(3) Lavin, K. D.; Riding, G. H.; Parvez, M.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1986**, 117.
(4) Allcock, H. R.; Lavin, K. D.; Riding, G. H.; Whittle, R. R.; Parvez, M. *Organometallics* **1986**, *5*, 1626.
(5) Allcock, H. R.; Lavin, K. D.; Riding, G. H, *Macromolecules* **1985**, *18*, 1340.
(6) A mixture of the two isomers was used to lower the melting point.
(7) However, polymerization occurs in the presence of $(NPCl_2)_3$.[5]
(8) Schmutzler, R. *Inorg. Synth.* **1967**, *9*, 75.
(9) Pertici, P.; Vitulli, G.; Paci, M.; Porri, J. *J. Chem. Soc., Dalton Trans.* **1980**, 1961.

Polymerization of 1-(Trimethylstannyl)alkyl Methacrylates: A New Class of Organotin Polymers and a Novel Case of Degradative Chain Transfer to Polymer

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ABSTRACT: The synthesis of poly[1-(trimethylstannyl)alkyl methacrylates], a new class of organotin polymers, is reported. The trimethyltin group is substituted on C-1 of the ester side chain, differing from conventional stannyl methacrylates where the tin is bonded directly to oxygen. The monomer synthesis was carried out by condensation of lithium trimethylstannate with a carbonyl compound, followed by esterification with methacryloyl chloride. Both homopolymers and MMA copolymers were prepared by radical polymerization. A reactivity ratio study showed copolymerization was perfectly random. A novel degradative chain transfer to polymer process was observed in the polymerization of monomers containing a secondary or benzylic hydrogen α to the trimethyltin group. The proposed mechanism involves a 5-membered cyclic transition state. The effect was most dramatic with tin substituted on a benzyl side chain, and the deuterium isotope effect for the polymerization of this monomer was determined to be 2.4. The effect of the trimethyltin group on the glass transition temperatures and the thermal stability of these materials is reported.

Introduction

Organotin polymers have been shown to be useful imaging materials for microlithography. For example, poly[(trimethylstannyl)styrene] is sensitive to electron beam radiation and also resistant to both oxygen- and fluorocarbon-based plasma degradation.[1,2] This combination of lithographic properties is not found in typical organic resist materials and is a consequence of the tin incorporated in the polymer.

Our recent work has focused on the synthesis of new organotin polymers for study as lithographic materials. We felt the area was ripe for the discovery of interesting new polymers, since research on organotin polymers has not kept pace with the use of organotin compounds as synthetic reagents.[3,4] Although several papers concerning organotin polymers have been published recently, they describe studies of well-known classes of organotin polymers and copolymers, including poly(stannylstyrenes)[5] and poly(stannyl methacrylates).[6] Utilization of current tin chemistry can potentially afford new organotin polymers with structural features that should impart both interesting polymer properties and the desired radiation sensitivity.

We chose to pursue organotin polymers that should degrade on irradiation, rather than cross-link, potentially functioning as positive tone resist materials. One approach to the design of an organotin polymer displaying this radiation chemistry is to incorporate tin pendent to a methacrylate polymer, since methacrylate-based polymers are well-known to undergo backbone scission upon irradiation and function as positive resist materials.[7] The materials we chose to prepare were homopolymers and copolymers of 1-(trimethylstannyl)alkyl methacrylates (1). This is a new class of methacrylate polymers where a trimethyltin group is substituted on the 1-position of the ester side chain, in contrast to conventional organotin methacrylates where tin is bonded directly to oxygen.[8] This paper will discuss the synthesis and characterization of these materials, as well as a unique degradative chain transfer to polymer process that occurs in the polymerization. The lithographic properties of homopolymers and methyl methacrylate copolymers of 1 have been published elsewhere.[2]

Experimental Section

Tetrahydrofuran (THF) and toluene were freshly distilled under nitrogen from sodium–benzophenone prior to use. Chloroform was purified by passage through basic alumina. Synthetic reactions were carried out under an argon atmosphere. Methyl methacrylate (MMA) was distilled from CaH_2 and stored at −10 °C. The petroleum ether utilized had a boiling point range of 35–60 °C. The α-deuteriobenzaldehyde was commercially available from Merck, Sharp, and Dohme, Isotope Division. Preparative HPLC was carried out on a Waters Prep 500 with silica gel columns.

(Trimethylstannyl)methyl Methacrylate (1a). Lithium trimethylstannate was prepared from 15 g (0.075 mol) of trimethyltin chloride and 2.5 g (0.36 mol) of lithium wire in 80 mL of THF.[9] The lithium trimethylstannate solution was cannula transferred to a 250-mL round-bottom flask and treated with 2.75 g (0.092 mol) of paraformaldehyde. The reaction was stirred 2.5 h at room temperature, quenched with 30 mL of half-saturated aqueous ammonium chloride, and then partitioned between petroleum ether and water. The organic layer was separated, washed with brine, and then dried (Na_2SO_4). Removal of the drying agent and solvents afforded 11 g of crude (hydroxymethyl)trimethylstannane as a colorless cloudy liquid. A solution of 8.4 mL (9.0 g, 0.086 mol) of methacryloyl chloride in 15 mL of chloroform was slowly added to a solution of the (hydroxymethyl)trimethylstannane, 3.7 g (0.030 mol) of (dimethylamino)pyridine (DMAP), and 30 mL of diisopropylethylamine in 40 mL of chloroform at room temperature. After stirring an hour, the reaction mixture was partitioned between petroleum ether and 0.5 N HCl and separated, and the organic layer was washed successively with 0.5 N HCl, water, aqueous sodium bicarbonate, and brine and

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Table I
Homopolymerization and MMA Copolymerization of 1-(Trimethylstannyl)alkyl Methacrylates (**1a–e**)

					elemental anal.			
					calcd		found	
entry	polymer	yield, %	$\bar{M}_n$[a]	$\bar{X}_n$	% C	% H	% C	% H
1	PMMA[b]	93	136 000	1360				
2	**2a**	87	144 000[c]	550[c]	36.55	6.14	36.78	6.26
3	**2b**	70	285 000	980	41.28	6.93	41.29	7.10
4	**2c**	86	270 000	930	41.28	6.93	41.25	7.05
5	**2d**	48	28 000	85	49.60	5.95	50.12	6.04
6	**2e**	54	68 000	200	49.45	5.64	49.53	6.11
7	MMA/**1b** (4:1)	82	165 000	1200				
8	MMA/**1c** (4:1)	95	190 000	1370				
9	MMA/**1d** (4:1)	63	67 000	460				
10	MMA/**1e** (4:1)	69	114 000	770				

[a] Measured by membrane osmometry. [b] 1.70 g of MMA, 3 mg of AIBN (0.1 mol %), 2 mL of toluene, 2 h at 70 °C. [c] Measured by GPC, calibrated with polystyrene standards.

then dried (Na_2SO_4). The crude product obtained was purified by preparative HPLC (0.5% ethyl acetate/hexane, silica gel) to give 7.5 g (38%) of **1a** as a clear colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9, $SnCH_3$), 1.95 (s, 3, CH_3), 4.2 (s, 2, $SnCH_2O$–), 5.5 (m, 1, =CH–), 6.1 (s, 1, =CH–); ^{13}C NMR ($CDCl_3$) δ -9.6 ($SnCH_3$), 18.4, 57.5 ($SnCH_2O$–), 124.6, 136.3, 168.4 (ester C=O); IR (neat) 1705 cm^{-1} (ester C=O). Anal. Calcd for $C_8H_{16}O_2Sn$: C, 36.55; H, 6.14. Found: C, 36.78; H, 6.26.

1-(Trimethylstannyl)propyl Methacrylate (1b). This compound was prepared in 48% yield by the same procedure as **1a**; however, the condensation of lithium trimethylstannate and propionaldehyde was carried out for 1 h at -78 °C: ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 9, $SnCH_3$), 1.0 (t, 3, J = 7 Hz, –CH_3), 1.8 (m, 2, CH_2), 1.9 (s, 3, =CCH_3), 4.5 (t, 1 J = 7 Hz, SnCHO–), 5.5 (m, 1, =CH–), 6.1 (m, 1, =CH–); ^{13}C NMR δ -9.6 ($SnCH_3$), 11.9, 18.2, 26.5, 74.0 (SnCHO–), 124.5, 136.5, 168.0 (ester C=O); IR (neat) 1703 cm^{-1} (ester C=O). Anal. Calcd for $C_{10}H_{20}O_2Sn$: C, 41.28; H, 6.93. Found: C, 41.45; H, 7.01.

2-(Trimethylstannyl)-2-propyl Methacrylate (1c). This compound was prepared in 31% yield by the same procedure as **1b** by use of acetone as the carbonyl compound: ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 9, $SnCH_3$), 1.4 (s, 6, $SnCCH_3$), 1.9 (s, 3, =CCH_3), 5.4 (m, 1, =CH–), 6.0 (s, 1, =CH–); ^{13}C NMR ($CDCl_3$), δ -8.7 ($SnCH_3$), 18.2, 26.8, 76.0 (SnCO–), 124.6, 136.8, 168.2 (ester C=O); IR (neat) 1701 cm^{-1} (ester C=O). Anal. Calcd for $C_{10}H_{20}O_2Sn$: C, 41.28; H, 6.93. Found: C, 41.08; H, 6.53.

α-(Trimethylstannyl)benzyl Methacrylate (1d). This compound was prepared in 30% yield by the same procedure as **1b** by use of benzaldehyde as the carbonyl compound: ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 9, $SnCH_3$), 2.0 (s, 3, =CCH_3), 5.5 (m, 1, =CH–), 5.75 (s, 1, SnCHO–), 6.15 (s, 1, =CH–), 7–7.3 (m, 5); ^{13}C NMR ($CDCl_3$) δ -9.4 ($SnCH_3$), 18.3, 74.0 (SnCHO–), 123.5, 125.2, 128.5, 136.3, 142.1, 167.4 (ester C=O); IR (neat) 1705 cm^{-1} (ester C=O). Anal. Calcd for $C_{14}H_{20}O_2Sn$: C, 49.60; H, 5.95. Found: C, 49.56; H, 5.86.

α-(Trimethylstannyl)-α-deuteriobenzyl Methacrylate (1e). This compound was prepared in 63% yield by a similar procedure as for **1b** by use of 14.0 g (0.0700 mol) of trimethyltin chloride, 3.3 g (0.48 mol) of lithium, and 5.0 g (0.047 mol) of α-deuteriobenzaldehyde (98.9% D): ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 9, $SnCH_3$), 2.0 (s, 3, =CCH_3), 5.5 (m, 1, =CH–), 6.15 (m, 1, =CH–), 7.0–7.3 (m, 5); ^{13}C NMR ($CDCl_3$) δ -9.4 ($SnCH_3$), 18.3, 73.6 (SnCDO–), 123.5, 125.2, 128.5, 136.3, 142.1, 167.4 (ester C=O); IR (neat) 1705 cm^{-1} (ester C=O). Anal. Calcd for $C_{14}H_{19}DO_2Sn$: C, 49.45; H, 5.64. Found: C, 49.57; H, 5.82.

Polymerization. Homopolymerization and MMA copolymerization of **1a–e** were carried out by combining a total of 17.0 mmol of the monomer(s) in the appropriate stoichiometry and 3 mg of azoisobutyronitrile (AIBN) (0.1 mol % to monomer) in 2 mL of toluene. The reaction mixture was degassed and then heated at 70 °C in a sealed tube under an argon atmosphere for 20 h. The resulting polymerization mixture was diluted with THF, and the polymer was precipitated by addition to methanol, isolated by filtration, and dried at 50 °C in a vacuum oven. Copolymer composition was determined by ^{1}H NMR, while the homopolymers **2a–e** were characterized by ^{1}H NMR, IR, and C,H combustion analysis (Table I).

Reactivity Ratio Determination. Reactivity ratios for **1b** and MMA (r_1 and r_2) were determined by carrying out copolymerizations to 7–10% extent of reaction with different monomer feed compositions. The composition of the resulting copolymers was determined by ^{1}H NMR and C,H combustion analysis.

1-(Trimethylstannyl)propyl Benzoate (3a). This compound was prepared by the same procedure utilized for **1b**. Purification by distillation under reduced pressure afforded **3a** was a clear colorless liquid in 48% yield: bp 80–82 °C (0.025 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9, $SnCH_3$), 1.05 (t, 3, J = 7 Hz), 2.0 (quint, 2, J = 7 Hz), 4.7 (t, 1, J = 7 Hz, SnCHO–), 7.4–7.6 (m, 3), 7.9–8.1 (m, 2); IR (neat) 1701 cm^{-1} (ester C=O); ^{13}C NMR ($CDCl_3$) δ -9.4, 12.0, 26.6, 74.3, 128.3, 129.3, 132.5, 167.2. Anal. Calcd for $C_{13}H_{20}O_2Sn$: C, 47.75; H, 6.17. Found: C, 47.57; H, 6.30.

α-(Trimethylstannyl)benzyl Benzoate (3b). This compound was prepared by the same procedure utilized for **1b**. Purification by distillation under reduced pressure afforded **3b** as a clear colorless liquid in 55% yield: bp 140 °C (0.02 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.1 (s, 9, $SnCH_3$), 5.9 (s, 1, SnCHO–), 7.1–7.5 (m, 8), 8.0–8.2 (m, 2); IR (neat) 1703 cm^{-1} (ester C=O); ^{13}C NMR ($CDCl_3$) δ -9.2, 74.3, 123.6, 125.3, 128.4, 128.5, 129.4, 130.3, 132.8, 142.2, 166.5. Anal. Calcd for $C_{17}H_{20}O_2Sn$: C, 54.45; H, 5.38. Found: C, 54.33; H, 5.32.

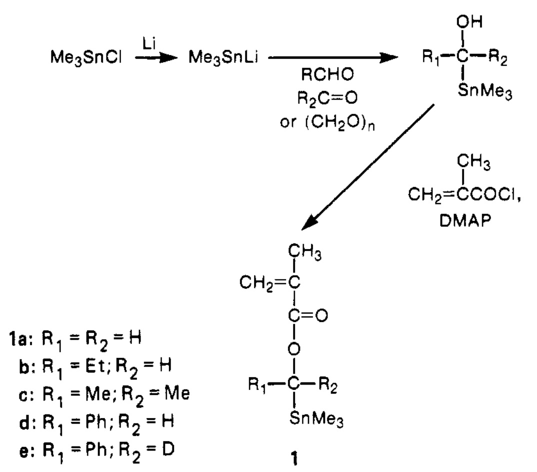
Chain Transfer to Monomer Experiments. A mixture of 1.28 mL (1.20 g, 12.0 mmol) of MMA, 2.0 mg (0.1 mol %) of AIBN, and 8 mmol of **3** was degassed and heated at 70 °C in a sealed tube under an argon atmosphere for 20 h. The resulting polymerization mixture was diluted with THF, and the polymer was precipitated into methanol, isolated by filtration, and dried at 50 °C in a vacuum oven.

Measurements. NMR spectra were obtained on Varian EM-390 (^{1}H), Varian CFT-20 (^{13}C), and IBM NR-80 (^{13}C) spectrometers. IR spectra were obtained on an IBM IR/32 spectrometer. C,H combustion analyses were performed by Galbraith Laboratories, Knoxville, TN. Molecular weight determinations were made with a Wescan Model 231 recording membrane osmometer with toluene solvent or a Waters Model 150C chromatograph equipped with six μStyragel columns using a THF mobile phase at 40 °C. The GPC calibration was made with polystyrene standards. TGA and DSC measurements were performed on a Du Pont 1090 instrument at a heating rate of 5 °C/min. TGA measurements were made under a nitrogen atmosphere.

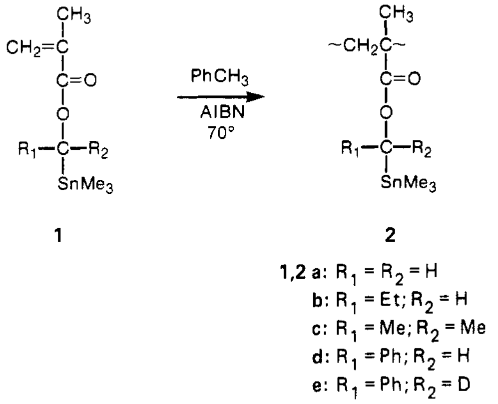
Results and Discussion

Monomer Synthesis. The synthesis of **1** was carried out by utilizing a route analogous to the preparation of α-alkoxyorganotin compounds (Scheme I).[10] Trimethyltin chloride was converted to lithium trimethylstannate by reaction with lithium wire.[9] Condensation of lithium trimethylstannate with the appropriate carbonyl compound afforded an α-hydroxyorganotin compound, which was esterified with methacryloyl chloride in the presence of DMAP to give **1** in 30–60% yield (based on trimethyltin chloride). The synthesis was general, as either aldehydes, ketones, or paraformaldehyde could be utilized as the

Scheme I
Synthesis of 1-(Trimethylstannyl)alkyl Methacrylates (1)



Scheme II
Polymerization of
1-(Trimethylstannyl)alkyl Methacrylates (1)



carbonyl compound. This synthetic flexibility allowed for control of the monomer structure about C-1 on the ester side chain. Thus, examples of 1 were prepared with the trimethyltin group substituted on primary, secondary, tertiary, and benzylic positions.

Polymerization. The radical polymerization of 1 could be carried out by utilizing 0.1 mol % AIBN in toluene at 70 °C (Scheme II). Polymers 2 were obtained as white powders in generally high yield and molecular weight (entries 2–6, Table I). A significantly lower yield and molecular weight were observed for the polymerization of **1d** due to a chain-transfer process (vide infra).

Copolymerization of **1b–e** was carried out with methyl methacrylate (entries 7–10, Table I). The copolymer composition was equal to the composition of the monomer feed in all cases, indicating the reactivity of 1 is equivalent to MMA. To conform this, a reactivity ratio study was carried out for the copolymerization of **1b** (M_1) and MMA (M_2). The copolymerizations were terminated at low conversion (7–10%), and the precipitated polymer was analyzed by ^{1}H NMR and C,H elemental analysis. It was found in all cases that the composition of the copolymer equaled the composition of the monomer feed; therefore, $r_1 = r_2 = 1$, and the copolymerization between **1b** and MMA was perfectly random (Figure 1). This demonstrates that the tin substituent does not affect the reactivity of the methacrylate double bond through coordination or electronic effects. It is anticipated that the reactivity of other stannylalkyl methacrylates will also be equivalent to that of MMA.

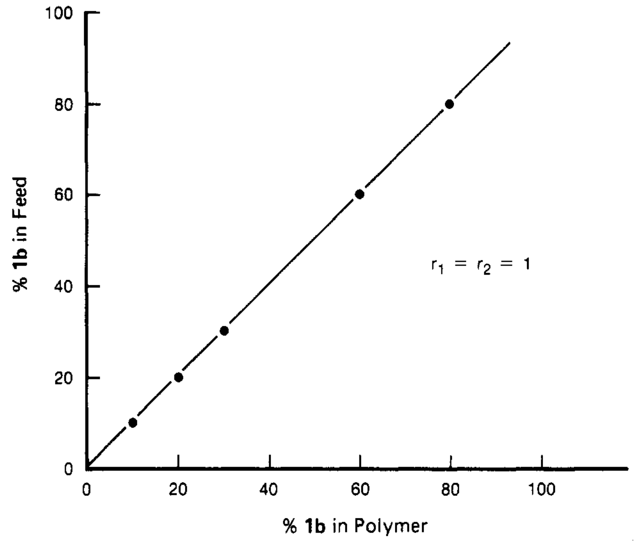


Figure 1. Reactivity ratio study for the copolymerization of **1b** and MMA.

Chain Transfer. The yield and degree of polymerization (X_n) for the homopolymerization of 1 showed a dependence on monomer structures and were particularly low for the polymerization of **1d** (entry 5, Table I). The polymerization of MMA was carried out as a control, affording PMMA in 93% yield and an X_n of 1360 (entry 1, Table I). These results should be contrasted with the polymerization of **1d**, which afforded polymer **2d** in 48% with an X_n of 85. A similar but less dramatic effect was observed in the preparation of **2b**, which was obtained in lower yield and X_n than PMMA (entry 3, Table I). The polymerization of **1c** gave **2c** in high yield; however, a drop in X_n was observed (entry 4, Table I). Likewise, **2a** was obtained in good yield (entry 2, Table I). It is apparent that the tin monomers can inhibit the polymerization, particularly in the case of **1d** where the tin substituent is on a benzylic position.

Copolymerization of MMA with 1 utilizing a 4:1 monomer feed ratio showed an analogous effect (entries 7–9, Table I). Copolymerization of MMA with **1d** occurred with a reduction of yield and X_n, whereas an analogous yet less significant reduction was observed for the copolymerization of MMA and **1b**. The copolymerization of MMA and **1c** was not affected and afforded copolymer comparable to the PMMA control in yield and X_n. The results indicate the hydrogen α to the trimethyltin group, particularly when benzylic, is participating in a chain-transfer process, either to monomer or to polymer. The abstraction of a hydrogen α to the trimethyltin group by the propagating polymer chain is reasonable, as the lability of hydrogens α to tin has been demonstrated for small-molecule organotin compounds.[11] Since chain transfer occurs with a concomitant reduction in yield, the resulting radical generated α to tin does not reinitiate polymerization, and the chain transfer is degradative. The low reactivity of this radical is probably due to stabilization through delocalization onto the tin metal center. The presence of tin is necessary for the process to occur, as a similar effect was not reported for the radical polymerization of benzyl methacrylate.[12-14] Likewise, diphenylmethyl methacrylate, which contains a more active hydrogen than the benzyl methacrylate, has been prepared in 90% yield by radical polymerization.[12]

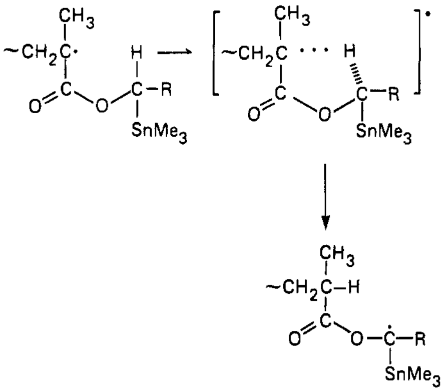
A study of 1-(trimethylstannyl)alkyl benzoates (3) as chain-transfer agents was carried out to determine if the polymerizations of **1b** and **1d** were inhibited by a chain

Table II
MMA Polymerization in the Presence of 1-(Trimethylstannyl)propyl Benzoate (3a) or α-(Trimethylstannyl)benzyl Benzoate (3b)

	PMMA	
solvent	yield, %	M_n[a]
toluene	93	83 000
3a	94	85 000
3b	93	60 000

[a] Measured By GPC, calibrated with polystyrene standards.

Scheme III
Proposed Degradative Chain Transfer to Polymer Process for the Polymerization of 1b and 1d



transfer to monomer process. The polymerization of MMA utilizing 1-(trimethylstannyl)propyl benzoate (**3a**) or α-(trimethylstannyl)benzyl benzoate (**3b**) as the solvent was compared to a control polymerization in toluene (Table II). The yield and molecular weight (M_n) of the PMMA isolated from the three cases showed **3a** had no affect on the PMMA isolated. The MMA polymerization in **3b** occurred with some reduction in M_n, but with no decrease in yield. Thus, the effect of **3a** and **3b** as chain-transfer agents was much less significant than the inhibition observed in the polymerizations of **1b** and **1d**, respectively. This demonstrates that chain transfer to monomer is not an important process in the polymerizations of **1b** and **1d**.

The results are best explained by considering an intramolecular chain transfer to polymer process (Scheme III). In this mechanism, the propagating radical can abstract a hydrogen via a 5-membered cyclic transition state. This intramolecular process should be considerably more facile than chain transfer to monomer, which requires intermolecular hydrogen abstraction. The most important case of intramolecular chain transfer to polymer has been observed in the high-pressure radical polymerization of ethylene, a process often referred to as backbiting.[15] Backbiting involves the abstraction of a secondary hydrogen on the same polymer chain as the propagating radical through a 6-membered cyclic transition state (Scheme IV). The resulting secondary radical continues propagation, affording short butyl branches along the polymer chain. The mechanism we propose for the chain transfer observed in the polymerizations of **1b** and **1d** is similar to classical backbiting as it involves a cyclic transition state; however, in the polymerizations of **1b** and **1d** the new radical site generated α to tin does not propagate further, causing a decrease in yield. The ^{13}C NMR spectra of **2b** and **2d** support this, since in both polymers only one signal was observed for the carbon α to the trimethyltin group.

To further substantiate the degradative chain transfer to polymer mechanism, a study of the deuterium isotope effect on the polymerization of **1d** was undertaken. A similar approach was utilized to demonstrate that a degradative chain transfer to monomer process occurs in the polymerization of allyl acetate.[16] The α-deuterio analogue of **1d** (**1e**) was prepared by the procedure outlined in Scheme I by use of α-deuteriobenzaldehyde as the carbonyl compound. Since a C–D bond is broken less readily than a C–H bond, the rate of chain transfer will be lower for the deuteriated monomer if abstraction of the hydrogen α to the trimethyltin group is involved in the rate-determining step. If the degradative chain-transfer process is occurring, the polymerization of the deuterio analogue (**1e**) should occur in higher yield and afford polymer with a higher X_n than that of **2d**. Polymerization of **1e** to give **2e** (entry 6, Table I) and copolymerization of **1e** with MMA (entry 10, Table I) afforded polymer in higher yield and X_n than the corresponding polymerization or MMA copolymerization with the protio analogue (**1d**) (entries 5 and 9, Table I). These results clearly demonstrate a deuterium isotope effect consistent with a chain transfer to polymer process as the source of the inhibition. Moreover, the degree of polymerization of **2e** is 2.4 times larger than that of **2d**, indicative of a primary isotope effect where the C–H bond is broken in the rate-determining step.[17] These data are all consistent with a degradative chain transfer to polymer process occurring in the polymerization of stannylalkyl methacrylates with available hydrogens α to the trimethyltin group, particularly when tin is substituted on a benzylic side chain. The key step in the process is hydrogen abstraction through a 5-membered cyclic transition state. To our knowledge, this is the first example of a degradative chain transfer to polymer process.

Scheme IV
Backbiting Process in the Radical Polymerization of Ethylene

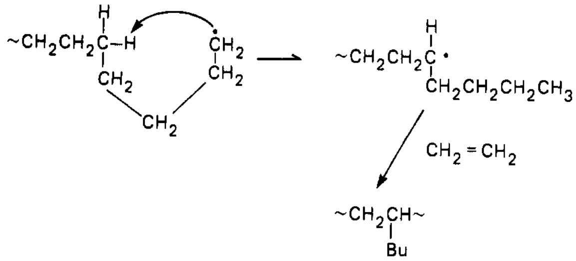


Table III
Glass Transition Temperatures for 2a–d

polymer	T_g,[a] °C
2a	40
2b	50
2c	145
2d	90
PMMA	115

[a] DSC, heating rate = 5 °C/min, results from second run.

Thermal Properties. The glass transition temperatures (T_g) of poly(alkyl methacrylates) are dependent on the structure of the ester alkyl group. Methacrylate polymers with linear side chains show a decrease in T_g with increasing carbon number, due to an increase in free volume in the polymer.[18,19] For nonlinear side chains, the T_g increases with branching, as branching creates steric hindrance to rotation about the carbon–carbon bonds in the polymer backbone. The glass transition temperatures (T_g) of **2a–d** and PMMA prepared under the same conditions are given in Table III. Comparison of **2a** and PMMA shows the T_g was depressed by 70 °C when a trimethyltin group was substituted on the methyl side

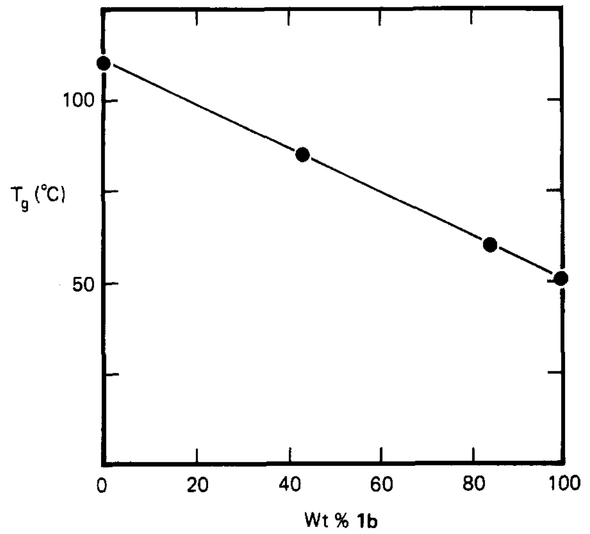


Figure 2. Effect of composition on T_g for copolymers of **1b** with MMA.

chain. Therefore, the effect of the trimethyltin substituent is to increase the free volume in the material, analogous to unbranched side chains, rather than to increase the energy barrier to rotation about the polymer backbone, as observed with branched side chains. The long tin–carbon mean bond distance (2.17 Å) relative to the mean carbon–carbon bond distance (1.54 Å) is probably the reason the large trimethyltin group does not lead to increased steric demands on carbon–carbon bond rotation in the polymer backbone. Moreover, the pendent trimethyltin group should encumber the packing of polymer chains, leading to an increase in free volume. The T_g increased to 50 °C for **2b** and 145 °C for **2c**, where the trimethyltin group is substituted on a secondary and tertiary carbon, respectively. Thus, as the substitution on C-1 of the ester side chain increases, branching increases and results in an elevation of the glass transition temperature. A T_g of 90 °C was observed for the polymer with trimethyltin on the benzylic side chain (**2d**).

The glass transition temperature of copolymers of **1b** with MMA varied linearly as a function of copolymer composition (weight percent) (Figure 2). The plot is in good agreement with the calculated values, as determined by eq 1 or 2.[20] The calculated T_g for the 4:1 MMA/**1b**

$$\frac{W_A}{T_{g_A}} + \frac{W_B}{T_{g_B}} = \frac{1}{T_g} \qquad W_x = \text{wt fraction} \tag{1}$$

$$W_A T_{g_A} + W_B T_{g_B} = T_g \tag{2}$$

copolymer (42 wt % **1b**) was 85 and 88 °C from eq 1 and 2, respectively. The calculated T_g for the 2:3 MMA/**1b** copolymer (81 wt % **1b**) was 61 °C using eq 1 and 62 °C with eq 2. The results are consistent with random copolymerization of **1b** and MMA, in agreement with the reactivity ratio analysis.

The thermal stability of **2** was similar to that of PMMA prepared under analogous conditions. The TGA measured under nitrogen showed weight loss characteristic of depolymerization.[21] In the case of **2b**, the onset of degradation occurred at 250 °C, while a second stage of weight loss occurred at 320 °C. This behavior is consistent with the depolymerization of **2b** with end group formed from a disproportionative termination. The disproportionation process leads to polymer chains with either unsaturated or saturated end groups, which have been found to depolymerize at 250 and 300 °C, respectively, in the case of PMMA.[22] The char yield was 25 wt % after heating to 440 °C, in contrast to PMMA which gave no char yield. The residue from **2b** is presumably composed of nonvolatile pyrolysis products containing some form of tin.

Summary

The poly[(trimethylstannyl)alkyl methacrylates] are an interesting new series of organotin polymers. Polymers were prepared with a trimethyltin substituent on primary, secondary, tertiary, and benzylic positions at C-1 of the ester side chain. Polymerization can occur with a competing chain transfer to polymer process, particularly if the tin substituent is on a benzylic side chain. The deuterium isotope effect in the case of the benzylic analogue was found to be 2.4, a value consistent with abstraction of the hydrogen α to the trimethyltin group in the rate-determining step. The proposed mechanism involves a 5-membered cyclic transition state for the intramolecular hydrogen abstraction occurring in the chain transfer to polymer process. The thermal properties of these materials were affected by the presence of the trimethyltin group, however, in a manner consistent with behavior of conventional methacrylate polymers.

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Registry No. **1a**, 103924-85-2; **1b**, 99542-83-3; **1c**, 99542-84-4; **1d**, 99542-85-5; **1e**, 105219-10-1; **2a**, 103924-86-3; **2b**, 99544-25-9; **2c**, 99552-93-9; **2d**, 99544-26-0; **2e**, 105219-11-2; **3a**, 105372-42-7; **3b**, 105372-43-8; MMA·**1b**, 99544-27-1; MMA·**1c**, 99544-28-2; MMA·**1d**, 99552-94-0; MMA·**1e**, 105219-12-3; MMA, 80-62-6; PMMA, 9011-14-7; Me_3SnLi, 17946-71-3; Me_3SnCl, 1066-45-1; Li, 7439-93-2; $HOCH_2SnMe_3$, 105220-81-3; $H_2C{=}C(Me)COCl$, 920-46-7; EtCHO, 123-38-6; MeCOMe, 67-64-1; PhCHO, 100-52-7; PhCDO, 3592-47-0; HCHO, 50-00-0.

References and Notes

(1) MacDonald, S. A.; Ito, H.; Willson, C. G. *Microelectron. Eng.* **1983**, *1*, 269.
(2) Labadie, J. W.; MacDonald, S. A.; Willson, C. G. *J. Imaging Sc.* **1986**, *30*, 169.
(3) (a) Bristow, G. S. *Aldrichimica Acta* **1984**, *17*, 75. (b) Stille, J. K. *Pure. Appl. Chem.* **1985**, *57*, 1771.
(4) For a recent review on organotin polymers: Kowalski, J.; Stanczyk, W.; Chojnowski, J. *Rev. Silicon, Germanium, Tin Lead Compd* **1982**, *6*, 225.
(5) Al-Diab, S. S.; Barcelon, M. A.; Mark, J. E.; Zimmer, H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, 298.
(6) Zeldin, M.; Lin, J. J. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2333.
(7) Willson, C. G. *Introduction to Microlithography: Theory, Materials and Processing*; Thompson, L. F., Willson, C. G., Bowden M. J., Eds.; ACS Symposium Series 219; American Chemical Society: Washington, DC, 1983; p 87.
(8) Yamada, B.; Yoneno, H.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2021.
(9) Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 237.
(10) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.
(11) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 6161.
(12) Yuki, H.; Hatada, K.; Niinomi, T.; Kikuchi, Y. *Polym. J. (Tokyo)* **1970**, *1*, 36.
(13) Matsuzaki, K.; Kanai, T.; Yamawaki, K.; Rung, K. P. S. *Makromol. Chem.* **1973**, *174*, 215.
(14) Yuki, H.; Hatada, K.; Ohta, K.; Okamoto, Y. *J. Macromol. Sci., Chem.* **1975**, *A9*, 983.
(15) Roedel, M. J. *J. Am. Chem. Soc.* **1953**, *75*, 6110.
(16) Bartlett, P. D.; Tate, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 91.
(17) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*; Plenum/Rosetta: New York, 1977; p 149.
(18) Kine, B. B.; Novak, R. W. *Kirk-Othmer Encycl. Chem. Tech., 3rd Ed..* **1980**, 377.

(19) Allen, R. D. Ph.D. Dissertation, Virginia Polytechnic Institute, Blacksburg, VA, 1985.
(20) Rudin, A. *The Elements of Polymer Science and Engineering*; Academic: New York, 1982; p 402.
(21) Grassie, N.; Melville, H. W. *Proc. R. Soc. London A*, **1949**, *199*, 24.
(22) Caciolo, P.; Mood, G.; Rizzardo, E.; Serelis, A. K.; Solomon, D. H. *Polym. Bull. (Berlin)* **1984**, *11*, 325.

Functional Capsule Membranes. 26.[1] Permeability Control of Polymer-Grafted Capsule Membranes Responding to Ambient pH Changes[2]

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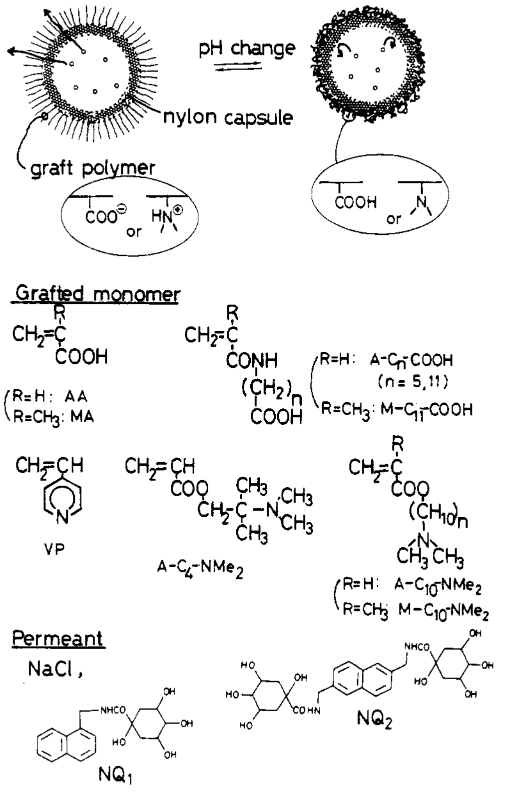
ABSTRACT: Large, ultrathin nylon capsule membranes were grafted with various kinds of polymers having dissociative side chains. The permeability of NaCl and large dyes stored in the inner aqueous core of the capsule could be reversibly controlled by pH changes of the outer medium. The pH dependence of the permeation rate and direct X-ray photoelectron spectroscopic analysis of the capsule surface confirmed that the graft-polymer chains acted as permeation valves where their conformation was changed in response to the dissociation of side chains by an ambient pH. Effects of the hydrophobic nature of the graft polymer, the amount of the graft polymer, and the molecular size of the permeant were also studied.

Introduction

Permeation behavior of microcapsules has been studied extensively because of its importance in designing and constructing sustained drug release devices and artificial cells.[3-5] Despite its potential usefulness, the chemical modification of and permeability control of the capsule membrane have not been fully explored. Capsule membranes are semipermeable and therefore have the disadvantage that they cannot store water-soluble small substances in the inner aqueous core. Conversely utilizing the disadvantage of the porous membrane, Chang and coworkers described the use of a capsule membrane for a model of an artificial cell by entrapping a large enzyme in the inner aqueous phase.[3,6,7] We have developed a nylon capsule whose porous membrane was corked with synthetic lipid bilayers.[8] Permeation of entrapped small substances was decreased very much and reversibly controlled by outside effects such as temperature,[9-11] photoirradiation,[12] and electric field.[13] Their signal-receptive permeability control could be explained by changes in the physical state (molecular packing or orientation) of corking bilayers, which act as a permeation valve.

In this paper, we report that a porous nylon capsule membrane with surface-grafted polyelectrolytes can be used as a pH-sensitive capsule, whose permeability is reversibly regulated by pH changes of the outer medium. We expect the graft polymers to act as permeation valves by changing their conformation in response to ambient pH changes. A schematic illustration of the capsule and structures of grafted monomers and permeants are shown in Scheme I. Acrylic acid (AA), methacrylic acid (MA), and vinyl monomers having a spacer alkyl chain and a carboxylic acid group (A–C_n–COOH (n = 5 and 11) and M–C_{11}–COOH) were selected as graft monomers having carboxylic acid side chains. For the tertiary amino group containing monomers, 4-vinylpyridine (VP) and vinyl monomers having a spacer alkyl chain and a dimethylamino group (A–C_n–NMe_2 (n = 4 and 10) and M–C_{10}–NMe_2) were used. NaCl and large, freely water-soluble naphthalene molecules (NQ_1 and NQ_2) were used as permeants.

Scheme I



Experimental Section

Materials. 4-Vinylpyridine (VP), acrylic acid (AA), and methacrylic acid (MA) were commercially available (Tokyo Kasei, Japan) and used after distillation.

Vinyl monomers containing a carboxylic acid, ω-(acryloylamino)alkanoic acid (A–C_n–COOH, n = 5, 11) and ω-(methacryloylamino)dodecanoic acid (M–C_{11}–COOH), were prepared

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