Synthesis and Characterization of Linear Poly(dialkylstannane)s

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Received July 2, 2007

ABSTRACT: A comprehensive study was made of the synthesis of a spectrum of poly(dialkylstannane)s by catalytic dehydropolymerization of dialkylstannanes (dialkyltin dihydrides, R_2SnH_2, prepared by reduction of R_2SnCl_2), with R = ethyl, propyl, butyl, pentyl, hexyl, octyl, and dodecyl. The polymerization reactions were followed by ^1H and ^{119}Sn NMR spectroscopy, IR spectroscopy (disappearance of the Sn−H vibration), and quantitative measurement of H_2 which evolved during the reaction. Among the numerous metal complexes employed as catalyst, $[RhCl(PPh_3)_3]$ was found to be particularly suited for the preparation of these inorganic polymers. The reaction parameters temperature, solvent, R_2SnH_2 concentration, and $[RhCl(PPh_3)_3]/R_2SnH_2$ ratio were varied, with the most prominent influence on the monomer conversion being the temperature. The number-average molar masses of the polystannanes were in the range of 1×10^4 to 1×10^5 g/mol, depending on the reaction conditions. For the generic case of the polymerization of Bu_2SnH_2 with $[RhCl(PPh_3)_3]$ as catalyst, it was demonstrated that poly(dibutylstannane) did not form by a random polycondensation, but by growth at a rhodium complex, whereby only a minor part of $[RhCl(PPh_3)_3]$ was converted to catalytically active species by reaction with tin hydrides. The polymers featured phase transitions into liquid-crystalline states, on occasion at remarkably low temperatures. A particularly high phase transition temperature was observed for poly(dipropylstannane), which also was characterized by a high density, indicative of a particularly favorable packing of the propyl groups.

1. Introduction

Polystannanes, i.e., polymers of the composition $(SnR_2)_n$, belong to the rare examples of polymers that comprise a backbone of covalently bonded metal atoms and are worth exploring already for that reason. As far as we are aware, compounds with the chemical composition of oligo- or polystannanes were prepared first by Löwig in 1852.[1] In an exothermic reaction, iodoethane was converted with a Sn/K or a Sn/Na alloy, in the presence of quartz sand which was used to control the reaction rate.[1] After evaporation of volatile components, extraction, and segregation procedures using diethyl ether and absolute ethanol, several fractions were collected which contained substances with elemental compositions close to those of oligo(diethylstannane)s or poly(diethylstannane). Similarly, Cahours obtained a few years later in 1860 in treatment of iodoethane with Na/Zn a compound comprising 27.30% C and 5.79% H (recalculated values).[2] Since the atomic masses of H, C and Sn at that early time were taken as 1, 6, and 59 g/mol, respectively, an ethyl group was represented with the formula C_4H_5 and, therefore, the composition of the tin compound was indicated with SnC_4H_5 and, accordingly, called stannic ethyl, stanethylium, stannäthyl, or stannéthyle in different languages.[1−6] Stannic ethyl was described as a high-viscous liquid[1,2,5] which still was not solid at −12 °C.[1] Already Löwig had assumed that stannic ethyl was formed from Na/Zn and iodoethane under release of NaI,[1] and, remarkably, Cahours attributed the formation of stannic ethyl to a reaction of the Wurtz type.[2,5] Indeed, the Wurtz reaction[7] has been shown to be suited for the preparation of poly(dialkylstannane)s by treatment of dialkyltin dichlorides with sodium.[8−14] Such reactions lead to polystannanes of high molar mass, however, in low yields as (cyclic) oligomers were also produced during the reactions. It should be noted that oligomers may also result by degradation processes of polystannanes.[14,15] These aspects may explain why stannic ethyl was gained as highly viscous liquid instead of a solid substance. Upon heating, stannic ethyl was found to decompose to elemental tin and tetraethyl tin (named distannethyl).[2,5] The attempt was also made to prepare stannic methyl by the Wurtz reaction, which would correspond to poly(dimethylstannane), but the elemental analyses do not justify the assumption that this compound was successfully prepared.[2,16]

It has been often mentioned[9,17−21] that stannic ethyl (or "diethyl tin") was also prepared by Frankland in 1852 or 1853.[3,4] Upon immersion of a zinc foil into a solution of diethyltin dichloride, this author obtained a highly viscous, brownish-yellow liquid which he attributed to stannic ethyl, suggesting that this compound was formed with release of $ZnCl_2$.[3,4] However, the reported elemental composition (C, 30.31%; H, 6.24%; recalculated from the quantities of the combustion gases CO_2 and H_2O),[3] is not consistent with that of poly(diethylstannane). Also, the experiment could not be reproduced by other authors.[8]

Interestingly, already in 1858, stannic ethyl had been formulated as a polymeric compound denoted with the composition $n(SnC_4H_5)$.[22] Nota bene in 1925, i.e., in the embryonic period of polymer science, it was explicitly proposed that dimethylstannane, prepared by a reaction of the Wurtz type, was present as a species of the formula $(R_2Sn)_x$.[17] Unfortunately, however,

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10.1021/ma071463t CCC: $37.00

only oxidation products of the latter compound were analyzed, and, therefore, it is not unequivoqually clear if poly(dimethylstannane) was indeed obtained. Attempts in 1939 to determine molar masses by freezing point depression yielded ambiguous results.[9] In 1943, it was postulated that "diphenyltin" exists as a type of polymeric material because of its yellow color,[23] and indeed a bathochromic shift of the wavelength at maximum absorption with increasing number of Sn atoms was found later in the case of oligo(dibutylstannane)s comprising up to 15 Sn atoms.[24,25] In 1961, so-called "hexameric diethyltin" was presented as a cyclic six-membered oligostannane,[26] and a few years after, the formation of crystalline cyclic nonamers and waxy cyclic hexamers of "diethyltin" was described.[27] It was reported in 1992 that the Wurtz reaction can yield linear poly(dibutylstannane) of high molar mass;[12] however, reinvestigation of this reaction resulted in materials of a bimodal molar mass distribution, with the product containing predominantly oligomers.[14] Also, the reaction of R_2SnCl_2 with 2 equiv of SmI_2 provided polystannanes, however of low molar masses and in moderate yields.[28,29] Finally, conclusive experimental evidence for a polystannane of a high molar mass was presented in 1993, which was synthesized by catalytic dehydropolymerization of dibutylstannane with zirconium catalysts.[30]

Besides the above-mentioned Wurtz reaction,[10−13] also electrochemical reactions have been shown to result in linear polystannanes,[31,32] which, however, in some cases were also thought to be branched.[33] A simple and effective way to produce polystannanes obviously is the catalytic dehydrocoupling of R_2SnH_2.[14,15,30,34−36] Unfortunately, the polymers prepared by those methods were frequently not isolated and typically contained significant fractions of cyclic oligomers.[14,30,34] Also, some of these synthetic efforts yielded polystannanes only in low yields.[35,36] Recently, however, we demonstrated that Wilkinson's catalyst[37] is well suited for the polymerization of dibutylstannane, Bu_2SnH_2, which produces not only linear poly(dibutylstannane) of high molar mass in high yields, but also does not give rise to the formation of cyclic byproducts.[15] Remarkably, the resulting poly(dibutylstannane) appeared to be present in a liquid-crystalline state at room temperature[15] and, interestingly, featured semiconductive properties as revealed by the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC).[38]

This article describes a comprehensive study of the preparation and characteristics of linear polystannanes synthesized by catalytic dehydrocoupling of a number of dialkylstannanes, including investigations of the polymerization process (influence of reaction parameters, kinetics, mechanistic aspects) and the thermal behavior and selected structural characteristics of the polymers produced.

2. Experimental Section

2.1. General Methods. Elemental analyses were performed by the Microelemental Analysis Laboratory of the Department of Chemistry at ETH Zürich.

Infrared 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, ^{13}C, and ^{119}Sn NMR spectra were obtained with a Bruker UltraShield 300 MHz/54 mm or a Bruker UltraShield 500 MHz/54 mm Fourier transform spectrometer. The NMR tubes were protected from light by complete enwrapping into aluminum foil. The aluminum foil was removed only immediately prior to the measurements. For quantitative analysis of poly(dibutylstannane)/cyclo-oligo(dibutylstannane) ratios by integrated intensities in ^{119}Sn NMR spectra, 1000 scans were accumulated with a delay time between the pulses of 0.5 s. The polymer signal was integrated from −186 to −195 ppm and that of the cycles from −197 to −206 ppm. The integrated values thus obtained represented poly(dibutylstannane)/cyclooligo(dibutylstannane) ratios without the need to apply a pronounced correction factor, as demonstrated by comparison with the corresponding ratios obtained from integrated signal intensities in ^1H NMR spectra in benzene and toluene (cf. Figure 1).

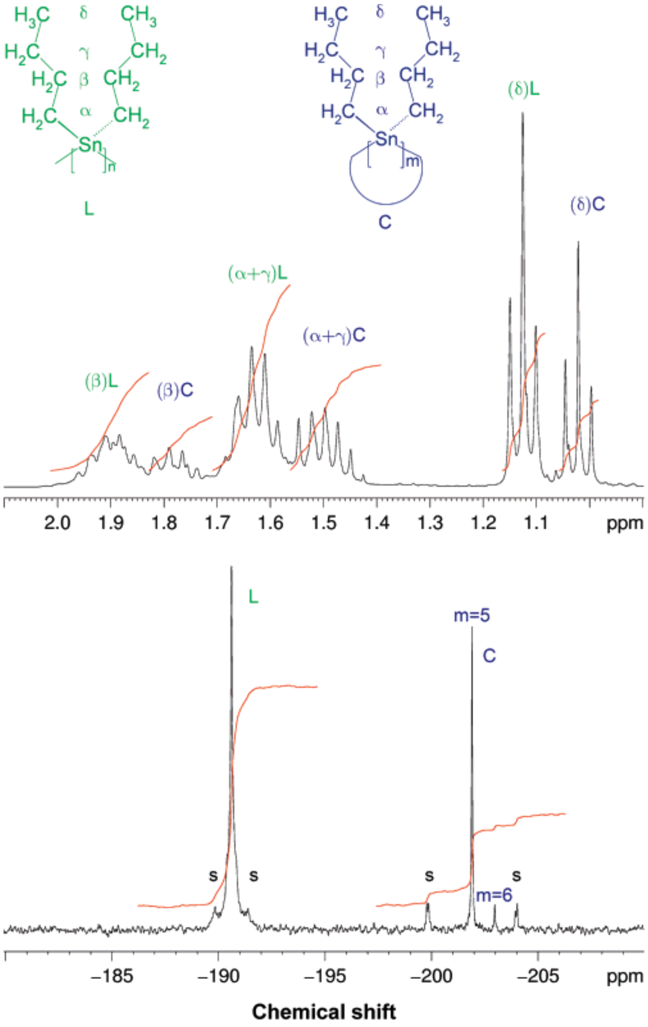


Figure 1. ^1H & ^{119}Sn NMR spectra of a sample containing a mixture of linear (L) poly(dibutylstannane) and cyclic (C) oligo(dibutylstannane)s. The signals labeled "s" are due to $^{119}Sn-^{119}Sn$ or $^{119}Sn-^{117}Sn$ couplings, respectively.

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

Membrane osmometry was conducted at 45 °C in toluene with an OSMOMAT 090 from Gonotec (Berlin, Germany), using a two-layer cellulose triacetate membrane with a cut off value of 5000 g/mol.

Thermal analysis was performed by differential scanning calorimetry (DSC) with a DSC822^e instrument (Mettler Toledo, Greifensee, Switzerland) equipped with an intracooler and thermogravimetric analysis (TGA) with a TGA/SDTA851^e from Mettler Toledo under nitrogen atmosphere or air at heating and cooling rates of 5 °C/min, if not otherwise indicated. Melting temperatures of monomer precursors and monomers were determined by DSC at a heating rate of 2 °C/min.

Simultaneous wide- and small-angle X-ray scattering (SWAXS) experiments were performed using a SAXSess instrument (Anton Paar) with a line collimation setup. The measurements were carried out in a total angular window ranging between 0.05° to 41° with

Table 1. Synthesis Parameters for the Polymers $(R_2Sn)_n$[a]

R	R_2SnH_2 [g (mmol)]	$[RhCl(PPh_3)_3]$ [mg (mmol)]	$-(R_2Sn)_n-$ [g (mmol)]	yield [%]	M_w/M_n [g mol^{-1}]	$\rho_{25\,°C}$ [g cm^{-3}]
Et	1.00 (5.59)	207 (0.22)	0.70 (3.95)	71	$3.1 \times 10^4/1.3 \times 10^4$	1.47
Pr	0.50 (2.42)	89 (0.10)	0.35 (1.71)	71	$2.7 \times 10^4/1.0 \times 10^4$	1.58
Bu	1.50 (6.38)	237 (0.26)	1.32 (5.67)	89	$9.1 \times 10^4/3.6 \times 10^4$	1.39
Pe	1.00 (3.80)	140 (0.15)	0.76 (2.91)	76	$4.8 \times 10^4/1.9 \times 10^4$	1.30
Hex	1.05 (3.61)	167 (0.18)	0.84 (2.91)	81	$7.6 \times 10^4/3.1 \times 10^4$	1.32
Oc	1.00 (2.88)	134 (0.14)	0.77 (2.23)	77	$9.7 \times 10^4/4.0 \times 10^4$	1.22
Dod	1.00 (2.17)	205 (0.22)	0.63 (1.38)	64	$2.8 \times 10^4/1.9 \times 10^4$	1.16

[a] Also included are selected analytical data of polymers like $\rho_{25°C}$ (density at 25 °C) and molar masses determined from the reaction mixture with GPC against poly(styrene) standards.

the scattering vector being defined as $q = 4\pi/\lambda \sin(\theta/2)$, using a Cu K$\alpha$ radiation ($\lambda = 0.1542$ nm). The beam was attenuated by a semitransparent nickel foil beam stop. A high sensitive SWAXS imaging plate slide positioned at 264.5 mm from the sample was used to collect the signal. The temperature of the sample holder was controlled between −30 and +160 °C. Samples were placed between two mica foils, which were clamped and sandwiched in a steel holder. Because of the high contrast to X-rays between Sn and alkyl side groups, 4 min of exposure time were sufficient for data acquisition. In temperature-dependent experiments, samples were first heated to 100 °C in order to eliminate the thermal history and then equilibrated for 30 min at a given temperature prior to collecting the scattering data. Diffractograms of mica were measured as a background and subtracted from the sample diffractograms to yield the data reported. All scattering signals were treated with Saxquant software by Anton Paar.

Optical microscopy at ambient was conducted with a Leica DM400 M polarizing microscope. For investigations at variable temperatures, a Leica DMRX polarizing microscope equipped with a Linkam THMS 600 heating-/cooling stage was used. The stage was flushed with argon and first cooled to −50 °C, followed by an increase in temperature (typically at a rate of 5 °C/min) up to 100 °C.

Densities of the polymers were determined by helium gas pycnometry at 25 °C (Ultrapycnometer-1000, Quantachrome, Odelzhausen, Germany, equipped with a Haake DC10 Thermostat).

2.2. Materials. All solvents were purchased in puriss p.a. purity from Fluka, Buchs (Switzerland) and were used without purification. All deuterated solvents were purchased from Cambridge Isotope Laboratories (Innerberg, Switzerland) with a deuterium fraction of >99%. Tetrachlorostannane was purchased from Fluka, Buchs (Switzerland), dicholorodiethylstannane and dichlorodioctylstannane from ABCR GmbH (Karlsruhe, Germany), all Grignard reagents from Sigma Aldrich (Buchs, Switzerland), dibutyldichlorostannane, $[RhCl(PPh_3)_3]$, $[RhCl(CO)(PPh_3)_2]$, $[Rh(\mu\text{-}Cl)Et_2]_2$, $[Ni(cod)_2]$, $[NiCl_2(PPh_3)_2]$, $[ZrH_2(cp)_2]$, $[Co_2(CO)_8]$, $[Rh(\mu\text{-}Cl)(CO)_2]_2$, $[Mo(cp)(CO)_3]_2$, $[IrH(CO)(PPh_3)_3]$, $[IrCl(CO)(PPh_3)_2]$, $[Ir(\mu\text{-}Cl)(cod)]_2$, $[PdCl_2(PEt_3)_2]$, and $[Rh(\mu\text{-}Cl)(cod)]_2$ from Johnson Matthey (Zürich, Switzerland), $[WH_2(cp)_2]$, $[Pd(PPh_3)_4]$, $[Pt(acac)_2]$, $[PdCl_2]$, $[Ir(acac)(cod)]$, $[ZrClH(cp)_2]$, $[TiCl_2(cp)_2]$, and $[PdCl_2(PPh_3)_2]$ from ABCR GmbH (Karlsruhe, Germany), and $H[AuCl_4]$ from Fluka (Buchs, Switzerland). $[RuCl_2(PCy_3)_2({=}CHSPh)]$ was kindly donated by Ciba Specialty Chemicals Inc. (Basel, Switzerland), and $[PtCl_2(PPh_3)_2]$ was synthesized from $[PtCl_2(styrene)_2]$ as described in the literature.[39] The above used acronyms refer to the following groups: Et = ethyl, Ph = phenyl, Cy = cyclohexyl, cod = 1,5-cyclooctadiene, cp = cyclopentadienyl, and acac = acetylacetonate (2,4-pentanedionate).

2.3. Important Remarks to the Treatment of Polystannanes. Note that polystannanes are sensitive to light[10,14,15,30] and moisture,[31] in particular in solution, where cyclic oligostannanes form upon degradation in, for instance, benzene.[15] We protected the synthesized poly(dialkylstannane)s from light, oxygen, and moisture as carefully as possible, to keep the exposure of the samples to a minimum. Therefore, reaction vessels were completely wrapped with soft tissue and subsequently surrounded with aluminum foil. Reactions were always carried out under argon atmosphere and the analyses of the polymers were performed either immediately after synthesis or after storage in argon-flushed brown glass vessels in a refrigerator at a temperature of ca. −20 °C.

Table 2. Calculated and Found Chemical Composition (in % m/m) of Poly(dialkylstannane)s

compound		C	H
$(SnEt_2)_n$	found	27.36	5.66
	calcd	27.17	5.70
$(SnPr_2)_n$	found	35.68	6.48
	calcd	35.17	6.89
$(SnBu_2)_n$	found	40.76	7.61
	calcd	41.25	7.79
$(SnPe_2)_n$	found	44.96	8.45
	calc	46.02	8.50
$(SnHex_2)_n$	found	48.19	8.49
	calcd	49.86	9.07
$(SnOc_2)_n$	found	53.96	9.61
	calcd	55.68	9.93
$(SnDod_2)_n$	found	62.62	10.68
	calcd	63.03	11.02

2.4. Synthesis and Isolation of Poly(dialkylstannane)s ($(R_2Sn)_n$). Polymerization of dialkylstannanes (quantities see Table 1) was conducted following the previously described procedure for poly(dibutylstannane).[15] A quantity of dialkylstannane (for synthesis, see the Supporting Information) was added with a syringe to a solution of $[RhCl(PPh_3)_3]$ (4% mol/mol with respect to R_2SnH_2) in dichloromethane. After 2 h (during which regularly a sample was withdrawn with a syringe for GPC analysis), the solution was cooled to −78 °C for at least 30 min. The precipitated yellow polymer was filtered off and washed with small amounts of cold dichloromethane (−78 °C). Thereafter, the isolated polymer was dried in vacuum (ca. 0.5 mbar) for 12 h. The product was stored in a refrigerator (−20 °C) in brown glass vessels which were flushed with argon. The resulting poly(dialkylstannane)s were analyzed by helium pycnometry (Table 1), GPC (Table 1), elemental analysis (Table 2), NMR spectroscopy (Table 3), TGA (Table 4), and DSC (Table 5). The absorption maxima in UV−vis spectra were in the range 360−400 nm.

2.5. Polymerization of Dibutylstannane by Continuous Addition of Catalyst. Typically, 2 g of dibutylstannane was placed in a Schlenk tube, which was entirely wrapped with soft tissue and aluminum foil and flushed with argon. Then 30 mL of toluene was added through a septum. A solution of 235 mg of $[RhCl(PPh_3)_3]$ in 2 mL of dichloromethane was slowly added (typically during 4 h) with a syringe pump (Razel Scientific Instruments, St. Albans, VT) up to a final ratio of 3% mol/mol $[RhCl(PPh_3)_3]/Bu_2SnH_2$ in the reaction solution. The polymer was subsequently isolated; because of its good solubility in cold toluene (−78 °C) an excess (10 times the toluene content) of cold methanol (−78 °C) needed to be added in order to cause the polymer to precipitate. Yields of 50−70% were achieved by this method.

2.6. Synthesis of Poly(dibutylstannane) for in Situ Investigations. An amount of 7.7 mg corresponding to 4% mol/mol catalyst (based on the ratio of rhodium atoms and Bu_2SnH_2 molecules) was placed in a Schlenk tube under argon, before 1 mL of deuterated solvent was added. The mixture was stirred under argon for a few minutes. Thereafter, 41.7 μL (48 mg, 0.2 mmol) Bu_2SnH_2 were added with a micro-pipet to the stirred solution under argon counter

Table 3. NMR Data for the Synthesized Poly(dialkylstannane)s, Where Chemical Shifts (δ) are Given in ppm

	^{1}H				^{13}C			^{119}Sn
R	$-CH_3$	$-CH_2-$	$Sn-CH_2$-	$Sn-CH_2-$and $-CH_3$	$-CH_3$	$Sn-CH_2-$	$-CH_2-$	
Et[a]				m, 10H 1.34	15.01	3.21		−172.2
Pr[c]	t, 6H 1.20	m, 4H 1.54	m, 4H 1.87		20.00	14.56	24.77	−194.8
Bu[b]	t, 6H 1.13	m, 8H 1.62	m, 4H 1.90		14.38	12.08	29.03; 34.02	−190.6
Pe[c]	t, 6H 1.10	m, 12H 1.63	m, 4H 1.97		14.13	11.67	22.63; 30.96; 37.80	−192.0
Hex[a]	t, 6H 0.81	m, 16H 1.22	m, 4H 1.45		14.07	11.42	23.00; 31.03; 31.81; 35.20	−192.5
Oc[a]	t, 6H 0.90	m, 24H 1.30	m, 4H 1.55		14.52	12.00	23.42; 30.18; 30.34; 31.63; 32.77; 36.12	−192.1
Dod[c]	m, 6H 0.96	m, 40H 1.38	m, 4H 1.97		14.39	12.49	23.27; 30.00 − 30.91;[d] 31.90; 32.60; 36.31	−189.0

[a] Measured in dichloromethane-d_2. [b] Measured in benzene-d_6. [c] Measured in toluene-d_8. [d] Broad, overlapping signals

Table 4. TGA Analysis of Linear Poly(dialkylstannane)s and Calculated Mass Fraction of Tin in the Polymers

polymer	atmosphere	temp at max rate of decomp [°C]	remaining mass at 450 °C [%]	mass fraction of tin in the polymer [%]
$(SnEt_2)_n$	nitrogen	283	27	66
	air	255	55	
$(SnPr_2)_n$	nitrogen	293	30	58
	air	261	50	
$(SnBu_2)_n$	nitrogen	302	31	51
	air	239	51	
$(SnPe_2)_n$	nitrogen	296	25	45
	air	275	49	
$(SnHex_2)_n$	nitrogen	295	36	41
	air	290	46	
$(SnOc_2)_n$	nitrogen	302	30	34
	air	299	41	
$(SnDod_2)_n$	nitrogen	289	28	26
	air	268	34	

Table 5. Transition Temperatures and Enthalpies of Poly(dialkylstannane)s; from Second Run DSC Thermograms

		transition temp [°C] from DSC		enthalpy [J g^{-1}]	
polymer		first transition	second transition	first transition	second transition
$(SnEt_2)_n$	heating	15		1.8	
	cooling	6		−1.6	
$(SnPr_2)_n$	heating	93		3.4	
	cooling	63		−6.6	
$(SnBu_2)_n$	heating	1		10.1	
	cooling	−26		−9.3	
$(SnPe_2)_n$	heating	6	57	10.6	1.5
	cooling	−16	42	−10.1	−2.1
$(SnHex_2)_n$	heating	34	68	10.1	6.7
	cooling	21	43	−7.2	−10.1
$(SnOc_2)_n$	heating	29	74	14.3	5.2
	cooling	13	58	−13.5	−5.8
$(SnDod_2)_n$	heating	55	91	12.7	2.1
	cooling	39	80	−24.9	−3.8

flow. After 2 h (if not otherwise indicated) the reaction mixture was transferred into an NMR tube. After NMR measurements, the reaction mixture was diluted with ca. 3 mL of tetrahydrofuran, and the molar masses were determined with GPC.

In order to monitor the reaction kinetics with $[RhCl(PPh_3)_3]$ at various temperatures, different quantities of $[RhCl(PPh_3)_3]$ (in the range of 1.90 − 37.95 mg) were placed in a Schlenk tube as described above; however, as solvent, typically 2 mL of toluene was employed. After the reaction mixture was stirred for 10 min, the catalyst dissolved completely or only partially at higher catalyst concentrations or lower temperatures. The reaction vessel was fixed onto a laboratory shaker (Heidolph Unimax 1010, shake velocity 100 min^{-1}, Merck, Dietikon, Switzerland) which was placed into a bath fitted with a thermostat (Julabo F26, from Merck). After 15 min of temperature equilibration, the Schlenk tube was disconnected from the argon counter flow and connected to a gas buret by Bunte[40] (the reaction vessel was rigorously protected from light as described above). Thereafter, an amount of Bu_2SnH_2 (typically 83.4 μL, 96 mg) was added with a micro-pipet through a septum. The evolution of gas, which accompanied the polymerization, was followed periodically in the gas buret until the volume did not change anymore over a period of 60 min. Thereafter a sample of 0.5 mL was taken from the reaction mixture and diluted with 2.5 mL of tetrahydrofuran. The resulting solution was subsequently used for GPC analysis.

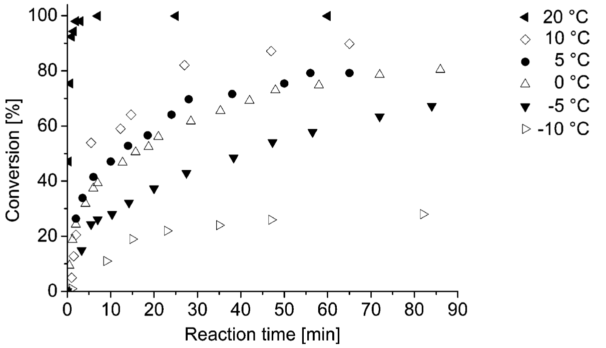


Figure 2. Conversion, determined by the volume of evolved H_2 of dibutylstannane to poly(dibutylstannane) as a function of reaction time during the first 90 min, in the presence of $[RhCl(PPh_3)_3]$ (4% mol/mol) in toluene at various temperatures.

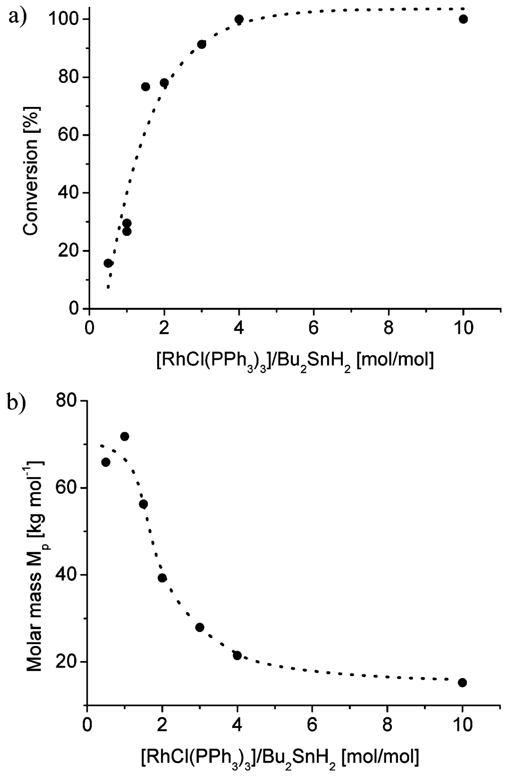


Figure 3. (a) Conversion of dibutylstannane in toluene at 20 °C after the evolved gas volume was constant over a period of 60 min and (b) molar mass of resulting poly(dibutylstannane) as a function of the $[RhCl(PPh_3)_3]/H_2SnBu_2$ ratio. Dotted lines are guides for the eye only.

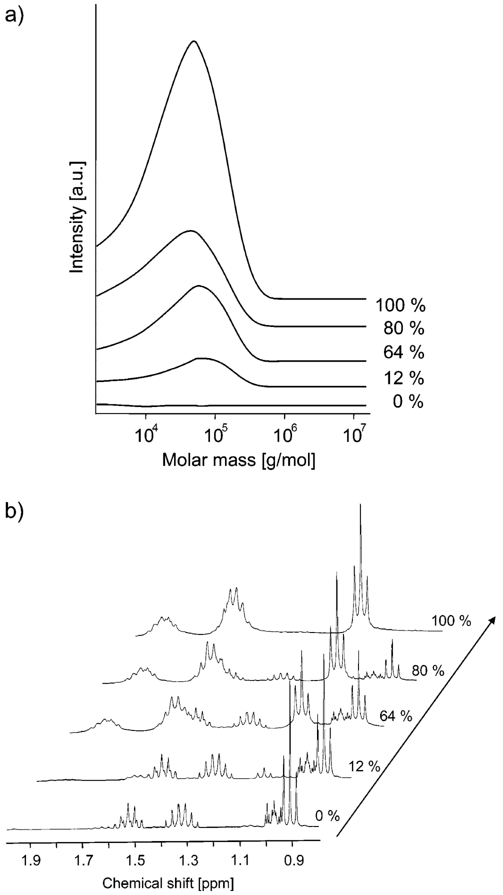


Figure 4. (a) Gel permeation chromatograms of dibutylstannane reaction mixtures at different dibutylstannane conversions, in reaction with continuous addition of [RhCl(PPh$_3$)$_3$]. (b) NMR spectra representative of the butyl groups in the reaction mixtures at the different conversions (indicated).

3. Results and Discussion

3.1. Determination of Monomer Conversion and Polymer Analysis. The conversion of the monomers R$_2$SnH$_2$ was monitored in situ by the decrease of the Sn−H signal in ^{1}H NMR spectra (around 4.7 ppm, see Supporting Information), ^{119}Sn NMR spectra (generally around −205 ppm, except poly(diethylstannane), see Supporting Information) or IR spectra (around 1835 cm^{-1}, see Supporting Information); note that the Sn−H signals in ^{1}H NMR and IR spectra were well separated from the other peaks of the respective compounds. For qualitative investigations, IR measurements using the ATR technique were particularly rapid and simple as a drop of the reaction solution can be placed directly on the ATR crystal without sample workup. In order to quantitatively determine the kinetics of the monomer conversion, in situ measurements in NMR tubes were not suited because of the evolution of H$_2$ gas which accompanies the polymerization. As an alternative, the volume of this gas was monitored with a gas buret by Bunte.[40]

Linear polymers and cyclic oligomers could be distinguished from each other most conveniently by ^{119}Sn NMR spectra (Figure 1).[10,14,15,41] The ^{119}Sn NMR shifts of poly(dialkylstannane)s appeared typically at ca. −190 ppm (with the exception of poly(diethylstannane), Table 3), while the corresponding cyclic oligomers were shifted to higher fields by approximately 10 ppm. It has been reported[14] that the signals of cyclic oligo(dialkylstannane)s and linear poly(dialkylstannane) are also separated in the ^{1}H NMR spectra—at least for the dibutyl and dihexyl derivatives. However, in our experiments a clear difference in chemical shifts of hydrogen atoms in propyl, butyl, or octyl groups was visible only in specific solvents such as benzene or toluene (shift difference ca. 0.1 ppm), while in, e.g., tetrahydrofuran or dichloromethane, the signals of the linear polymer and the cyclic oligomers essentially coincided. Hence ^{1}H NMR spectra allowed a quantitative determination of the fraction of cyclic oligomers dissolved in toluene or benzene, preferentially by evaluation of the signals of the methyl groups (Figure 1), provided, however, that the dialkylstannanes reacted completely without formation of additional products. On the other hand, the signals of the cyclic products were well separated from other signals in ^{119}Sn NMR spectra, and therefore, the fraction of the cyclic products could be estimated readily by integration of the corresponding signal intensities in ^{119}Sn NMR spectra. However, it has to be considered that the signal intensities in ^{119}Sn NMR spectra might not be proportional to the concentration of related species due to differences in relaxation time or NOE (nuclear Overhauser effect). Two samples of reaction mixtures with 100% monomer conversion comprising both linear polymer and cyclic oligomers resulted in a polystannane/cyclic oligomers ratio of, respectively, 81:19 and 66:34 from ^{1}H NMR spectra compared to 86:14 and 71:29 from ^{119}Sn NMR analysis (Figure 1), using the NMR parameters indicated in the Experimental Section. Hence, it appears that evaluation of ^{119}Sn NMR spectra leads to a reasonable estimation of the fraction of cyclic oligomers. Remarkably, the time required for recording ^{119}Sn NMR spectra with sufficient signal/noise ratio was relatively short (10 min).

In the studies previously reported, molar masses of polystannanes were quantified with gel permeation chromatography (GPC) on the basis of poly(styrene) standards.[10,14,15,31,34,42] Of course, because of that these results may feature a considerable systematic error. On the other hand, GPC is an efficient method and, in fact, well suited for a *relative* comparison of the molar masses of polymers of the same chemical structure, thus allowing semiquantitative studies of the influence of reaction parameters on the molar mass. Moreover, GPC allowed molar mass determination of polystannanes in their reaction solutions. In the following, mainly molar masses at the peak maximum (M_p) elution curves are indicated since those values could be determined most accurately in reaction solutions. These values were frequently in the range of 2×10^4 to 3×10^4 g/mol, and number-average molar masses (M_n) amounted to 2×10^4 to 3.5×10^4 g/mol and weight-average molar masses (M_w) to 5.5×10^4 to 8×10^4 g/mol. Thus, M_p appeared to be somewhat, but not markedly, below M_n. Regarding the issue of reproducibility, it is important to note that the molar mass varied within some limits when experiments were repeated under the same conditions. Typically, when a number of poly(dibutylstannane)s were prepared in separate experiments or with different batches of monomer but under otherwise similar conditions for instance (polymerization of dibutylstannane at room temperature in toluene at a [RhCl(PPh$_3$)$_3$]/Bu$_2$SnH$_2$ ratio of 4% mol/mol), M_p was found in the range of 1.5×10^4 and 3.0×10^4 g/mol. We attribute these differences to, among other things, differences in the purity of the monomer or small variations in the experimental conditions which could critically affect the quantity of the catalytic active species. Therefore, in order to compare the influence of reaction parameters on M_p, all experiments of the corresponding reaction series were performed with the same batch of Bu$_2$SnH$_2$ and during the same day. In the following, we considered differences in M_p to be significant only if the values differed by more than a factor of 2.

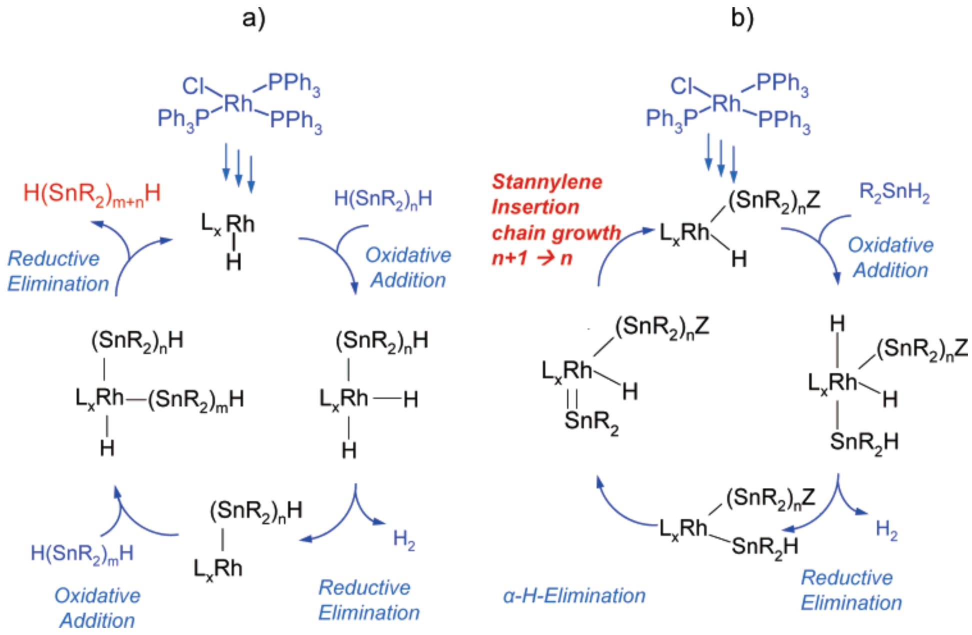


Figure 5. Schemeatic of two different polymerization mechanisms. (a) A modified path as proposed for zirconium catalysts, where the molar mass should follow Carothers' equation (see text). (b) Mechanism involving chain growth at a rhodium atom by stannylene insertion.

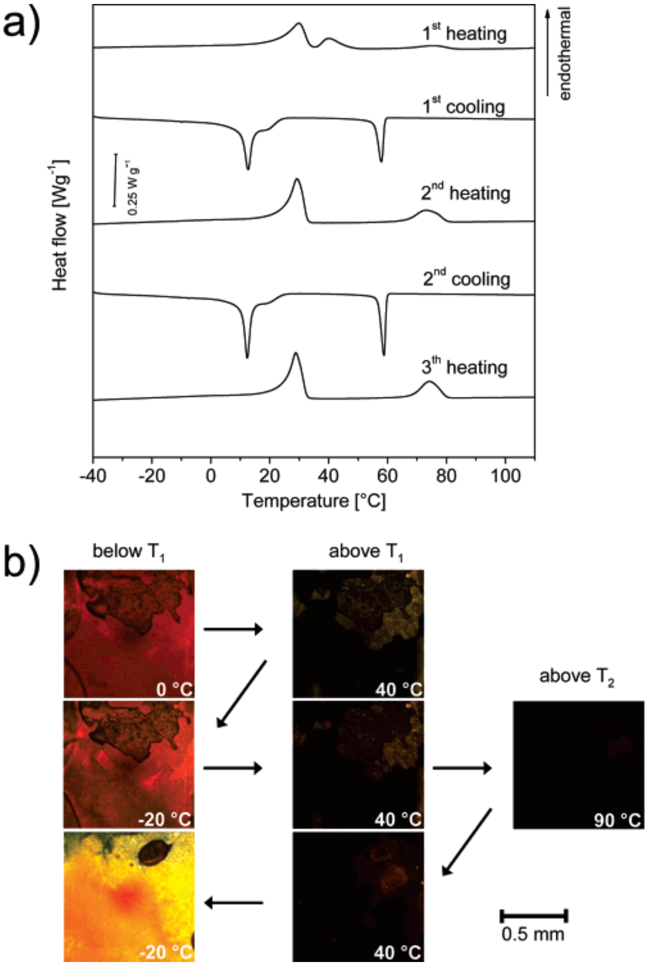


Figure 6. (a) DSC thermograms of poly(dioctylstannane); recorded for subsequent heating /cooling cycles (under N_2, rate 5 °C/min). (b) Optical microscopy images of the sample at the various temperatures indicated; crossed polarizers. The sequence of the heating/cooling steps proceeded is indicated with the arrows (under argon, rate 5 °C/min).

Extensive investigations were performed also with membrane osmometry using samples of poly(dibutylstannane) (M_n from GPC: 2.1×10^4 g/mol) and of poly(didodecylstannane) (M_n from GPC: 1.0×10^4 g/mol). Because of the degradation sensitivity of poly(dialkylstannane)s to light and the ambient atmosphere, the samples were dissolved immediately before the measurements were carried out. As could be concluded from the development of the osmotic pressure, low molar mass components slowly penetrated the membrane (size exclusion limit M ca. 0.5×10^4 g/mol), thus yielding an apparent increase in molar mass of the dissolved poly(dialkylstannane) with time. For instance, the apparent M_n of a poly(dibutylstannane) sample increased during an equilibrium time from 2 to 60 min from 3.0×10^4 to 4.8×10^4 g/mol and of poly(didodecylstannane) from 1.6×10^4 to 2.9×10^4 g/mol. Experiments with a poly(styrene) standard sample suggested that the equilibrium between the osmosis chambers was established essentially within 2 min and, therefore, the measurements of the polystannanes at 2 min equilibrium time were taken to be the more reliable. The results from membrane osmometry indicate that the M_n obtained from GPC are somewhat lower but still in the same order as those obtained from membrane osmosis.

3.2. Catalytic Activity of Selected Metal Complexes. The activity of a group of 25 transition metal compounds, including [$RhCl(PPh_3)_3$] (indicated in Table 6 and below) were scrutinized for their activity for the catalytic polymerization of dibutylstannane (Bu_2SnH_2), here used as a model system. Polymerizations were carried out in four different deuterated solvents (benzene, toluene, tetrahydrofuran, and dichloromethane) under argon atmosphere for 2 h with each of the 25 metal complexes, and the reaction solutions were subsequently poured into NMR tubes for ^{1}H NMR and ^{119}Sn NMR analysis. In addition, each of the as-prepared reaction mixtures was also analyzed with GPC.

When dibutylstannane was added to the transition metal compounds, hydrogen evolved in most cases, suggesting the formation of Sn−Sn bonds. However, poly(dibutylstannane)s of considerable molar mass were formed only under the action of seven metal complexes, four of which were based on rhodium, two on zirconium and one on nickel, see Table 6. The ratios of cyclic and linear reaction products indicated in this table were estimated from ^{119}Sn NMR spectra. ^{1}H NMR evaluation of reaction mixtures in benzene or toluene confirmed

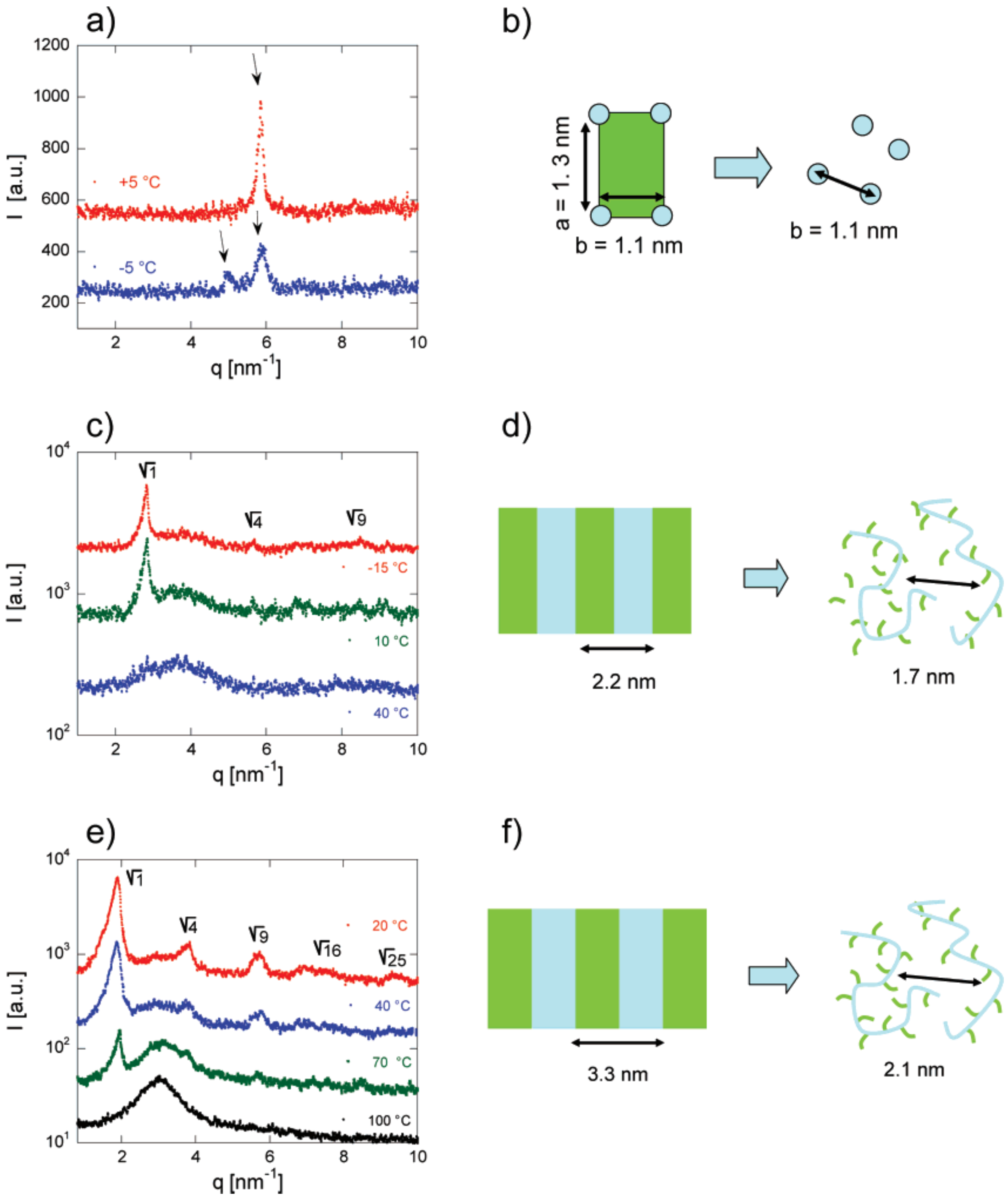


Figure 7. (a) SAXS patterns of poly(dibutylstannane) at temperatures below and above T_1, at −5 and +5 °C, respectively. (b) Scheme of proposed changes in the structure of liquid-crystalline polymers below and above T_1. (c) SAXS patterns of poly(dioctylstannane) at −15 °C, 10 °C (below T_1) and 40 °C (above T_1). (d) Scheme of proposed order−disorder changes in the structure of the polymers below and above T_1. (e) SAXS patterns of poly(didodecylstannane) at 20, 40, 70, and 100 °C. (f) Scheme of proposed changes in liquid-crystalline structures below and above T_1.

corresponding results from ^{119}Sn NMR spectra (in tetrahydrofuran or dichloromethane, ^{1}H NMR spectra of samples could not be evaluated because of overlapping signals, as indicated above). The compounds H[AuCl$_4$], [Co$_2$(CO)$_8$], [Ir(acac)(cod)], [NiCl$_2$(PPh$_3$)$_2$], [PdCl$_2$(PEt$_3$)$_2$], [PdCl$_2$(PPh$_3$)$_2$], [Pd(PPh$_3$)$_4$], [PdCl$_2$], [Pt(acac)$_2$], and [PtCl$_2$(PPh$_3$)$_2$] also caused the formation of H$_2$ upon addition of Bu$_2$SnH$_2$, however, significant amounts of high molar mass products were not detected. Finally, the complexes [IrCl(CO)(PPh$_3$)$_2$], [Ir(μ-Cl)(cod)]$_2$, [IrH(CO)(PPh$_3$)$_3$], [Mo(cp)(CO)$_3$]$_2$, [TiCl$_2$(cp)$_2$], [WH$_2$(cp)$_2$], [Rh(μ-Cl)(CO)$_2$]$_2$, [RuCl$_2$(PCy$_3$)$_2$(═CHSPh)] did not display any catalytical activity when contacted with Bu$_2$SnH$_2$.

While the choice of the solvent influenced the monomer conversion markedly, the molar mass of the polymer principally depended on the transition metal compound. Since all reaction mixtures were homogeneous—the latest after dibutylstannane addition—the dependence of the conversion on the nature of the solvents is attributed to different reaction processes or reaction rates and not directly to differences in the solubility of the catalyst or of reaction intermediates. Generally, conversion in dichloromethane or tetrahydrofuran reached at best that in benzene or toluene, although reactions with the catalyst [RhCl(PPh$_3$)$_3$] and [Ni(cod)$_2$] also reached 100% conversion in at least one of the former two solvents.

Four catalysts yielded 100% conversion of dibutylstannane in at least one solvent (cf. Table 6). However, detectable amounts of cyclic oligomers in the resulting reaction mixtures were absent only in the experiments with [RhCl(PPh$_3$)$_3$] and possibly in those with [Ni(cod)$_2$]; in the latter case the detection limit of cyclic products was only ca. 30% as a result of the

Table 6. Polymerization of Dibutylstannane in the Presence of 4% mol/mol of the Most Reactive Catalysts in Different Solvents, and Molar Masses of the Resulting Polymers (M_p in g/mol, i.e., Molar Mass at the Peak Maximum in GPC Analysis), after 2 h Reaction Time at Room Temperature[c]

	solvent											
	benzene-d_6			toluene-d_8			THF-d_8			CD_2Cl_2		
catalyst	conversion[c]		M_p	conversion[c]		M_p	conversion[c]		M_p	conversion[c]		M_p
$[RhCl(PPh_3)_3]$	100	(0)	1.9×10^4	100	(0)	1.7×10^4	37	(0)	1.6×10^4	100	(0)	1.9×10^4
$[RhCl(CO)(PPh_3)_2]$	100	(1)	1.8×10^4	100	(2)	0.7×10^4	82	(2)	0.7×10^4	41	(0)	1.6×10^4
$[Rh(cod)(\mu\text{-}Cl)]_2$	32	*d*	6.9×10^4	78	*d*	5.5×10^4	0		--	2	(0)	--
$[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$	13	*d*	4.5×10^4	12	*d*	5.9×10^4	6	*d*	--	3	*d*	3.6×10^4
$[Ni(cod)_2]$	100	*e*	0.7×10^4	100	*e*	0.6×10^4	100	*e*	0.5×10^4	100	*e*	0.6×10^4
$[ZrH_2(cp)_2]$	100	(29)	2.4×10^4	100	(14)	2.7×10^4	65	(29)	2.5×10^4	0		--
$[ZrClH(cp)_2]$	47	(10)	1.8×10^4	3	(0)	2.5×10^4	7	(0)	2.5×10^4	0		--

[a] Conversion of Bu_2SnH_2 determined by integration of the tin hydride signal in ^1H NMR spectra. [b] Amount of cyclic products determined by comparison of the linear and cyclic signals in ^{119}Sn NMR spectra. [c] Key: Left column, conversion in %[a] (in brackets % of cyclic byproduct[b]); right column, M_p in g/mol. Only catalysts yielding poly(dibutylstannane) with $M_p > 6000$ g/mol are listed. Ligands: cod = 1,5-cyclooctadiene, cp = cyclopentadienyl, and acac = acetylacetonate (2,4-pentanedionate). [d] Small amount of unidentified product at ca. −88 ppm in ^{119}Sn NMR. [e] No cyclic species observed, however, due to the very broad NMR signals caused by the presence of paramagnetic nickel species; the detection limit of the cyclic products was only ca. 30%.

NMR signal broadening, likely to be due to the paramagnetic nature of nickel species present in the reaction solution, which obscures the results.

The complex $[RhCl(CO)(PPh_3)_2]$ yielded small, and $[ZrH_2(cp)_2]$ large amounts of cyclic oligomers. Polymers of the highest molar masses (M_p up to 6.9×10^4 g/mol) were found in the reaction systems containing the rhodium-olefin compounds $[Rh(cod)(\mu\text{-}Cl)]_2$ or $[Rh(C_2H_4)(\mu\text{-}Cl)]_2$, but the conversions were well below 100% and in addition a signature of an unidentified byproduct was evident in ^{119}Sn NMR spectra around −88 ppm. While most of the rhodium complexes examined were catalytically active, none of the iridium compounds yielded noteworthy amounts of linear poly(dibutylstannane); in particular $[IrCl(CO)(PPh_3)_2]$ was completely inactive although the corresponding rhodium complex lead to 100% conversion of dibutylstannane.

The data failed to reveal a systematic dependency of the catalytic activity of the complexes on particular ligands or the metal atom. Thus, the catalytic activity seems to be delicately dependent on the entire metal−ligand system, although rhodium and, as known from the literature,[14] zirconium complexes appear to be catalytically active with a variety of coordinated ligands. The most suited catalyst with respect to complete monomer conversion and exclusive formation of linear polymer was $[RhCl(PPh_3)_3]$; $[Ni(cod)_2]$ might also be appropriate, but conclusive evidence was hampered due to very broad NMR signals. Hence, further studies were conducted with $[RhCl(PPh_3)_3]$ as the catalyst.

3.3. Polymerization of Bu_2SnH_2 with $[RhCl(PPh_3)_3]$.

A detailed study was conducted of the influence of the reaction temperature and the $[RhCl(PPh_3)_3]/Bu_2SnH_2$ ratio on the conversion of dibutylstannane, on the product distribution (linear polymer vs cyclic oligomers) and on the molar mass of the resulting polymer in toluene—a solvent which enabled the distinction of linear polymer and cyclic oligomers also by ^1H NMR spectroscopy.

In order to monitor the kinetics of monomer conversion at different reaction conditions, the volume of the formed H_2 gas was measured with a gas buret by Bunte.[49] Samples were removed from the reaction mixtures at various times, subsequently diluted under ambient conditions with a 5-fold volume of tetrahydrofuran (THF), to arrest the polymerization at ambient atmosphere and immediately injected in the GPC instrument in order to analyze molar masses.

Influence of Polymerization Temperature. At a catalyst/monomer $[RhCl(PPh_3)_3]/Bu_2SnH_2$ ratio of 4% mol/mol, the rate of Bu_2SnH_2 conversion depended markedly on the reaction temperature in the range of −10 to +20 °C (Figure 2). The polymerization rate rapidly decreased with decreasing temperature. At 20 °C, reaction was finished within 2 min, while completion of the reaction at 10 °C required ca. 2 h. Further, it was found that, even over more extended periods of time, 100% conversion was not attained at temperatures below 0 °C. At −5 °C, for instance, final Bu_2SnH_2 conversion of ca. 75% was obtained after ca. 2.5 h, and at −10 °C the catalytic activity virtually expired after ca. 3.5 h when the monomer conversion amounted only to ca. 30%. The rate of monomer consumption could not be described with an integer order kinetics.

Importantly, at the end of the reactions, which was considered to be that moment when no gas evolution was observed during a period of 1 h, the molar masses M_p evaluated from GPC (2×10^4 to 3×10^4 g mol^{-1}) were not significantly influenced by the reaction temperature.

After 30 min at 20 °C and a $[RhCl(PPh_3)_3]/Bu_2SnH_2$ ratio of 4% mol/mol, i.e., under conditions where the monomer was virtually completely converted, the two dominating peaks at +24.5 and −5.1 ppm in the ^{31}P NMR spectra indicated the presence of $[RhCl(PPh_3)_3]$ and free PPh_3. The remaining $[RhCl(PPh_3)_3]$ induced complete polymerization of supplementary added Bu_2SnH_2 (25% of the initial Bu_2SnH_2 quantity), as suggested from the absence of the Sn−H stretching vibration in IR spectra. Repetition of this procedure (in 30 min intervals) lead to a weak signal of the Sn−H vibration after the third and a strong signal after the fourth addition, indicating that the catalytic system became essentially inactive after the third addition of monomer. The value of M_p in the reaction solution (1.5×10^{-4} g/mol) did not change upon the first supplementary Bu_2SnH_2 addition and decreased thereafter by ca. 15% after the second and by ca. 30% in total after the third and fourth supplementary addition.

Catalyst/Monomer Ratio. Further, experiments were performed at a reaction temperature of 20 °C at constant initial Bu_2SnH_2 concentration, but different $[RhCl(PPh_3)_3]/Bu_2SnH_2$ ratios. This ratio was found to significantly affect the maximum Bu_2SnH_2 conversion, which became incomplete below a $[RhCl(PPh_3)_3]/Bu_2SnH_2$ ratio of 4% mol/mol, reaching only 16% at a 0.5% mol/mol (Figure 3). On the other hand, a lower catalyst/monomer ratio lead to a (nonlinear) *increase* in molar mass of the resulting poly(dibutylstannane). The highest M_p values (around 7×10^4 g mol^{-1}) were found at $[RhCl(PPh_3)_3]/Bu_2SnH_2$ ratios of 0.5−1% mol/mol. Since the increase in molar mass of the polymer was accompanied by a significant decrease in conversion of Bu_2SnH_2, the preparation of polymers with higher molar mass was judged to be inefficient under such experimental conditions. On the basis of the above observations, however, polymers of high molar mass and 100% monomer conversion could be prepared when the concentration of active catalyst was kept low by very slow and continuous addition with a syringe pump of [RhCl(PPh$_3$)$_3$] in dichloromethane ([RhCl(PPh$_3$)$_3$] is soluble in dichloromethane in higher concentrations than in toluene) to a Bu$_2$SnH$_2$ solution in toluene. Here, the catalyst was added to the monomer solution, while in the above procedures the reverse was true; i.e., the monomer was added to the catalyst. During the reaction, small amounts of samples were removed from the reaction mixture and immediately diluted with tetrahydrofuran-*d*$_8$ in order to interrupt the polymerization reaction. Analysis of these samples with ^{1}H NMR spectroscopy disclosed that monomer conversion was not yet completed at a [RhCl(PPh$_3$)$_3$]/Bu$_2$SnH$_2$ ratio of 2% mol/mol (80% monomer conversion) while the Bu$_2$SnH$_2$ was completely polymerized at a [RhCl(PPh$_3$)$_3$]/Bu$_2$SnH$_2$ ratio of 3% mol/mol (Figure 4). The M_p decreased from 9.3 × 10^4 at a [RhCl(PPh$_3$)$_3$]/Bu$_2$SnH$_2$ ratio of 0.5% mol/mol (12% monomer conversion) to 6.0 × 10^4 at 2% mol/mol ($M_n = 7.2 \times 10^4$ g/mol, $M_w = 13.4 \times 10^4$ g/mol) and remained at this level at a ratio of 3% mol/mol (Figure 4).

Monomer Concentration. In order to investigate if variations of the monomer Bu$_2$SnH$_2$ concentration in toluene could result in poly(dibutylstannane) with high molar mass and 100% monomer conversion, the volume of the solvent was varied by a factor of 20 (0.25−5 times the volume of solvent used in the above experiments, [RhCl(PPh$_3$)$_3$]/Bu$_2$SnH$_2$ ratio 1% mol/mol). However, monomer conversion after 120 min never exceeded 50% and there was no unambiguous trend for a dependence of the monomer conversion on the solvent volume; also, the values of M_p did not differ significantly from each other (4.3 × 10^4 to 5.6 × 10^4 g mol^{-1}). When the polymerization was carried out in neat Bu$_2$SnH$_2$, i.e. in the absence of solvent, monomer conversion was not complete after 120 min and the molar mass of the formed polymer was M_p of 0.99 × 10^4 g/mol only.

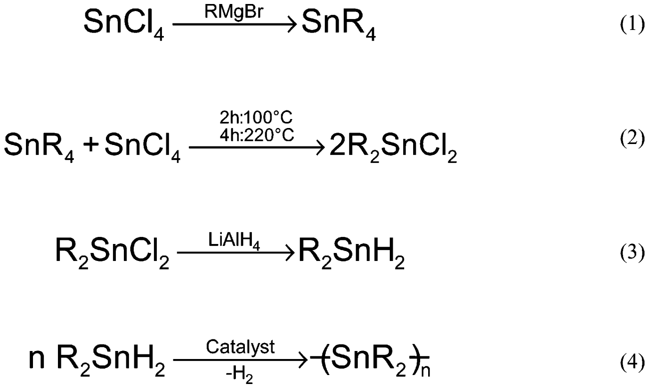
Mechanism. The results of the above experiments provide some insights into the mechanism of the polymerization process:

If the Sn−H bonds would react randomly with each other, the molar mass should increase with conversion according to that for simple polycondensation as proposed by Carothers;[43] i.e., high molar masses would be obtained only at very high monomer conversions. Evidently, this is not substantiated by the experimental findings, as shown in Figure 3; quite to the contrary, the highest molar masses were obtained at low Bu$_2$SnH$_2$ conversion. Accordingly, a polymerization mechanism analogous to that proposed for catalysts based on elements of the group IV in the periodic table[44,45] (Figure 5) can be excluded in the present case.

The development of molar mass with monomer conversion, however, is in agreement with polymerization proceeding by a catalytic active rhodium complex site at which the polymer grows, for instance, via formation of stannylene intermediates, which may arise from α-H elimination, similar to a mechanism suggested for the formation of polygermanes (Figure 5).[46]

At [RhCl(PPh$_3$)$_3$]/Bu$_2$SnH$_2$ ratios of 1.5, 2 and 3% mol/mol (also at 20 °C), the maximum monomer conversion was 77, 78 and 91%, respectively, indicating that [RhCl(PPh$_3$)$_3$] had finally reacted completely to catalytic inactive species. Accordingly, if each of the rhodium atoms had initiated one polystannane chain, the ratio of tin atoms in one polymer chain was at most 51, 39, and 30, respectively (i.e., if the Bu$_2$SnH$_2$ would have been converted exclusively to polymer). However, the average number of tin atoms in a polymer chain, estimated from M_p, is 4−5 times larger (i.e., 240, 167 and 119, respectively), and therefore, it appears that a considerable fraction of rhodium atoms was most likely never involved in the polymerization process. Thus, it cannot be excluded that each catalytically active rhodium atom initiates the growth of only one polymer chain. The reaction of [RhCl(PPh$_3$)$_3$] with Bu$_2$SnH$_2$ probably leads to several compounds of which only a part is catalytically active. Indeed, oxidative addition of Bu$_3$SnH to [RhCl(PPh$_3$)$_3$] proceeds at room temperature under release of PPh$_3$ and formation of [RhClH(SnBu$_3$)(PPh$_3$)$_2$][47] and analogous reactions may occur with Bu$_2$SnH$_2$. Therefore, the free PPh$_3$ which was present after addition of Bu$_2$SnH$_2$ to [RhCl(PPh$_3$)$_3$] (see above) could be a consequence of the formation of Rh−Sn complexes. Since Rh complexes with even five coordinated tin atoms are known,[48] the reaction of [RhCl(PPh$_3$)$_3$] with Bu$_2$SnH$_2$ can readily result in a number of different complexes.

Scheme 1. Reaction Scheme for the Preparation of the Monomer Precursors, the Monomers, and the Polystannanes[a]



[a] Key: (1) Grignard reaction of SnCl$_4$ with alkylmagnesuim halides; (2) comproportionation reaction of tetraalkylstannanes with SnCl$_4$; (3) reduction of dialkyldichlorostannanes with Li[AlH$_4$]; (4) catalytic dehydropolymerization of dialkylstannanes to polystannanes.

Upon a decrease in temperature from 20 to 10 °C, the time required for complete Bu$_2$SnH$_2$ conversion increased by a factor of ca. 50. Such an extreme sensitivity to temperature is uncommon. The molar mass of poly(dibutylstannane) obtained in this temperature range was little affected, indicating that the ratio between the polymer growth rate and the termination rate was only slightly temperature dependent; i.e., the lower monomer conversion is likely to be due to a decrease in the ratio of the formation of catalytic active and inactive species. Hence, it appears that the reaction rate of [RhCl(PPh$_3$)$_3$] to catalytic active species markedly decreases with decreasing temperature, and the extreme temperature dependency of the overall reaction suggests that the formation of the catalytic active species is a complex process which involves many reaction steps.

3.4. Other Poly(dialkylstannane)s. Monomers. In addition to Bu$_2$SnH$_2$, the compounds R$_2$SnH$_2$ with R = ethyl (Et), propyl (Pr), pentyl (Pe), hexyl (Hex), octyl (Oc), and dodecyl (Dod) were also employed as monomers. These compounds were prepared by reduction of the corresponding dialkyldichlorostannanes (R$_2$SnCl$_2$) with lithium aluminum hydride (Scheme 1, eq 3).[49−52] Dialkyldichlorostannanes that were not commercially available were synthesized according to Scheme 1 (eqs 1 and 2). First, tetraalkylstannanes (SnR$_4$) were prepared by the Grignard reaction[53] of SnCl$_4$ with alkylmagnesium halides in diethylether/hexane solutions (Scheme 1, eq 1);[54−62] after the reaction was initiated, half of the solvent was exchanged by toluene, thus allowing one to increase the reaction temperature, which is known to increase the yield of Grignard reactions.[63] The tetraalkylstannanes thus obtained were subsequently converted with stoichiometric quantities of $SnCl_4$ to the dialkyldichlorostannanes (Scheme 1, eq 2; erroneously referred to as Kocheshkov comproportionation reaction[64−68] as it was obviously overlooked that Buckton had already described this reaction type in 1859[6,69]). Nota bene: the Grignard method has been reported not to be suited for the direct synthesis of dialkyltindichlorides from $SnCl_4$.[70]

Polymerization. Polymerization of the above monomers was carried out with 4% mol/mol $[RhCl(PPh_3)_3]$/dialkylstannane ratio in dichloromethane at room temperature for 2 h. Only in the case of $(Dod)_2SnH_2$ this was not sufficient to convert the entire amount of dialkylstannane (only ca. 50% had reacted after 2 h); therefore the same amount of catalyst was added again for complete monomer conversion. The molar masses of the polymers, as analyzed by GPC, are collected in Table 1 (M_w and M_n between 2.7×10^4 to 9.7×10^4 and 1.0×10^4 to 4.0×10^4 g mol^{-1}, respectively). After conversion of the monomer, ^{119}Sn, ^{1}H, and ^{13}C NMR spectra of the reaction mixtures revealed only one type of dialkylstannane moiety (Table 3) with chemical shifts in ^{119}Sn NMR spectra that are characteristic for the linear polymers[14,15,30,41] (a deviation of ca. 20 ppm in the case of $(SnEt_2)_n$ is attributed to the limited length of the ethyl groups). Generally, signals of cyclic oligostannanes emerged only when solutions of the polymers were exposed to light.

Characterization. The polystannanes precipitated from the reaction mixtures by cooling to −78 °C (yields 65−90%, Table 1). The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of the collected products did not distinguish significantly from the spectra recorded in the reaction solutions. However, the molar masses of the isolated products invariably were found to be below the corresponding values determined in the reaction mixtures. For example, for a poly(dibutylstannane) sample M_n decreased from 3.6×10^4 to 2.1×10^4 g/mol and M_w from 9.1×10^4 to 5.9×10^4 g/mol, and for a poly(dioctylstannane) sample M_n changed from 4.0×10^4 to 2.8×10^4 g/mol and M_w from 9.7×10^4 to 7.1×10^4 g/mol, which may be due to disruption of Sn−Sn bonds in the polymer main chain during the isolation process or during redissolving.

In the solid state, all polymers were thermally quite stable. Thermogravimetric analysis (TGA) did not reveal significant evidence for decomposition below 200 °C under nitrogen as well as in air. The maximum rate of decomposition was detected in the range 280−300 °C in nitrogen atmosphere and 240−300 °C in air (Table 4). There was no systematic dependency of the thermal stability on the length of the alkyl groups. In most cases, the residual masses at 450 °C did not correspond to the tin content of the polymers. Lower residual masses are obviously due to the formation of volatile tin compounds, while higher masses might originate in the formation of tin carbides or, in the presence of air, tin oxides.

Differential scanning calorimetry (DSC) of the polystannanes in the temperature range between −50 and +120 °C revealed one thermally reversible phase transition for polymers with the shorter (up to butyl) and two for the longer alkyl groups (Figure 6a). In the following, the lower (or single) phase transition temperatures are designated T_1 and the higher phase transition temperatures (if existing) T_2. In repeated heating−cooling cycles, the transition temperatures in the first heating traces differed from the reversible transition temperatures in the further traces by a few degrees only. This is not uncommon and ascribed to differences in crystallite sizes when solids are obtained by precipitation (first heating trace) or by solidification of a melt (further traces). The phase transition temperatures obtained from melting-crystallization cycles are collected in Table 5. As commonly observed for polymeric species, the transition temperatures recorded upon heating were shifted to lower temperatures upon cooling (ca. 10−30 °C). Finally, the first crystallization enthalpies were significantly lower for the two poly(dialkylstannane)s with the shortest alkyl groups (ca. 2−3 J/g) than with the longer alkyl groups (ca. 10−15 J/g), and the enthalpies of the second phase transition (ca. 2−7 J/g, observed only for longer alkyl groups) were lower than those of the first transition. While T_2 increased with increasing length of the alkyl group there was no systematic trend in T_1. T_1 values of $(SnBu_2)_n$ (1 °C) and $(SnPe_2)_n$ (6 °C) were low and also the T_1 of $(SnEt_2)_n$ was below room temperature. By contrast, the T_1 of $(SnPr_2)_n$ was unexpectedly high (93 °C). Interestingly, $(SnPr_2)_n$ also showed a particularly high density, which for the different poly(dialkylstannane)s ranged from 1.16 to 1.58 g/cm at 25 °C (Table 1). It was expected that the densities decreased continuously with increasing length of the alkyl groups due to a decrease in content of the heavier element Sn. As noted, a conspicuous exception to this trend, however was $(SnPr_2)_n$, for which a density was measured that significantly exceeded that of $(SnEt_2)_n$. The unusually high values of both T_1 and density of $(SnPr_2)_n$ may originate in a favorable packing of propyl groups in this particular poly(dialkylstannane).

In order to investigate the phase transitions qualitatively with other methods, all polymers were examined in the optical microscope between crossed polarizers, and selected polystannanes also with X-ray diffraction. Films of all compounds were found to be birefringent below the first phase transition temperature. Since the polymers are sensitive to light, attention was paid when thin films were examined in the microscope at elevated temperature. Flushing with argon permitted observations at temperatures up to ca. 100 °C. No change in birefringence was evident upon heating above the first phase transition of thin films of $(SnEt_2)_n$, $(SnPr_2)_n$, $(SnBu_2)_n$, and $(SnPe_2)_n$, even at 100 °C. In the case of the $(SnHex_2)_n$ and $(SnDod_2)_n$, birefringence became significantly weaker above the first transition temperature, while for $(SnOc_2)_n$ it vanished above T_1. For $(SnHex_2)_n$ and $(SnDod_2)_n$, birefringence disappeared only above the second transition temperatures. Upon cooling of $(SnHex_2)_n$, $(SnOc_2)_n$, $(SnDod_2)_n$, the materials became notably birefringent only at the temperatures below the first phase transition (Table 5, Figure 6b). On the basis of the optical microscope images alone, one might conclude that all samples except $(SnOc_2)_n$ show still some order after the first phase transition. Remarkably, however, when samples of $(SnOc_2)_n$ were oriented by smearing with a spatula (as reported previously for $(SnBu_2)_n$),[15] and subsequently heated above the first phase transition temperature followed by cooling, the initial orientation evident from the birefringence did not change: only heating above T_2 lead to a loss in orientation, which was not recovered by cooling. The observed transition temperatures in $(SnHex_2)_n$, $(SnOc_2)_n$, and $(SnDod_2)_n$ are in general agreement with transition temperatures detected in DSC thermograms.

Figure 7a shows the small-angle X-ray scattering (SAXS) of poly(dibutylstannane) at temperatures below and above the first DSC endothermic transition, i.e., at −5 and +5 °C. At −5 °C, two peaks were observed, at 5 and 6 nm^{-1}, respectively, while at +5 °C only the peak at 6 nm^{-1} remained. The presence of two peaks, with the one at lower q less intense, and the persistent birefringence are consistent with a columnar rectangular phase at −5 °C, in which the scattered intensity maxima are observed at q values given by

$$q = 2\pi\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2}} \qquad (1)$$

where the Miller indices $(h,k) = (1,0)$ and $(0,1)$ yield the lattice parameters $a = 1.3$ nm and $b = 1.1$ nm, respectively. Similar rectangular structures have been indeed reported recently for dendronized comblike polymers with alkyl tails decorating the polymer backbone.[71] The calculated distance between two extended butyl chains connected to a Sn atom, with the standard bond lengths for Sn−C, C−C, and C−H of 220, 150, and 110 pm, respectively, and the standard bond angles at the carbon and tin atoms of 109° results in 1.3 nm. These data also suggest that polystannane backbones occupy the edges of the rectangular lattice, while the butyl tails fill the volume within the rectangular unit cell by adopting a bilayer-like structure. When the temperature is increased above T_1, the only remaining peak at 6 nm^{-1} indicates that the two-dimensional order is lost, although relatively sharp interfaces between the alkyl tails and polymer backbone are still present. Because the resulting phase is still birefringent, these data suggest the presence of a nematic phase above T_1, where polymer−alkyl tail interfaces are still preferentially aligned along the original columnar direction, but with a liquidlike two-dimensional order with a correlation length of 1.1 nm. Wide-angle X-ray scattering (WAXS) data at larger q indicate that the alkyl tails remain amorphous within the considered temperature range and the corresponding endothermic peak observed by DSC at 0 °C can then be attributed to a transition from a columnar rectangular to a nematic phase, which remained stable up to degradation. Figure 7b, depicts this transition from a columnar rectangular phase to a nematic structure.

Figure 7c shows X-ray patterns of poly(dioctylstannane) at −15, +10 ($<T_1$), and 40 °C ($>T_1$). At −15 °C, a sharp peak and two very weak peaks spaced as $q_1{:}q_2{:}q_3 = \sqrt{1}{:}\sqrt{4}{:}\sqrt{9}$ were identifiable, consistent with the presence of a lamellar phase with a period of 2.2 nm. Indeed, the second and third reflections (q_2,q_3), although very weak, appear systematically. At 10 °C, the diffractogram closely resembled to that measured at −15 °C, whereas the first reflection is sharp and the second and third weak but still noticeable. However, at 40 °C, the first peak became weaker, much broader and shifted to larger q, while the second and third reflections disappeared completely. These findings indicate a transition to an isotropic polymer fluid with an interchain distance of 1.7 nm, as also supported by the complete loss of birefringence at and beyond this temperature. The increase from 1.1 to 2.2 nm in the correlation length of the interfaces in the liquid-crystalline phases from poly(dibutylstannane) to poly(dioctylstannane) is consistent with the calculation of an extended $SnOc_2$ distance of 2.3 nm, which suggests that the lamellar phase is of the smectic A type—that is with the alkyl tails orthogonal to lamellar planes. Again, WAXS data indicate the alkyl tail to be present in the amorphous state, which allows the attribution of the corresponding endothermic transition in DSC to a first-order smectic−isotropic transition, as sketched in Figure 7d.

Figure 7e, finally, shows the diffractograms for poly(didodecylstannane) at different temperatures. At 20 °C ($<T_1$), the polymer is organized into a well-ordered lamellar phase of a periodicity of 3.3 nm (up to five pronounced reflections, labeled as $q_1{:}q_2{:}q_3{:}q_4{:}q_5$, $\sqrt{1}{:}\sqrt{4}{:}\sqrt{9}{:}\sqrt{16}{:}\sqrt{25}$, can be distinguished). Also in this case, the period increases consistently and fits with the calculation of an extended $SnDod_2$ length of 3.3 nm, indicating that the alkyl tails could be organized as a bilayer and adopted a smectic A arrangement. When the temperature was increased to 40 °C, the higher order reflections of the lamellar phase decreased in intensity and a shoulder appeared at 3 nm^{-1}, indicating that liquid crystalline order decreased. At 70 °C, i.e., well above T_1, all the high order peaks from q_2 upward disappeared and the first-order peak was present together with a broad amorphous liquidlike peak. Finally at 100 °C ($>T_2$) the diffractogram is typical for an isotropic polymer fluid with 2.1 nm interchain distance. The gradual appearance of a broad isotropic peak and disappearance of the lamellar phase are consistent with the progressive loss of the birefringence above the temperature T_1. At the same time, the endothermic enthalpy measured by DSC for T_1 can be attributed to the lamellar-isotropic order−disorder transition, although in the DSC thermograms this transition appears to occur in a sharper way than what revealed by SAXS. Figure 7f depicts the lamellar−isotropic transition and the changes in typical length scales as measured by SAXS.

4. Conclusions

Among a variety of complexes, the compound $[RhCl(PPh_3)_3]$ was found to be particularly suited as a catalyst (precursor) for the polymerization of dialkylstannanes with the alkyl groups ranging from ethyl to dodecyl. In all cases, only linear polymers were obtained, i.e., detectable amounts of cyclic oligomers were absent, independent of the reaction conditions examined (temperature, solvent, dialkylstannane concentration, $[RhCl(PPh_3)_3]/R_2SnH_2$ ratio). However, the influence of the temperature on the polymerization reaction itself was particularly pronounced. While at room temperature invariably monomer conversion of 100% was achieved, already at slightly lower temperatures the conversion, as well as the reaction rate considerably decreased. Further, polymerization was less efficient at low $[RhCl(PPh_3)_3]/R_2SnH_2$ ratios. Finally, also the nature of the solvent in which the reaction was conducted affected the monomer conversion (tetrahydrofuran less suited than dichloromethane, benzene or toluene).

The number-average molar masses of the polymers generally were in the range of 1×10^4 to 1×10^5 g/mol, depending on the reaction conditions and the alkyl substituents. Polystannanes of the highest molar masses were obtained under conditions where the monomer was not fully converted to polymer, or when the catalyst was added slowly to the reaction solution; in which case also 100% monomer conversion was observed. The reaction temperature, on the other hand, did not have a pronounced influence on the molar mass of the resulting polymer. The molar mass of poly(dibutylstannane) formed at low monomer conversion appeared to be somewhat higher than that at high monomer conversion. This finding is not compatible with random condensation of Sn−H groups, but is consistent with polymer growth at a catalytic active rhodium species. In our studies we concluded that $[RhCl(PPh_3)_3]$ itself is not active, but is converted by reaction with dialkylstannanes into a catalytic species. Since a relatively high $[RhCl(PPh_3)_3]/R_2SnH_2$ ratio (3−4% mol/mol) was required to obtain 100% monomer conversion, it appears that most of the $[RhCl(PPh_3)_3]$ molecules reacted to catalytically inactive compounds.

The poly(dialkylstannane)s were isolated by precipitation in yields of 65−90%. The polymers featured a phase transition from a solid to a soft, ordered state. This transition occurred at relatively low temperatures (0−15 °C) in the case of $(SnEt_2)_n$, $(SnBu_2)_n$, and $(SnPe_2)_n$ and at a remarkably high temperature for $(SnPr_2)_n$ (91 °C). The latter polymer was also characterized by a particularly high density, possibly due to a particularly favored packing of the alkyl groups. In addition, the polymers with pentyl or longer alkyl groups exhibited a second phase transition at higher temperature. For $(SnBu_2)_n$ the endothermic transition around 0 °C was attributed to the transition from a liquid-crystalline columnar rectangular to a liquid-crystalline nematic phase. For $(SnOc_2)_n$ and $(SnDod_2)_n$, however the first transitions at T_1 were identified as transitions between lamellar smectic phases to isotropic phases and that at T_2 to an isotropic polymer melt.

Acknowledgment. We thank Drs. Niklaus Bühler and Andreas Mühlebach both from Ciba Specialty Chemicals for fruitful discussions. Ciba Specialty Chemicals (Basel, Switzerland) is gratefully acknowledged for financial support.

Supporting Information Available: Text giving experimental detail regarding the preparation of the monomeric precursors and tables giving synthesis parameters, NMR data, and elemental analysis data for the precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA071463T