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Poly(alkylnylstannanes)

A new class of main chain organotin polymers

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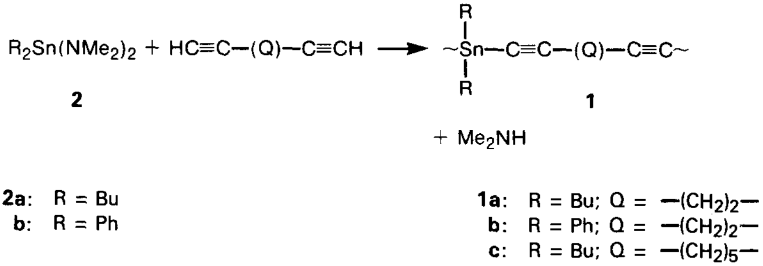
SUMMARY

The synthesis of poly(alkynylstannanes) was achieved by the step-growth polymerization of bisaminostannanes and α,ω-diynes. This is a new class of organotin polymers containing tin-alkyne linkages in the polymer backbone. The polymers were obtained in good yield, albeit with relatively low molecular weight. The polymers underwent crosslinking on standing to give insoluble material and required stabilization with radical inhibitors. The thermal properties of these materials, and the influence of the group pendent to tin are discussed.

INTRODUCTION

Organotin polymers have been shown to be an interesting new class of resist materials for microlithographic applications (1),(2). For example, poly[4-(trimethyl- stannyl)styrene] is very sensitive to electron beam radiation, crosslinking on exposure to give negative tone relief images after development. We were interested in examining the radiation sensitivity of other classes of organotin polymers, particularly polymers which seemed likely to undergo main chain degradation. This type of polymer could potentially function as a positive resist, which is desirable since positive resists are easier to develop without swelling, which limits the resolution attainable with crosslinking negative resist materials. We chose to pursue polymers containing tin atoms in the polymer main chain, as these could be designed with weak tin-carbon bonds in the polymer backbone. The assumption that the tin-carbon bonds should rupture on exposure to electron beam radiation, is based on analogy to the γ-radiolysis of small molecule organotin compounds (3). Moreover, if irradiation causes rupture of tin-carbon bonds in the main chain, then properly designed polymers of this type should undergo degradation and function as positive resist materials.

Currently, the most useful method of preparing organotin polymers with carbon-tin bonds in the main chain is through the polyaddition of organotin dihydrides with dienes or diynes (4)-(9). However, these polymers often have poor physical properties, including low glass transition temperatures and poor solubility. Since reports of new polymers with tin-carbon bonds in the polymer backbone have been sparse, we decided to investigate new synthetic routes towards these types of polymers. The preparation of a polymer containing tin-alkyne bonds in the backbone appeared particularly interesting, as these bonds are known to be quite weak (10). One potential method for the synthesis of alkynylstannane polymers would utilize the coupling of aminostannanes and terminal alkynes as the polycondensation reaction. This reaction has been shown to be an efficient method for the synthesis of small molecule alkynyltin compounds (11). We report here the synthesis of poly(alkynylstannanes) (1) *via* the condensation of bis(dimethylamino)- dialkylstannanes (2) with α,ω-diynes (Scheme I). This represents the first example of organotin polymers containing tin-alkyne linkages in the polymer backbone.



$$R_2Sn(NMe_2)_2 + HC{\equiv}C{-}(Q){-}C{\equiv}CH \longrightarrow {\sim}\overset{R}{\underset{R}{Sn}}{-}C{\equiv}C{-}(Q){-}C{\equiv}C{\sim} + Me_2NH$$

Scheme I. Synthesis of poly(alkynylstannanes) (1).

EXPERIMENTAL

Materials

1,5-Hexadiyne and 1,8-nonadiyne were obtained from Fairchan Chemicals and distilled from sodium borohydride before use. Dimethylamine was obtained from Matheson and purified by passage through a potassium hydroxide column. Dibutyl- and diphenyltin chloride were obtained from Alfa chemicals and used as received. Tetrahydrofuran (THF) was purified by distillation from sodium-benzophenone ketyl under a nitrogen atmosphere. Bis(dimethylamino)dibutylstannane (**2a**) and bis(dimethylamino)diphenylstannane (**2b**) were prepared according to the published procedure (12).

Poly[(1,6-hexadiynyl)dibutylstannane](1a)

A side arm flask purged with an argon atmosphere was charged with 2.23g (6.95 mmole) of **2a** and cooled to 0°C. To the stirred monomer was added 0.68 ml (0.54g, 7.0 mmole) of 1,5-hexadiyne. The ice bath was removed, and the reaction proceeded with steady evolution of dimethylamine. The reaction mixture solidified after 5 min, was diluted with 4 ml of THF, and then stirred for 1.5h. The polymerization was quenched by adding 0.20 cc (0.19g, 1.9 mmole) phenylacetylene, followed by stirring for an additional 1h. The polymer was isolated by precipitation into methanol followed by filtration to afford 1.88g of **1a** (87%) as a white powder. The polymer was dissolved in dioxane, centrifuged and treated with 0.2 mole% of 4-methoxyphenol (MEHQ) or 2,6-Di-tert-butyl-4-methylphenol (BHT). The resulting solution was freeze-dried to afford the stabilized polymer as a fluffy white solid: ^{1}H NMR ($CDCl_3$) δ 0.8–1.5(m,18H,Sn-Bu), 2.5 (s,4H,$\equiv$C–CH_2–); IR (film) 2155 cm^{-1} (C$\equiv$C str).

Poly[(1,6-hexadiynyl)diphenylstannane] (1b)

This polymer was prepared by the same procedure as for **1a** utilizing **2b** as the tin monomer. This afforded **1b** in 83% yield as a white powder: ^{1}H NMR ($CDCl_3$) δ 2.5 (br s, 4H, $\equiv CCH_2$–), 7.3–7.8 (m,10H,Sn-Ph); IR (film) 2163 cm^{-1} (C$\equiv$C str). Anal. calcd. for $C_{18}H_{14}Sn$: C, 61.95, H, 4.04; Sn, 34.01. Found: C, 62.16; H, 4.12; Sn, 34.07.

Poly[(1,9-nonadiynyl)dibutylstannane] (1c)

This polymer was prepared by reaction of **2a** with nonadiyne utilizing a similar procedure as for **1a**. Addition of the polymer solution to methanol afforded an oil rather than a solid. After decantation of the mother liquor, the oil was washed twice with methanol, then dried under vacuum to give **1c** in 88% yield as a thick clear colorless oil: ^{1}H NMR($CDCl_3$) δ 0.8–1.6(m,24H), 2.2 (br t, 4H,$\equiv CCH_2$–, J=7 Hz); IR (neat) 2155 cm^{-1} (C$\equiv$C str). Polymer **1c** was not stabilized with a radical inhibitor, and on standing, slowly transformed into an insoluble white solid.

Measurements

^1H NMR spectra were obtained on a Varian EM-390. IR spectra were obtained on an IBM IR/32 spectrometer. C,H combustion analysis of **1b** was performed by Galbraith Laboratories, Knoxville, Tennessee. Molecular weight determinations were made with a Waters Model 150 Chromatograph equipped with 6 μstyragel columns using a THF mobile phase at 40°C. Molecular weights are reported relative to polystyrene standards. TGA and DSC measurements were made on a Dupont 1090 instrument at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

The polycondensation of bisaminostannanes with α,ω-diynes occurred smoothly, liberating dimethylamine. Since the polymerization was exothermic, mixing of the monomers at 0°C afforded a more controlled polymerization avoiding evolution of dimethylamine at too rapid a rate. After the polymerization solidified, it was diluted with THF and stirred an additional 1.5h in an attempt to maximize conversion. In the synthesis of **1a**, solution polymerizations in THF or toluene were carried out, but gave a slightly lower molecular weight polymer than the bulk method. The polymerization was terminated by addition of excess phenylacetylene as a capping reagent, in order to convert unreacted stannylamine end groups to tin-acetylide units. The polymers were isolated in 83–88% yield by precipitation in methanol (Table 1). The number average molecular weight (M_n) of the isolated materials ranged from 3–6,000 (Table 1). The two most important influences contributing to the low M_n are likely the purity of **2** and side reactions associated with the condensation of aminostannanes and terminal alkynes (13). Aminostannanes are very sensitive to atmospheric moisture, which causes difficulty in obtaining the highly pure samples of **2** required for the polymerization. In setting up the polymerization, care must be taken to avoid atmospheric contact of **2** in transfer procedures. Moreover, the condensation of aminostannanes and terminal alkynes possibly does not occur in the exceptionally high selectivity and yield (99%+) required for high molecular weight polymer in a step-growth polymerization. Although, isolated yields of up to 93% have been reported for the synthesis of alkynyltin compounds by this method (11).

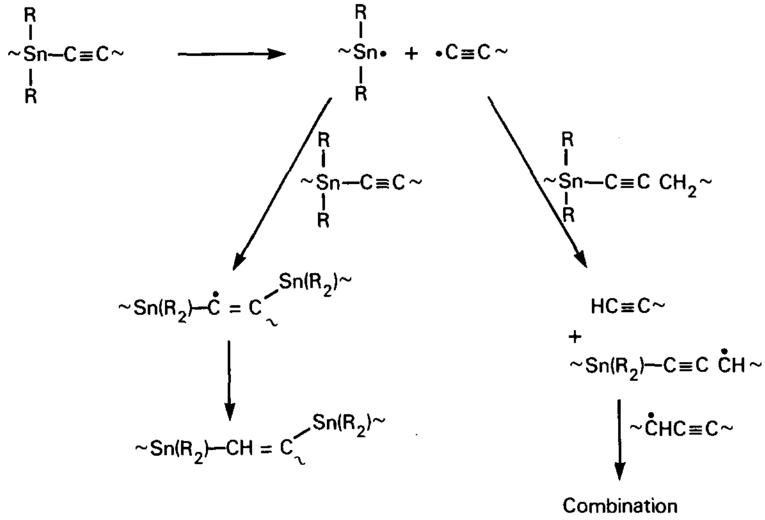
Table 1
Polymerization of Bisaminostannanes with α,ω-Diynes

Polymer	Aminostannane	Diyne	Yield	M_n^a
1a	2a	1,5-hexadiyne	87	6,000
1b	2b	1,5-hexadiyne	83	3,000
1c	2a	1,8-nonadiyne	88	3,500

a) Measured by GPC, relative to polyst,rene standards.

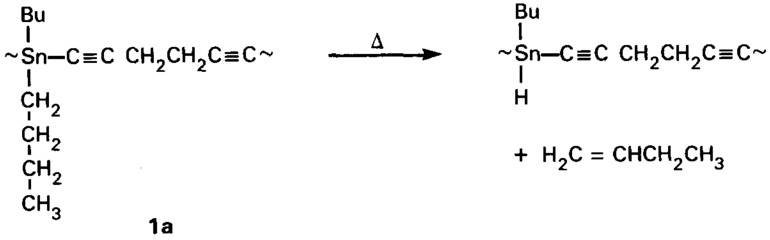
An interesting property associated with **1a-1c** was their thermal instability. The polymers were freely soluble in THF, chloroform and chlorobenzene, yet after the polymers were isolated and stored for more than 12h under ambient conditions they were not completely soluble. The insoluble white powder appeared to be crosslinked polymer. The insoluble powder could be removed by centrifugation and purified polymer re-isolated by precipitation. However, after standing, the formation of more insoluble material occurred. This behavior could be avoided by the addition of a inhibitor, either MEHQ or BHT. The stabilized polymer was found to be completely soluble after standing for extended periods of time.

The rate of the crosslinking process was observed to accelerate with increasing temperature, and could be followed by IR spectroscopy. A film of **1b** was heated at 135°C for 8 min, which rendered it insoluble. IR spectra showed heating **1b** resulted in a significant decrease in the alkyne stretch band (ν=2163 cm^{-1}). Thus, it appears that the polymers undergo a thermally induced crosslinking reaction, which occurs with a decrease in the number of alkyne units. The crosslinking does not occur with weight loss as the TGA of **1a** and **1b** showed no weight loss under nitrogen up to 200°C and 320°C, respectively. We postulate that the crosslinking is initiated by homolytic cleavage of the weak tin-alkyne bond (D=40 kcal/mole) (10). The stannyl and alkynyl radicals generated can participate in crosslinking processes by a variety of mechanisms, including addition to alkynes and propargyl radical coupling (Scheme II). The addition of a tin radical to an alkyne is likely as this is known to be a facile process, and occurs in the hydrostannation of alkynes (14). This process would also lead to the observed decrease in the alkyne stretch absorption. The crosslinking is certainly free radical in nature as indicated by the inhibiting effect of radical scavengers.



Scheme II. Proposed crosslinking processes for poly(alkynylstannanes) (1).

The thermal decomposition of **1a** and **1b** to give volatile products occurred at significantly different temperatures. The TGA of **1b** showed the onset of weight loss at 200°C, while **1b** showed no weight loss until 320°C. Thus, phenyl groups pendent to tin gives a considerably more stable structure than pendent butyl groups. The TGA of **1a** showed the most rapid weight loss between 200–320°C, corresponding to 35% of the material. A plausible explanation for the lower thermal stability of **1a** is the facile elimination of the pendent butyl groups to generate butylene (Scheme III). This can be considered the reverse of a hydrostannation reaction. Such reactions are known to be reversible reactions (15). The elimination of two moles of butylene would correspond to a 32% weight loss, which is in good agreement with the 35% weight loss observed between 200°C and 320°C.



Scheme III. Proposed thermal degradation of 1a via butylene elimination.

The glass transition temperatures (Tg) of the poly(alkynylstannanes) were also influenced by the group pendent to tin. In the case of **1b**, which has pendent phenyl groups, the Tg was 55°C. This was an amorphous polymer and showed no evidence of crystallinity. In contrast, **1a** showed an exotherm at 70°C and an endotherm at 90°C. We attribute these transitions to crystallization and melting, respectively. A Tg was not observed above 25°C, and was presumably below room temperature. The formation of crystalline regions possibly occurs through crystallization of the butyl side chains driven by either dipole-dipole interactions between tin-alkyne groups or tin-alkyne coordination. It is unusual to observe crystallinity in an organotin polymer with tin-carbon bonds in the main chain. Hydrostannation polymers derived from dibutyltin dihydride are invariably amorphous solids or oils. It is interesting to compare the physical behavior of **1a** and**1c**. The dibutyltin-hexadiyne polymer (**1a**) appears semicrystalline, while the dibutyltin-nonadiyne polymer (**1c**) is an oil. The reason **1c** does not form crystalline regions is probably due to the longer alkyl unit present in the polymer backbone and/or an odd-even effect due to the odd number of methylene groups between the bis(alkynyl)tin units (5) for **1c**, as compared to the even number for **1b** (2).

CONCLUSIONS

The synthesis of poly(alkynylstannanes) was achieved by the step-growth polymerization of bis(dimethylamino)stannanes and α,ω-diynes. The polymers were obtained in 83–88% yield over a molecular weight range of 3–6,000. The polymers underwent crosslinking on standing and required stabilization with radical inhibitors for extended storage. The polymers show interesting thermal properties which were influenced by both the groups pendent to tin and the alkyl segment in the polymer backbone. The polymerization should be effective with a broad scope of different bisaminostannanes and α,ω-dynes, affording a variety of different polymers of this type. The properties of these materials did not warrant detailed investigation of their radiation chemistry.

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