146. Anion Selectivities of Triorganyltin Acetates and Halides in Solvent Polymeric Membranes

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A series of triorganyltin compounds of the type R_3SnY and $R_2^1R^2SnY$ has been studied in view of their anion selectivities exhibited in solvent polymeric membranes. A large variety of selectivity patterns has been observed first by varying the concentration of a given ionophore in the membrane phase, and second by using ionophores which differ in the organic substituents R on the Sn centre. With more space consuming substituents R, the observed selectivity patterns become more and more similar to that of a blank membrane, suggesting steric hindrance for the pentacoordination of the corresponding ionophores by sample anions.

Introduction. – Certain organotin compounds induce anion selectivity in membranes [1–6] and act as electrically neutral carriers for anions [4] [6] (see also [7]). They are attractive candidates for anion sensors with a selectivity sequence deviating from the one observed with classical anion-exchanger membranes [5] [6] (*Hofmeister* lyotropic anion selectivity sequence:

$$ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- \sim AcO^- \sim SO_4^{2-} \sim HPO_4^{2-}$$
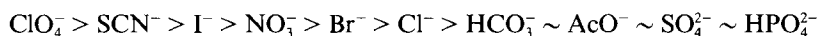
[8] [9]). Since the selectivity sequences induced in membranes by Bu_3SnCl and $(CH_3(CH_2)_7)_3SnCl$ show a significantly different pattern [5], we studied a series of trioganyltin compounds **1–12** (R_3SnY and $R_2^1R^2SnY$). Here, we report on the selectivities of membranes containing these compounds.

$$\begin{array}{ccc} R^1 & & R^2 \\ & \diagdown \diagup & \\ & Sn & \\ & \diagup \diagdown & \\ R^1 & & Y \end{array}$$
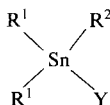
	R^1	R^2	Y
1	$CH_3-(CH_2)_3$	$CH_3-(CH_2)_3$	Cl
2	$CH_3-(CH_2)_3$	$CH_3-(CH_2)_3$	AcO
3	$CH_3-(CH_2)_7$	$CH_3-(CH_2)_7$	Cl
4	$CH_3-(CH_2)_3-CH(Et)CH_2$	$CH_3-(CH_2)_3-CH(Et)CH_2$	Cl
5	$CH_3-(CH_2)_{13}$	$CH_3-(CH_2)_{13}$	AcO
6	CH_3-CH_2	$CH_3-(CH_2)_5$	AcO
7	CH_3-CH_2	$CH_3-(CH_2)_7$	AcO
8	CH_3-CH_2	$CH_3-(CH_2)_{13}$	AcO
9	$CH_3-(CH_2)_3$	$CH_3-(CH_2)_{17}$	AcO
10	Cyclohexyl	Cyclohexyl	Br
11	Ph	Ph	Cl
12	$PhCH_2$	$PhCH_2$	Cl

Results and Discussion. – When solvent polymeric membranes with ionophores of the type shown are contacted with aqueous sample solutions containing various anions, an equilibrium distribution of triorganyltin compounds with different electronegative substituents Y will ultimately be established [5]. The selectivities exhibited by such membranes are, therefore, not strongly dependent on the original substituent Y (Cl, Br, AcO) on the Sn-centre of the ionophore used for preparing the membranes. Exceptions, however, may occur for some substituents Y (e.g. trialkyltin stearates behave differently from the corresponding trialkyltin acetates [10]).
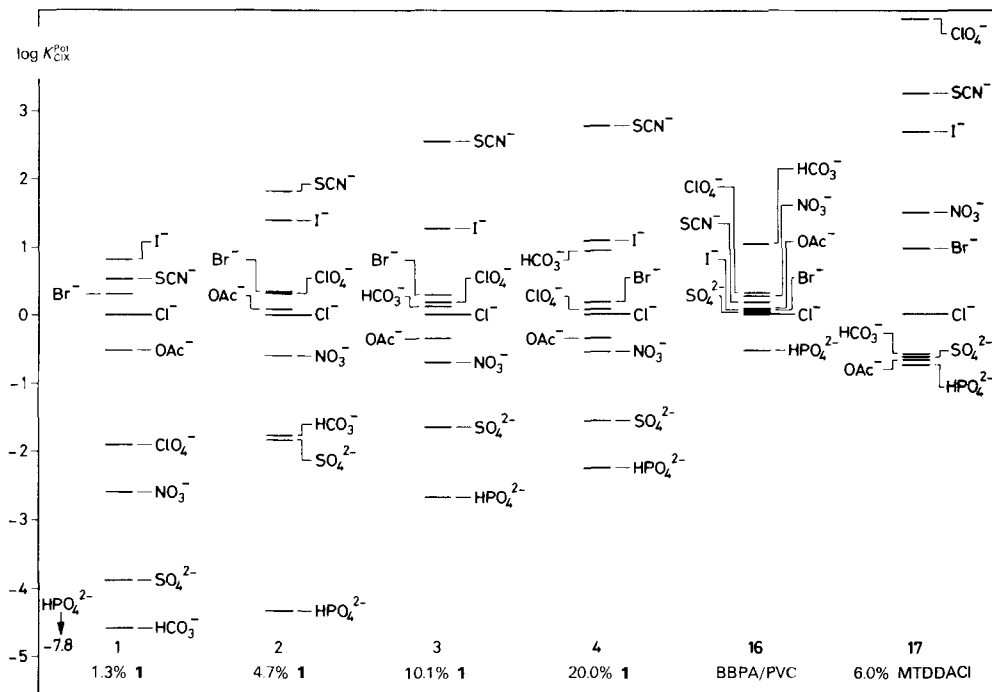

Fig. 1. *Influence of the ionophore concentration in the membrane phase on the selectivity induced by* **1** *(Columns 1 to 4). The selectivity patterns of a blank membrane (Column 5) and a membrane with a typical anion exchanger (Column 6) are also given (see last two lines in the Table).*

As described earlier, the selectivity pattern of a membrane containing a compound of the type R_3SnY heavily depends on the concentration of the ionophore in question (see *Fig. 1*). The selectivity factors (K_{ClX}^{Pot}) presented in *Fig. 1* reflect the preference of the anions X indicated relative to Cl^- observed for each membrane. Large positive values of log K_{ClX}^{Pot} reflect a high selectivity of the corresponding membrane for X over Cl^-. Membranes containing Bu_3SnCl as ionophore (*Columns 1 to 4*) exhibit selectivity sequences which clearly deviate from those found with blank membranes *(Column 5)* or with classical anion exchangers (*Hofmeister* series, *Column 6*). Because of the large dependence of the selectivity pattern on the carrier concentration, further discussions will be based on virtually constant molarities for the different organyltin anion carriers in the membrane

Table. *Compositions of the Membranes Used*

Membrane No.	Ion-selective component			Plasticizer (BBPA)[a] %	Membrane matrix (PVC)[a] %
	Constitution	%	mol/membrane		
1	**1**	1.3	$5.0 \cdot 10^{-7}$	65.7	33.0
2	**1**	4.7	$16.9 \cdot 10^{-7}$	63.4	31.9
3	**1**	10.1	$37.4 \cdot 10^{-7}$	59.6	30.3
4	**1**	20.0	$74.1 \cdot 10^{-7}$	52.8	27.2
5	**2**	1.0	$4.0 \cdot 10^{-7}$	65.2	33.8
6	**3**	1.5	$4.2 \cdot 10^{-7}$	65.7	32.8
7	**4**	1.8	$4.5 \cdot 10^{-7}$	64.6	33.6
8	**5**	1.0	$1.4 \cdot 10^{-7}$	66.3	32.7
9	**6**	1.1	$4.2 \cdot 10^{-7}$	66.1	32.8
10	**7**	1.3	$4.6 \cdot 10^{-7}$	65.8	32.9
11	**8**	1.5	$4.5 \cdot 10^{-7}$	66.1	32.4
12	**9**	2.1	$4.8 \cdot 10^{-7}$	65.3	32.6
13	**10**	1.6	$4.5 \cdot 10^{-7}$	65.1	33.3
14	**11**	1.4	$4.5 \cdot 10^{-7}$	65.6	33.0
15	**12**	1.6	$4.6 \cdot 10^{-7}$	65.2	33.2
16	–		–	66.5	33.5
17	MTDDACl[a]	6.0	$13.5 \cdot 10^{-7}$	65.2	28.8

[a]　PVC = Poly(vinyl chloride), BBPA = bis(1-butylpentyl) adipate,
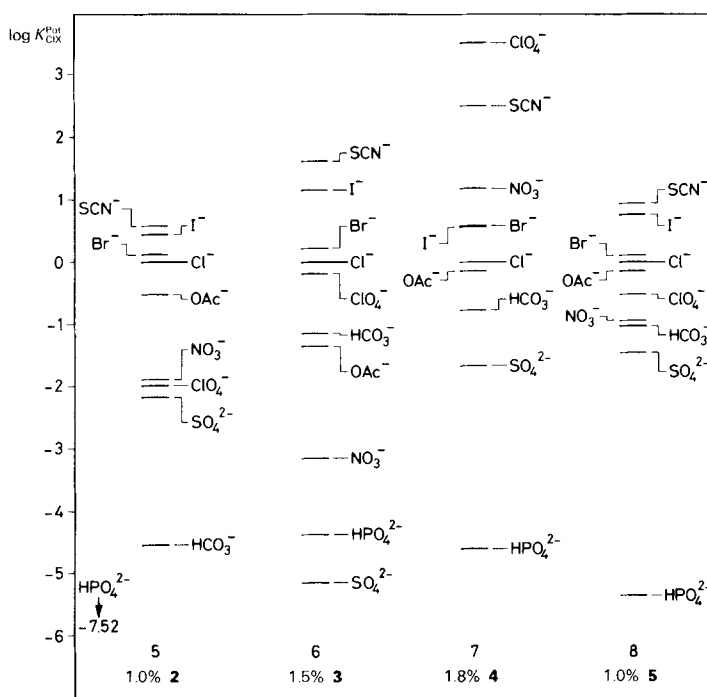　　MTDDACl = (tridodecyl)methylammonium chloride.

Fig. 2. *Selectivity sequences of membranes containing organyltin carriers of the type R_3SnY with R of different chain lengths*

(see the *Table*). The only exception is tritetradecyltin acetate which is not soluble enough in the membrane phase used.

There are some impressive changes with regard to membrane selectivity, when the chain lengths of the R_3SnCl or R_3SnOAc are varied *(Fig. 2)*. Branching of the alkyl chains *(Column 3)* leads to a preference of the ClO_4^- and NO_3^- ions by a factor of approximately 10^4 as compared with the corresponding isomers with unbranched chains *(Column 2)*. Ionophore **4** exhibits a selectivity pattern never observed before which somewhat deviates from the *Hofmeister* series and shows an unusual rejection of the SO_4^{2-} and HPO_4^{2-} ions in respect to Cl^-. Some influence of the carrier chain lengths on the sensors selectivity is also observed for the trialkyltin acetates ($R_2^1R^2SnY$) **6** to **9** *(Fig. 3)*.
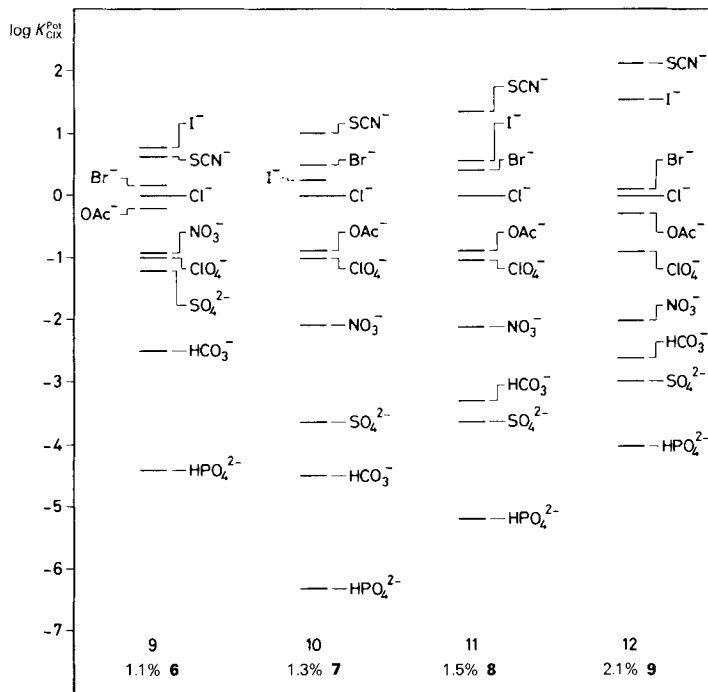

Fig. 3. *Selectivity sequences of membranes containing organyltin carriers of the type $R_2^1R^2SnY$ with R^1 and R^2 of different chain lengths*

A wide variety of anion sensor selectivities is accessible by incorporating compounds of the type R_3SnY with bulky substituents R into membranes *(Fig. 4)*. Apparently, substituents which are too bulky lead to an almost complete breakdown in the anion selectivity. Membranes with $(PhCH_2)_3SnCl$ (**12**), for instance, exhibit selectivities which are close to those of blank membranes (see *Column 4* in *Fig. 4* and *Column 5* in *Fig. 1*). There seems to be a tendency that an increase in the bulkiness of the substituents R on the Sn-centre of the ionophore leads to a decrease in the range of the log K_{CIX}^{Pot} values for the corresponding membranes. This behaviour is in line with the formation of negatively charged pentacoordinated species which could offer an explanation for the mode of
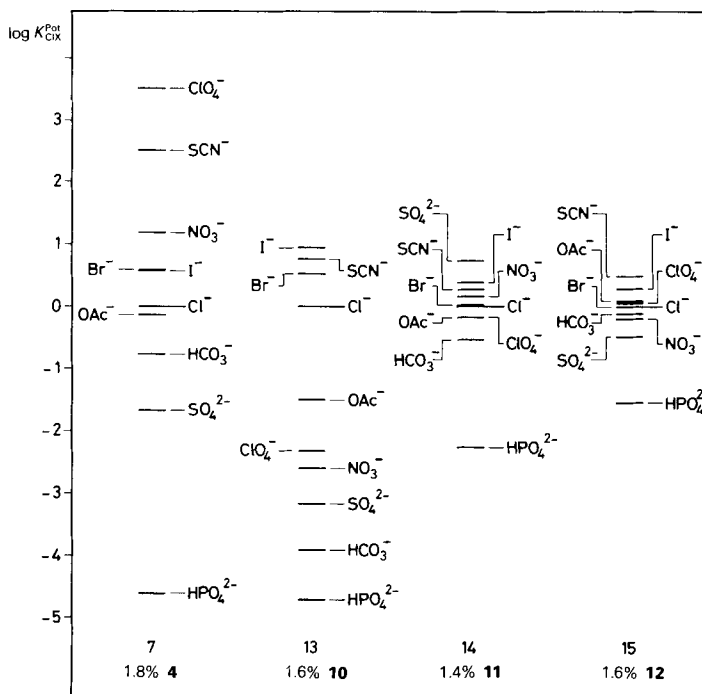
Fig. 4. *Selectivity sequences of membranes containing organyltin carriers of the type R_3SnY with substituents R of different steric shielding of the Sn-centre*

action of the neutral ionophores R_3SnY and $R_2^1R^2SnY$. It is also consistent with the increasing configurational stability of triorganyltin halides with bulky groups (*e.g.* trityl groups) at the Sn-centre in the presence of nucleophiles [11].

Experimental Part

Membranes. The compositions of the membranes used are given in the *Table.* The components totalled 200 mg and were dissolved in *ca.* 3 ml of THF and were then poured into a glass ring (diameter 27 mm) resting on a glass plate. After evaporation of the solvent, circular membrane pieces with a diameter of 7 mm were stamped out. They were incorporated into *Philips IS-561* electrode bodies (*N. V. Philips' Gloeilampenfabrieken,* Eindhoven, Holland) containing 0.01M NaCl as internal filling solution.

EMF-Measuring Device. Reference and ion-selective electrodes were connected to FET operational amplifiers *AD 515 KH (Analog Devices,* Norwood, MA, USA), and the analog signal of the difference amplifier (input impedance $10^{13}\ \Omega \| 2$ pF) was processed by an analog interface board *DT 1744 (Data Translation,* Natick, MA, USA). A single-board computer (*SBC 80/20-4; SBC 116A; Intel Corp.,* Santa Clara, CA, USA) served to store the data for further manipulation with the built-in arithmetic processor *AMC 95/6011 (Advanced Micro Computers,* Santa Clara, CA, USA). A display terminal (*ADDS Regent 20, Applied Digital Data Systems, Inc.,* Hauppauge, NY, USA) and a printer (*Matrix Drucker Print Swiss, Wenger, Wenger Print Swiss Matrix,* CH–4000 Basle) were used for viewing the data which were processed off-line on a *Hewlett Packard HP 85* calculator system.

Selectivity Factors. All measurements were carried out on cells of the following type:

Hg; Hg_2Cl_2, KCl (sat.) | 1M $LiOCOCH_3$ | sample sol. ‖ membrane ‖ 0.01M NaCl, AgCl; Ag
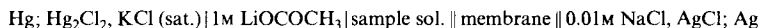
A description of the reference electrode used is given in [12]. Selectivity factors were determined by the separate soln. method (SSM) [13] at 21° with 0.1M Na salts of the different anions which were buffered with Tris (hydroxymethyl) aminomethane (tris) and H_2SO_4 to pH 7.5. The EMF was monitored during 20 min in ca. 25 ml of sample soln. (recording of the EMF values every 60 s), and the average of the last 5 min (i.e. 6 values) was used for further processing. Although some membranes exhibited super-*Nernstian* electrode response in the electrode function for Cl⁻ (see [5] [6]), calculations were carried out using the theoretical slope for 21° (−58.37 mV). All EMF values were corrected for changes in the liquid junction potentials for the various sample solns. according to the *Henderson* formalism [14] [15]. Single ion activities were calculated using the extended *Debye-Hückel* equation [16]. For this purpose, a program for the *HP 85* calculator system developed in this laboratory was used.

Commercial Reagents. The Na salts and buffer reagents used for the sample solns. were of the highest purity available (*Fluka AG*, CH–9470 Buchs; *E. Merck*, D–Darmstadt). H_2O used was distilled twice in a quartz glass apparatus. Poly(vinyl chloride) (PVC), THF, and bis (1-butylpentyl) adipate (BBPA) were supplied by *Fluka AG*; (tridodecyl)methylammonium chloride (MTDDACl) by *Polysciences, Inc.*, Warrington, PA, USA. $(PhCH_2)_3SnCl$ (12) and tricyclohexyltin bromide (10) were obtained from *Ventrom GmbH*, D–Karlsruhe; diethyl(hexyl)tin acetate (6) and diethyl(octyl)tin acetate (7) from *Aldrich GmbH*, D–Steinheim; Ph_3SnCl (11) and Bu_3SnCl (1) from *Fluka AG*. These compounds were distilled in a *Kugelrohr* apparatus or recrystallized until only one signal could be observed in the ¹¹⁹Sn-NMR spectra. The purity was also checked by size-exclusion chromatography.

Syntheses. – *Tributyltin Acetate* (2). Bis (tributyltin) oxide (11.9 g, 0.02 mol) and 2.4 g (0.04 mol) of AcOH were stirred for 30 min at 130°. After cooling to about 50°, hexane was added to the mixture which was then filtered immediately. Further cooling led to precipitation of the raw product which was filtered by suction and recrystalized 2 × from hexane: 3.7 mg (0.01 mol, 25% of the theoretical amount) of 2, m.p. 84–84.5° were obtained. Anal. calc. for $C_{14}H_{30}SnO_2$ (349.13): C 48.17, H 8.66; found: C 48.15, H 8.77.

Trioctyltin Chloride (3). Tetraoctyltin (28.6 g, 0.05 mol) was cooled to 0° in an ice bath, and 13.6 g (0.05 mol) of ice-cold $SnCl_4$ were added in small portions. The mixture was stirred for 5 h. After addition of 400 ml of EtOH, the raw product precipitated. It was filtered off and washed with 400 ml of 5% aq. NaOH soln. in a separatory funnel. To eliminate octyltin trichloride which is a side-product of the disproportioning reaction, the aq. phase was extracted twice with 300 ml of benzene. After filtration of the org. phase, it was transferred into a two-necked flask, where 400 ml of a 5% aq. HCl were added dropwise, while H_2O was removed simultaneously by azeotropic distillation. The raw product was first purified by flash chromatography (3× with hexane/AcOEt 4:1 over silica gel 60 230–400 mesh ASTM), then by distilling it 2× in a *Kugelrohr* apparatus (190°/0.06 Torr): 4.9 g (0.01 mol, 20%) of the theoretical amount of 3. Anal. calc. for $C_{24}H_{51}SnCl$ (493.89): C 58.37, H 10.41; found: C 58.53, H 10.45.

Tritetradecyltin Acetate (5). Mg Cuttings (0.97 g, 0.04 mol) were heated with a small amount of I_2 for a short time, then 30 ml of Et_2O was added, and 11.1 g (0.04 mol) of tetradecyl bromide in 70 ml of Et_2O were added dropwise. The reaction started immediately, and the mixture was refluxed for 1 h. Then, 2.1 g (0.008 mol) of $SnCl_4$ were given to the mixture resulting in a vigorous reaction. The mixture was then refluxed for another 2 h. Afterwards, 10 ml of H_2O were added, the soln. was filtered, and the solvent evaporated. Recrystallization from AcOEt and ensuing flash chromatography over silica gel 60 with hexane yielded 3.2 g (0.0035 mol, 44% of the theoretical amount) of tetra(tetradecyl)tin.

Tetra(tetradecyl)tin (0.45 g, 0.0005 mol) was added to a soln. of 0.13 g (0.0005 mol) of I_2 in Et_2O. The mixture was refluxed for 30 min, whereby tritetradecyltin iodide was formed. To the unpurified product, 5 ml of 20% aq. NaOH soln. were added, and the mixture was stirred for 30 min at r.t. The org. phase was separated and filtered, 20 drops of AcOH were added, and the mixture was stirred for another 30 min at r.t. After evaporating of the solvent, the raw product was recrystallized 3× from pentane to give 0.07 g (0.00009 mol, 18% of the theoretical amount) of 5, m.p. 70–70.5°. Anal. calc. for $C_{44}H_{90}SnO_2$ (769.88): C 68.64, H 11.78; found: C 68.55, H 11.75.

Dibutyl(octadecyl)tin Acetate (9). To 0.24 g (0.01 mol) of Mg cuttings, a small I_2 crystal and 20 ml of Et_2O were added. A soln. of 3.3 g (0.01 mol) of octadecyl bromide in 40 ml of Et_2O was added dropwise. One drop of 1,2-dibromoethane and moderate heating started the *Grignard* reaction. The mixture was refluxed for 10 min, and 3.3 g (0.01 mol) of Bu_3SnCl in 40 ml of, Et_2O were added, whereupon a precipitation occurred. The mixture was stirred overnight at r.t. Then, 50 ml of H_2O and 50 ml of 1M HCl were added. The mixture was extracted 3× with Et_2O. The Et_2O phase was washed with H_2O and evaporated. After distillation in a *Kugelrohr* apparatus (200–220°/0.08 Torr), 1.9 g (0.003 mol, 35% of the theoretical amount) of tributyl(octadecyl)tin were obtained.

Tributyl(octadecyl)tin (0.54 g, 0.001 mol) and 0.25 g (0.001 mol) of I_2 were dissolved in 20 ml of Et_2O and refluxed for 3 h. After evaporation of the solvent and distillation in *Kugelrohr* apparatus (210–220°/0.15 Torr), 0.35 g (0.0006 mol, 62% of the theoretical amount) of dibutyl(octadecyl)tin iodide were obtained.

Dibutyl(octadecyl)tin iodide (0.32 g, 0.00057 mol) was dissolved in 10 ml of Et_2O, 10 ml of 20% aq. KOH soln. were added, and the mixture was stirred for 1 h at r.t. After separation of the org. phase, it was washed with H_2O, and Et_2O was evaporated: 0.26 g (0.00026 mol, 92% of the theoretical amount) of bis[dibutyl(octadecyl)tin] oxide.

Bis[dibutyl(octadecyl)tin] oxide (0.23 g, 0.00023 mol) was dissolved in 10 ml of Et_2O, and 5 drops of AcOH were added. After stirring the mixture for 1 h at r.t., the solvent was evaporated, and the crude product was recrystallized 2× from pentane: 0.1 g (0.00018 mol, 40% of the theoretical amount) of 9, p.m. 53–54°. Anal. calc. for $C_{28}H_{58}SnO_2$ (545.46): C 61.66, H 10.72; found: C 61.80, H 11.07.

(Tetradecyl)diethyltin Acetate (**8**). This synthesis was carried out analogous to that of **9**. Starting reagents in this case were tetradecyl bromide and Et_3SnCl. Anal. calc. for $C_{20}H_{42}SnO_2$ (433.24): C 55.45, H 9.77; found: C 55.60, H 10.06.

Tris(2-ethylhexyl)tin Chloride (**4**). The first step of this synthesis was analogous to the *Grignard* reaction in the preparation of tetra(tetradecyl)tin in the synthesis of **5** (see above), using $SnCl_4$ and 2-ethylhexyl bromide as the starting materials to give tetrakis(2-ethylhexyl)tin. From then on, the same procedure as in the synthesis of **3** with tetraoctyltin and $SnCl_4$ was applied (see above). In this case, however, the disproportionation reaction was carried out with tetrakis (2-ethylhexyl)tin and $SnCl_4$ to yield **4**. Anal. calc. for $C_{24}H_{51}SnCl$ (493.89): C 58.37, H 10.41; found: C 58.57, H 10.15.

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