting solution was added 25 ml of dry benzene and the entire contents of the flask were filtered through Celite in air. The clarified solution was poured into 250 ml of light petroleum ether (b.p. 30–60 °C) to precipitate the polymer. The solution was decanted from the solid polymer and the latter was washed with 250 ml of light petroleum ether and dried under vacuum at room temperature for 24 h to gie 5.0 g (*ca* 70% yield, based on the weight of starting materials) of a slightly yellow, viscous oil (much more viscous than the starting polymer). ^1H NMR spectroscopy showed that extensive hydrostannation had taken place. the $^{119}Sn\{^1H\}$ NMR spectrum of **P3** showed little or no concentration dependence in the range of 15–25 polymer wt % solution in benzene-d_6. GPC analysis on this polymer was not performed, because of the reactive nature of the Sn—Cl bond.

Analysis: Calcd for 70% hydrostannation: C, 50.40; H, 8.07; Sn, 16.92; Cl, 5.06%. Found: C, 50.17; H, 8.04; Sn, 16.84; Cl, 5.77%.

^1H NMR (benzene-d_6): δ 0.9–2.9 (broad m, aliphatic); 2.9–4.5 (broad, m, aliphatic); 5.0–5.4 (broad m, unreacted allyl groups, $—CH_2CH=C\underline{H}_2$); 5.7–6.0 ppm (broad m, unreacted allyl groups, $—CH_2C\underline{H}=CH_2$).

$^{119}Sn\{^1H\}$ (benzene-d_6): δ 66.1 ppm (s, five-coordinate tin) (Fig. 4).

$^{119}Sn\{^1H\}$ (benzene-d_6 + 5 equiv. DMSO): δ 50.5 ppm (s, five-coordinate DMSO adduct).

3.4 Preparation and testing of the crosslinked tin-containing coatings

3.4.1 General testing procedure

Office of Naval Research protocol was followed. The subject coatings were tested against AF121 (common, commercially available marine antifoulant) and G10 epoxy and/or glass control rods. Twenty rods of each type where immersed in a test tank under throughflow seawater conditions. In the case of coating **C1**, a three-day preliminary immersion was performed before the test was started. This procedure was not carried out on coating **C2**. Five rods were removed each week during the testing period for four weeks. The extent of fouling for each set of rods removed was determined, so that a week-by-week update on the antifouling properties of the rods was obtained. Nonparametric statistics were used to determine if there were significant differences between the subject coatings and the control rods.

Organisms against which the antifouling characteristics of the coatings were measured were aborescent bryozoa, barnacles, tube worms, bivalves, tunicates, amphipods, colonial hydroids and encrusting bryozoa. All values were recorded as counts of individuals, except those for colonial hydroids and encrusting bryozoa, which were recorded as percentages of surface covered.

3.4.2 Preparation of coatings

(a) Coating **C1** *from polymer* **P1**

A 100 ml graduated cylinder containing 10 mg of AIBN was charged with 1.0 g of the polybutadiene-based tin acetate polymer, **P1**, and 70 ml of benzene. This mixture was stirred for *ca* 5 min to dissolve the polymer completely. Glass rods (23 in total, of which 21 were for testing and two for elemental analysis) of dimensions 11 cm × 7 mm were sanded with garnet paper and then

washed and dried. These rods were dipped into the solution a total of three times, allowing 15 min of drying time in the air between dips. After the dipping process, the rods were hung from an apparatus constructed from copper wire that could accommodate all the rods at once and air-dried for 2 h. After this time, the rods were tacky to the touch. The entire appratus containing the 23 rods was placed in a cylindrical, 16-lamp, Rayonet (Southern New England Ultraviolet Company) photochemical reactor. The lamps of this reactor were of the low-pressure mercury-vapor type, which delivered a wavelength of 254 nm. The rods were irradiated at room temperature for 12 h; after this time the coatings on the rods were clear, durable and non-tacky. Such coatings could not be removed by any solvent, but could be scraped from the rods with a razor. Each rod produced in this fashion contained 5–10 mg of material. Elemental analysis of the coating gave 20.10% tin, which is close to the value obtained for **P1**. The IR spectrum of this coating showed the presence of a tin acetate, as evidenced by strong absorptions at 1581 and 1439 cm^{-1}. In addition to these absorbances, there were also strong bands at 1723 and *ca* 3400 cm^{-1}, which can be attributed to acetic acid (and water), due to hydrolysis. It is likely that the polymer crosslinked via bis-oxide linkages, as well as through C=C unsaturation, with UV light aiding in hydrolysis. High 1,2-polybutadiene, under identical conditions, formed crosslinked, insoluble coatings as well.

(b) *Coating* **C2** *from polymer* **P3**

A 100 ml crystallizing dish containing 100 mg of AIBN was charged with 2.0 g of the linear 1,2-poly(tetraethylene glycol monoallyl ether methacrylate)-based tin chloride polymer, **P3**, and 20 ml of benzene. This mixture was swirled for *ca* 5 min to dissolve the polymer and the AIBN completely. The rods (21 G10 epoxy for testing and two glass for elemental analysis) of dimensions 11 cm × 7 mm were sanded with garnet paper and then washed and dried. These rods were painted twice, allowing a 15 min drying time between coats, and then the rods were hung on the apparatus described above and allowed to air-dry for an additional 2 h, after which they were tacky to the touch. The rods were irradiated in the photochemical reactor. After 24 h at room temperature, the rods were still slightly tacky, so irradiation was continued for an additional 48 h, after which time the rods were clear and tack-free. Such coatings appear to remain indefinitely in water. Elemental analysis of the coating showed that it contained 21.83% tin, which is consistent with the tin content found in polymer **P3**.

This coating, **C2**, as was the case with **C1**, was found to be ineffective as an aquatic antifoulant. 'Fouling on the test coating and the G10 epoxy controls was dominated by hydroids. Barnacles were also present but in low numbers. The AF 121 rods were not significantly fouled after the testing interval. Clearly, no significant difference in fouling exists between the test coating and the G10 epoxy controls (J. W. Reisenweber, personal communication, 6 January 1993).

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