Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Charles E. Carraher Jr.[a]; Timothy J. Gehrke[a]; David J. Giron[a]; Delie Roselyn Cerutis[a]; H. M. Molloy[a]
[a] Departments of Chemistry and Microbiology and Immunology, Wright State University, Dayton, Ohio

To cite this Article Carraher Jr., Charles E. , Gehrke, Timothy J. , Giron, David J. , Cerutis, Delie Roselyn and Molloy, H. M.(1983) 'Structure and Characterization of the Condensation Products of Dextran and Organostannane Halides', Journal of Macromolecular Science, Part A, 19: 8, 1121 — 1135

To link to this Article: DOI: 10.1080/00222338308081089

URL: http://dx.doi.org/10.1080/00222338308081089

J. MACROMOL. SCI.–CHEM., A19(8&9), pp. 1121-1135 (1983)

Structure and Characterization of the Condensation Products of Dextran and Organostannane Halides

CHARLES E. CARRAHER, JR., TIMOTHY J. GEHRKE,
DAVID J. GIRON, DELIE ROSELYN CERUTIS, and H. M. MOLLOY

Departments of Chemistry and Microbiology and Immunology
Wright State University
Dayton, Ohio 45435

ABSTRACT

The modification of dextran, a water-soluble polysaccharide, through condensation with organostannane halides was accomplished utilizing the interfacial technique. Structural analysis agreed with condensation of the dextran-hydroxyls forming tin ether linkages with the dextran. Thermal degradation occurs through several stability plateaus and in air occurs through an oxidative pathway(s). Some of the products inhibit bacteria commonly responsible for mildew and rot.

INTRODUCTION

Currently, because the ready sources of feedstocks, such as petroleum-based compounds, are being consumed at a faster rate than they are being discovered, there is a need for conservation, renewing of feedstocks, and development of readily available, regenerable natural feedstocks. Polysaccharides are one such readily available, natural feedstock.

Carraher and co-workers synthesized a number of metal-containing polymers through reaction with a wide variety of diols including

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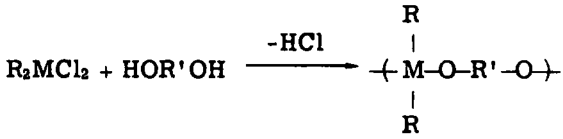
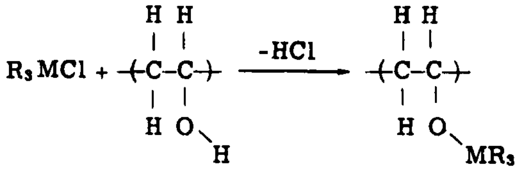
ethylene glycol and hydroquinone including M=tin (such as Refs. 1-6):



$$R_2MCl_2 + HOR'OH \xrightarrow{-HCl} \left(\overset{R}{\underset{R}{M}}-O-R'-O \right)$$

1

Further, polyvinyl alcohol has been successfully modified through condensation with a wide variety of organometallic halides (for instance, Refs. 7-9):



$$R_3MCl + \left(\overset{H}{\underset{H}{C}}-\overset{H}{\underset{O-H}{C}} \right) \xrightarrow{-HCl} \left(\overset{H}{\underset{H}{C}}-\overset{H}{\underset{O-MR_3}{C}} \right)$$

2

In general there is a direct correlation between reactions with the hydroxyl contained on a polymer and the reactions employing diols [3, 10]. An extension is the modification of polysaccharides through condensation of the hydroxyl groups of the polysaccharides to give products of varying exact structure containing a variety of units with varying metal content including unreacted units.

Carbohydrates are the most abundant class of naturally occurring organic compounds. They constitute three-fourths of the dry weight of the plant world and are widely distributed in both plant and animal forms of life. Thus the vegetation of the earth contains large quantities of chemically combined polysaccharides. Polysaccharides are typically high molecular weight (~25,000 to 15,000,000) polymers composed of monosaccharide units. These polysaccharides are exceedingly complex with the general composition varying according to the source and the exact structure varying from chain to chain even when derived from the same source. An exact structure for these polymers cannot be written but the general structure can be described in a reasonable degree of completion.

Dextran was the polysaccharide chosen for preliminary study. It is water soluble, permitting the evaluation of aqueous reaction systems. Also, it is readily available on a large scale in a wide variety of molecular weights, the latter permitting modification of dextran to be studied as a function of chain length.

Dextrans are primarily found in yeast and bacteria and are branched storage polysaccharides of D-glucose with the major backbone predominantly connected through the 1→6 sites. Additional linking and branching may be of the 1→2, 1→3, and 1→4 forms.

Here we present evidence related to the structure of the condensation products derived from dextran and organostannane halides and the results of some preliminary thermal and biological studies.

EXPERIMENTAL

Dextran (molecular weight 2 to 3 × 10^5, United States Biochemical Corporation, Cleveland, Ohio); dibutyltin dichloride (Fisher, Fairlawn, New Jersey); diphenyltin dichloride (Metallomer Labs., Maynard, Massachusetts); diethyltin dichloride (Ventron-Alfa Inorganics, Beverly, Massachusetts); tri-n-propyltin chloride (Alfa); tri-n-butyltin chloride (Aldrich, Milwaukee, Wisconsin); dioctyltin dichloride (Alfa); dilauryltin dichloride (Metallomer); dimethyltin dichloride (Alfa); tricyclohexyltin bromide (Alfa); triethylene diamine (Eastman Kodak Co., Rochester, New York); triethylamine (Eastman); piperdine (Matheson, Coleman and Bell, Cincinnati, Ohio); N,N-dimethylaniline (Fisher); 3,5-latidine (Aldrich); and pyridine (J. T. Baker Chemical Co., Phillipsburg, New Jersey) were used as received.

The reaction procedure and apparatus is fully described elsewhere [11]. Briefly, the dextran in water along with added base is added to rapidly stirred solutions of stannane in an appropriate organic liquid.

Infrared spectra were obtained using a Perkin-Elmer 457 Grating Infrared Spectrophotometer and a Nicolet MX-1 Fourier Transform Infrared Spectrophotometer employing KBr pellets.

Thermogravimetric analysis (TG) was carried out utilizing a DuPont 951 Thermogravimetric Analyzer. Differential scanning calorimetry (DSC) was carried out using a DuPont cell base connected to a DuPont 990 Thermal Analyzer console employing a linear baseline compensator to insure a constant energy baseline. A Mettler H-20 semimicro balance was employed for weighing the DSC samples. DSC measurements were obtained in open aluminum cups to allow the volatilized materials to flow freely away from the solid. This closely simulates the conditions employed for TG measurements. A purge gas (helium, nitrogen, argon, or air) flow rate of about 50 mL/min was employed.

Mass spectrometry results were obtained utilizing a double-focusing DuPont 21-491 Mass Spectrometer employing a Hewlett-Packard HP-2116C computer having a disk-oriented data system especially developed for the DuPont 21-491 MS. The MS system is under the control of the HP 2116C computer operating with a dual 2.5M byte disk drive, a Hewlett-Packard Cathode Ray Tube terminal, a Tektronix storage scope, driven by a dual 12 bit digital-to-analog converter, and a Versatec printer-plotter. Data are acquired using a 14-bit analog-to-converter. The system can operate and process data at rates to 8 kHz.

Elemental analyses for tin were conducted as described in Ref. 12 except that one drop of water and concentrated nitric acid (10 drops) are added subsequent to the sodium fusion and this mixture is heated until brown fumes are evolved. Also, the stannic sulfide is heated in air converting it to stannic oxide which is weighed and this weight utilized in determining the percentage tin. This process is not suitable for volatile organostannanes such as dibutyltin dichloride, but is suitable for tin polyesters, polyethers, and polyamines. Tin polyesters were utilized as control compounds. Thus the polyester derived from disodium adipate and dibutyltin dichloride has been found to contain 31% tin with the calculated value being 31%.

Biological assays were carried out as follows. Tryptic soy agar plates were seeded with suspensions of the test organism to produce an acceptable lawn of test organism after 24 h of incubation. Shortly after the plates were seeded (less than 2 h), the tested compounds were weighed out and deposited (either as solids or in solution) on the plates as small round dots. The plates were then incubated 244 h and the inhibition noted. The results are averages of at least duplicate examinations.

Solubility tests were conducted by placing about 1 mg of sample in 3 mL of liquid at room temperature. The mixtures were periodically shaken and observed for 1 to 3 d.

RESULTS AND DISCUSSION

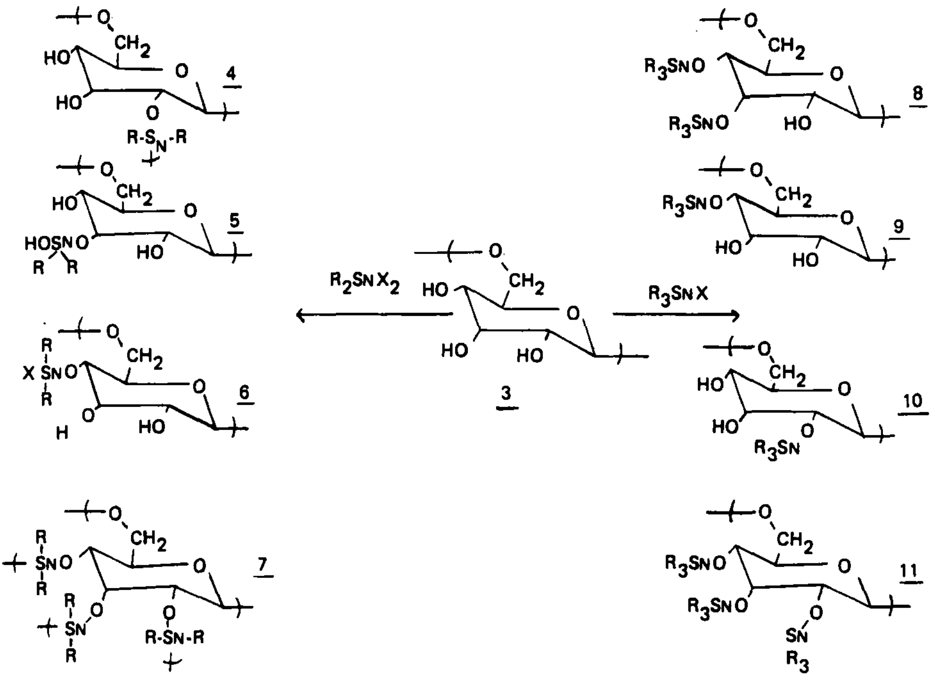
Structure

General

Physical characterization data will be presented in this section aimed at the identification of the condensation products formed through the condensation of hydroxyl groups, present in dextran, with an organotin halide. Several possible units which could contribute to the overall structure of the products are given in Forms 3, 8-11 for products derived from monohalostannanes and as 3-7 for products derived from dihalostannanes. It is reasonable to assume that the actual structure will vary from chain to chain, each being composed of a mixture of the hexose units, the proportion of each unit per chain being dependent on the nature of the stannane and the reaction conditions.

Historical

As noted in the Introduction, the condensation of organostannane halides with hydroxyls contained in the dextran is a direct extension of the reaction of organostannane dihalides with diols and of organostannane mono- and dihalides with polyvinyl alcohol under similar reaction conditions.



Control Reactions

The term "control reactions" describes conducting reaction sequences in the usual manner except omitting one of the reactants. For instance, in the aqueous interfacial system, the reaction sequence was carried out except omitting the organotin halide for one reaction attempt and dextran for another reaction attempt. Neither reaction attempt produced precipitate. When both reactants are present, along with added base, a white precipitate is formed. The above is consistent with the precipitate containing components of both the dextran and organostannane.

Elemental Analysis

Elemental analyses were conducted on the samples to determine the amount of tin present. Results varied depending on the nature of the organostannane halide (Table 1) but were fairly constant over a wide variety of reaction conditions when employing dibutyltin dichloride (% Sn = 22-26). The results are consistent with the product containing about one tin moiety per hexose unit.

Infrared Spectroscopy

Analysis of the infrared spectra of the products are consistent with the dextran being modified by the formation of Sn–O–R ether linkages

TABLE 1. Yield and Tin Content as a Function of Organotin Halide[a]

Organotin halide	Organotin halide (mmol)	Dextran (mmol)	Yield (%)	Yield (g)	Sn (%)	Sn % at 100 substitution
ϕ_2SnCl_2	6	4	77	1.7	12	30
Me_2SnCl_2	6	4	65	1.0	33	47
$(C_8H_{17})_2SnCl_2$	6	4	92	2.6	23	26
$(C_8H_{17})_2SnCl_2$[b]	6	4	67	1.9	18	26
$(C_{12}H_{25})_2SnCl_2$	6	4	76	2.6	15	21
$(C_4H_9)_2SnCl_2$	6	4	81	1.7	23	35
ϕ_3SnCl	12	4	95	4.7	14	29
ϕ_3SnCl	8	4	100	3.7	-	29
$(C_4H_9)_3SnCl$	12	4	2	0.05	-	35
$(C_6H_5CH_2)_3SnCl$	12	4	13	0.7	14	26
$(C_6H_5CH_2)_3SnCl$	6	2	11	0.3	14	26
$(C_6H_{11})_3SnBr$	6	2	11	0.3	16	29

[a] Reaction conditions: Dextran and sodium hydroxide (held at a 3:1 NaOH:dextran ratio) in 40 mL of aqueous solution is added to stirred (18,000 rpm) chloroform (40 mL) containing organotin halide at 25°C for a stirring time of 30 s.

[b] In CCl_4 instead of chloroform.

TABLE 2. Positions of Sn–O–R Bands as a Function of Employed Stannane

Stannane	Sn–O–R asymmetric stretch (cm^{-1})	Sn–O–R symmetric stretch (cm^{-1})
Bu_2SnCl_2 [a]	665	598, 570
Bu_2SnCl_2	665	598, 570
Bu_3SnCl	670	598, 570
$(C_6H_{11})_3SnBr$	660	580, 555
$(CH_3)_2SnCl_2$	660	570, 555
$(C_8H_{17})_2SnCl_2$	665	595, 560
$(C_6H_5CH_2)_3SnCl$	690	580, 560

[a] Cellulose derived from cotton.

through condensation of the stannane at hexose hydroxyl sties. Formation of the ether linkage is indicated by the presence of bands between 660 and 690 cm^{-1}, which are characteristic of the asymmetric stretch of tin ethers, and a doublet in the region of 550 to 600 cm^{-1}, which is attributed to the symmetric stretch of tin ethers (Table 2 and Figs. 1-3).

Bands characteristic of the organotin moiety are also present in the spectra of the products. For instance, for the product made from Bu_2SnCl_2 (Fig. 1), bands characteristic of methylene (CH_2) deformation are present at 1470 and 1150 cm^{-1}; bands characteristic of the presence of the methyl group are present at 1420 (assymetric stretching) and 1380 (symmetric stretching) cm^{-1}; a quartet of hands characteristic of the C–H stretch present in n-butyl groups are present at 2955, 2910, 2870, and 2855 cm^{-1}; and bands at 665, 598, and 570 cm^{-1} which are attributed to the presence of the Sn–O–R moiety (Table 2). Further bands attributed to the symmetric C–O stretch are present at 1010, 885, and 865 cm^{-1} and bands attributed to assymmetric C–O stretching are present at 1070 cm^{-1}. A broad band from 3500 to 3200 cm^{-1} is present and is attributed to the presence of unreacted hydroxyl groups and/or water trapped during reactions employing water. This band is also present in products made in nonaqueous systems; thus it must be due to the presence of unreacted hydroxyl groups for at least these systems.

For the products derived from dihalostannanes there are two additional groupings which should be considered. These are the Sn–Cl and Sn–OH moieties. Bands characteristic of the Sn–OH moiety vary between 3400 to 3500 cm^{-1}, making identification and differentiation of the Sn–OH from the R–OH moiety difficult. Bands characteristic of the

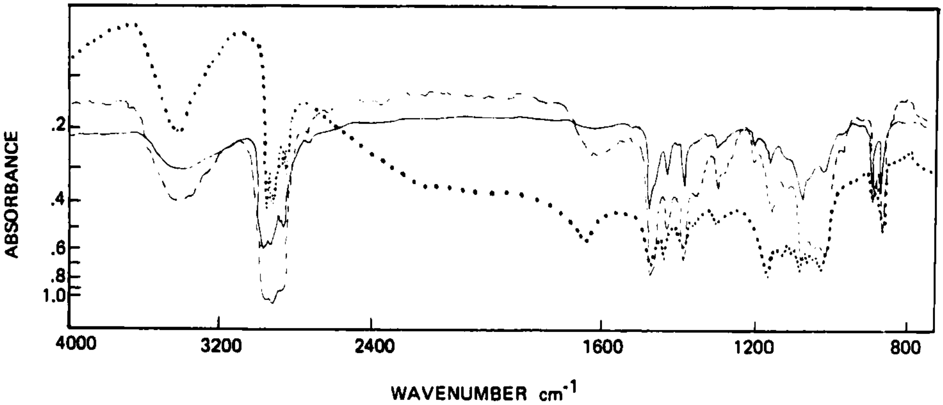


FIG. 1. Infrared spectrum of dextran modified through reaction with $(C_4H_9)_2SnCl_2$ utilizing conventional infrared spectroscopy (- -) and Fourier-transform infrared spectroscopy (•••••) and cellulose derived from cotton modified through reaction with $(C_4H_9)_2SnCl_2$ utilizing conventional infrared spectroscopy (—).

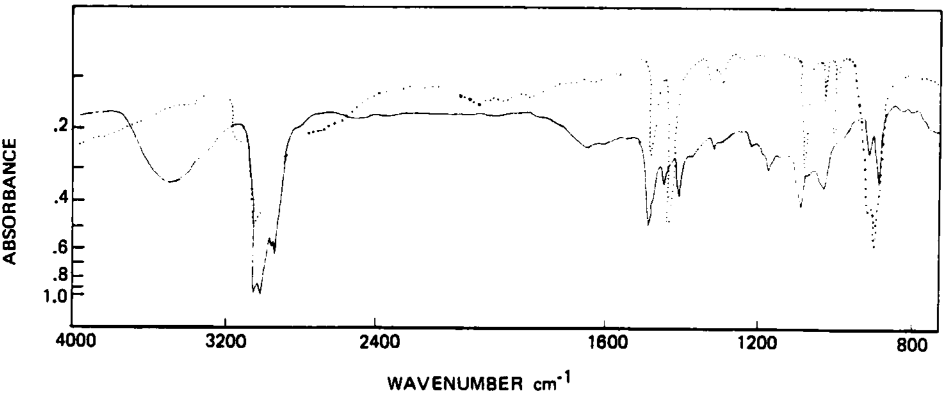


FIG. 2. Infrared spectrum of dextran modified through reaction with ϕ_3SnCl (•••••) and $(C_4H_9)_3SnCl$ (——).

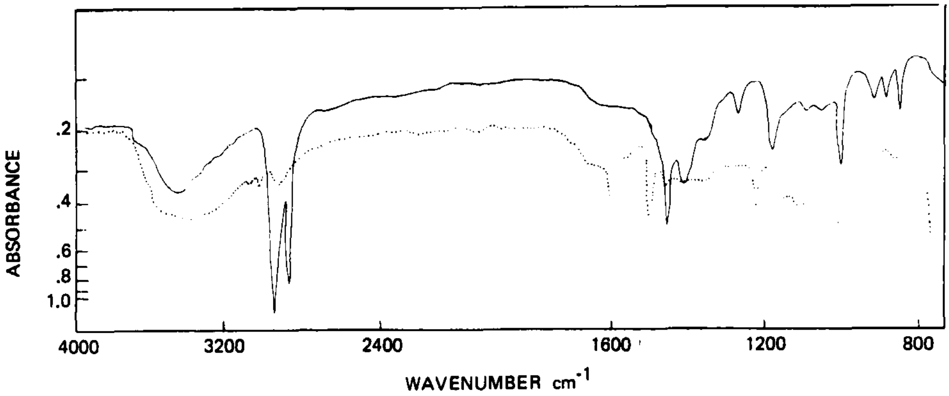


FIG. 3. Infrared spectrum of dextran modified through reaction with $(C_6H_5CH_2)_3SnCl$ (•••••) and $(C_6H_{11})_3SnBr$ (——).

OH stretch in Sn–OH groups reach a maximum at about 3470 to 3500 cm^{-1} and can often be identified or eliminated through the observation of breaks in the R–OH band located between 3200 to 3500 cm^{-1}. For the products reported here, this region is typically smooth, indicating the absence of significant Sn–OH groups (which would be formed from the hydrolysis of Sn–Cl). Thus the presence of significant quantities of units containing Sn–OH groups such as Structure 5 is eliminated. The Sn–Cl stretching occurs between 320 and 350 cm^{-1}, depending upon the tin substitution [13]. There exists quite a variety in intensity and/or the presence of bands in this region, depending on the mode of synthesis. Thus conclusions based solely on the presence of bands in this region are uncertain. For instance, the product derived from the aqueous interfacial condensation of dioctyltin dichloride with dextran shows a moderate band at 350 cm^{-1} and a smooth broad band in the 3500 to 3100 cm^{-1} region, which is characteristic of the presence of Sn–Cl groups, but not Sn–OH groups. This is consistent of products containing units such as 6. The product derived from the aqueous interfacial condensation employing Me_2SnCl_2 shows the absence of a band in the 400 to 300 cm^{-1} region and a smooth, broad band between 3500 to 3100 cm^{-1}, indicating the absence of a significant number of Sn–OH and/or Sn–Cl units consistent with the presence of units such as 4 and 7.

Furthermore, Fig. 1 includes a companion infrared spectrum of the condensation product derived from cotton and dibutyltin dichloride. This spectrum appears identical to that of the product derived from dextran. Comparisons of other spectra of modified cellulosic products derived from cotton and dextran are also identical, as expected, in agreement with the similarity of cellulose derived from cotton and dextran. Figure 1 also includes a spectrum determined by using a Fourier-Transfer infrared spectrophotometer. The most striking difference concerns the sharpening of the bands due to C–H stretching in the 3000 to 2700 cm^{-1} region. The FT-IR exhibits seven distinct bands: five due to the presence of the butyl group derived from the dibutyltin moiety (at 2960, 2935, 2920, 2875, and 2855 cm^{-1}) and two weaker bands derived from the dextran (at 2895 and 2885 cm^{-1}). Though many of the cellulose C–H stretching vibrations are lost, the stronger bands due to the butyltin moiety are present within ±5 cm^{-1} of that found for dibutyltin dichloride itself and in the same general display pattern with respect to relative length. Thus the presence of both tin moieties is indicated by the spectral evidence given by the FT-IR.

In summary, infrared spectroscopy is consistent with the formation of tin ether groups through condensation of the halostannane with hydroxyl groups on the dextran. For dihalostannanes, the absence of significant quantities of Sn–OH groups is indicated.

Product Solubility

Extensive solubility tests were conducted on two representative products. One was dextran modified using a monohalo-organostannane (triphenyltin chloride) while the other was dextran modified employing a dihalostannane (diphenyltin dichloride). Tested liquids included chloroform, carbon tetrachloride, dimethylsulfoxide (DMSO), dimethylformamide (DMF), acetone, hexamethylphosphoramide (HMPA), hexachloroacetone, triethyl phosphate, and cyclohexane.

Products derived from the diphenyltin dichloride should be insoluble if cross-linking occurs. This is what was found. The use of monohalostannanes does not lead to cross-linking, thus such products may be soluble in appropriate liquids. However, the products derived from triphenyltin chloride were also insoluble in all attempted liquids.

Mass Spectrophotometry

The mass spectra contains ion fragments characteristic of the presence of both the polysaccharide (here cellulose) and organostannane units. For instance, for the product derived from triphenyltin chloride and polysaccharide, significant (normalized intensities of one and greater compared to the mass intensity of the most abundant ion fragment, here m/e of 28 derived from nitrogen) ions are found at (all ion locations are given in m/e units unless noted otherwise) 79, 78 (parent for benzene), 77, 76, 74, 61, 52, 51, 50, and 39 characteristic of the phyenyl group and 121, 120, 117, 73, 70, 57, 56, 55, 53, 51, 50, 49, 42, 37, 31, 29, 27, and 26 derived from the hexose unit with ion fragments present from 176 to 182 derived from one hexose unit plus two ether oxygens, 162-168 from one hexose unit including one ether oxygen, and 147-152 from one hexose unit excluding ether oxygens. There are trace (less than 10^{-2}% normalized intensity) amounts of higher (instrumental calibration to 400) ion fragments at 358 (one hexose unit plus ϕSn, 327 (two hexose units), 351-353 (ϕ_3Sn), 271 (ϕ_2Sn), 197 (ϕSn), and 311 (two hexose units minus one hydroxyl).

For the product derived from dibutyltin dichloride, ion fragments characteristic of the hexose unit appear at 121, 120, 116, 73, 70, 57, 56, 55, 53, 51, 50, 49, 42, 37, 31, 29, 27, and 26 with ions at 15, 27, 29, 39, 41, and 43 (ion fragments at 27 and 29 are derived from both moieties) derived from the n-butyl moiety, with ion fragments characteristic of one hexose unit plus two ether oxygens present at 176 to 182, 161-167 from one hexose unit including one ether oxygen, and 149-153 from one hexose unit excluding ether oxygens. Again there are trace (less than 10^{-2}% normalized intensity) amounts of higher ion fragments at 309 (hexose unit plus BuSn minus CH_2OH), 329-325 (two hexose units), 381 (hexose unit plus Bu_2Sn minus hydroxyl), 232-236 (Bu_2Sn minus hydroxyl), 232-236 (Bu_2Sn), and 174-177 (BuSn).

While units containing tin were found, these represented no more than 10^{-2}% by weight of the tin present in the product assuming one organostannane per hexose unit. Thus the vast majority of tin remained within the residue.

Summary

Physical characterization of the products resulting from combining dextran with organotin halides under various reaction conditions is consistent with a tin-modified product composed of units such as those depicted in 3 through 11. Results from the elemental analysis shows tin present consistent with the presence of the organotin moiety. Results from studying control reactions are consistent with the product being derived from both the organotin halide and dextran. The presence of the organotin moiety, dextran, and the tin-ether linkage is indicated by infrared spectroscopy. Mass spectral results are also consistent with the presence of both reactants.

Characterization

Thermal Properties

The organostannane-dextran products exhibited thermogravimetric (TG) thermograms characteristic of other organometallic polymers showing regions where weight loss is relatively low over a given temperature range compared with other regions where weight loss is considerably greater over the same temperature range [3, 10]. Weight losses typically began at about 150°C with the majority of weight lost before 400°C. Representative TG thermograms appear as Figs. 4 and 5. TG thermograms in air and under inert conditions, nitrogen, or helium atmosphere are typically dissimilar.

Differential scanning calorimetry (DSC) thermograms are similar up to about 125 to 150°C with no accompanying weight loss by TG (Figs. 4-6). These initially mild energy changes are probably associated with some type of internal phase transitions but not degradation of the prod-

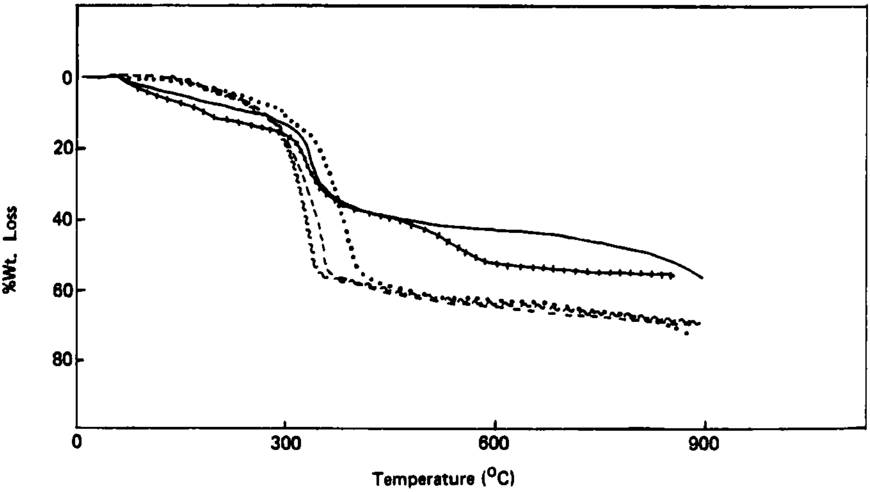


FIG. 4. Thermogravimetric analysis thermograms of dextran modified through reaction with Bu_2SnCl_2 in helium (~ ~ ~); $(C_6H_5CH_2)_3SnCl$ in air (-++-) and nitrogen (—); and $(C_{12}H_{25})_2SnCl_2$ in air (- -) and nitrogen (•••••) using 0.100 g of sample with a gas flow rate of 50 mL/min and a heating rate of 20°C/min.

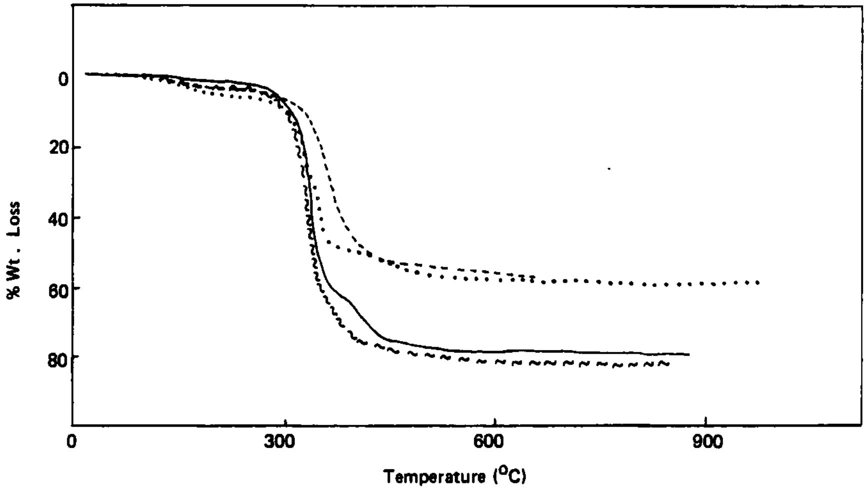


FIG. 5. Thermogravimetric analysis of dextran modified through reaction with $(C_6H_5)_3SnCl$ in air (~ ~ ~) and nitrogen (—), and $(CH_3)_2SnCl_2$ in air (•••••) and nitrogen (- -) using 0.100 g of sample with a gas flow rate of 50 mL/min and a heating rate of 20°C/min.

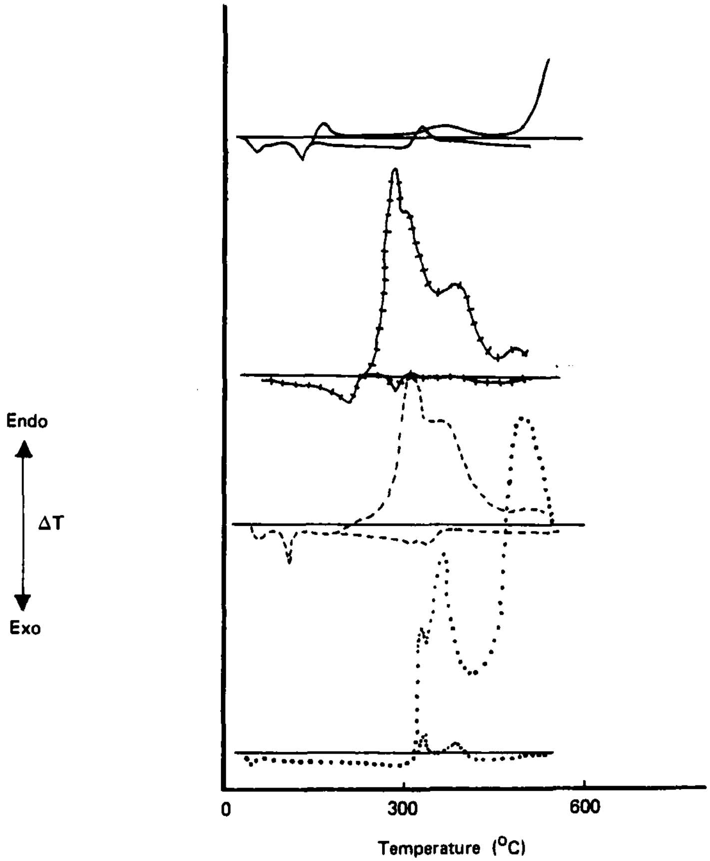


FIG. 6. Differential scanning calorimetry thermograms of dextran modified through reaction with (from top to bottom) $(C_6H_5CH_2)_3SnCl$ in air (upper portion after 275°C) and nitrogen, $(C_6H_{11})_3SnBr$ in air (upper portion after 275°C) and nitrogen, and $(CH_3)_2SnCl_2$ in air (upper portion after 300°C) and argon. Measurements obtained using 0.100 g of sample with a gas flow rate of 50 mL/min and a heating rate of 20°C/min. The straight line indicates where $\Delta T = 0$.

duct. The DSC thermograms (Fig. 6) are dissimilar above 150°C and are accompanied by weight losses as observed through TG. Net energy exchanges, as evidenced by DSC, are relatively mildly endothermic and/or exothermic under inert conditions but are highly exothermic under an air atmosphere. This is characteristic of degradation occurring through oxidative routes in air [10]. Oxidative degradation in air is typical for metal-containing polymers [10].

TABLE 3. Inhibition of Organostannane Modified Dextran Samples

Organostannane	Weight of compound (mg)	Pseudomonas aeruginosa inhibition zone (mm)	E. coli inhibition zone (mm)
$(C_{12}H_{25})_2SnCl_2$	5	0	0
$(C_6H_5CH_2)_3SnCl$	20	0	1.4
	10	0	1.0
	5	0	0.8
$(CH_3)_2SnCl_2$	20	2.0	1.7
	10	1.8	1.5
	5	1.7	1.3
$(C_6H_{11})_3SnCl$	5	0	0
$(C_6H_5)_3SnCl$	5	0	0
$(C_8H_{17})_2SnCl_2$	5	0	0

Biological Characterization

Preliminary biological assays were conducted on organostannane modified dextran samples (Table 3). Tests were performed using dry samples, thus closely approximating the conditions under which the modified dextran products may be utilized, i.e., as bandages, paper-product additives, insulation, coatings additive. The compound derived from the dimethyltin dichloride exhibited good inhibition against the two test species while the dextran modified with tribenzyltin chloride inhibited Pseudomonas aeruginosa. The two tested bacteria are commonly responsible for mildew and rot. Further biological testing is underway.

ACKNOWLEDGMENT

The authors are pleased to acknowledge partial support from the American Chemical Society–Petroleum Research Foundation Grant 3682-Y3.

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Accepted by editor October 5, 1982
Received for publication November 5, 1982