Soluble Polystyrenes Functionalized by Triorgano[(1-oxoalkyl)oxy]-stannanes (= Triorganotin Carboxylates): Synthesis, Structure, and Anion-Recognition Characteristics

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Polystyrene copolymers of the type $(\mathbf{P}-H)_{1-x}(\mathbf{P}-(CH_2)_n-COOSnR_3)_x$ containing [(1-oxoalkyl)oxy]triphenylstannane or tributyl[(1-oxoalkyl)oxy]stannanes as side chains ($\mathbf{P}-H$ = styrene; $\mathbf{P}-(CH_2)_n-COOSnR_3$ = *para*-substituted styrene-like monomeric unit with R = Ph ($x = 0.1$), Bu ($x = 0.5$); $n = 2-4$) were investigated. The tributyl[(1-oxoalkyl)oxy]stannane copolymer was prepared by direct conversion of the corresponding copolymeric methyl esters with hexabutyldistannoxane. By contrast, the [(1-oxoalkyl)oxy]triphenylstannane copolymer could be prepared only by a procedure involving two reaction steps consisting of a preliminary hydrolysis of the related methyl ester $(\mathbf{P}-H)_{1-x}(\mathbf{P}-(CH_2)_n-COOMe)_x$ followed by functionalization of the corresponding poly(carboxylic acid) $(\mathbf{P}-H)_{1-x}(\mathbf{P}-(CH_{2n}-COOH)_x$ with hydroxytriphenylstannane. Attempts to directly convert the methyl ester with hydroxytriphenylstannane or hexaphenyldistannoxane led to the formation of uncompletely functionalized product. The structure of the stannane-functionalized polymers was investigated in solution and solid state by NMR, IR, and thermal analysis. The tributylstannane and triphenylstannane copolymers were assessed as chloride-selective anion carriers in polymeric-liquid-membrane potentiometric ion-selective electrodes.

1. Introduction. – Triorganostannane moieties linked to organic polymers have been used as stable, film-forming resinous antifouling coatings and biocide agents [1–3]. Linking triorganostannane moieties to polymeric matrices such as polycarboxylates is of great interest because of the potential to produce a chemically very active and stable membrane or coating. In addition, nonpolymeric triorganostannane derivatives have been found to selectively bind and transport anions in biological membranes [4–6]. Tributyl[(1-oxoalkyl)oxy]stannanes (= tributyltin carboxylates) have also been investigated for their properties as very selective anion carriers in plasticized PVC membrane-based ion-selective electrodes (ISEs) [7]. The major drawback of these very selective electroactive species is their limited stability. Polymer-grafted Sn-carriers could offer a solution to this problem, which most probably originates from the leaching of the carriers from the membrane to the aqueous test solution [8][9]. Overcoming this problem could, thus, drastically increase the lifetime and signal stability of the sensors, rendering them suitable for applications [10].

Polystyrene-containing triorgano[(1-oxoalkyl)oxy]stannanes linked to polymethylene spacers as side chains have been synthesized by radical polymerization of organostannane-functionalized monomers [11–13]. The method has, however, some limitations with regard to the control of molecular mass and stereoregularity of the main chain as well as to very long polymerization times [14].

Such soluble polystyrenes with tributyl[(1-oxoalkyl)oxy]stannane moieties were also synthesized by a novel method [15] that by-passes complications from radical polymerization inhibition due to the presence of Sn in the monomers. It involved an early radical copolymerization of *ω*-(*para*-styryl)alkanoic acid methyl ester with styrene prior to stannylation, followed by the direct conversion of the methyl ester function of the corresponding copolymer to the associated tributyl-[(1-oxoalkyl)oxy]stannanes by using hexabutyldistannoxane (= bis(tributyltin) oxide; BTBTO).

The purpose of the present work is threefold. *i*) It assesses the possibility of extending the direct conversion of the methyl ester function to the corresponding tributyl[(1-oxoalkyl)oxy]stannanes to the synthesis of polystyrenes functionalized by tributyl[(1-oxoalkyl)oxy]stannane with higher degree of functionality than previously [15]. *ii*) It examines to what extent this synthetic method could be applicable to the synthesis of [(1-oxoalkyl)oxy]triphenylstannane-functionalized polystyrenes. *iii*) It evaluates the possibility of utilizing the triorgano[(1-oxoalkyl)oxy]stannane-functionalized polymers, which are based on organostannane monomers established to have excellent anion-recognition characteristics [7], to form stable electrochemical-sensor membrane elements.

The resulting copolymers are characterized by NMR in solution and solid state, IR, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

2. Experimental. – 2.1. *Spectroscopic Characterization.* IR Spectra: *Perkin-Elmer FT-IR-1720X* instrument; KBr pellets; in cm^{-1}. ^1H-, ^{13}C- and ^{117}Sn-NMR Spectra: *Bruker DRX-250* spectrometer at 250.13, 62.93, and 89.15 MHz, resp., for soln. spectra; *Bruker DRX-250* spectrometer at 89.15 MHz for solid-state CP-MAS ^{117}Sn-NMR spectra, as described previously [16], $\delta(H)$ and $\delta(C)$ in ppm rel. to $SiMe_4$ (= 0 ppm) and coupling constants J in Hz ^{117}Sn chemical shifts are referenced to $\Xi_{^{117}Sn} = 35.632295$ [17]; proton assignments from homonuclear coupling patterns and constants, as well as, together with the C-atom assignments, from 2D ^1H,^{13}C HMQC and HMBC NMR spectra, recorded with a *Bruker AMX-500* spectrometer, as described previously [18]; arbitrary atom numbering according to *Scheme 1*, C(α) being the atom of the $(CH_2)_n$COO moiety directly bound to the benzene moiety and C(β), C(γ), and C(δ) being the atoms further away from the benzene moiety; u = unresolved. For the cases $n = 2$ and $n = 4$, data from a previous report [15] were used and extrapolated straightforwardly, as described there, while, for $n = 3$, novel data from 2D ^1H,^{13}C HMQC, and HMBC spectra of *4-(1-hydroxyethyl)benzenebutanoic acid methyl ester* (**4b**) and *4-ethenylbenzenebutanoic acid methyl ester* (**5b**) (see below) were used as a basis.

2.2. *Thermal Characterizations.* Thermogravimetric analyses were carried out with a *Perkin-Elmer TGA-7* analyser by heating the sample in air at a rate of 20°/min. Differential scanning calorimetric measurements were performed with a *TA-Instruments DSC-2920* apparatus adopting a temp. program consisting of one heating ramp starting from r.t. at a heating rate of 10°/min under N_2.

2.3. *Molar-Mass Determinations.* The average molecular masses of the polymers were determined by GPC in THF soln. at 20° on a *Lab-Flow-2000* chromatograph equipped with a UV detector *Linear Instrument UVIS-200* operating at 254 nm and a *Phenogel column MXM*. Monodisperse polystyrene standards were used for calibration.

2.4. *Electrochemical Anionic-Response Measurements.* All potentiometric measurements were performed with a *Xenon-CI-317* 8-channel electrometer (*Halandri*, Athens, Greece) *vs.* an *Orion 900200* double-junction reference electrode (*Orion Research, Inc.*, Beverly, MA, USA). The data were collected with a personal

computer, with a home-written program in BASIC, for storage and further analysis. Nanopure water (18.3 MΩ) and potassium salts of high purity (*p.a. Fluka*) were used for the preparation of all electrolyte solns. Morpholine-2-ethanesulfonic acid (MES; *Merck*) was used to prepare the pH buffer. For the membrane setup, polyvinylchloride (PVC) (high molecular mass; *Selectophore*®; *Fluka*) was used as a membrane matrix, bis(2-ethynylhexyl) sebacate (DOS; *Selectophore*®; *Fluka*) as a plasticizer, and tetrahydrofuran (THF; *p.a.*, *Merck*; distilled before use) as a membrane solvent. The preparation of the membranes is described elsewhere [7]. The internal soln. of the electrodes for all membranes was 0.01M KCl.

2.5. *Synthesis and Characteristics of the Monomers. 4-Ethenylbenzenepropanoic Acid Methyl Ester* (**5a**) *and 4-Ethenylbenzenepentanoic Acid Methyl Ester* (**5c**) were prepared and characterized as described in [15].

4-Ethenylbenzenebutanoic Acid Methyl Ester (**5b**) was also prepared according to [15] starting from benzenebutanoic acid (**1b**) *via* its methyl ester derivative **2b**, subsequently the 4-acetyl derivative **3b**, and finally the 4-(1-hydroxyethyl) derivative **4b**. Relevant data for **2b**–**5b** are reported below (see *Scheme 1*).

Benzenebutanoic Acid Methyl Ester (**2b**). As described in [15] according to a procedure reported earlier [19]. Purification by vacuum distillation at 90°/0.2 Torr. Yield 90%. FT-IR: 3063, 3027 (arom. CH); 2951, 2861 (aliph. CH); 1739 (CO, ester); 1603 (arom. C); 747 (monosubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.29–7.14 (*m*, 5 arom. H); 3.63 (*s*, Me); 2.63 (*t*, $J=7$, $CH_2(\alpha)$); 2.30 (*t*, $J=7$, $CH_2(\gamma)$); 1.94 (*tt*, $J=7$, $CH_2(\beta)$). ^{13}C-NMR ($CDCl_3$): 174.4 (COO); 142.0 (C_i); 129.1 (C_o); 129.0 (C_m); 126.6 (C_p); 52.0 (Me); 35.7 (C(α)); 34.0 (C(γ)); 27.1 (C(β)).

4-Acetylbenzenebutanoic Acid Methyl Ester (**3b**). As described in [15]. Purification by vacuum distillation at 130°/0.1 Torr. Yield 70%. FT-IR: 3033, 3002 (arom. CH); 2952, 2863 (aliph. CH); 1737 (CO, ester); 1682 (CO, ketone); 1607 (arom. C=C); 845 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.83 (u. *dd*, $J=8$, 2 H_o); 7.22 (u. *dd*, $J=8$, 2 H_m); 3.62 (*s*, MeO); 2.66 (*t*, $J=7$), $CH_2(\alpha)$; 2.53 (*s*, MeCO); 2.29 (*t*, $J=7$, $CH_2(\gamma)$; 1.93 (*tt*, $J=7$, $CH_2(\beta)$). ^{13}C-NMR ($CDCl_3$): 197.6 (CO); 173.5 (COO); 147.0 (C_p); 135.1 (C_i); 128.4 (C_o, C_m); 51.4 (MeO); 34.9 (C(α)); 33.1 (C(γ)), 26.4 (*Me*CO); 25.9 (C(β)).

4-(1-Hydroxyethyl)benzenebutanoic Acid Methyl Ester (**4b**). As described in [15]. Purification by column chromatography ($CHCl_3$/AcOEt 8:2). Yield 80%. FT-IR: 3425 (OH); 3036, 3003 (arom. CH); 2951, 2866 (aliph. CH); 1737, (CO, ester); 1607 (arom. C=C); 841 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.25 (2 H_o) and 7.12 (2 H_m) (*AA′,BB′*, $J_{AB}=8$); 4.83 (*q*, $J=7$, CH); 3.63 (*s*, MeO); 2.61 (*t*, $J=7$, $CH_2(\alpha)$); 2.29 (*t*, $J=7$, $CH_2(\gamma)$); 2.00 (br. *s*, OH); 1.91 (*tt*, $J=7$, $CH_2(\beta)$); 1.45 (*d*, $J=7$, Me). ^{13}C-NMR ($CDCl_3$): 173.9 (COO); 143.5 (C_i); 140.5 (C_p); 128.5 (C_m); 125.4 (C_o); 70.1 (CH); 51.4 (MeO); 34.7 (C(α)); 33.3 (C(γ)); 27.0 (C(β)); 25.6 (Me).

4-Ethenylbenzenebutanoic Acid Methyl Ester (**5b**). As described in [15]. Purification by column chromatography ($CHCl_3$). Yield 60%. FT-IR: 3085, 3005 (arom. CH); 2950, 2860 (aliph. CH); 1737 (CO, ester); 1629 (C=C); 1607 (arom. C=C); 906 CH=CH_2); 844 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.31 (2 H_o) and 7.12 (2 H_m) (*AA′BB′*, $J_{AB}=8$); 6.61 (*dd*, $J=17.6$, 11.0, CH_2=C*H*); 5.69 *dd*, $J=17.6$, 0.9, H_{trans} of CH_2=CH); 5.18 (*dd*, $J=11.0$, 0.9, H_{cis} of CH_2=CH); 3.65 (*s*, Me); 2.63 (*t*, $J=7$, $CH_2(\alpha)$); 2.32 (*t*, $J=7$, $CH_2(\gamma)$); 1.91 (*tt*, $J=7$, $CH_2(\beta)$). ^{13}C-NMR ($CDCl_3$): 174.3 (COO); 141.5 (C_p); 137.1 (CH_2=*C*H); 135.9 (C_i); 128.6 (C_m); 126.2 (C_o); 113.0 (*C*H_2=CH); 51.4 (MeO); 34.8 (C(α)); 33.3 (C(γ)); 26.3 (C(β)).

2.6. *Determination of the Composition of the Polymers.* The composition of the copolymers **7a**–**c** and **8a**–**c** was determined from ^{1}H-NMR spectra, by using the integration ratio of the aromatic to aliphatic proton signals according to the following expressions (x = molar fraction of COO-substituted co-units):

Aliphatic ^{1}H/aromatic ^{1}H = $[3+2xn]/[5\text{-}x]$, where $n=2$ for **7a**, 3 for **7b**, and 4 for **7c**.

Aliphatic ^{1}H/aromatic ^{1}H = $[3+2xn]/[5+14x]$, where $n=2$ for **8a**, 3 for **8b**, and 4 for **8c**.

The composition of **6b** and of the copolymers with higher degree of functionalization **6a′**–**6c′**, and **9a′**–**9c′** was determined as described in [15].

Ethenylbenzene Copolymers with 4-Ethenylbenzenealkanoic Acid Methyl Esters ($(\mathbf{P}-H)_{1-x}$-$(\mathbf{P}-CH_2)_n-COOMe)_x$). Copolymers **6a**, **6a′** ($n=2$), **6b**, **6b′** ($n=3$), and **6c**, **6c′** ($n=4$) were prepared by a similar procedure as in [15].

6a: Yield 82%; $x=0.12$; $\overline{M_n}=16400$ g/mol, $\overline{M_w}/\overline{M_n}=1.9$.

6b: Yield 80%; $x=0.12$; $\overline{M_n}=14400$ g/mol, $\overline{M_w}/\overline{M_n}=1.7$.

6c: Yield 74%; $x=0.11$; $\overline{M_n}=15200$ g/mol, $\overline{M_w}/\overline{M_n}=1.8$.

6a′: Yield 77%; $x=0.54$; $\overline{M_n}=4000$ g/mol, $\overline{M_w}/\overline{M_n}=2.0$.

6b′: Yield 75%; $x=0.54$; $\overline{M_n}=11000$ g/mol, $\overline{M_w}/\overline{M_n}=2.1$.

6c′: Yield 68%; $x=0.56$; $\overline{M_n}=16100$ g/mol, $\overline{M_w}/\overline{M_n}=1.6$.

Ethenylbenzene Copolymers with 4-Ethenylbenzenealkanoic Acids ($(\mathbf{P}-H)_{1-x}(\mathbf{P}-(CH_2)_n-COOH)_x$). The copolymers **7a**–**c** ($x=0.11$) were prepared from the corresponding methyl ester derivatized copolymers **6a** (1 g,

8.8 mmol), **6b**, (1 g, 8.6 mmol), and **6c**, (1 g, 8.5 mmol), respectively, in CH_2Cl_2 (100 ml) by reaction with KOH (0.5 g, 8.9 mmol) in EtOH (10 ml) under stirring at r.t. for 2 days. The mixture was then acidified with 5% H_2SO_4 soln., the residue extracted with CH_2Cl_2 and the solvent evaporated. Subsequently, the copolymer was precipitated with MeOH, dissolved in CH_2Cl_2, and reprecipitated from MeOH three times.

7a: Yield 80%; $x = 0.12$; $\overline{M_n} = 36500$ g/mol, $\overline{M_w}/\overline{M_n} = 1.7$.

7b: Yield 78%; $x = 0.12$; $\overline{M_n} = 25900$ g/mol, $\overline{M_w}/\overline{M_n} = 1.6$.

7c: Yield (72%; $x = 0.12$; $\overline{M_n} = 24100$ g/mol, $\overline{M_w}/\overline{M_n} = 1.9$.

Ethenylbenzene Copolymers with {[ω-(4-Ethenylphenyl)-1-oxoalkyl]oxy}triphenylstannanes ($(\mathbf{P}-H)_{1-x}$-$(\mathbf{P}-(CH_2)_n-COOSnPh_3)x$). The copolymers **8a-c** were prepared from stoichiometric amounts of copolymers **7a** (1 g, 8.87 mmol), **7b** (1 g, 8.74 mmol), and **7c** (1 g, 8.61 mmol), respectively, and hydroxytriphenylstannane (= triphenyltin hydroxide); *Aldrich*; 0.390 g (8.87 mmol) for **7a**; 0.384 g (8.74 mmol) for **7b**, and 0.379 g (8.61 mmol) for **7c**) in toluene (100 ml) under reflux for 12 h. The solvent was evaporated and the copolymer purified by precipitation with hexane.

8a: Yield 85%; $x = 0.11$; $\overline{M_n} = 30900$ g/mol, $\overline{M_w}/\overline{M_n} = 1.9$. Elem. anal.: C 80.80, H 6.58, Sn 8.86.

8b: Yield 80%; $x = 0.11$; $\overline{M_n} = 26100$ g/mol, $\overline{M_w}/\overline{M_n} = 2.1$. Elem. anal.: C 80.39, H 6.55, Sn 8.71.

8c: Yield 78%; $x = 0.10$; $\overline{M_n} = 25700$ g/mol, $\overline{M_w}/\overline{M_n} = 2.0$. Elem. anal.: C 79.43, H 6.70, Sn 8.10.

Ethenylbenzene Copolymers with Tributyl{[ω-(4-ethenylphenyl)-1-oxoalkyl]oxy}stannanes ($(\mathbf{P}-H)_{1-x}$-$(\mathbf{P}-(CH_2)_n-COOSnBu_3)_x$). The copolymers with higher degree of functionalization **9a′–c′** were synthesized by a similar procedure as in [15].

9a′: Yield 76%; $x = 0.51$; $\overline{M_n} = 8400$ g/mol, $\overline{M_w}/\overline{M_n} = 2.0$. Elem. anal.: C 63.83, H 8.10, Sn 21.21.

9b′: Yield 73%; $x = 0.50$; $\overline{M_n} = 22800$ g/mol, $\overline{M_w}/\overline{M_n} = 2.2$. Elem. anal.: C 65.48, H 8.18, Sn 21.38.

9c′: Yield 70%; $x = 0.54$; $\overline{M_n} = 33200$ g/mol, $\overline{M_w}/\overline{M_n} = 1.9$. Elem. anal.: C 64.31, H 8.59, Sn 21.02.

The copolymers with lower degree of functionalization **9a** and **9c** were described previously [15]. Copolymer **9b** was synthesized by a similar procedure as in [15]. **9b:** Yield 68%; $x = 0.11$, $\overline{M_n} = 14900$, $\overline{M_w}/\overline{M_n} = 1.9$. Elem. anal.: C 80.89, H 8.11, Sn 8.82.

2.7. Spectroscopic Data of the Polymers. Ethenylbenzene Copolymer with 4-Ethenylbenzenepropanoic Acid (**7a**, $n = 2$). FT-IR: 3082, 3025 (arom. CH); 2922 (aliph. CH); 1709 (CO, acid); 1601 (arom. C=C); 840 (*p*-disubst. arom.) ^{1}H-NMR ($CDCl_3$) 7.24–6.69 (*m*, arom. H); 3.07 (br. *s*, $CH_2(\alpha)$); 2.82 (br. *s*, $CH_2(\beta)$); 2.03–1.62 (*m*, CH_2-CH). ^{13}C-NMR ($CDCl_3$): 180.0 (COO); 144.9 (C_i, $C_{i'}$); 136.0 (C_p); 128.6 (C_o, $C_{o'}$, C_m, $C_{m'}$); 126.3 ($C_{p'}$); 44.0 (CH_2-CH); 41.1 (CH_2-CH); 35.3 (C(β)); 29.9 (C(α)).

Ethenylbenzene Copolymer with 4-Ethenylbenzenebutanoic Acid (**7b**, $n = 3$). FT-IR: 3082, 3025 (arom. CH); 2922 (aliph. CH); 1708 (CO, acid), 1601, (arom. C=C); 839 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.03–6.48 (*m*, arom. H); 2.57 (br. *s*, $CH_2(\alpha)$); 2.33 (br. *s*, $CH_2(\gamma)$); 1.88–1.43 (*m*, $CH_2(\beta)$, CH_2-CH). ^{13}C-NMR ($CDCl_3$): 179.9 (COO); 145.3 (C_i, $C_{i'}$); 138.2 (C_p); 127.9, 127.7 (C_o, $C_{o'}$, C_m, $C_{m'}$); 125.6 ($C_{p'}$); 44.5 (CH_2-CH); 41.0 (CH_2-CH); 35.2 (C(α)); 34.0 (C(γ)); 26.9 (C(β)).

Ethenylbenzene Copolymer with 4-Ethenylbenzenepentanoic Acid (**7c**, $n = 4$). FT-IR: 3082, 3025 (arom. CH); 2922 (aliph. CH); 1706 (CO, acid); 1601 (arom. C=C); 839 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.04–6.48 (*m*, arom. H); 2.54 (br. *s*, $CH_2(\alpha)$); 2.37 (br. *s*, $CH_2(\delta)$); 1.84–1.43 (*m*, $CH_2(\beta)$, $CH_2(\gamma)$, CH_2-CH). ^{13}C-NMR ($CDCl_3$): 180.0 (COO); 145.9 (C_i, $C_{i'}$); 139.7 (C_p); 128.6, (C_o, $C_{o'}$, C_m, $C_{m'}$); 126.3 ($C_{p'}$); 44.3 (CH_2-CH); 41.0 (CH_2-CH), 35.7 (C(α)); 34.5 (C(δ)); 31.3 (C(β)); 24.9 (C(γ)).

Ethenylbenzene Copolymer with [3-(4-Ethenylphenyl)-1-oxopropoxy]triphenylstannane **8a**, $n = 2$). FT-IR: 3082, 3025 (arom. CH); 2922, 2849 (aliph. CH); 1636 (CO, ester); 1601 (arom. C=C); 840 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.75–7.70 (*m*, $^3J(^1H,^{119/117}Sn) \approx 55$, H_o(PhSn)); 7.42–7.34 (*m*, H_m(PhSn), H_p(PhSn)); 7.03–6.46 (*m*, arom. H); 2.86 (br. *s*, $CH_2(\alpha)$); 2.64 (br. *s*, $CH_2(\beta)$); 1.82–1.41 (*m*, CH_2-CH). ^{13}C-NMR ($CDCl_3$): 180.5 (COO); 145.9 (C_i, $C_{i'}$); 138.9 ($^1J(^{13}C,^{119/117}Sn) = 650, 618$, C_i(PhSn)); 138.5 (C_p); 137.5 ($^2J(^{13}C,^{119/117}Sn) \approx 47$, C_o(PhSn)); 130.7 (C_p(PhSn)); 129.5 ($^3J(^{13}C,^{119/117}Sn) \approx 64$, C_m(PhSn)); 128.6, 128.3, (C_o, $C_{o'}$, C_m, $C_{m'}$);126.3 ($C_{p'}$); 44.7 (CH_2-CH); 41.0 (CH_2-CH); 36.5 (C(β)); 31.9 (C(α)). ^{117}Sn-NMR ($CDCl_3$): −113.

Ethenylbenzene Copolymer with [4-(4-Ethenylphenyl)-1-oxobutoxy]triphenylstannane (**8b**, $n = 3$). FT-IR: 3082, 3025 (arom. CH); 2922, 2850 (aliph. CH); 1635 (CO, ester); 1601 (arom. C=C); 839 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.75–7.70 (*m*, $^3J(^1H,^{119/117}Sn) \approx 59$, H_o(PhSn)); 7.42–7.34 (*m*, H_m(PhSn), H_p(PhSn)); 7.03–6.46 (*m*, arom. H); 2.48 (br. *s*, $CH_2(\alpha)$); 2.37 (br. *s*, $CH_2(\gamma)$); 1.86–1.41 (*m*, $CH_2(\beta)$, CH_2CH). ^{13}C-NMR ($CDCl_3$): 180.6 (COO); 145.3 (C_i, $C_{i'}$); 138.5 ($^1J(^{13}C,^{119/117}Sn) = 647, 620$, C_i(PhSn)); 137.9 (C_p); 136.9 ($^2J(^{13}C,^{119/117}Sn) \approx 46$, C_o(PhSn)); 130.1 (C_p(PhSn)); 128.9 ($^3J(^{13}C,^{119/117}Sn) \approx 63$, C_m(PhSn)); 127.9, 127.6 (C_o, $C_{o'}$, C_m, $C_{m'}$); 125.6 ($C_{p'}$); 43.9 (CH_2-CH); 40.4 (CH_2-CH); 34.9 (C(α)); 33.6 (C(γ)); 27.4 (C(β)). ^{117}Sn-NMR ($CDCl_3$): −115.

Ethenylbenzene Copolymer with {[5-(4-Ethenylphenyl)-1-oxopentyl]oxy}triphenylstannane (**8c**, $n=4$). FT-IR: 3080, 3025 (arom. CH); 2922, 2850, (aliph. CH); 1635 (CO, ester); 1601 (arom. C=C); 839 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.75–7.70 (*m*, $^3J(^1H,^{119/117}Sn)\approx 59$, H_o(PhSn)); 7.42–7.34 (*m*, H_m(PhSn), H_p(PhSn)); 7.03–6.45 (*m*, arom. H); 2.43 (br. *s*, $CH_2(\alpha)$); 2.37 (br. *s*, $CH_2(\delta)$); 1.82–1.41 (*m*, $CH_2(\beta)$, $CH_2(\gamma)$ CH_2-CH). ^{13}C-NMR ($CDCl_3$): 180.7 (COO); 145.2 (C_i, $C_{i'}$); 138.4 ($^1J(^{13}C,^{119/117}Sn)=649$, 619, C_i(PhSn)); 138.0 (C_p); 136.8 ($^2J(^{13}C,^{119/117}Sn)\approx 48$, C_o(PhSn)); 130.1 (C_p(PhSn)); 128.8 ($^3J(^{13}C,^{119/117}Sn)\approx 64$, C_m(PhSn)); 128.3, 127.9 (C_o, $C_{o'}$, C_m, $C_{m'}$); 125.6 ($C_{p'}$); 43.8 (CH_2-CH); 41.3, (CH_2-CH); 35.1 (C(α)); 33.9 (C(δ)); 31.0 (C(β)); 25.5 (C(γ)). ^{117}Sn-NMR ($CDCl_3$): −116.

Ethenylbenzene Copolymer with Tributyl[3-(4-ethenylphenyl)-1-oxopropoxy]stannane (**9a′**, $n=2$). FT-IR: 3083, 3025 (arom. CH); 2923, 2853 (aliph. CH); 1648, 1561 (CO, ester); 1601 (arom. C=C); 840 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 6.98–6.39 (*m*, arom. H); 2.81 (br. *s*, $CH_2(\alpha)$); 2.53 (br. *s*, $CH_2(\beta)$); 1.73–1.14 (*m*, CH_2-CH), $CH_2(\alpha)$(Bu), $CH_2(\beta)$(Bu), $CH_2(\gamma)$(Bu)); 0.91 (*t*, $J=7$, Me(Bu)). ^{13}C-NMR ($CDCl_3$): 178.5 (COO); 145.2 (C_i, $C_{i'}$); 138.2 (C_p); 127.7 (C_o, $C_{o'}$, C_m, $C_{m'}$); 125.5 ($C_{p'}$); 44.0 (CH_2-CH); 40.3 (CH_2-CH); 36.6 (C(β)); 31.5 (C(α)); 27.8 ($^2J(^{13}C,^{119/117}Sn)\approx 20$, $CH_2(\beta$(Bu)); 27.0 ($^3J(^{13}C,^{119/117}Sn)\approx 64$, $CH_2(\gamma)$(Bu)); 16.4 ($^1J(^{13}C,^{119/117}Sn)=360$, 344, $CH_2(\alpha)$(Bu)); 13.6 (Me(Bu)). ^{117}Sn-NMR ($CDCl_3$): 104.

Ethenylbenzene Copolymer with Tributyl[4-(4-ethenylphenyl)-1-oxobutoxy]stannane (**9b′**, $n=3$). FT-IR 3082, 3025 (arom. CH); 2923, 2853 (aliph. CH); 1651, 1558 (CO, ester);1601 (arom. C=C); 839 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 6.99–6.41 (*m*, arom. H); 2.50 (br. *s*, $CH_2(\alpha)$); 2.28 (br. *s*, $CH_2(\gamma)$); 1.84–1.14 (*m*, $CH_2(\beta)$, CH_2-CH), $CH_2(\alpha)$(Bu), $CH_2(\beta)$(Bu), $CH_2(\gamma)$(Bu)); 0.90 (*t*, $J=7$, Me(Bu)). ^{13}C-NMR ($CDCl_3$): 179.1 (COO); 145.3 (C_i, $C_{i'}$); 138.8 (C_p); 127.8 (C_o, $C_{o'}$, C_m, $C_{m'}$); 125.4 ($C_{p'}$); 44.3 (CH_2-CH); 40.5 (CH_2-CH); 35.0 (C(α)); 34.4 (C(γ)); 27.9 ($^2J(^{13}C,^{119/117}Sn)\approx 21$, $CH_2(\beta)$(Bu)); 27.6 (C(β)); 27.1 ($^3J(^{13}C,^{119/117}Sn)\approx 65$, $CH_2(\gamma)$(Bu)); 16.4 ($^1J(^{13}C,^{119/117}Sn)=360$, 344, $CH_2(\alpha)$(Bu)); 13.6 (Me(Bu)). ^{117}Sn-NMR ($CDCl_3$): 102.

Ethenylbenzene Copolymer with Tributyl{[5-(4-ethenylphenyl)-1-oxopentyl]oxy}stannane (**9c′**, $n=4$). FT-IR 3082, 3025 (arom. CH); 2923, 2853 (aliph. CH); 1651, 1556 (CO, ester); 1601 (arom. C=C); 839 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.00–6.41 (*m*, arom. H); 2.48 (br. *s*, $CH_2(\alpha)$); 2.31 (br. *s*, $CH_2(\delta)$); 1.73–1.14 (*m*, $CH_2(\beta)$, $CH_2(\gamma)$, CH_2-CH, $CH_2(\alpha)$Bu), $CH_2(\beta)$(Bu), $CH_2(\gamma)$(Bu)); 0.89 (*t*, $J=7$, Me(Bu)). ^{13}C-NMR ($CDCl_3$): 179.2 (COO); 145.3 (C_i, $C_{i'}$); 139.2 (C_p); 127.8 (C_o, $C_{o'}$, C_m, $C_{m'}$); 125.5 ($C_{p'}$); 44.4 (CH_2-CH); 40.3 (CH_2-CH); 35.9 C(α)); 35.3 (C(δ)); 31.8 (C(β)); 27.8 ($^2J(^{13}C,^{119/117}Sn)\approx 20$, $CH_2(\beta)$(Bu)); 27.0 ($^3J(^{13}C,^{119/117}Sn)\approx 63$, $CH_2(\gamma)$(Bu)); 26.3 (C(γ)); 16.9 ($^1J(^{13}C,^{119/117}Sn)\approx 350$, $CH_2(\alpha)$(Bu)); 14.2 (Me(Bu)). ^{117}Sn-NMR ($CDCl_3$): 102.

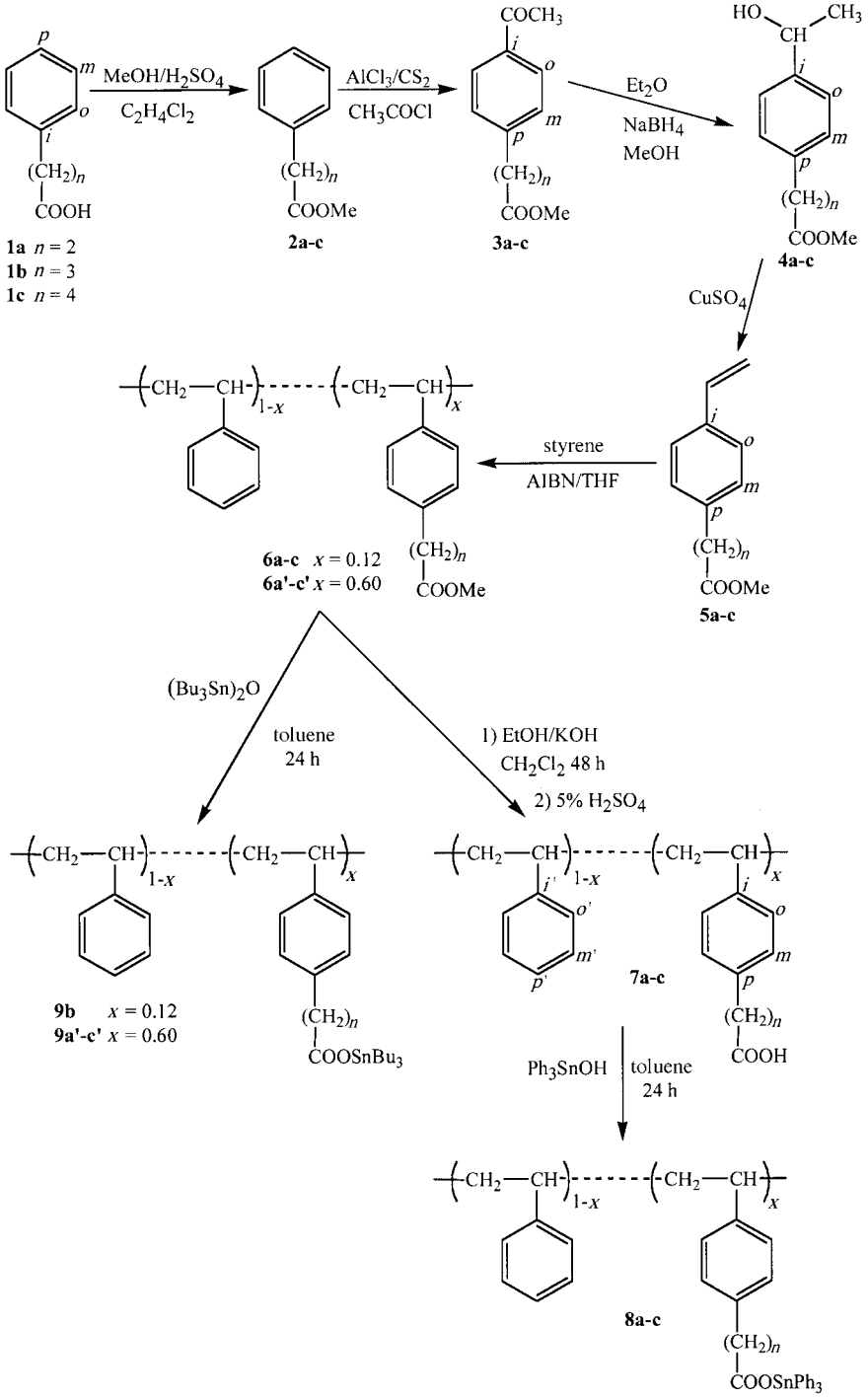
Ethenylbenzene Copolymer with 4-Ethenylbenzenebutanoic Acid Methyl Ester (**6b**, $n=3$). FT-IR 3082, 3025 (arom. CH); 2922 (aliph. CH); 1737 (CO, ester); 1601 (arom. C=C); 840 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.06–6.37 (*m*, arom. H); 3.65 (*s*, Me); 2.53 (br. *s*, $CH_2(\alpha)$); 2.28 (br. *s*, $CH_2(\gamma)$); 1.87–1.42 (*m*, $CH_2(\beta)$, CH_2-CH). ^{13}C-NMR ($CDCl_3$): 173.9 (COO); 145.3 (C_i, $C_{i'}$); 138.3 (C_p); 127.9, 127.6 (C_o, $C_{o'}$, C_m, $C_{m'}$); 125.6 ($C_{p'}$); 51.4 (MeO); 44.8 (CH_2-CH); 41.1, (CH_2-CH); 35.4 (C(α)); 34.1 (C(γ)); 27.2 (C(β)).

Ethenylbenzene Copolymer with Tributyl[4-(4-ethenylphenyl)-1-oxobutoxy]stannane (**9b**, $n=3$). FT-IR 3081, 3026 (arom. CH); 2922, 2850 (aliph. CH); 1648 (CO, ester); 1601 (arom. C=C); 840 (*p*-disubst. arom.). ^{1}H-NMR ($CDCl_3$): 7.21–6.46 (*m*, arom. H); 2.53 (br. *s*, $CH_2(\alpha)$); 2.31 (br. *s*, $CH_2(\gamma)$); 1.86–1.13 (*m*, $CH_2(\beta)$, CH_2-CH, $CH_2(\alpha)$(Bu), $CH_2(\beta)$(Bu), $CH_2(\gamma)$(Bu)); 0.91 (*t*, $J=7$, Me(Bu)). ^{13}C-NMR ($CDCl_3$): 179.2 (COO); 145.3 (C_i, $C_{i'}$); 138.7 (C_p); 127.9, 127.7 (C_o, $C_{o'}$, C_m, $C_{m'}$); 125.6 ($C_{p'}$); 44.6 (CH_2-CH); 41.0 (CH_2-CH); 35.6 (C(α)); 34.4 (C(γ)); 28.5 ($^2J(^{13}C,^{119/117}Sn)\approx 21$, $CH_2(\beta)$(Bu)); 27.7 (C(β)); 27.1 ($^3J(^{13}C,^{119/117}Sn)\approx 65$, $CH_2(\gamma)$(Bu)); 17.1 ($^1J(^{13}C,^{119/117}Sn)=360$, 344, $CH_2(\alpha)$(Bu)); 14.3 (Me(Bu)).

Copolymers **9a** *and* **9c**. For data, see [15].

3. Results and Discussion. – 3.1. *Synthesis.* The monomeric precursor of the polymers **6b**, **6b′**, **7b**, **8b**, **9b**, and **9b′**, *i.e.*, 4-ethenylbenzenebutanoic acid methyl ester (**5b**), not described in our previous work [15], was synthesized starting from benzenebutanoic acid (**1b**) by the procedure shown in *Scheme 1* (see also *Exper. Part*). From **5b**, the copolymer **6b**, was synthesized in analogy with the procedure previously described for the synthesis of the polymers **6a** and **6c** [15]. Copolymers **7a–c** were prepared by reaction of **6a–c**, respectively, with KOH in EtOH for 48 h, followed by acidification with 5% H_2SO_4 solution. Subsequently, **7a–c** were converted to the corresponding [(1-oxoalkyl)oxy]triphenylstannane analogues **8a–c** with hydroxytri-

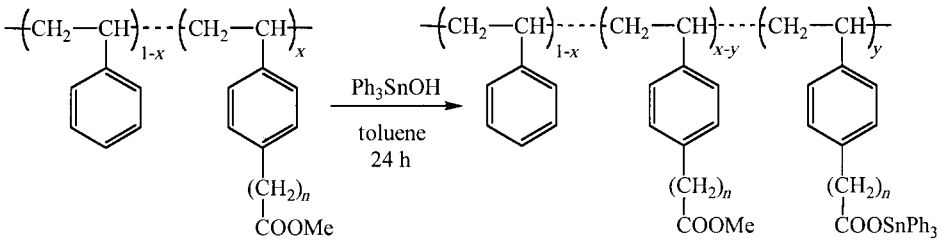
Scheme 1. *Synthesis of the [(1-Oxoalkyl)oxy]triphenylstannane and Tributyl[(1-oxoalkyl)oxy]stannane Polymers* **8a–8c** *and* **9a'–9c', 9b**, *respectively.* Arbitrary numberings.



phenylstannane. Copolymers **6a′–c′**, with higher degrees of functionalization than **6a–c**, were prepared in THF solution by copolymerization of the monomeric 4-ethenylbenzenealkanoic acid methyl esters [15] (60 mol-%) with styrene (40 mol-%) for 72 h in the presence of a thermal radical initiator (azoisobutyronitrile (=2,2′-azo[2-methylpropanenitrile] AIBN, 0.5%). Under these conditions, the methyl ester copolymers were obtained in reasonable yields (see *Exper. Part*). The tributyl[(1-oxoalkyl)oxy]stannane copolymers were synthesized by reaction of the poly(carboxylic acid methyl esters) **6a′–c′** with hexabutyldistannoxane ($(Bu_3Sn)_2O$) yielding, **9a′–c′**, respectively. Since the copolymers **9a′–c′**, purified by precipitation [15], appeared very sticky, we dissolved the copolymers, after purification, in small amounts of dry, freshly distilled $CHCl_3$, the latter being then evaporated slowly for several hours, which eventually gave glassy copolymers which were easier to handle.

In previous work [15], we reported on the use of $(Bu_3Sn)_2O$ as a reagent that enables direct conversion of the methyl ester functions of polystyrene copolymers to their corresponding tributyl[(1-oxoalkyl)oxy]stannanes. This approach avoids all disadvantages related to polymerization of stannane-containing monomers [14][15], as well as as the need for acid-hydrolysis reactions on monomers containing styrene moieties, which could lead to undesired polymerization. It also avoids the involvement of poly(carboxylic acids) as synthetic intermediates. Since it is known that hydroxytriphenylstannane (Ph_3SnOH) and hexaphenyldistannoxane (=bis(triphenyltin) oxide; $(Ph_3Sn)_2O$; BTPTO) cleave methyl and isopropyl benzene acetate [20], it was expected that direct conversion of the polymeric methyl esters into the corresponding [(1-oxoalkyl)oxy]triphenylstannanes with these reagents would be likewise possible, in analogy with the preparation of the tributyl[(1-oxoalkyl)oxy]stannanes **9a′–c′**. Surprisingly, pure polystyrenes **8a–c** with the [(1-oxoalkyl)oxy]triphenylstannane functionality only could not be obtained in this way, as derivatives containing both the unreacted methyl ester and the [(1-oxoalkyl)oxy]triphenylstannane moieties were generated (*Scheme 2*), as evidenced by IR and ^{1}H-NMR spectroscopy. Thus, when copolymers **6a** or **6b**, respectively, were heated at 113° in toluene for 72 h with 2 or 4 mol-equiv. of Ph_3SnOH or $(Ph_3Sn)_2O$, only *ca.* 37% of the methyl ester functions were converted into the [(1-oxoalkyl)oxy]triphenylstannanes. The presence of both methyl ester and [(1-oxoalkyl)oxy]triphenylstannane functions was assessed by ^{1}H- and ^{117}Sn-NMR and IR spectroscopy. No evidence for the presence of a carboxylic acid functionality could be found in these copolymers, as unambiguously established by the presence of both methyl ester (*ca.* 1740 cm^{-1}) and organo[(1-oxoalkyl)oxy]stannane bands (*ca.* 1635 and 1605 cm^{-1}) and the absence of carboxylic acid bands (*ca.* 1705 cm^{-1}) in the IR spectrum. This result indicates that even an excess of stannane reagent does not allow complete conversion of the methyl ester functions into the [(1-oxoalkyl)oxy]triphenylstannanes. Obviously, the presence of hydroxy protons is not determinant, since the use of Ph_3SnOH rather than $(Ph_3Sn)_2O$ has no influence on the reaction course. Apparently, the steric demand of the copolymer does not allow the complete conversion since it has been shown that the cleavage of carboxylic esters by Ph_3SnOH or $(Ph_3Sn)_2O$ can depend on the steric demand of the ester [20]. Alternatively, that the reactivity of the methyl ester functions might be quenched by the COOMe function being stabilized by an O→Sn interaction of the type

Scheme 2. *Incomplete Conversion of Methyl Ester Functions into [(1-Oxoalkyl)oxy]triphenylstannane Moieties with the Reagent Ph_3SnOH*



$-COO-Sn(Ph_3)\leftarrow O=C(OMe)-$ is excluded by the fact that ^{117}Sn-NMR data in solution do not indicate coordination expansion at the Sn-atom.

By contrast, the direct reaction of $(Bu_3Sn)_2O$ with copolymers **6a′–c′** having a high content of methyl ester monomer was successful and led directly to the desired corresponding tributyl[(1-oxoalkyl)oxy]stannane copolymer in reasonable yields. This result indicates that Ph_3SnOH and $(Ph_3Sn)_2O$ are less reactive than $(Bu_3Sn)_2O$, and are not suitable for straightforward synthesis of [(1-oxoalkyl)oxy]triphenylstannanes from the corresponding methyl esters. Therefore, the preparation of the poly(carboxylic acids) **7a–c** as reaction intermediates in the synthetic scheme was needed. Noteworthy is that the molar-mass determination of the latter polymers indicated, when compared to that of the starting methyl esters, that they are self-associated in solution, as is usual for non-polymeric carboxylic acids in the liquid state.

The results of the functionalization degrees, as obtained from elemental-analysis data, as well as from ^{1}H-NMR signal integrations, are given in *Table 1* for the polystyrenes derivatized by [(1-oxoalkyl)oxy]triphenylstannanes (**8a–c**) and tributyl[(1-oxoalkyl)oxy]stannanes (**9a′–c′**).

Table 1. *Functionality Degrees* x *of Styrene Copolymers with [(1-Oxoalkyl)oxy]triphenylstannanes and Tributyl[(1-oxoalkyl)oxy]stannanes of the Type* $(\mathbf{P}-H)_{1-x}(\mathbf{P}-(CH_2)_n-COOSnR_3)_x$

	n	R	x^a)	x^b)
8a	2	Ph	0.11	0.11
b	3	Ph	0.11	0.11
c	4	Ph	0.10	0.10
9b	3	Bu	0.11	0.11
9a′	2	Bu	0.52	0.51
b′	3	Bu	0.49	0.50
c′	4	Bu	0.53	0.54

[a]) As calculated from tin elemental analysis data. [b]) As calculated from ^{1}H-NMR data.

3.2. *Characterization of the Poly(carboxylic acids)* **7a–c**, *the Poly{[(1-oxoalkyl)-oxy]triphenylstannanes}* **8a–c** *and the Poly{tributyl[(1-oxoalkyl)oxy]stannanes}* **9a′–c′**.
3.2.1. *FT-IR Spectra*. In the FT-IR spectra of the poly(carboxylic acids) **7a–c**, the vibrations associated with the COOMe group [21] of the copolymers **6a** (1739 and 1172 cm^{-1}), **6b** (1737 and 1174 cm^{-1}), and **6c** (1739 and 1195 cm^{-1}) have disappeared

and been replaced by new absorptions corresponding to the COOH group [22] (1709 and 1292 cm^{-1} for **7a**, 1708 and 1289 cm^{-1} for **7b**, and 1706 and 1286 cm^{-1} for **7c**).

In the solid state, nonpolymeric triorgano[(1-oxoalkyl)oxy]stannanes can belong to the three basic classes of structures **A – C** (*Fig. 1*). Structure class **A** is polymeric, with pentacoordinate Sn-atoms. Structure classes **B** and **C** correspond to monomeric structures, varying from a purely tetrahedral tetracoordinate geometry (type **C**) to a similar one with a weak additional intramolecular coordination from the carbonyl O-atom to the Sn-atom (type **B**) [23].

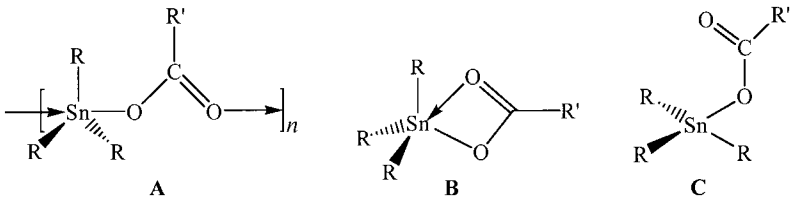


Fig. 1. *Structure classes* **A – C** *for triorgano[(1-oxoalkyl)oxy]stannanes in the solid state*

The observed IR absorption frequencies for the asymmetric carbonyl stretching vibration $\tilde{\nu}_{as}$(COO) at *ca.* 1635 cm^{-1} and the symmetric $\tilde{\nu}_s$ (COO) at 1303 cm^{-1} for copolymers **8a – c** are shown in *Table 2*. The $\Delta\tilde{\nu}$ values of 332 – 333 cm^{-1} are in the range 230 – 350 cm^{-1}, characteristic for the monodentate bonding mode of type **C** [24]. In previous work [15], these absorptions were likewise found at *ca.* 1650 and 1300 cm^{-1} for the corresponding lower functionalized poly{tributyl[(1-oxoalkyl)oxy]stannanes} **9a** and **9c**. They correspond to a structure involving exclusively tetracoordinated Sn-moieties [15]. In the case of the tributyl[(1-oxoalkyl)oxy]stannane copolymers **9a′ – c′**, the intensities of these absorptions around 1650 and 1300 cm^{-1} are lower when compared with the copolymers **9a** and **9c** [15], being coupled with the simultaneous appearance of bands located around 1560 and 1418 cm^{-1}. This results from the higher content of the tributyl[(1-oxoalkyl)oxy]stannane co-units in the copolymers **9a′ – c′** which causes part of the tributylstannane moieties to adopt an oligomeric structure of type **A**, involving pentacoordinated Sn-atoms. The observed $\Delta\tilde{\nu}$ values, which are less than 150 cm^{-1}, are characteristic for bridging or chelating carboxylato groups, as widely observed in the infrared spectra of triorgano[(1-oxoalkyl)oxy]stannanes [25][26]. Hence both tetra- and pentacoordinated Sn-atoms are present in the copolymers **9a′ – c′** with a tributyl[(1-oxoalkyl)oxy]stannane co-unit molar content of *ca.* 50%.

Table 2. *Infrared COO-Stretching Frequencies* [cm^{-1}] *of* **8a – c**, **9b**, *and* **9a′ – c′** *in the Solid State* (KBr pellet)

	$\tilde{\nu}_{as}$	$\tilde{\nu}_s$	$\tilde{\nu}_{as}$	$\tilde{\nu}_s$	$\Delta\nu$
8a	1636	1304	–	–	332
b	1635	1302	–	–	333
c	1635	1303	–	–	332
9b	1648	1304	–	–	344
9a′	1648	1302	1561	1417	346, 144
b′	1651	1309	1558	1418	342, 140
c′	1651	1306	1556	1418	345, 138

3.2.2. *NMR Characterization*. The ^{1}H- and ^{13}C-NMR data (*Exper. Part*) of the polymeric methyl esters **6a′–c′**, carboxylic acids **7a–c**, and triorgano[(1-oxoalkyl)-oxy]stannanes **8a–c** and **9a′–c′** are all in agreement with the proposed structures. The ^{1}H-NMR resonance intensities are in good agreement with the functionalization degrees calculated from elemental analyses (*Table 1*). The ^{117}Sn-NMR chemical shifts ($CDCl_3$) of the polymeric [(1-oxoalkyl)oxy]triphenylstannanes **8a–c** and tributyl[(1-oxoalkyl)oxy]stannanes **9a′–c′** are given in *Table 3*. The single resonances at *ca.* −115 and 103 ppm for the triphenyl- and tributylstannanes, respectively, is compatible with the tetrahedral geometry proposed for the solution structure [27][28]. Thus, in solution, the Sn-configuration is affected by neither the substituent nature nor the functionalization degree. The $^1J(^{13}C,^{119/117}Sn)$ coupling constants of copolymers **8a–c** and **9a′–c′** are likewise typical for tetrahedral Sn-atoms [15][26][29].

Table 3. *^{117}Sn-NMR Chemical Shifts, Both in $CDCl_3$ Solution and in the Solid State, and ^{1}J(^{13}C,$^{119/117}$Sn) Coupling Constants in $CDCl_3$ Solution for the Styrene Copolymers with Triorgano[(1-oxoalkyl)oxy]stannanes* **8a–c**, **9b**, *and* **9a′–c′**. δ in ppm rel. to $SnMe_4$, J in Hz.

	$\delta(^{117}Sn)$ ($CDCl_3$)	$^1J(^{13}C,^{119/117}Sn)$($CDCl_3$)	$\delta(^{117}Sn)$ (solid)
8a	−113	650, 618	−114
b	−115	647, 620	−117
c	−116	649, 619	−115
9b	103	360, 344	92
9a′	104	360, 344	92, −39 (65)[a])
b′	102	360, 344	89, −43 (71)[a])
c′	102	350[b])	87, −40 (73)[a])

[a]) Values in parentheses indicate the percentage of pentacoordinated Sn-atoms. [b]) A single value is given because of broad, unresolved coupling satellites.

The solid-state CP-MAS ^{117}Sn-NMR spectra of copolymers **8a–c** show also a single broad resonance at −114, −117, and −115 ppm, respectively, without any chemical-shift anisotropy pattern, unambiguously confirming tetrahedral configuration at the Sn-atom and indicating identical structures in solution and in the solid state without any intramolecular donor-acceptor interactions involving the Sn-atom. The solid-state ^{117}Sn spectra of copolymers **9a′–c′** exhibit two isotropic resonances. One resonance is located around 90 ppm, a value which is close to the chemical-shift value observed in solution and confirming tetrahedral Sn-atoms. The second, around −40 ppm, with an anisotropy pattern similar to that found in previous pentacoordinated Sn copolymers [26], reveals pentacoordinated Sn-atoms; however, this pentacoordination is lost in solution, as characterized by the single ^{117}Sn-NMR resonance in $CDCl_3$ solution around 100 ppm. These results are in complete agreement with the FT-IR data. The relative amounts of tetra- and pentacoordinated Sn-atoms, roughly estimated by the integration of the corresponding resonances in the CP-MAS ^{117}Sn-NMR spectra [30], are given in *Table 3*. Noteworthy is that there is only a slight trend in the increase of the fraction of pentacoordinated Sn as a function of the number of methylene groups in the spacer. Upon increasing the polymethylene chain length from 2 to 4 C-atoms, an enhanced capability of the macromolecules to give rise to a more ordered system can be suggested as a consequence of the slight increase of the fraction of pentacoordinated

Sn. This can be stated on the basis of the very close functionalization degree of polymers **9a′–c′**.

3.2.3. *Thermal Properties.* The thermogravimetric analysis of triphenylstannane copolymers **8a–c** reveals a thermal stability not much dissimilar from that of the previously reported tributylstannane analogues **9a** and **9c** [15] having a closely related composition, with initial decomposition-temperature values (T_d) above in the range 214–240° (*Table 4*). The stability of copolymers **9a′–c′** appears lower with respect to copolymers **9a–c** [15]. This can be ascribed to the presence of increased amounts of the labile tributyl[(1-oxoalkyl)oxy]stannane moieties in the copolymers **9a′–c′**. As expected, the tributyl[(1-oxoalkyl)oxy]stannane moieties are more prone to decompose at lower temperature upon increasing the size and flexibility of the polymethylene spacer. Accordingly, the initial decomposition temperatures for the methyl ester copolymer **6c′** and the poly(carboxylic acid) copolymer **7c** appear appreciably lower than those observed for the compounds **6a′**, **6b′** and **7a**, **7b**, respectively, with a smaller spacer length. The inorganic SnO_2 residue left after heating copolymers **8a–c** at 800° has lower mass than expected on the basis of the copolymer composition determined by ^{1}H-NMR (see *Table 4*). Partial decomposition through volatile organostannanes is a likely explanation, even if this effect seems not to be present in the polymers having the higher content in tributyl[(1-oxoalkyl)oxy]stannane functionality.

Table 4. *Thermal Data of Styrene Copolymers with Triorgano[(1-oxoalkyl)oxy]stannanes* **8a–c**, *and* **9a′–c′**, *and with the Corresponding Methyl Ester and Carboxylic Acid Precursors*

	T_g [a])	T_d [b])	SnO_2 weight [%] [c])	
			Calc.	Found
6a′	44	282	–	–
b′	37	288	–	–
c′	21	269	–	–
7a	116	304	–	–
b	108	302	–	–
c	67	269	–	–
8a	104	241	11.0	8.3
b	92	224	10.9	8.1
c	90	214	10.8	8.8
9a [d])	61	266	11.5	8.0
b	64	245	11.4	8.8
c [d])	65	220	11.3	7.0
9a′	50 [e])	231	21.9	22.7
b′	47 [e])	228	21.4	21.5
c′	34, 56 [e])	173	21.5	21.6

[a]) Glass transition temperature determined by DSC (heating rate 10°/min). [b]) Decomposition temperature at 1% weight loss under air (heating rate 20°/min). [c]) Residual material at 800°, calculated as SnO_2. [d]) Ref. [15]. [e]) Melting transitions.

The DSC analysis exhibits higher glass transition temperatures (T_g) for the poly(carboxylic acids) **7a–c** and their corresponding poly{[(1-oxyalkyl)oxy]triphenylstannanes} **8a–c** with respect to the more mobile tributyl[(1-oxoalkyl)oxy]stannane analogues [15] (see *Table 4*). The T_g values of copolymers **8a–c** decrease upon increasing the spacer length, due to the plasticizing effect related to the increased

length of the polymethylene segment in the side chain of the macromolecules. Their corresponding tributyl[(1-oxoalkyl)oxy]stannanes **9a′–c′** possessing a higher content of organostannane co-units, display somewhat dissimilar behavior, as they exhibit melting transitions rather than glass transitions, due to the crystalline domains originating from the quite important presence (*Table 3*) of cross-linked structures formed upon pentacoordination at the Sn-atom [26].

3.3. *Anion Recognition Based on Electrochemical Studies.* Liquid polymeric membranes doped with anion-selective carriers with specific chemical and physical characteristics are utilized for the selective and reversible anion monitoring in ion-selective electrodes (ISEs). The carriers should have a selective and reversible binding affinity to the analyte of interest, they must be chemically stable and have a very high partition coefficient toward the lipophilic membrane phase. It has been shown that the lipophilicity of the carrier determines to a large extent the signal stability and lifetime of the carrier-based chemical sensors [10]. It is thus postulated that one of the reasons for the short lifetime of organostannane-based sensors is indeed their rather low lipophilicity. For this reason, it is expected that grafting highly selective triorgano[(1-oxoalkyl)oxy]stannane monomers [7] to a polystyrene backbone should drastically increase the lipophilicity of the ion-recognition moiety and could thus eliminate the problem of carrier leaching into the aqueous phase. For this purpose, the triphenylstannane copolymers **8a–c**, the tributylstannane copolymers **9a–c** [15] with low functionality degree, as well as the tributylstannane copolymers **9a′–c′** with higher functionality degree were incorporated into a liquid membrane to assess their physical and chemical stabilities on the basis of their electrochemical response towards the Cl^- ion [7]. In all membranes, the same molar amount of active Sn-sites, independently of the degree of functionality of the triorganostannane moiety in the polymer, was used. The effect of the polymer grafting on the sensor stability was investigated with the poly(tributylstannanes), since the corresponding monomers were shown previously [7] to provide higher potentiometric response as well as selectivities towards Cl^- ion over their triphenylstannane analogues. As can be seen from *Fig. 2*, the tributylstannane copolymers **9c** and **9c′** ($n=4$) show the highest overall potentiometric response to Cl^-. However, this response drastically decreases within 24 h. On the other hand, the other copolymers exhibit low potentiometric responses, even at time zero. From these results, it is concluded that grafting triorgano[(1-oxoalkyl)oxy]stannanes to polystyrene does not overcome the problem of signal stability of the electrodes. This suggests that, at least in the case of triorgano[(1-oxoalkyl)oxy]stannanes, the physical leaching based on a possible low lipophilicity of the carrier is not the primary cause for the loss of the potentiometric response.

Since the diffusion of the polymer out of the membrane is not plausible, it can be postulated that either hydrolysis of the triorgano[(1-oxoalkyl)oxy]stannane, or poisoning of the carrier due to the strong coordination of the Sn-centers by Cl^- causes the weakening of the response with time. Evidence against hydrolysis of Sn from the polymers is provided by the fact that no hydrolysis at all is observed in similar polymeric triorgano[(1-oxoalkyl)oxy]stannanes even after stirring in an aqueous 0.1M KCl suspension at room temperature for two weeks, as checked by FT-IR spectroscopy [31]. In addition, it is postulated that grafting the triorgano[(1-oxoalkyl)oxy]stannane to the polymeric support should introduce some steric demand, hampering the facile

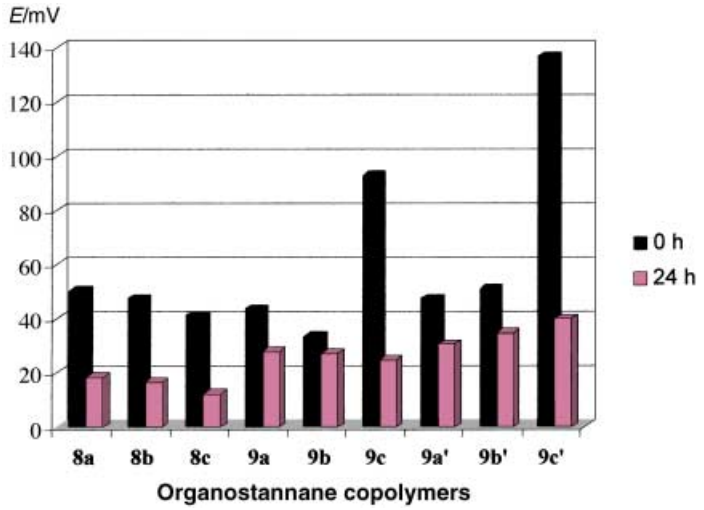


Fig. 2. *Potentiometric response of stannane-functionalized polymer-based ion-selective electrodes to chloride*

and reversible coordination of the ionic ligand to the Sn-center. For these reasons, the monomeric tributyl(1-oxo-2-phenylethoxy)stannane (=tributyltin phenylacetate) and its perfluorophenyl analogue have previously shown a higher response to Cl^- [7] than that obtained with the present polymeric tributyl[(1-oxoalkyl)oxy]stannanes. Another important fact to consider is that reasonably high overall potentiometric response is only obtained when the membranes are doped with polymers grafted with tributyl[(1-oxoalkyl)oxy]stannanes having a long spacer unit ($n=4$ in **9c** and **9c′**). This phenomenon can be due to the fact that either the spacer end is far enough from the sterically demanding polymer backbone, or that it has sufficient flexibility to prevent steric hindrance of the Cl^- ion coordination to the Sn-atom. The fact that the above observations do not hold true in the case of the triphenylstannane analogue **8c** can be attributed to two factors. It could be traced either to their well-established very low overall potentiometric responses to Cl^-, as compared to the tributylstannane ones [7], or to the fact that the triphenylstannane moiety reduces the flexibility of the polymer side chain in the membrane. It is, indeed, likely that some membrane swelling by the solvent is needed to induce the response, which is certainly easier with more flexible structural units.

Fig. 3 shows the potentiometric selectivity coefficients of carriers **9c** and **9c′** as representative examples of the polymers evaluated. The value of $\log K^{pot}_{Cl^-,X^-}$ is taken as zero for the Cl^- ion. It should be mentioned here that the separate solution method (SSM) is used to evaluate this value [32] with *Eqn. 1*, where a_I is the activity of the primary ion, z_I the charge of the primary ion, z_J the charge of the interfering ion, E_I the potentiometric responce of the ISE to the primary ion *I*, and E_J the potentiometric response of the ISE to the interfering ion *J*. As can be seen from *Eqn. 1*, the larger the overall potentiometric response to the Cl^- ion, the more negative the $\log K^{pot}_{Cl^-,X^-}$ value is, and thus, the more selective the sensor is to Cl^-. From *Fig. 3*, it can be seen that the idea that the polystyrene backbone acts as a hydrophobic barrier to the anion ability to

penetrate into the membrane is well supported. It can also be observed that the sensor retains a very unique selectivity towards Cl^-.

$$\log K_{IJ}^{pot} = \frac{z_I F[E_J - E_I]}{2.303RT} + \left(1 - \frac{z_I}{z_J}\right) \log a_I \quad (1)$$

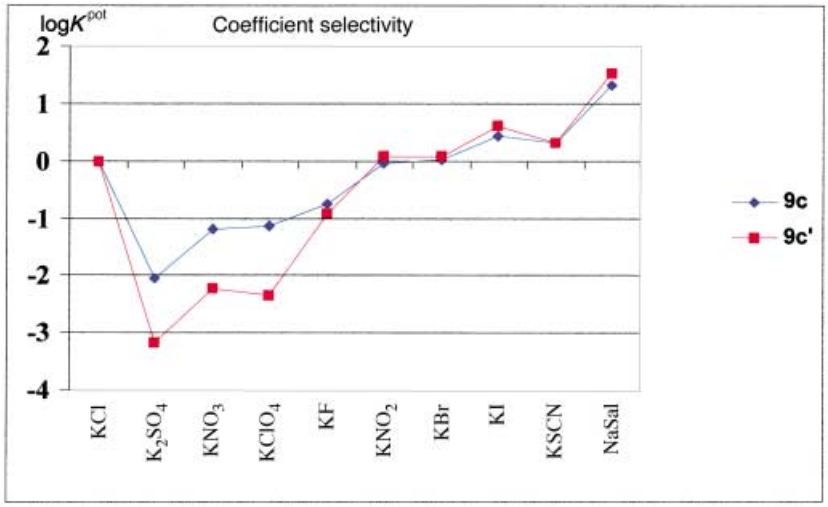


Fig. 3. *Anion-selectivity coefficients of electrodes prepared with copolymers* **9c** *and* **9c′**. Sal = salicylate.

The selectivity of the polymeric compounds **9c** and **9c′** towards chloride is higher than nitrate and perchlorate, but not than thiocyanate or iodide. However, the selectivity sequence obtained with the polymers in the present work is very different from the selectivity induced by classical anion exchangers which is based solely on the lipophilicity of the anion (*Hoffmeister* selectivity sequence: organic anions > ClO_4^- > SCN^- > I^- > salicylate$^-$ > NO_3^- > Br^- > Cl^- > HCO_3^- > SO_4^{2-} > HPO_4^{2-} ≈ F^-) [33].

4. Conclusions. – This work establishes that the one-pot conversion of polymeric carboxylic acid methyl esters into the corresponding polymeric tributyl[(1-oxoalkyl)oxy]stannanes can be applied successfully to the synthesis of copolymers with higher degree of functionalization, without being affected by undesired side reactions. However, analogous experiments with hydroxytriphenylstannane or hexaphenyldistannoxane with poly(carboxylic acid methyl esters) did not allow the complete conversion of the methyl ester functions into the corresponding [(1-oxoalkyl)oxy]triphenylstannanes. In the solid state, the Sn-atoms of polymeric [(1-oxoalkyl)oxy]triphenylstannane derivatives are tetracoordinated, while, by contrast, their tributylstannane analogues with high functionality degree exhibit both penta- and tetracoordinated Sn-atoms. In solution, no pentacoordinated Sn-atom at all is observed. Unlike similar monomeric tributyl[(1-oxoalkyl)oxy]stannanes, the overall potentiometric response to Cl^- is low, a fact that is mainly attributed to the lipophilic barrier induced by the polystyrene-like backbone. On the other hand, the good selectivity retained by

the some of the functionalized polymers is promising for the design of selective and stable anion carriers.

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