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Poly(di(ω -alkylphenyl)stannane)s

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Abstract Poly(di(ω -alkylphenyl)stannane)s, $[\text{Sn}(\text{C}_n\text{H}_{2n}\text{Ph})_2]_m$ with $n = 2-4$, and a copolymer of di(3-propylphenyl)stannane and dibutylstannane of weight-average molar masses of $2-8 \cdot 10^4$ g/mol were synthesized by dehydro-polymerization of stannanes of the composition H_2SnR_2 using Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$. At least two methylene groups were required as spacers between the phenyl group and the tin atom for polymerization to occur. The polystannanes were characterized by, among other techniques, ^1H , ^{13}C and ^{119}Sn NMR spectroscopy, thermal analysis and X-ray diffraction. The polymers featured properties different from those of the corresponding poly(dialkylstannane)s. Specifically, the $[\text{Sn}(\text{C}_n\text{H}_{2n}\text{Ph})_2]_m$ family displayed glass transitions at remarkably low temperatures, down to ca. -50 °C, and a lower value for a copolymer (-68 °C). Polymers $[\text{Sn}(\text{C}_n\text{H}_{2n}\text{Ph})_2]_m$ with $n = 2$ and 3 and a copolymer at room temperature were of a gel-like consistence, which enabled facile orientation with shear forces. Finally, the temperature-dependent electrical conductivity was determined for poly(di(3-propylphenyl)stannane), which followed the law of typical semiconductors, with an activation energy for conduction of 0.12 eV.

Keywords Polystannanes · Organometallic polymers · Semi-conducting polymers · Orientation · ^{119}Sn NMR spectroscopy

1 Introduction

Only few reports describe polymers of the composition $(\text{SnR}_2)_n$ (polystannanes), which are of potential interest because of their demonstrated semi-conductive properties [1]. Remarkably compounds with that chemical composition were synthesized already by Löwig as early as 1852 by reaction of iodoethane with a Sn/K or a Sn/Na alloy, in the presence of quartz sand—which was used to control the reaction rate [2]. The conversion of iodoethane with Sn/Na alloy was attributed to a reaction of the Wurtz type in 1860 [3, 4]. More than 80 years later, this synthetic approach was reapplied for the preparation of poly(dialkylstannane)s by treatment of dialkyltin dichlorides with sodium [5–7]. Products of high molar mass were obtained with this method [6], however, in low yields and with (cyclic) oligomers as byproducts.

In the past 15 years, alternative routes for the preparation of polystannanes have been developed, such as electrochemical reactions [8, 9] or catalytic dehydropolymerizations of dialkylstannanes (dialkyltin dihydrides) or diarylstannanes (R_2SnH_2 , where R represents an alkyl or aryl group) [10–14]. Unfortunately, the polymers prepared by those methods typically contained significant fractions of cyclic oligomers [10, 11] and were frequently not isolated and characterized. Recently, however, we demonstrated that $[\text{RhCl}(\text{PPh}_3)_3]$ (Wilkinson's catalyst) is suited for polymerization of R_2SnH_2 yielding linear polystannanes of high molar mass and in high yields without detectable amounts of cyclic byproducts [12, 13].

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Remarkably, these polymers at room temperature are in liquid-crystalline state, which facilitates orientation of them by simple methods such as tensile deformation, shearing or crystallization on oriented substrates [15].

In this work, we sought to expand the family of polystannanes and synthesized ω -alkylphenyl-substituted derivatives in order to investigate the influence of a terminal phenyl side group on their properties.

2 Experimental

2.1 Materials

All non-deuterated solvents were purchased in puriss p.a. grade from Fluka (Buchs, Switzerland) and were used without purification, and deuterated solvents from Cambridge Isotope Laboratories (Innerberg, Switzerland) with a deuterium fraction of >99%. Tetrachlorostannane from Fluka (Buchs, Switzerland), 1-bromo-2-phenylethane (98%) from Acros Organics (Basel, Switzerland), 1-bromo-3-phenylpropane (98%) from ABCR (Karlsruhe, Germany), 1-bromo-4-phenylbutane (97%) from TCI (Zwijndrecht, Belgium), and chlorotris(triphenylphosphine)rhodium(I) [RhCl(PPh₃)₃] from Johnson Matthey (Zürich, Switzerland).

2.2 Methods

Elemental analyses were performed by the Microelemental Analysis Laboratory of the Department of Chemistry of ETH Zurich.

Infrared (IR) spectra of liquid samples were recorded with a Bruker Vertex 70 FTIR spectrometer with the attenuated total reflection (ATR) technique by use of a Si-crystal.

¹H, ¹³C and ¹¹⁹Sn NMR spectra were obtained with a Bruker UltraShield 300 MHz/54 mm Fourier transform spectrometer. The NMR tubes were protected from light by wrapping in aluminum foil, which was removed only immediately before the analyses were carried out.

Molar masses were determined with gel permeation chromatography (GPC), employing a PL gel 5 μ m Mixed-D column from Polymer Laboratories Ltd. (Shropshire, United Kingdom) with tetrahydrofuran (THF) as the eluent. For calibration, atactic-poly(styrene) standards from Fluka (Buchs, Switzerland) were used.

Differential scanning calorimetry (DSC) was performed with a DSC822^c instrument (Mettler Toledo, Greifensee, Switzerland) equipped with an intracooler; thermogravimetric analysis (TGA) with a TGA/SDTA851^c (Mettler Toledo) under nitrogen atmosphere or air at heating and cooling rates of 5 °C/min; and dynamic mechanical thermal analysis (DMTA) in shear mode with a DMA861^c instrument (Mettler Toledo) in the temperature range of

–110 to 20 °C at a heating rate of 1 °C/min, and a frequency of 10 Hz, a force amplitude of 1 N and a displacement amplitude of 5 μ m. Samples were placed in poly(dimethylsiloxane) rings of a diameter of ca. 3 mm and a thickness of 1 mm in order to assure a constant geometry of the sample, N.B. the polysiloxane ring alone did not show any phase transition in this temperature range.

Electrical resistance measurements were conducted with samples placed in a small cylinder equipped with two nickel electrodes at temperatures between 300 and 370 K in argon, employing a Keithley 2002 Multimeter/236 Source Measure Unit system.

Optical microscopy was performed at ambient with a Leica DM400 M polarizing microscope. For observations at variable temperatures, a Leica DMRX polarizing microscope equipped with an argon-flushed Linkam THMS 600 heating-/cooling stage was used (cooling and heating rate 5 °C/min).

Wide-angle X-ray diffractions (WAXD) patterns were recorded with a Diffraction XcaliburTM PX (Oxford Instruments, Scotts Valley, USA), using MoK α radiation (wavelength 0.71 Å). The temperature was controlled with a Cryojet Controller.

2.3 Syntheses of Monomer Precursors, Monomers and Polymers

Polystannanes are sensitive to light [10–12, 16] and moisture [8]; hence, these polymers were protected from light, oxygen and moisture as carefully as possible. Reaction vessels were fully wrapped with aluminum foil. Reactions were always carried out under argon atmosphere and analysis of the polymers was performed either immediately after synthesis or after storage in argon-flushed brown glass vessels in a refrigerator kept at a temperature of ca. –20 °C.

2.3.1 Tetra(ω -alkylphenyl)stannanes [(PhC_nH_{2n})₄Sn]

Magnesium beads (for quantities see Table 1a) were heated with a blow drier under vacuum (ca. 0.1 mbar) for a few minutes and then covered with diethyl ether. An amount of alkylphenyl bromide was dissolved in diethyl ether and added during 0.5 h with a dropping funnel to the stirred magnesium suspension, under argon. Thereafter, the solution was kept under reflux for additional 2 h and, subsequently, cooled with ice. To this solution, tetrachlorostannane dissolved in toluene was added slowly (typically during a period of 1 h) with a dropping funnel. After the addition of the tetrachlorostannane solution was completed, the reaction mixture was kept under reflux for 2 h. Thereafter, the mixture was cooled with ice water, and a saturated NH₄Cl solution in water was slowly added until

Table 1 Synthesis parameters (reaction mixture composition and yield) for the monomer precursors (PhC_nH_{2n})₄Sn (**a**), (PhC_nH_{2n})₂SnCl₂ (**b**), monomers (PhC_nH_{2n})₂SnH₂ (**c**) and polymers [(PhC_nH_{2n})₂Sn]_n (**d**)

R	Mg m (g (mmol))	Alkylphenyl bromide m (g (mmol))	Diethyl ether V (ml)	SnCl ₄ m (g (mmol))	Toluene V (ml)	R ₄ Sn m (g (mmol))	Yield (%)
(a)							
-C ₂ H ₄ Ph	5.78 (238)	40.0 (216)	400	11.2 (43)	100	22.3	96
-C ₃ H ₆ Ph	5.34 (220)	40.0 (201)	400	10.3 (40)	100	21.5	90
-C ₄ H ₈ Ph	2.80 (115)	22.9 (107)	200	5.7 (22)	100	14.1	98
R	SnCl ₄ m (g (mmol))	R ₄ Sn m (g (mmol))	R ₂ SnCl ₂ m (g (mmol))	Yield (%)	T _m (°C)		
(b)							
-C ₂ H ₄ Ph	10.4 (40)	21.6 (40)	14.7 (37)	46	58		
-C ₃ H ₆ Ph	7.7 (30)	17.8 (30)	11.9 (40)	67	77		
-C ₄ H ₈ Ph	5.32 (20)	13.3 (20)	12.0 (26)	65	61 ^a		
R	R ₂ SnCl ₂ m (g (mmol))	Li[AlH ₄] m (g (mmol))	R ₂ SnH ₂ m (g (mmol))	Yield (%)	v (Sn-H) (cm ⁻¹)		
(c)							
-C ₂ H ₄ Ph	13.7 (34)	2.4 (62)	10.2 (30)	90	1833		
-C ₃ H ₆ Ph	9.3 (22)	1.2 (33)	7.2 (20)	92	1830		
-C ₄ H ₈ Ph	5.0 (11)	0.5 (13)	4.3 (10)	96	1833		
R	R ₂ SnH ₂ m (g (mmol))	[RhCl(PPh ₃) ₃] m (mg (mmol))	Solvent V (ml)	-(R ₂ Sn) _n m (g)	Yield (%)	Isolation method	M _w /M _n (kg mol ⁻¹)
(d)							
-C ₂ H ₄ Ph	1.0 (3.0)	84 (0.1)	Toluene (14)	0.1	14	Centrifugation	22/11
-C ₃ H ₆ Ph	1.0 (2.8)	77 (0.1)	CH ₂ Cl (14)	0.8	78	Precipitation	80/34
-C ₄ H ₈ Ph	1.0 (2.6)	96 (0.1)	Toluene (14)	0.4	39	Centrifugation	80/35

Also included are selected analytical data (T_m: melting temperature at ambient pressure, v(Sn-H): IR-absorption vibration of the Sn-H bond). The number- and weight-average molar masses M_n and M_w were determined by gel permeation chromatography

^a Upon heating, an exothermic signal at 14 °C was present in DSC traces, possibly due to crystallization

the aqueous phase became clear. The organic phase, which separated from the aqueous one, was removed with a separating funnel, dried with anhydrous magnesium sulfate and filtered through celite. The solvents were removed with a rotary evaporator and the resulting product dried overnight in vacuum (~0.1 mbar) at room temperature. The tetra(*ω*-alkylphenyl)stannanes thus obtained were analyzed with NMR spectroscopy (Tables 2, 3) and used without further purification for the preparation of di(*ω*-alkylphenyl)dichlorostannanes.

2.3.2 Di(*ω*-alkylphenyl)dichlorostannanes [(PhC_nH_{2n})₂SnCl₂]

Tetra(*ω*-alkylphenyl)stannane was poured into a two-necked round-bottom flask equipped with reflux condenser (quantities in Table 1b). The top of the condenser was

connected to a balloon filled with argon to protect the reaction mixture from oxygen and moisture. The second neck was closed by a septum through which tetrachlorostannane was added with a syringe. Thereafter, the reaction mixture was heated to 100 °C for 1 h and to 200 °C for an additional 2 h. Small aliquots were analyzed with ¹¹⁹Sn NMR spectroscopy from time to time; if small signals of R₃SnCl or RSnCl₃ beside the one of R₂SnCl₂ were detected, small amounts of SnCl₄ or R₂SnCl₂ were added until only the signal for the R₂SnCl₂ was visible in the ¹¹⁹Sn NMR spectrum. The resulting product was recrystallized from hot (~95 °C) heptane (~100 mL/20 g) and dried in vacuum (~0.5 mbar) for 24 h. The compounds were obtained in the shape of colorless crystals and were analyzed with NMR spectroscopy (Tables 2, 3), elemental analysis (Table 4) and DSC for the determination of the melting temperature (Table 1b).

Table 2 ^{13}C and ^{119}Sn NMR data for monomer precursors and monomers in dichloromethane- d^2

Compound	C	–CH=	–CH ₂ –	Sn–CH ₂		Sn	
	δ ^{13}C	δ ^{13}C	δ ^{13}C	J ($^{117/119}\text{Sn,C}$)	δ ^{13}C	J ($^{117/119}\text{Sn,C}$)	δ ^{119}Sn
(PhC ₂ H ₄) ₄ Sn	145.83	125.77 ^a 127.90 128.48	32.84	² <i>J</i> 17	11.16	¹ <i>J</i> 296/309	–13.35
(PhC ₃ H ₆) ₄ Sn	142.59	125.58 ^a 128.19 128.46	29.26 40.72	² <i>J</i> 17 ^b ³ <i>J</i> 55 ^b	8.76	¹ <i>J</i> 298/312	–11.83
(PhC ₄ H ₈) ₄ Sn	143.12	125.74 ^a 128.41 128.61	26.90 35.75 36.47	² <i>J</i> 19 ^b ³ <i>J</i> 50 ^b	9.11	¹ <i>J</i> 298/311	–11.37
(PhC ₂ H ₄) ₂ SnCl ₂	142.52	126.90 ^a 127.93 129.09	30.37		29.85		108.06
(PhC ₃ H ₆) ₂ SnCl ₂	140.76	126.25 ^a 128.53 128.60	26.49 38.53	<i>J</i> 35 <i>J</i> 82/85	26.02	¹ <i>J</i> 407/425	120.56
(PhC ₄ H ₈) ₂ SnCl ₂	142.01	125.83 ^a 128.33 128.37	26.68 34.84 35.22		24.51		124.51
(PhC ₂ H ₄) ₂ SnH ₂	144.92	125.86 ^a 127.91 128.41	33.95	² <i>J</i> 21	9.24	¹ <i>J</i> 358/375	–203.13
(PhC ₃ H ₆) ₂ SnH ₂	142.30	125.82 ^a 128.36 128.62	30.34 40.07	² <i>J</i> 26 ^b ³ <i>J</i> 59/62 ^b	6.99	¹ <i>J</i> 357/374	–200.89
(PhC ₄ H ₈) ₂ SnH ₂	142.82	125.58 ^a 128.23 128.40	27.79 35.45 35.65	² <i>J</i> 23 ^b	7.05	¹ <i>J</i> 360/376	–202.48

Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz

^a Carbon signal of half intensity of the other –CH= signals, attributed to the CH-group of the aromatic carbon atom in para position to the alkyl group

^b The coupling constants were derived by comparison with the 2-ethylphenyl compounds, where ³*J*(Sn,C) is not featured

2.3.3 Di(ω -alkylphenyl)stannanes [(PhC_{*n*}H_{2*n*})₂SnH₂]

Di(ω -alkylphenyl)dichlorostannanes (quantities see Table 1c) were reduced with an excess of Li[AlH₄]. A solution of di(ω -alkylphenyl)dichlorostannane in diethyl ether (typically 0.4 M) was added dropwise with a funnel during approximately 0.5 h to the same volume of ice-cooled Li[AlH₄] suspension in diethyl ether, which was protected from air by argon counter flow. After addition, the reaction mixture was stirred for an additional 0.5 h at 0 °C, before the ice bath was removed in order to allow the mixture to warm up to room temperature, at which point the reaction mixture was stirred for additional 2 h. The latter was then very slowly mixed with ice water (until excess of Li[AlH₄] was hydrolyzed) and the organic phase was separated from the aqueous

phase with a separating funnel. The ether phase was dried over anhydrous magnesium sulfate. The solution was filtered through celite and the solvent was removed with a rotary evaporator at 40 °C and ambient pressure. Due to the high boiling temperature and very low crystallization temperatures of the tin dihydrides, the resulting liquids could not be purified by distillation or crystallization, and, hence, were only carefully degassed by bubbling argon with a needle through the solution and subsequently dried under vacuum (ca. 0.1 mbar) at room temperature for 0.5 h. Thereafter, the liquids were collected in vessels which were closed with a septum and immediately wrapped completely with soft tissue and aluminum foil to protect them from light. Finally, the compounds were stored in a refrigerator at –20 °C. The di(ω -alkylphenyl)stannanes were analyzed by NMR

Table 3 ^1H NMR data of monomer precursors and monomers in dichloromethane- d^2

Compound	-CH=		-(CH ₂) _n -			-Sn-CH ₂ -		Sn-H	
		δ ^1H	δ ^1H	J		δ ^1H	J	δ ^1H	J
(PhC ₂ H ₄) ₄ Sn	m, 12H	7.34	t, 8H	2.88	$^3J(\text{Sn,H})$ 48	m, 8H	1.24	$^2J(^{117}\text{Sn,H})$ 46	
	m, 8H	7.45			$^3J(\text{H,H})$ 8			$^2J(^{119}\text{Sn,H})$ 49	
(PhC ₃ H ₆) ₄ Sn	m, 12H	7.22	m, 8H	1.87	$^3J(^{117}\text{Sn,H})$ 41	m, 8H	0.98	$^2J(^{117}\text{Sn,H})$ 47	
	m, 8H	7.33	t, 8H	2.68	$^3J(^{119}\text{Sn,H})$ 44			$^2J(^{119}\text{Sn,H})$ 49	
(PhC ₄ H ₈) ₄ Sn	m, 12H	7.42	m, 16H	1.85	$^3J(\text{H,H})$ 8	m, 8H	1.12	$^2J(\text{Sn,H})$ 49	
	m, 8H	7.51	m, 8H	2.86				$^3J(\text{H,H})$ 8	
(PhC ₂ H ₄) ₂ SnCl ₂	m, 4H	7.19	t, 4H	2.95	$^3J(^{117}\text{Sn,H})$ 119	t, 4H	1.88	$^2J(\text{Sn,H})$ 57	
	m, 2H	7.29			$^3J(^{119}\text{Sn,H})$ 124			$^3J(\text{H,H})$ 8	
	m, 4H	7.38			$^3J(\text{H,H})$ 8				
(PhC ₃ H ₆) ₂ SnCl ₂	m, 6H	7.25	m, 4H	2.15	$^3J(\text{Sn,H})$ 104	m, 4H	1.76	$^2J(^{117}\text{Sn,H})$ 50	
	m, 4H	7.34	t, 4H	2.74	$^3J(\text{H,H})$ 8			$^2J(^{119}\text{Sn,H})$ 53	
(PhC ₄ H ₈) ₂ SnCl ₂	m, 6H	7.25	m, 8H	1.88	$^3J(\text{H,H})$ 8	m, 4H	1.77		
	m, 4H	7.34	t, 4H	2.71					
(PhC ₂ H ₄) ₂ SnH ₂	m, 6H	7.27	t, 4H	1.90	$^3J(\text{Sn,H})$ 62	m, 4H	1.36	$^2J(\text{Sn,H})$ 53	m, 2H 4.61 $^1J(^{117}\text{Sn,H})$ 1628
	m, 4H	7.37			$^3J(\text{H,H})$ 8				$^1J(^{119}\text{Sn,H})$ 1700
(PhC ₃ H ₆) ₂ SnH ₂	m, 4H	7.25	m, 4H	1.98	$^3J(\text{Sn,H})$ 57	txt, 4H	1.19	$^2J(\text{Sn,H})$ 54	q, 2H 4.66 $^3J(\text{H,H})$ 2
	m, 6H	7.26	t, 4H	2.73	$^3J(\text{H,H})$ 8			$^3J(\text{H,H})$ 8	
								$^3J(\text{H,Sn-H})$ 2	
(PhC ₄ H ₈) ₂ SnH ₂ ^a	m, 4H	7.09	m, 8H	1.55	$^3J(\text{H,H})$ 8	m, 4H	0.93	$^2J(^{117}\text{Sn,H})$ 52	q, 2H 4.74 $^1J(^{117}\text{Sn,H})$ 1607
	m, 6H	7.19	t, 4H	2.50				$^2J(^{119}\text{Sn,H})$ 54	$^1J(^{119}\text{Sn,H})$ 1681 $^3J(\text{H,H})$ 2

Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz; t = triplet, q = quintet, m = multiplet

^a Measured in toluene- d^8

spectroscopy (Tables 2, 3), infrared spectroscopy (Table 1c) and elemental analysis (Table 4).

2.3.4 Poly(*di*(ω -alkylphenyl)stannane)s, $[\text{Sn}(\text{C}_n\text{H}_{2n}\text{Ph})_2]_m$

Polymerizations of *di*(ω -alkylphenyl)stannanes were done according to previously described procedures for poly(dialkylstannane)s (parameters see Table 1d) [12, 13]. A quantity of *di*(ω -alkylphenyl)stannane was added with a syringe to a solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (4% mol/mol with respect to $(\text{PhC}_n\text{H}_{2n})_2\text{SnH}_2$) in dichloromethane or toluene (cf. Table 1d). After 2 h, the solution was cooled to -78 °C for at least 30 min. The cooled solution, which was still clear, was poured into an excess (5 times) of cold methanol (-78 °C), after which the solution became turbid, or a yellow solid began to precipitate (after 2–3 h). If the polymer precipitated, it was filtered off and washed with small amounts of cold methanol (-78 °C) (cf. Table 1d). If no precipitation occurred (cf. Table 1d), the resulting turbid solutions were subjected to centrifugation (8,000 revolutions per minute), after which polymer that settled at the bottom was collected by decanting. The different polymers

were dried in vacuum (ca. 0.1 mbar) at room temperature for 12 h, and stored in a refrigerator (-20 °C) in brown glass vessels which were flushed with argon. The poly(*di*(ω -alkylphenyl)stannane)s thus obtained were, finally, analyzed by GPC, elemental analysis, NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric (TGA), dynamic mechanical thermal analysis (DMTA), optical microscopy, and X-ray scattering.

2.3.5 Poly(dibutylstannane)-*co*-(*di*(3-propylphenyl)stannane) ($[\text{SnR}_2]_p$ - $[\text{Sn}(\text{C}_n\text{H}_{2n}\text{Ph})_2]_q$)

A quantity of 0.5 mL *di*(3-propylphenyl)stannane and 0.5 mL dibutylstannane (corresponding to a total mass of both stannanes of 1.15 g) was rapidly mixed at ambient and poured into a solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (140 mg, 0.15 mmol) in 20 mL dichloromethane, under argon and exclusion of light as described above. After 1 h stirring under light exclusion, the solution was cooled to -78 °C for 30 min, after which it was poured into 100 mL cold methanol (-78 °C). Thereafter, the mixture became turbid yielding a yellow precipitate after ~ 1 h, which was

Table 4 Calculated and found elemental composition (in % m/m) of di(ω -alkylphenyl)dichlorostannanes, di(ω -alkylphenyl)stannanes and poly(di(ω -alkylphenyl)stannane)s

Compound		C	H	Cl
(PhC ₂ H ₄) ₂ SnCl ₂	Found	47.78	4.73	17.81
	Calc.	48.05	4.54	17.73
(PhC ₃ H ₆) ₂ SnCl ₂	Found	50.65	5.28	16.33
	Calc.	50.52	5.18	16.57
(PhC ₄ H ₈) ₂ SnCl ₂	Found	52.82	5.78	15.30
	Calc.	52.68	5.75	15.55
(PhC ₂ H ₄) ₂ SnH ₂	Found	58.27	6.19	n.a.
	Calc.	58.05	6.09	n.a.
(PhC ₃ H ₆) ₂ SnH ₂	Found	60.19	6.61	n.a.
	Calc.	60.21	6.74	n.a.
(PhC ₄ H ₈) ₂ SnH ₂	Found	62.46	7.40	n.a.
	Calc.	62.05	7.29	n.a.
-(PhC ₃ H ₆) ₂ Sn] _n	Found	55.12	5.23	n.a.
	Calc.	58.41	5.51	n.a.
-(PhC ₃ H ₆) ₂ Sn] _n	Found	59.98	6.07	n.a.
	Calc.	60.55	6.21	n.a.
-(PhC ₄ H ₈) ₂ Sn] _n	Found	61.02	6.49	n.a.
	Calc.	62.37	6.80	n.a.

n.a. Not applicable

subsequently filtered off and washed with cold methanol ($-78\text{ }^{\circ}\text{C}$). The isolated polymer 0.72 g (62%) was then dried in vacuum (~ 0.1 mbar) at room temperature for 12 h and stored in a refrigerator ($-20\text{ }^{\circ}\text{C}$) in a brown glass vessel flushed with argon until further use.

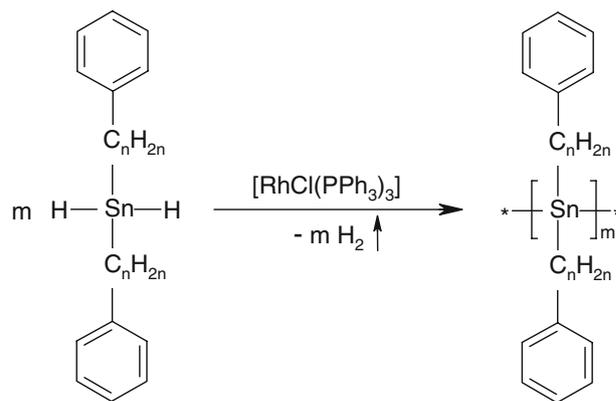
2.3.6 Degradation of Polystannanes

Separately, the stability towards light was investigated with an Osram Dulux[®] S Luminux[®] 7 W/860 (Daylight) lamp (Jeker Leuchten AG, Zurich, Switzerland) placed in a box of the dimensions $25 \times 85 \times 40$ cm, using in situ synthesized polystannane solutions in toluene- d^8 . After 90 min illumination, a ^{119}Sn NMR spectrum was recorded and contrasted with its spectrum prior to illumination.

3 Results and Discussion

3.1 Homopolymers

Monomers were prepared following well-established reactions. First, the compounds (PhC_{*n*}H_{*2n*})₄Sn were prepared with Grignard's reaction [17] using SnCl₄ and ω -phenylalkyl magnesium bromide (Grignard reagent), as essentially described already more a 100 years ago [18, 19]. The (PhC_{*n*}H_{*2n*})₄Sn was then converted with stoichiometric quantities of SnCl₄ to (PhC_{*n*}H_{*2n*})₂SnCl₂, a reaction which is

**Scheme 1** Schematic of synthesis of poly(di(ω -alkylphenyl)stannane)s

known at least since 1856 [20, 21]. Finally, (PhC_{*n*}H_{*2n*})₂SnCl₂ was reduced with an excess of Li[AlH₄], yielding the monomer (PhC_{*n*}H_{*2n*})₂SnH₂, as shown 60 years ago [22, 23].

Linear poly(di(ω -alkylphenyl)stannane)s were synthesized at room temperature by dehydropolymerization of tin dihydrides with [RhCl(PPh₃)₃] (Wilkinson's catalyst) under protection from ambient light (Scheme 1). As mentioned in the introduction, [RhCl(PPh₃)₃] was found to be extremely suitable for the polymerization of various compounds of the composition R₂SnH₂. Indeed, this catalyst was also of use for the formation of poly(di(2-ethylphenyl)stannane), **P(D2ØSn)**, poly(di(3-propylphenyl)stannane), **P(D3ØSn)**, and poly(di(4-butylphenyl)stannane), **P(D4ØSn)**. NMR data of the polymers synthesized are collected in Table 5. The chemical shifts of the Sn-atoms in the polymer backbones in ^{119}Sn NMR spectra were around -190 ppm, i.e. in the range of those reported for other polystannanes [10–13, 24]. The lack of the characteristic signals of the monomer, in particular of the Sn signal between -201 and -203 ppm in ^{119}Sn NMR spectra and of the Sn–H signal at ca. 4.7 ppm in ^1H -NMR spectra, implied that complete monomer conversion was achieved. In addition, there was no evidence for cyclic oligomers in ^{119}Sn and ^1H NMR spectra. However, when the polystannanes were isolated, the elemental analysis of the resulting materials in the case of **P(D2ØSn)** showed pronounced deviations from the expected values (cf. Table 4). This is most likely due to difficulties in precipitation from the reaction solution. While poly(dialkylstannane)s were readily isolated by precipitation from cold solvents [12, 13], poly(di(ω -alkylphenyl)stannane)s turned out to be more soluble and did not precipitate even upon prolonged cooling at $-78\text{ }^{\circ}\text{C}$. Addition of cold methanol ($-78\text{ }^{\circ}\text{C}$), which is known as poor solvent for polystannanes [11], was only successful for the precipitation of **P(D3ØSn)**. However, solutions of **P(D2ØSn)** and **P(D4ØSn)** became only turbid after to 2 h at $-78\text{ }^{\circ}\text{C}$.

Table 5 NMR data for poly(di(ω -alkylphenyl)stannane)s in dichloromethane- d^2

R	^1H		^{13}C			^{119}Sn
	–CH=	–CH ₂ –	C	–CH=	–CH ₂ –	Sn
–{PhC ₂ H ₄)} ₂ Sn– _n	m, 4H, 6.87	m, 4H, 1.69	144.62	125.37 ^b	13.03	–187.43
	m, 6H, 7.01	m, 4H, 2.87		127.37	36.87	
–{PhC ₃ H ₆)} ₂ Sn– _n	m, 4H, 7.02	m, 4H, 1.11	141.87	125.27 ^b	10.95	–192.12
	m, 6H, 7.20	m, 4H, 1.68		128.27	32.55	
		m, 4H, 2.41		128.37	41.02	
–{PhC ₄ H ₈)} ₂ Sn– _n	m, 10H, 7.11 ^a	m, 4H, 1.31	142.37	125.56 ^b	11.21	–190.48
		m, 8H, 1.66		128.18	30.89	
		m, 4H, 2.60		128.22	35.71	

Chemical shifts (δ) are given in ppm, t = triplet, m = multiplet

^a Broad, overlapping signals

^b Carbon signal of half intensity of the other –CH= signals, attributed to the CH-group of the aromatic carbon atom in para position to the alkyl group

These polymers settled only upon centrifugation. Hence, the resulting solids might also contain catalyst residues.

TGA, carried out under nitrogen at a heating rate of 5 °C/min, indicated that thermal decomposition of all polymers commenced at ca. 200 °C. Their thermal stability was thus quite similar to that reported for poly(dialkylstannane)s [11–13]. Above 350 °C, the mass remained constant at values which were close the calculated tin contents of 36, 33, and 31% w/w for **P(D2ØSn)**, **P(D3ØSn)** and **P(D4ØSn)**, respectively.

All poly(di(ω -alkylphenyl)stannane)s were yellow-orange (λ_{max} between 380 and 400 nm), soft, and sticky at room temperature; **P(D4ØSn)** showed the consistency of liquid honey, whereas **P(D2ØSn)** and **P(D3ØSn)** were of a relatively solid gel nature. Thermal analysis of the polystannanes by DSC revealed pronounced, remarkably low glass transition temperatures (T_g): ca. –20 °C for **P(D2ØSn)**, around –45 °C for **P(D3ØSn)** and –52 °C for **P(D4ØSn)** (cf. Fig. 1). The latter was close to the measuring limits of ca. –60 °C of the DSC, and, therefore, the glass transition temperature of **P(D4ØSn)** was also measured by DMTA [25, 26]. **P(D4ØSn)** was analyzed in shear mode, as described in the experimental part. Often T_g is determined in DMTA measurements to be the onset of the storage-modulus (G'), which corresponds to maximum of the loss modulus (G''), although sometimes the peak maximum of $\tan \delta$ is also employed. In this work, we used the maximum of the loss modulus (G''). This value (–46 °C) was relatively close to that derived from DSC measurements (–52 °C). Interestingly, the present polystannanes displayed a different phase behaviour from poly(dialkylstannane)s. Instead of first-order transitions reported for the latter polymers [12, 13], only glass transitions were found for the former.

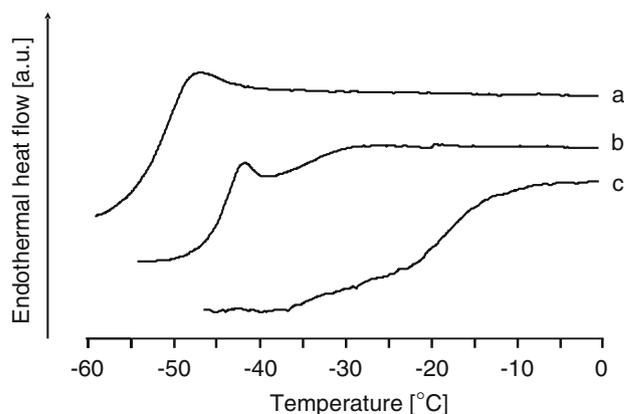


Fig. 1 DSC heating thermograms of **a** poly(di(4-butylphenyl)stannane), **b** poly(di(3-propylphenyl)stannane) and **c** poly(di(2-ethylphenyl)stannane) (under nitrogen, heating rate 5 °C/min)

Wide-angle X-ray diffraction (WAXD) patterns of the poly(di(ω -alkylphenyl)stannane)s were characterized by diffuse halos both above and below the glass transition temperatures indicating that the polymers were largely amorphous. The diffraction patterns did not change significantly in the temperature range between –70 and 90 °C. Yet weak but sharp reflections were found (at 2θ of 3.5°, 6.3°, 9.8° and 18.9°), for **P(D3ØSn)** suggestive a low degree of crystallinity of this polymer. Consistent with this observation, **P(D2ØSn)** and **P(D3ØSn)** were slightly birefringent in the temperature range of –70–90 °C; no striking changes in birefringence were observed in cooling- and heating cycles. **P(D4ØSn)** was only weakly birefringent.

P(D2ØSn) and **P(D3ØSn)** could easily be oriented by shearing of bulk samples above T_g on a glass slide with a razor blade, analogous to poly(dialkylstannane)s [12, 15] as

indicated by the pronounced birefringence observed between crossed polarizers in an optical microscope. Persistent orientation, induced by shearing could not be achieved for **P(D4OSn)**.

The poly(di(ω -alkylphenyl)stannane)s were readily soluble at room temperature in common organic solvents, e.g. benzene, dichloromethane and tetrahydrofuran. Such solutions were employed for molar mass determinations by GPC (Table 1d), using atactic-poly(styrene) standards for calibration, as previously conducted for poly(dialkylstannane)s [13]. The number-average molar masses of the poly(di(ω -alkylphenyl)stannane)s M_n were between 11 and 35 kg/mol⁻¹ and weight-average molar masses M_w between 22 and 80 kg/mol, i.e. in the range of the corresponding values of poly(dialkylstannane)s [13]. The lowest molar mass was obtained for **P(D2OSn)**; and, in fact, it appears that polymerization of (PhC_nH_{2n})₂SnH₂ with the catalyst [RhCl(PPh₃)₃] becomes increasingly difficult at low values of n . Attempts to polymerize the stannanes with $n = 1$ (dibenzylstannane) or $n = 0$ (diphenylstannane) with [RhCl(PPh₃)₃] failed. In addition, di-*tert*-butylstannane, (C(CH₃)₃)₂SnH₂, could not be polymerized either, which indicates that bulky groups such as phenyl, in close proximity to Sn atom hamper the polymerization, at least with [RhCl(PPh₃)₃]. These sterically hindered stannanes did release hydrogen upon contact with [RhCl(PPh₃)₃], but no high molar-mass products were detected by GPC, and in ¹¹⁹Sn NMR spectra no signal was found which could be attributed to a polymer.

In order to investigate the stability of the poly(di(ω -alkylphenyl)stannane)s towards light, polymerizations were performed in toluene-d⁸ and ¹¹⁹Sn NMR spectra of the reaction mixtures were recorded. Thereafter, the in situ prepared polystannanes were exposed to a light source (cf. experimental section) in a box for 90 min. Polymer degradation was quantified by the decrease in the polystannane signal in ¹¹⁹Sn NMR spectra. All three poly(di(ω -alkylphenyl)stannane)s after illumination decomposed completely into cyclic oligomers (chemical shift in ppm and (coupling constant $J(\text{Sn}, \text{Sn})$ in Hz) of the more pronounced cycle **cyclo-D2OSn**-199.1 (437); **cyclo-D3OSn**-203.5 (459) and **cyclo-D4OSn**-203.7 (444).

The conductivity of one of the poly(di(ω -alkylphenyl)stannane)s, **P(D3OSn)**, was investigated by a two-point measurement at various temperatures. At 300 K, a conductivity of $3 \cdot 10^{-8}$ S/cm was found. This conductivity increased with higher temperature, indicating that the amount of charge-carriers increased at higher temperatures, characteristic for semi-conducting materials, for which the electrical conductivity follows the expression [27]:

$$\sigma = \sigma_0 e^{-\frac{E_a}{k_B T}} \quad (1)$$

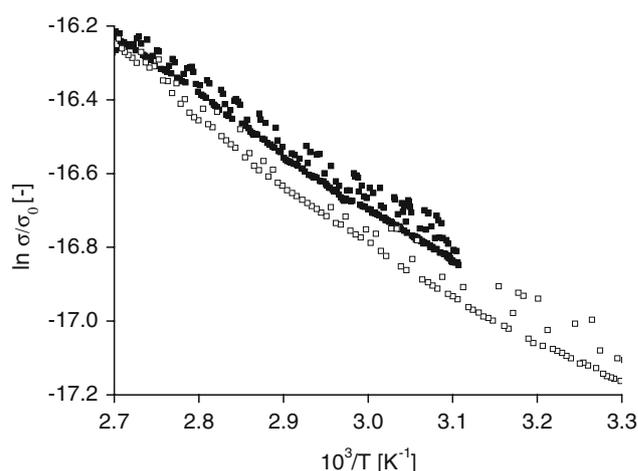


Fig. 2 Plot of the logarithm of the normalized conductivity (σ/σ_0 , with $\sigma_0 = 1$ S/cm) of poly(di(3-propylphenyl)stannane) as a function of the inverse temperature (T): heating from room temperature to 370 K (■) and subsequent cooling to 300 K (□)

where σ refers to the electrical conductivity, σ_0 is an arbitrary constant (usually taken to be 1 S/cm), E_a the activation energy for a thermally induced excitation of an electron from the valence band to the conduction band, k_B Boltzmann's constant, and T the temperature (in K). Thus, a logarithmic representation of the conductivity as function of the inverse temperature resulted in a linear dependence (Fig. 2), in agreement with the above equation. From the slope, an activation energy (E_a) of 0.12 eV was calculated, which is in the range of other polymeric systems with metal atoms in their backbone, such as Magnus' green salt [27]. Unfortunately, the conductivity of **P(D2OSn)** was below the detection limit of 10^{-10} S/cm (at room temperature), and **P(D4OSn)** was too liquid to be addressed with the available experimental set-up.

3.2 Copolymer

Interestingly, a copolymer could be created with the catalytic dehydropolymerization method using two different tin dihydrides. Upon addition of [RhCl(PPh₃)₃] to a mixture of (PhC₃H₆)₂SnH₂ and Bu₂SnH₂, poly(dibutylstannane-*co*-di(3-propylphenyl)stannane), **P(D3OSn-*co*-D4Sn)**, formed. After 1 h, ¹H-NMR spectra no longer featured the Sn-H signals of both monomers and concomitantly the signals of the monomers were also missing in ¹¹⁹Sn-NMR spectra, indicating conversion of both monomers. The ¹¹⁹Sn NMR spectrum of the reaction mixture displayed two broad signals between -200 and -190 ppm, which is in the range of polystannanes (Fig. 3); however, the position and line width of these signal clearly differed from those in a spectrum recorded for a reference mixture of the two homopolymers poly(dibutylstannane)

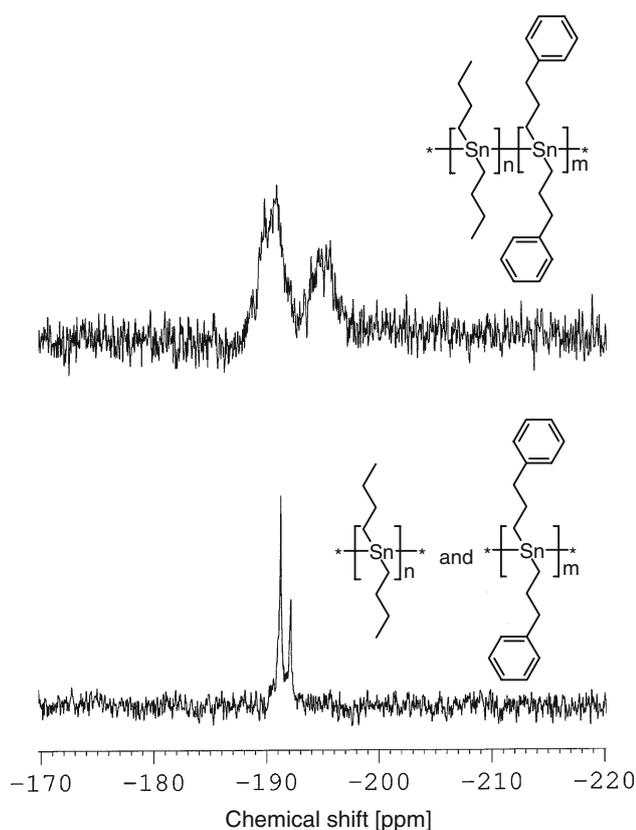


Fig. 3 ^{119}Sn NMR spectra of poly(dibutylstannane-*co*-di(3-propylphenyl)stannane) (top) and a reference mixture of poly(dibutylstannane) and poly(di(3-propylphenyl)stannane) (bottom)

and poly(di(3-propylphenyl)stannane) (two sharp signals at -191 ppm and -192 ppm, cf. Fig. 3). This finding implies indeed that a copolymer, **P(D3ØSn-*co*-D4Sn)**, resulted upon simultaneous polymerization of H_2SnBu_2 and $\text{H}_2\text{Sn}(\text{C}_3\text{H}_6\text{Ph})_2$, and the considerable broadness of the signals indicates that the tin atoms comprised in the two different monomer units are present in different surroundings, i.e. the monomers were arranged in the copolymer not in alternate or block-like arrangement, but in a random sequence. Broadening of the signals was also visible in ^1H NMR spectra of the copolymer. In particular, the normally sharp butyl signals of poly(dibutylstannane) [13] arose in the copolymer as broad peaks, where ^1H - ^1H couplings were not resolved anymore. Even in ^{13}C NMR spectra of the copolymer the signals were broad. Finally, there was no evidence for the formation of cyclic oligomers or co-oligomers.

GPC of the isolated copolymer **P(D3ØSn-*co*-D4Sn)**, resulted in $M_w = 3.5 \cdot 10^4$ g/mol and $M_n = 1.7 \cdot 10^4$ g/mol. These values were in the range of the poly(di(ω -alkylphenyl)stannane) homopolymers (cf. Table 1d).

P(D3ØSn-*co*-D4Sn) was of viscous gel-like nature at room temperature, as seen for some di(ω -alkylphenyl)stannane homopolymers. Also weak birefringence was

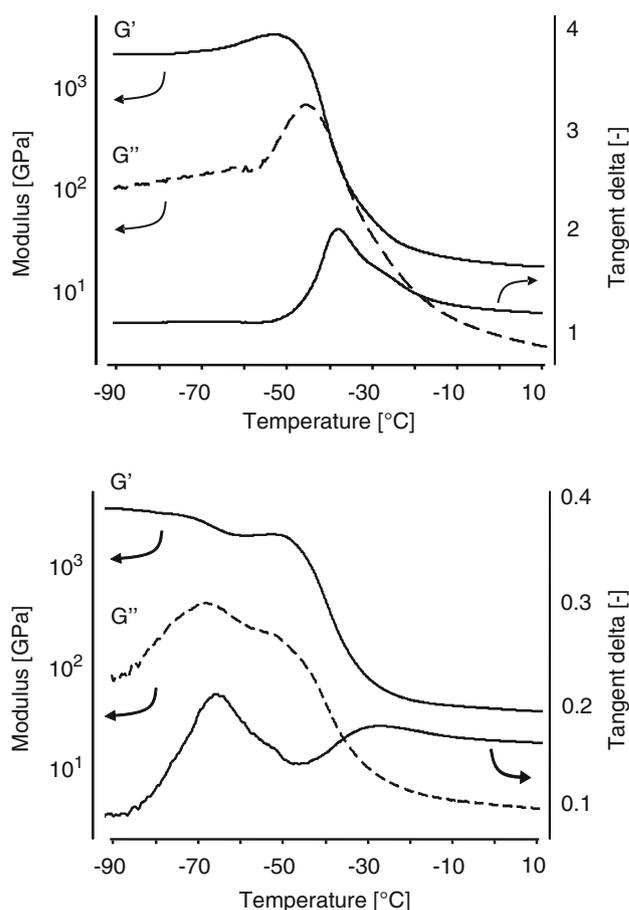


Fig. 4 Semi-logarithmic plot of the storage-modulus (G'), the loss modulus (G'') and $\tan \delta$ of poly(di(4-butylphenyl)stannane) (top) and poly(dibutylstannane-*co*-di(3-propylphenyl)stannane) (bottom); placed in poly(dimethylsiloxane) rings; determined by DMTA in shearing mode

observed in a polarized microscope, indicating some crystallinity. DSC analysis in the temperature range of -60 to 120 °C did, however, not reveal any transition. DMTA measurements, by contrast displayed a maximum of the loss modulus at ca. -68 °C (Fig. 4). The phase behavior of **P(D3ØSn-*co*-D4Sn)** was, thus, very similar to that of the poly(di(ω -alkylphenyl)stannane) homopolymers, which also featured only second order transitions, instead of the first-order transitions of poly(dialkylstannane) homopolymers [13].

As with the di(ω -alkylphenyl)stannane homopolymers, shearing of the copolymer with a razor blade at room temperature yielded films oriented along the shearing direction, as was evident in polarized optical microscopy at different angles between shearing direction and orientation of the polarizers.

Unfortunately, as for **P(D4ØSn)**, the electrical conductivity of **P(D3ØSn-*co*-D4Sn)** could not be determined with the available equipment because it was too liquid.

4 Conclusions

In summary, we demonstrated that polymerization of di(ω -alkylphenyl)stannanes can efficiently be conducted with [RhCl(PPh₃)] as catalyst, provided that the phenyl group was separated from the tin atom by at least two methylene groups. All poly(di(ω -alkylphenyl)stannane)s were obtained without any cyclic impurities. In contrast to poly(dialkylphenylstannane)s, the poly(di(ω -alkylphenyl)stannane)s did not show a first-order phase transition before decomposition, but only a glass transition at remarkably low temperatures, between -20 and -60 °C, depending on the length of the alkyl spacing groups.

Furthermore, polymerization mixtures of di(3-propylphenyl)stannane and dibutylstannane in the presence of [RhCl(PPh₃)] yielded copolymers in which the two components were randomly distributed, and that displayed a phase behavior similar to that of poly(di(ω -alkylphenyl)stannane) homopolymers.

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