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ARTICLE

Multihydroxy-Functional Polysilanes via an Acetal Protecting Group Strategy

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ABSTRACT: A new acetal-protected monomer for Wurtz-type coupling to polysilanes, dichloro(3-(2,2-dimethyl-1,3-dioxolane-4-yloxy)propyl)methylsilane, referred to as dichloro(isopropylidene glyceryl propyl ether)methylsilane (DCIMS), has been introduced to synthesize a series of protected linear polysilane copolymers, poly[di-*n*-hexylsilane-*co*-(isopropylidene glyceryl propyl ether)methylsilane] (P(DHS-*co*-IMS)) via alkali-mediated reductive Wurtz-type coupling. The acetal protecting group proved stable under the harsh polymerization conditions. Differential scanning calorimetry combined with ^{1}H, ^{13}C, and ^{29}Si NMR measurements confirmed composition and random structure of the obtained copolymers. After separation of the cylic fraction, this route yielded defined linear polysilane copolymers with monomodal molecular weight distributions (2000−98700 g mol^{-1} (SEC)) and polydispersities in the range 1.61−2.60. Subsequent cleavage of the acetal protecting groups under acidic conditions resulted in the multihydroxy-functional polysilanes poly[di-*n*-hexylsilane-*co*-(glyceryl propyl ether)methylsilane] (P(DHS-*co*-GMS)).

Introduction

Polysilanes,[1−3] sometimes called polysilylenes, consist of a one-dimensional silicon backbone with organic substituents and exhibit extraordinary electronic and photophysical properties such as UV absorption,[2] thermochromism,[4] solvatochromism,[5] and electroluminescence,[4] caused by the delocalization of the σ-electrons along the Si-chain. Because of these unique characteristics, polysilanes have attracted broad attention in academia and industry in the last 2 decades. They can be used as functional materials in semiconductors, radical photoinitiators, precursors for silicon carbide syntheses, and sensors.[6] Variation of substituents and copolymerization of different dichlorodiorganosilanes $SiCl_2R_2$ offers countless possibilities for tailoring chemical and physical properties, e.g., solubility, morphology, and optical characteristics.[7−9] Optically active polysilanes have been obtained by polymerizing monomers with enantiopure chiral side groups,[10] which, among other things, can be used for chiroptical switching and memory systems for data storage.[11] Functional polysilanes have rarely been described, since the main synthetic route to polysilanes via sodium-mediated reductive Wurtz coupling of $SiCl_2R_2$ is inherently intolerant toward functional groups.[12] Oftentimes, post-polymerization functionalization sequences have to be employed.

In consequence, only few functional polyorganosilanes are known to date. For example, trimethylammonium moieties bound to phenethyl substituents have been reported by Seki et al.[13] Aromatic hydroxyl functionalities at polysilanes have been introduced by way of trimethoxysilane protected phenols by Horiguchi et al.[14] Möller and co-workers[15] employed polymer modification reactions including hydrosilylation with unsaturated polysilane substituents to generate aliphatic hydroxyl substituents.

Ether moieties are known to be stable under the harsh polymerization conditions of the Wurtz coupling reaction.[16−21] Thus, ether-substituted polysilanes can be obtained from the corresponding dichlorosilane monomers directly. However, it is crucial that the position of the ether moiety is chosen at least three methylene units away from the silicon backbone to avoid possible β-elimination of the electron-withdrawing group during polymerization.[21] The obtained polymers show enhanced solubility in polar solvents such as alcohols and ethers. These mostly viscous substances do not exhibit the typical bulk properties of poly(di-*n*-alkylsilanes), namely crystallization and formation of a columnar mesophase. For instance, poly(di-*n*-hexylsilane) (PDHS), soluble in nonpolar organic solvents only, approximates a trans-planar conformation of the backbone at room temperature.[22] At 45 °C, a transition to a liquid-crystalline, hexagonal columnar mesophase (hcm) with conformational disorder of the side chains takes place, which can be followed by calorimetric measurements (DSC) or UV spectroscopy as well as many other techniques.

The preparation of polar polysilanes containing randomly distributed OH groups at the backbone has remained a challenge to date, mostly because of the inherently sensitive chemistry entailed by the synthetic approaches. Such materials could provide fascinating potential in the field of polysilane-based networks or hydrogels with unusual electrooptical properties. Multiple hydroxyl moieties attached to the linear polymer chain should also provide intriguing possibilities for further functionalization sequences and the synthesis of complex macromolecular architectures.

Here we present the synthesis and characterization of multihydroxy-functional polysilane copolymers (Scheme 1). To the best of our knowledge, the employed sequential acetal protecting group strategy has not been used in polysilane synthesis to date. The protected substituents of a new monomer, dichloro-(3-(2,2-dimethyl-1,3-dioxolane-4-yloxy)propyl)methylsilane, which will be referred to as dichloro(isopropylidene glyceryl propyl ether)methylsilane (DCIMS) for reasons of simplicity and clarity, release the desired functional groups upon deprotection, thus offering numerous pathways to entirely new polysilane-based materials.

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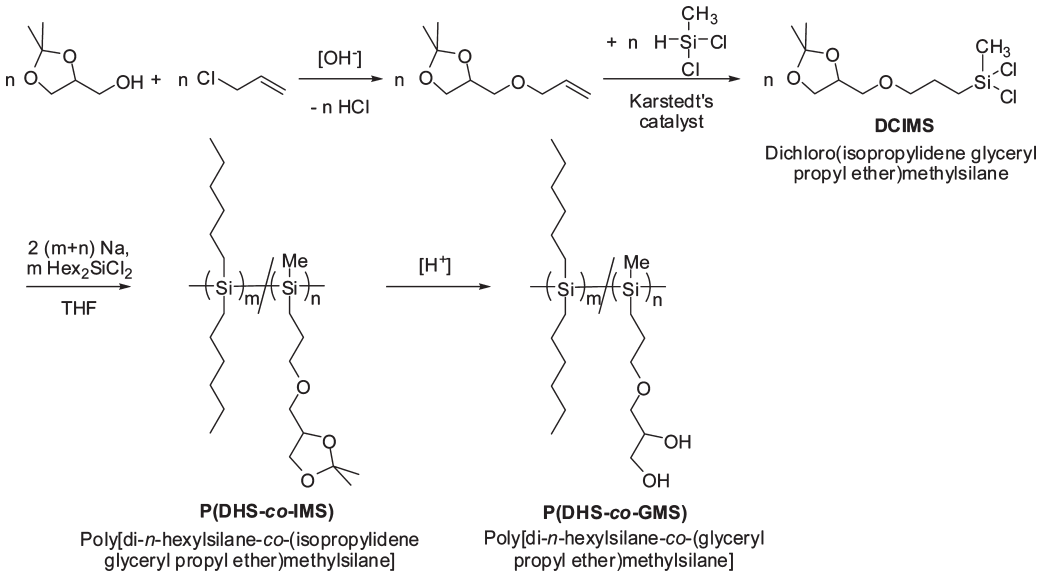
Scheme 1. Synthesis of P(DHS-*co*-IMS) and P(DHS-*co*-GMS) Copolymers



Experimental Section

Instrumentation. ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC 300. All spectra were referenced internally to residual proton signals of the deuterated solvent. ^{29}Si NMR spectra (79.5 MHz) were obtained on a Bruker AMX 400. Size exclusion chromatography (SEC) measurements were performed on a setup consisting of a Waters 717 plus Autosampler, a TSP Spectra Series P 100 pump, and three PSS-HEMA-5 μL-columns with 100, 1000, and 10000 Å pore diameter, respectively. THF was used as an eluent at 30 °C and at a flow rate of 1 mL/min. UV absorptions were detected by a SpectraSYSTEM UV2000. The specific refractive index increment (dn/dc) was measured at 30 °C, using an Optilab DSP interferometric refractometer (also RI detector) and determined with the Wyatt ASTRA IV software (Version 4.90.08). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service. DSC measurements were carried out using a Perkin-Elmer DSC 7 with a Perkin-Elmer thermal analysis controller TAC7/DX in the temperature range of −100 to +100 °C using heating rates of 40 and 20 K/min for the copolymer samples and 40 and 5 K/min for the PDHS sample. The melting points of indium (T_m = 156.6 °C) and Millipore water (T_m = 0 °C) were used for calibration. Polarized light microscopy was carried out using a Leitz Ortholux II POL-BK microscope with crossed polarizers. Sodium dispersions were prepared using an EuroTurrax T20b homogenizer purchased from IKA Labortechnik.

Materials. All reagents and solvents were purchased from Acros Organics or Sigma-Aldrich and used without further purification unless otherwise stated. Solvents for the polymerizations (THF, xylene) were purified according to literature procedures.[23] Dry chlorobenzene over molecular sieves was purchased from Fluka. Karstedt's catalyst, platinum(0)-divinyltetramethyldisiloxane complex (in xylene, 2.1−2.4% Pt), and dichlorodi-*n*-hexylsilane (DCDHS) were obtained from ABCR GmbH & Co. KG. DCDHS was purified by fractionating distillation prior to use. Allyl solketyl ether was prepared according to the literature.[24] Deuterated solvents were purchased from Deutero GmbH and stored over molecular sieves (3 Å).

Monomer Preparation: Dichloro(isopropylidene glyceryl propyl ether)methylsilane (DCIMS). The synthesis was carried out under argon atmosphere. Allyl solketyl ether (2.60 g, 15.1 mmol, 1 equiv) was placed in a Schlenk flask. Chlorobenzene (3.5 mL), 90 μL of Karstedt's catalyst solution, and 3.5 mL of dichloromethylsilane (33.5 mmol, 2.2 equiv) were added via syringe. After stirring at room temperature overnight, excess dichloromethylsilane and chlorobenzene were removed under reduced pressure. Fractional distillation (105 °C/0.001 mbar) yielded 2.36 g (54%) of colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 4.28 (quintuplet, 1 H, ^{3}J = 9 Hz, CH), 4.07 (dd, 1 H, J_{AB} = 9 Hz, ^{3}J = 6 Hz, CH−CH'H″−O−C$(CH_3)_2$), 3.74 (dd, 1 H, J_{AB} = 9 Hz, ^{3}J = 6 Hz, CH−CH′H″−O−C$(CH_3)_2$), 3.56−3.42 (m, 4 H, CH_2−O−CH_2), 1.85−1.75 (m, 2 H, Si−CH_2−CH_2), 1.43 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.20−1.14 (m, 2 H, Si−CH_2), 0.79 (s, 3 H, Si−CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ [ppm] = 109.37 (s, $C(CH_3)_2$), 74.65 (s, CH), 72.64 (s, Si−$(CH_2)_2$−CH_2), 71.80 (s, CH_2−O−CH_2−CH), 66.73 (s, CH−CH_2−O−C$(CH_3)_2$), 26.70 (s, CH_3), 25.36 (s, CH_3), 22.63 (s, Si−CH_2−CH_2), 18.00 (s, Si−CH_2), 5.11 (s, Si−CH_3).

General Procedures for the Copolymerization of DCIMS and DCDHS. In a glovebox, 0.828 g (36 mmol, 2 equiv) sodium and 20 mL xylene were placed in a Schlenk flask, transferred to the vacuum line, and heated to 135 °C. The mixture was transformed into a fine dispersion using a preheated homogenizer (EuroTurrax T20b, IKA Labortechnik). After evaporation of xylene in high vacuum, 20 mL of THF and 0.018 mol of dichlorodiorganosilane were added via syringe. The mixture turned purple after 30 min and was stirred vigorously for 22 h at room temperature. The reaction was then quenched with 120 mL of methanol. The precipitated polymer was filtered, washed with water and methanol, and dried in high vacuum. The cyclic fraction was separated via fractional precipitation from THF/2-propanol. Yields: 21−50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 4.35−4.15 (CH), 4.15−3.95 (CH-CH'H″−O−C$(CH_3)_2$), 3.85−3.65 (CH−CH′H″−O−C$(CH_3)_2$), 3.65−3.20 (CH_2−O−CH_2), 1.80−1.55 (CH_3−Si−CH_2−CH_2), 1.55−0.50 (C$(CH_3)_2$, Si−$(CH_2)_4$−CH_3, and CH_3−Si−CH_2), 0.40−0.25 (Si−CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ [ppm] = 109.13 ($C(CH_3)_2$), 74.54 (CH), 71.94 (Si−$(CH_2)_2$−CH_2−O), 67.80 (O-CH_2−CH), 67.02 (CH−CH_2−O−C$(CH_3)_2$), 34.28 (Si−$(CH_2)_2$−CH_2−Pr), 31.72 (Si−$(CH_2)_3$−CH_2−Et), 27.42 (Si−CH_2−CH_2−Bu), 26.66 (C($C'H_3$)), 25.49 (Si−CH_2−CH_2−CH_2−O), 25.28 (C($C''H_3$)), 22.74 (Si−$(CH_2)_4$−CH_2−Me), 14.95 (Si−CH_2−$(CH_2)_2$−O), 14.00 (Si−$(CH_2)_5$−CH_3), 10.41 (Si-CH_2−CH_2−Bu), −3.34 (Si−CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ [ppm] = −24.5 to −27.0 (Hex_2Si), −29.5 to −32.5 (MeSiR).

Cleavage of Acetal Protecting Groups. In a round-bottom flask, 400 mg P(DHS-*co*-IMS) were dissolved in 400 mL THF (dest.). Subsequently, 12 mL of trifluoroacetic acid and 8 mL of water were added. After refluxing for 72 h, the solution was neutralized with saturated K_2CO_3 solution and filtered. The volatiles were removed under reduced pressure. The residue was

dispersed in chloroform, filtered, and the solvent removed under reduced pressure. Yields: ≥95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.95−3.80 (C*H*−OH), 3.75− 3.65 (CH−C*H*′H″−OH), 3.65−3.55 (O−C*H*′H″−CH), 3.55−3.25 (CH−CH′*H*″−OH, O−CH′*H*″−CH, and Si−$(CH_2)_2$−CH_2−O), 1.85−1.55 (CH_3−Si−CH_2−CH_2), 1.55−0.60 (Si−$(CH_2)_4$−CH_3, and CH_3−Si−CH_2), 0.45−0.25 (Si−CH_3).

Results and Discussion

Monomer Synthesis. In order to obtain multihydroxy-functional polysilanes, a monomer containing a protected hydroxyl group had to be designed that both withstands the conditions of the polysilane formation in the Wurtz-type coupling reaction and can be deprotected easily subsequent to polymer synthesis. The accordingly developed synthetic strategy affording the new acetal protected monomer dichloro(isopropylidene glyceryl propyl ether)methylsilane (DCIMS) for Wurtz-type polymerization is shown in Scheme 1. The isopropylidene acetal group is stable toward most reaction conditions except for protic media and Lewis acids. Therefore, it serves as an ideal candidate for survival of the reductive conditions during polysilane formation and subsequent acidic cleavage to release the desired hydroxyl functionalities and acetone.

Starting from allyl chloride and solketal ((2,2-dimethyl-1,3-dioxolane-4-yl)methanol), the monomer was synthesized in two steps. First, the corresponding allyl solketyl ether was obtained by Williamson ether synthesis, followed by a hydrosilylation reaction with dichloromethylsilane in presence of Karstedt's catalyst, platinum(0)-divinyltetramethyldisiloxane, resulting in the desired acetal protected silane with a yield of 54% after optimization of reaction conditions. The hydrosilylation product was purified by fractional distillation, which was difficult due to the formation of side products at elevated temperatures (≥140 °C), indicated by a color change to dark yellow or brown, diminishing yield and purity of the obtained monomer. This phenomenon is well-known in silane chemistry and has already been reported for dichlorosilane monomers containing ether linkages.[17,21] This detrimental behavior has been proposed to be caused by inter- and intramolecular reactions of the polar Si−Cl bonds with the oxygen atoms in the substituents, leading to thermodynamically favored Si−O bonds as well as C−Cl compounds. Only freshly distilled DCIMS was used for all further reactions and characterization due to the limited shelf life of the monomer. After 2 days storage under argon at 6 °C, the liquid turned dark yellow to brown, indicating the side reactions described above taking place. An NMR spectrum of the new monomer is shown in Figure 1 and detailed in the Supporting Information.

Polymer Synthesis. The dichlorosilanes were polymerized using a dispersion of sodium in THF at room temperature. This approach was chosen because of the superior yields compared to classical Wurtz coupling polymerization with molten sodium in refluxing toluene[15] (Table 1). The dispersion was prepared in analogy to the method described by Jones and co-workers,[25] replacing toluene with xylene because of the higher boiling point of this solvent. This prevents solidification of sodium contacting the inserted homogenizer, which is externally preheated to approximately 200 °C for this reason. Furthermore, this change of solvent obviously reduces the danger of solvent vapor ignition.

Polymer Characterization. The polysilanes were obtained as colorless, crystalline to amorphous, highly viscous compounds. The characterization data of the obtained P(DHS-*co*-IMS) copolymers and the respective homopolymers are listed in Table 1. The corresponding SEC elugrams can be seen in Figure 2, showing monomodal distributions with polydispersities in the range 1.61−2.60, which represent typical values for polysilane structures. Molecular weights were in the range 2000−98700 *g* mol^{-1}.

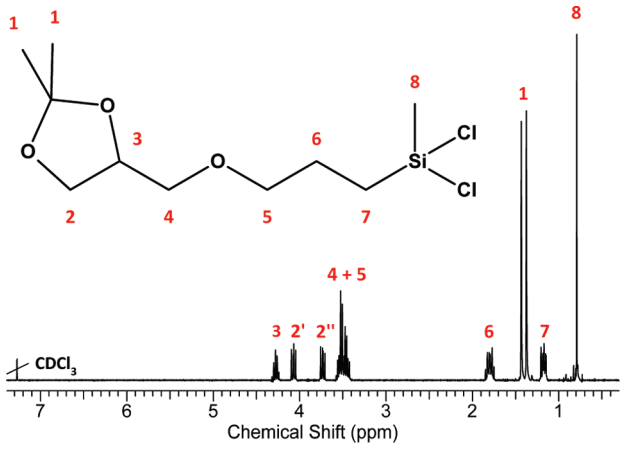


Figure 1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of dichloro(isopropylidene glyceryl propyl ether)methylsilane (DCIMS) and peak assignment.

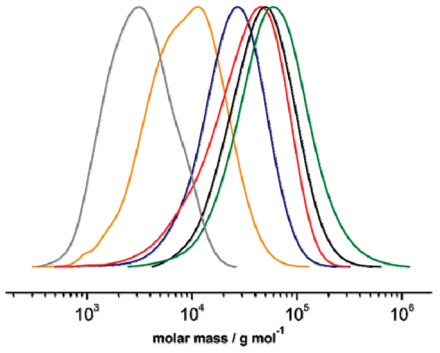


Figure 2. SEC elugrams of the polysilane copolymer series (THF, PS standards): PDHS (red); P(DHS-*co*-IMS) (6%, green; 11%, blue; 17%, black; 40%, yellow); PIMS (gray).

Table 1. Characterization Data for Polysilane Homo- and Copolymers

polymer	solvent	content[a]/ %	M_w[b]/ g mol^{-1}	PDI[b]	yield[c]/ %
PDHS	toluene	0 (0)	98 700	2.60	17
	THF	0 (0)	60 700	2.34	58
P(DHS-*co*-IMS)	toluene	7 (10)	51 900	2.09	1
	THF	6 (10)	63 100	2.00	47
		11 (20)	30 700	1.60	24
		17 (30)	57 900	1.72	21
		40 (50)	11 700	1.93	34
PIMS	THF	100 (100)	2000	1.30	50[d]
	[e]	100 (100)	4000	1.61	10

[a] DCIMS content determined via ^{1}H NMR spectroscopy after separation of the cyclic fraction by fractionating precipitation. The value in parentheses denotes the DCIMS fraction in the monomer feed. [b] Determined by SEC in THF, polystyrene standards, RI detection. [c] After separation of the cyclic fraction by fractionating precipitation. [d] Separation of the cyclic from the linear fraction not possible due to similar molecular weights. [e] Polymer synthesis was carried out using C_8K in THF at room temperature.[26]

With increasing DCIMS fraction, the preparation of copolymers with high molecular weight became increasingly difficult. This might be due to an alteration of the solution equilibrium at the sodium surface by the polar substituents, similar to the previously reported effect observed after adding ethylene glycol (glyme) or diethylene glycol dimethyl

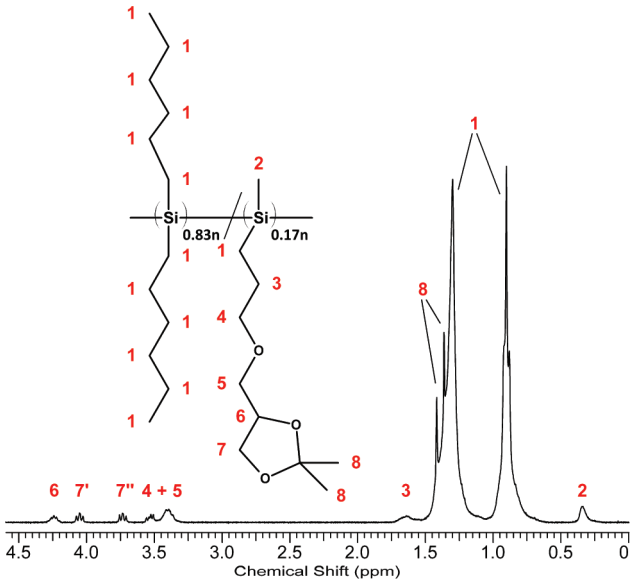


Figure 3. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of P(DHS-*co*-IMS) (17% IMS content) and peak assignment.

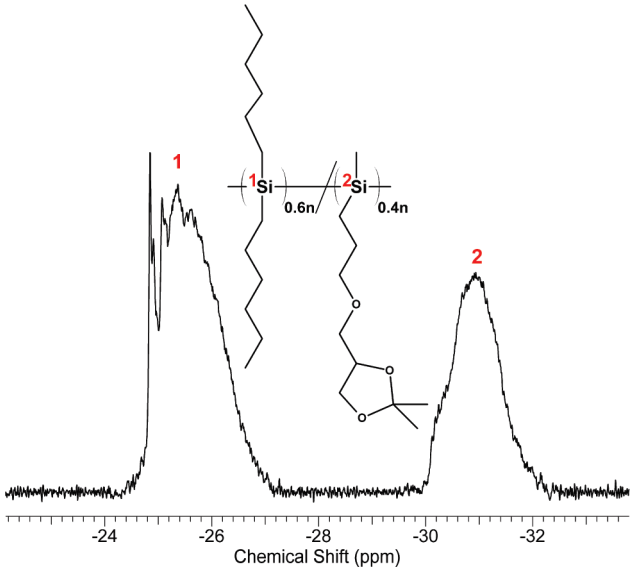


Figure 4. Inverse gated ^{29}Si NMR spectrum ($CDCl_3$, 79.5 MHz) of P(DHS-*co*-IMS) (40% IMS content) and peak assignment.

ether (diglyme) to the heterogeneous reaction mixture of a poly(dialkylsilane) synthesis, resulting in a rapid reduction of molecular weight of the product.[27]

The assignment of the ^{1}H and ^{13}C NMR signals of the protected polysilane copolymers P(DHS-*co*-IMS) was performed in analogy to the monomer spectra, taking the upfield shift of the units directly bound to the silicon backbone induced by the removal of the electron-withdrawing chlorine atoms into account, see Figure 3 and the Supporting Information.

^{29}Si NMR spectroscopy is a powerful tool for the determination of the microstructure of polysilane copolymers with respect to the distribution of comonomer units in the backbone. The spectrum of a copolymer with 40% DCIMS content is exemplarily shown in Figure 4. Two broad signals at −24.5 to −27 ppm and −30 to −32.5 ppm can be seen. Only a small sharp signal at −24.85 ppm is visible, induced by longer runs of directly connected di-*n*-hexylsilane repeating units. The intensity of this signal decreases with increasing comonomer content (5% for the observed polymer). The asymmetry of the (isopropylidene glyceryl propyl ether)methylsilane building blocks adjacent to the other di-*n*-hexylsilane units generates the broad signal at −24.5 to −27 ppm, which possesses a considerably higher intensity than the sharp signal of the homoruns. This indicates a predominantly random composition of the P(DHS-*co*-IMS) copolymers interrupted by few di-*n*-hexylsilane homosequences only. The observed broad resonance around −31 ppm supports this conclusion, since it can be assigned to the IMS units. The chemical shift of the silicon atoms incorporated in polysilanes is influenced by the chain conformation and therefore by steric effects of the substituents. If a large steric constraint is imposed on the Si atom, a downfield shift can be observed.[28] According to the ^{29}Si NMR spectrum, repeat units emerging from DCIMS are sterically less demanding than di-*n*-hexylsilane units, presumably due to the monosubstitution of the DCIMS with the bulky side chain. Surprisingly, the sterically less demanding monomer DCIMS seems to be present at a higher percentage in the cyclic than in the linear fraction, comparing ^{1}H NMR spectra of the samples before and after work-up. The remaining difference between monomer feed ratio and incorporation ratio, existent even before separation of the cyclic oligomers, can be explained by slow decomposition of DCIMS monomer during the extended reaction time (22 h) by the side reactions discussed above.

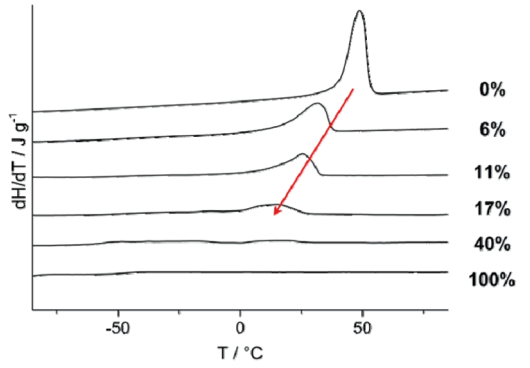


Figure 5. DSC traces of the second heating run for P(DHS-*co*-IMS) copolymers with IMS fractions from 0 to 100%, as denoted to the right of each trace. The arrow indicates the decrease of the transition temperature to the conformationally disordered mesophase with increasing fraction of IMS.

Polysilanes with symmetric alkyl side chain substitution pattern have long been known to exhibit unusual mesomorphic behavior, forming conformationally disordered mesophases with hexagonal columnar order. Thus, it was an intriguing issue in the context of this work to investigate the thermal properties of the obtained P(DHS-*co*-IMS) copolymers with IMS fractions ranging from 0 to 100%, using differential scanning calorimetry (DSC). The main differences in properties could be seen with the naked eye, the PDHS being a crystalline powder, while incorporation of IMS generally led to a colorless, viscous material. The corresponding DSC traces of the copolymers with varying fractions of IMS are depicted in Figure 5, and the corresponding calorimetric data are listed in Table 2. While pure PDHS shows the typical endothermic phase transition from crystalline to a liquid-crystalline hexagonal columnar mesophase at 45 °C,[22] a gradual decrease of the transition temperature as well as transition enthalpy is observed for the P(DHS-*co*-IMS) copolymers. This is caused by the comonomer-induced irregularities and consequent disturbance of the crystalline order in comparison to PDHS. The gradual character of the decrease of both transition temperature and enthalpy with increasing comonomer fraction represents another confirmation for the existence of random P(DHS-*co*-IMS) copolymers. To exclude the possibility of PDHS homopolymer fractions in the copolymer samples

Table 2. Calorimetric Data for Polysilane Homo- and Copolymers (DSC)

polymer	fraction[a]/%	T_g/°C	T_p[b]/°C	ΔH[c]/J g^{-1}
PDHS	0		45	92
P(DHS-*co*-IMS)	7	−46	31	54
	11	−48	26	32
	17	−47	15	16
	40	−58		
P(DHS-*co*-GMS)	17	−46	29	17
PIMS	100	−48		

[a] DCIMS fraction determined via ^{1}H NMR spectroscopy after separation of the cyclic fraction by fractional precipitation. [b] Peak temperature of the endothermic transition observed in the second heating run of the DSC measurements. [c] Enthalpy of the endothermic transition determined via DSC (second heating run). The determination of the exact enthalpy is impeded by the broadness of the phase transition.

causing an error in DSC characterization, 50 wt % mixtures of PDHS and P(DHS-*co*-IMS) with 17 and 40% IMS fraction, respectively, were also measured. The DSC traces showed the combined thermal behavior of both components and immiscibility due to crystallization, indicating once more absence of PDHS homopolymer in the copolymer samples.

Remarkably, copolymers with IMS fractions up to 17% are still capable of forming mesophases above the respective transition temperature. The anisotropic character was confirmed by polarized light microscopy using crossed polarizers, demonstrating birefringence above the disordering temperature. The observed phase transition is fully reversible, showing the expected hysteresis of the transition temperatures due to kinetically controlled nucleation. Furthermore, a glass transition temperature of approximately −48 °C was observed after incorporation of DCIMS monomer in a polysilane sample, indicating an increasing amorphous fraction. In line with expectation, P(DHS-*co*-IMS) samples with more than 40% IMS fraction were not able to form a mesophase and were obtained as amorphous isotropic materials above the glass transition temperature, as confirmed by polarized light microscopy. The thermal behavior of the materials after deprotection will be discussed below.

Cleavage of Acetal Protecting Groups. The deprotection is exemplified here for the copolymer containing 17% DCIMS. Since the polysilane backbone has been described as acid-sensitive,[29] mild conditions were initially employed to cleave the acetal protecting groups of the polysilane copolymers while avoiding degradation of the polysilane chain. Systems consisting of 1 M HCl, concentrated HCl, BCl_3, and the acidic ion-exchanger Dowex 50WX8 did not prove successful. Release of the hydroxyl groups was eventually achieved by refluxing the respective copolymer in THF and water with trifluoroacetic acid for 72 h. The difficulties in deprotection may be explained by the pronounced shielding effect of the nonpolar, superiorly soluble *n*-hexyl substituents. The cleavage of 90% of the protecting groups was proven by ^{1}H NMR spectroscopy by the disappearance of the respective methyl protons (see Supporting Information). SEC analysis yielded a shift in molecular weight from M_w(protected) = 57900 g mol^{-1} to M_w(deprotected) = 45000 g mol^{-1}, a value smaller than the estimated M_w based on the loss of the protecting groups. This is tentatively explained by the interactions between the released hydroxyl groups and the polar SEC column material, causing a slower elution of the deprotected polymer and a smaller apparent molecular weight. No degradation of the polysilane main chain took place, confirmed by virtually unaltered polydispersities (1.72 and 1.73, respectively). The obtained glycerol-functional polysilanes show remarkable stability versus acids and solubility in polar solvents, such as 2-propanol, which cannot be used for precipitation any more.

Concerning the thermal properties of the deprotected compounds, it had been expected that the phase transition temperature to the mesophase would be at comparable or lowered temperatures upon deprotection due to the hydroxyl moieties, which are immiscible with the nonpolar surroundings, thereby destabilizing the crystalline packing. Comparing the DSC traces of the polymer before and after deprotection, it can be noted that the glass transition temperature T_g remains almost constant, while the phase transition temperature to the thermotropic mesophase increases by 14 K to 29 °C. This leads to the conclusion that the stability of the crystalline order has been increased by release of the hydroxyl moieties. Shortening of the substituents and loss of sterically demanding cyclic units after deprotection may disturb the packing of the chains less than in the case of the protected comonomer. Furthermore, formation of hydrogen bonds between the hydroxyl moieties and the subsequent order stabilizing effect through noncovalent interactions may have a similar influence.

Conclusions

The synthesis of a novel functional dichlorosilane monomer, dichloro(isopropylidene glyceryl propyl ether)methylsilane, and its subsequent copolymerization with dichlorodi-*n*-hexylsilane, yielding linear, functional polysilanes of moderate polydispersity has been accomplished. The random character of the copolymer series has been confirmed using NMR spectroscopy and is also reflected by the thermal properties observed by DSC measurements. The acetal protecting group strategy has been successfully employed to obtain a series of polysilane copolymers bearing hydroxyl moieties. This pathway provides versatile access to new multifunctional polysilanes and unusual polysilane-based structures, such as hydrogels and polysilane nanoparticles. Work in this direction is currently in progress.

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Supporting Information Available: Figures showing polymer samples, NMR spectra and signal assignment, and additional DSC traces and an equation showing the calculation of the IMS content. This material is available free of charge via the Internet at http://pubs.acs.org.

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