Synthesis and Properties of Poly[bis(γ-ethoxypropyl)silylene]

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ABSTRACT: Bis(γ-ethoxypropyl)dichlorosilane was synthesized by hydrosilylation of dichlorosilane. Polymerization yielded monomodal high molecular weight poly[bis(γ-ethoxypropyl)silylene] (PDEPS). PDEPS is soluble in alcohols with longer alkyl groups and acetone. Bulk PDEPS exhibits a blue shift of λ_{max} from 362 to 315 nm correlated with the mesomorphic transition occurring at 25 °C. Above 25 °C, PDEPS transforms into a highly mobile columnarlike mesophase. Transition enthalpy, wavelength of the absorption maximum, and ^{29}Si MAS CP solid-state NMR indicate that PDEPS crystallizes in a disturbed all-trans-like structure. In addition to PDEPS, some copolymers with di-*n*-hexyl-substituted units were studied.

Introduction

The research interest in polysilylenes (polysilanes) is stimulated by their peculiar optical and charge transport properties.[1] Polysilylenes are σ-conjugated, Si-catenated polymers (i.e., 1D silicon), with promising potential for electrophotography,[2] nonlinear optics,[3] data storage,[4] and microlithography.[1]

Symmetrically *n*-alkyl-substituted polysilylenes with side chains consisting of at least two methylene units[11] are crystalline polymers, which form columnarlike mesophases with conformational disorder at elevated temperature.[5,24] Analogous mobile phases have been observed for various other inorganic/organic hybrid polymers, such as polysiloxanes[6,7] and polyphosphazenes.[8] Contrary to classical liquid crystals, the formation of ordered mesophases is not induced by rigid, mesogenic units.[9] Prerequisites for the formation of conformationally disordered phases are flexibility of the molecular backbone and a rather symmetrical substitution pattern.[10] Incompatibility between the backbone and side chains might also play a role.

We have shown previously that subtle variations of the substitution pattern of poly(di-*n*-alkylsilylene) copolymers did not impede crystallization but allowed us to control and modify the backbone conformation and thus to manipulate the optoelectronic properties.[12,13]

In this paper, we describe the synthesis and properties of poly[bis(γ-ethoxypropyl)silylene] (PDEPS). This polymer can formally be considered as an oxygenated analog of poly(di-*n*-hexylsilylene)[14,15] (PDHS), the fourth methylene group being replaced by an oxygen linkage. In comparison to PDHS, we expected peculiar variations of the phase behavior and the electronic properties due to higher flexibility and different minimum energy conformations of the ether units. Furthermore, the ether linkages represent reactive functionalities, which may be used to graft side chains onto polysilylenes and may eventually lead to materials with altered solubility and processing properties.

We will also give a first account of the synthesis and characterization of some copolymers consisting of bis(γ-ethoxypropyl)-substituted units and di-*n*-hexylsilylene units.

Experimental Section

Synthesis of Bis(γ-ethoxypropyl)dichlorosilane.[22] A 500-mL stainless steel vessel, pressure proof up to 400 bar, thoroughly dried, and argon purged, was used for the hydrosilylation reaction. The reaction vessel was equipped with a needle valve and a magnetic stirring bar. All manipulations were carried out under Ar. A total of 144 g (1.67 mol) of the ethoxyallyl ether (Aldrich) was syringed into the reaction flask. Subsequently 0.5 mL of a solution of Speier's catalyst (H_2PtCl_6 in anhydrous isopropyl alcohol) or a Pt–cyclovinylmethylsiloxane catalyst (PC 085, obtained from ABCR/Petrarch) was added, and the reaction vessel was then closed and cooled to the temperature of liquid nitrogen. After evacuation, 82 g (0.81 mol) of H_2SiCl_2 (Union Carbide)[26] was condensed into the steel cylinder. The cold apparatus was placed in a waterbath at 50 °C and allowed to warm up in a bunker under remote control. (It occurs that the exothermic symmetrical hydrosilylation reaction can proceed extremely violently. Resulting high pressures and high temperatures can expand or even burst the reaction vessel. Generally, the reaction proceeded smoothly with high yields of the respective substituted dichlorosilane but sometimes became uncontrollable. This unwanted effect can be avoided by dilution with saturated hydrocarbons.) After several minutes under stirring, an exothermic reaction started, which lasted 5–10 min. This could be monitored by a temperature increase of the waterbath. The product mixture was allowed to cool down overnight, before the reaction vessel was opened to release volatile products. The dark crude product mixture was distilled twice to separate the bis(γ-ethoxypropyl)dichlorosilane from the lighter byproduct fractions [bp 75–95 °C (0.4 mmHg)]. A total of 61 g of a light yellow liquid was obtained; the purity according to ^{1}H NMR was >95%. The monomer was distilled twice more via a spinning band column [bp 91–93 °C (0.4 mmHg)]; 42 g (19%) of bis(γ-ethoxypropyl)dichlorosilane was obtained as a light yellow liquid. ^{1}H NMR (200 MHz, C_6D_6): 1.06 (t, CH_2, 2H), 1.10 (t, CH_3, 3H), 1.65 (m, CH_2, 2H), 3.12 (t, CH_2O, 2H), 3.22 (q, CH_2O, 2H). Analysis of the purity of the final product by GC was not possible due to partial decomposition in the column.

Polymerizations were carried out using a slightly modified "normal" addition mode[16] procedure. A total of 10 mL of dry toluene and 1.01 g of Na (44 mmol) were added into a dried, Ar-purged 25-mL flask equipped with a gas inlet, condenser, and magnetic stirrer. Under strong stirring and reflux a fine Na dispersion was formed. Subsequently, 6.01 g of bis(γ-ethoxypropyl)dichlorosilane (22 mmol) in 2 mL of dry toluene was syringed into the reaction flask. Very rapidly a dark blue color

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Table I. PDEPS

polymer	yield (%)	$M_w \times 10^{-3}$ [a]	M_w/M_n [a]
PDEPS I	6	257	2.5
PDEPS II	13	219	2.3
PDEPS III	9	640	2.9
PDEPS III-m		389	8.0

[a] Apparent M_w, as obtained from GPC based on polystyrene calibration; for PDEPS I, II, and III different monomer batches slightly varying in purity were used, which may account for the difference in molecular weight.

developed, that deepened over the course of the reaction. The reaction was quenched after 5 h by the addition of 2 mL of methanol; 20 mL of toluene was added, and after filtration the organic phase was washed with water several times in order to remove the NaCl formed in the reaction. No precipitation was observed when 100 mL of methanol was added. Only after evaporation of most of the solvent (toluene/methanol) could a white polymer be separated. Final yield after reprecipitation: 400 mg (9%) (PDEPS III; Table I). For the copolymers, the work-up procedure was modified in such a way that after almost complete removal of the solvent the polymeric fraction was precipitated with cold methanol. Separation of cyclics and oligomers was achieved by repeating the procedure.

Methods. GPC analysis was performed in THF using Styragel 10^5-, 10^4-, and 10^3- and 500-Å columns. The molecular weights are referenced to narrow polystyrene standards.

Solution ^{13}C and ^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer in C_6D_6, at 62.8 and 250.1 MHz, respectively.

Solubility: "slightly soluble" in the text indicates that clear 0.03% solutions in the respective solvent could be prepared at room temperature; the solutions were inspected visually and by UV spectroscopy. "Good" solubility means that >1% solutions could be prepared.

Thermal transitions were monitored by means of a Perkin-Elmer DSC 7. The instrument was calibrated with high-purity samples of indium and cyclohexane. The transition temperatures were recorded with a heating rate of 3 K/min. Typically, the sample weight was chosen to be between 3 and 5 mg. Polymer samples were used as obtained after the second reprecipitation (ambient atmosphere, but closed pans during measurements). Transition enthalpies of the three different PDEPS samples varied by less than 5%. The transition entropy was calculated assuming thermal equilibrium ($\Delta H_{dis} = T_{dis}\Delta S_{dis}$).

Polarizing microscopy was carried out using a Leitz Ortholux II-Pol-BK microscope equipped with a Mettler hotstage FP-82.

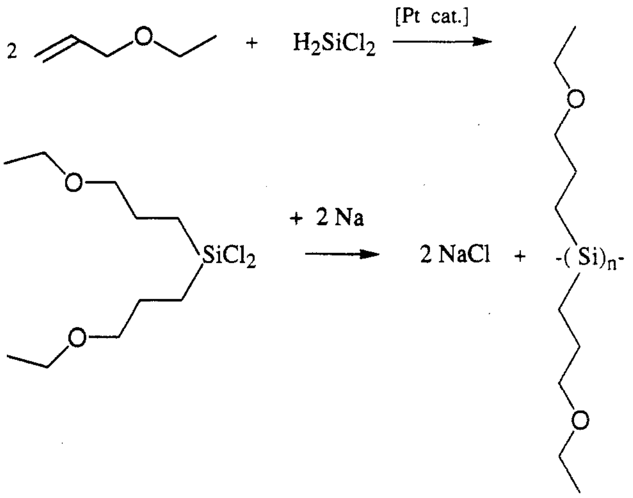
UV spectra of films cast on quartz substrates and solutions were measured with a Kontron UVIKON 930 spectrometer.

Solid-state ^{29}Si and ^{13}C NMR spectra were recorded on a Bruker CXP 300 spectrometer at 59.63 and 75.47 MHz, respectively. A double-bearing MAS probe (Bruker), modified for variable-temperature experiments, was used. Line narrowing was achieved by high-power decoupling and magic-angle spinning. Spinning rates were set to 3000 Hz. The usual cross-polarization sequence was applied for the spectra marked with "CP". ^{13}C NMR chemical shifts are referenced to TMS. ^{29}Si chemical shifts are referenced to TMS indirectly by taking the signal of a silicon rubber fitting of the sample container as the calibrated reference signal.

Results and Discussion

Synthesis. A crucial problem encountered in the synthesis of polysilylenes bearing functional groups within their side chain is the possible side reactions during the polymerization of the di-*n*-alkyldichlorosilane monomers in the Na dispersion.[16] Etheric side chains are one of the few moieties able to survive the polymerization. A number of reports have described the synthesis of symmetrically substituted polysilylenes with arylalkoxy side chains.[17,18] To our knowledge no reports have appeared so far on the synthesis of symmetrically substituted polysilylenes with linear side chains containing oxygen linkages. This may partly be due to the difficulties associated with the monomer synthesis. In our hands, the synthesis of bis(γ-ethoxypropyl)dichlorosilane via Grignard attachment of the respective alkoxyalkyl halides to $SiCl_4$ was not successful. Attempts to react 1-chloro-3-ethoxypropane with $SiCl_4$ in the presence of Mg (in situ Grignard formation) also failed. The formation of complex salts impeded further workup of the reaction products, and also the product mixture could not be distilled. Therefore, we applied the hydrosilylation route to prepare bis(γ-ethoxypropyl)dichlorosilane. H_2SiCl_2 reacts with 2 equiv of the respective alkene, using either Speier's[19] catalyst or other Pt-based catalysts[20] to produce the dialkyldichlorosilane monomers. In the case of 1-alkenes, this reaction is highly exothermic and gives the substituted dichlorosilanes in high yield.[22] Monomer synthesis and polymerization are shown in Scheme I. Synthetic details are given in the Experimental Section.

Scheme I



The monomer synthesis using either a solution of Speier's catalyst or a Pt–cyclovinylmethylsiloxane catalyst yielded only about 20% of bis(γ-ethoxypropyl)dichlorosilane. No significant difference was observed for the different catalysts. The hydrosilylation proceeded less exothermically than for 1-alkenes and had to be carried out at slightly elevated temperature. We attribute the low yields of bis(γ-ethoxypropyl)dichlorosilane to cleavage of the ether bonds, a proposal which is supported by the formation of a variety of lower boiling side products found upon analysis of the reaction products by GC. After distillation, bis(γ-ethoxypropyl)dichlorosilane was obtained as a light yellow liquid, which rapidly turned dark yellow in spite of handling the product under an inert gas. We have no explanation for this yet. As shown by ^{13}C and ^{1}H NMR, bis(γ-ethoxypropyl)dichlorosilane was obtained in more than 95% purity after distillation using a spinning band column. Partial decomposition occurred during GC analysis, and GC-MS characterization confirmed that bis(γ-ethoxypropyl)dichlorosilane is a labile compound at elevated temperature.[22]

Polymerizations of the bis(γ-ethoxypropyl)dichlorosilane were carried out in a Na dispersion in refluxing toluene. Apparently, the impurities did not impede the polymerization. The reactivity of the bis(γ-ethoxypropyl)dichlorosilane appeared to be considerably higher than that of di-*n*-hexyldichlorosilane. A rapid change of the color of the reaction mixture is observed upon addition of the monomer to a Na dispersion. The shorter induction period than observed in the case of di-*n*-alkyldichlorosilanes may be compared to the enhancement of the reactivity found using high boiling ethers as cosolvents in the polymerization of di-*n*-alkyldichlorosilanes.[16] The

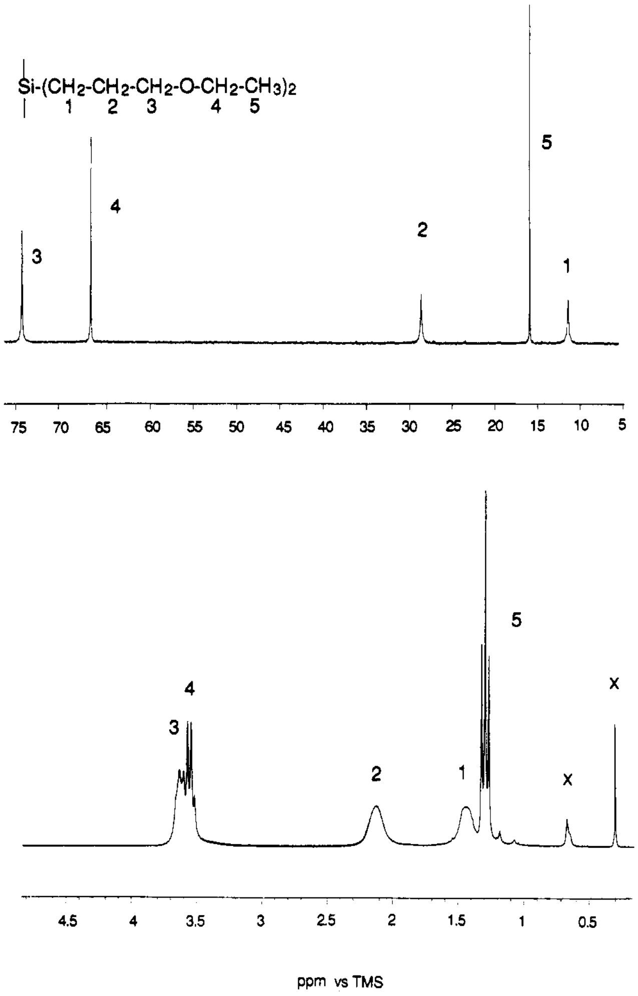


Figure 1. Top: ^{13}C NMR spectrum of PDEPS. Bottom: ^{1}H NMR spectrum of PDEPS. Both in C_6D_6 (× = impurity).

yields of linear high polymer, poly[bis(γ-ethoxypropyl)-silylene] (PDEPS), were lower than usually obtained in the synthesis of poly(di-*n*-alkylsilylenes)[16] and ranged between 6 and 13%. It is not understood whether the low yields of polymer are due to side reactions involving the impurities in the monomer or interaction of the ether groups with sodium resulting in preferential formation of cyclic products.

The usual procedure for the isolation of high molecular weight polymer had to be modified because PDEPS was soluble in a mixture of toluene and methanol and thus could not be precipitated from toluene by addition of methanol. Yields and molecular weights of PDEPS as determined by GPC are summarized in Table I for different batches. In contrast to samples I and II, PDEPS III was prepared from monomer that had been repeatedly distilled using a spinning band column.

Figure 1 shows ^{1}H and ^{13}C NMR spectra of PDEPS (sample PDEPS III). Although a small amount of some impurity is seen (marked ×), the spectra demonstrate that the polymer was obtained rather pure and free from cyclic side products, an observation which is also confirmed by the UV spectra (vide infra). This is a major requirement for the ensuing structural investigation. The peak assignment was made in analogy to the spectra of the *n*-alkyl-substituted homopolymers.[21] Due to higher mobility and increased spin–spin relaxation times, the spectral line width decreases when moving outward from the polysilylene backbone. Also the ^{1}H spectrum indicates a higher mobility for C4 and C5, which in contrast to C1 and C2 lead to resolved triplet and quartet signals, respectively.

Properties in Solution. Similar to PDHS and its homologues, PDEPS dissolves readily in THF and nonpolar solvents, such as hexane or toluene. Furthermore, PDEPS is slightly soluble in a wide range of polar solvents such as alcohols with alkyl groups longer than ethyl. PDEPS shows good solubility ($\geq$1 wt %) in diethyl ether, acetone, and cyclohexanol, which are poor solvents for PDHS. The material shows limited solubility ($\geq$0.03 wt %) even in ethanol but is completely insoluble in water.

The UV spectrum of PDEPS in cyclohexane solution is almost identical with the spectrum observed for PDHS. The absorption maximum is found at 316 nm; the extinction coefficient in cyclohexane, ϵ = 9000, is also similar to that observed for PDHS.[1] It may be concluded that while the replacement of the fourth methylene group by an oxygen linkage has a significant effect on solubility, there is little impact on the conformation of the Si-catenated backbone in solution. The latter mainly determines the electronic structure in alkyl-substituted polysilylenes.

Solid-State Properties. One objective of this work was the comparison of the solid-state properties of PDHS and the newly synthesized PDEPS. PDHS crystallizes in an all-trans conformation and is transformed into a columnar mesophase at 42 °C, with a transition enthalpy of 14–16 kJ/mol.[14] This transition is accompanied by a strong thermochromic blue shift from 373 to 317 nm in the formation of the mesophase. Up to the decomposition temperature above 300 °C, PDHS remains in the mesophase. As the PDEPS structure is of similar symmetry, it was expected that the material would show a similar phase behavior with the phase transformation occurring at lower temperature because of enhanced side-chain flexibility. Furthermore, a different backbone structure may be expected for the crystalline phase, as the all-trans conformation of PDHS depends on side-chain crystallization.

At room temperature, PDEPS is a white solid, which appears slightly yellow in thicker layers and exhibits a strong blue fluorescence, resembling PDHS. In this state, PDEPS is strongly birefringent. Upon heating, the sample softens slightly above room temperature. Under crossed polarizers, no distinct loss of birefringence correlated to this transition could be discerned. This suggests that the transformation observed is not isotropization but, in analogy to PDHS, a transition to a mobile phase with a high degree of intermolecular order. When heated further, above 210 °C, the polymer started to flow freely and became isotropic. So far, reversible melting of an *n*-alkyl-substituted polysilylene has been reported only for the unsymmetrically substituted poly(*n*-butyl-*n*-hexylsilylene)[23] (PBHS); for symmetrically substituted poly(di-*n*-alkylsilylenes) melting occurs simultaneously with degradation.[24]

In order to assure that the observed isotropization is true melting and not degradation, a small sample of PDEPS III was heated to 230 °C for 3 min and then characterized again by GPC (listed in Table I under PDEPS III-m). Figure 2 shows a comparison of the GPC diagrams of the virgin PDEPS with the material heated to 230 °C. A decrease of the weight-average molecular weight from 640 000 to 327 000 resulted, and the polydispersity increased by a factor of 2.7. The spectroscopic properties were not affected. The relatively minor degradation confirmed the observation of melting of the polymer mesophase. Thus, PDEPS can be regarded as one of the few examples of a crystallizable, yet meltable, polysilylene.

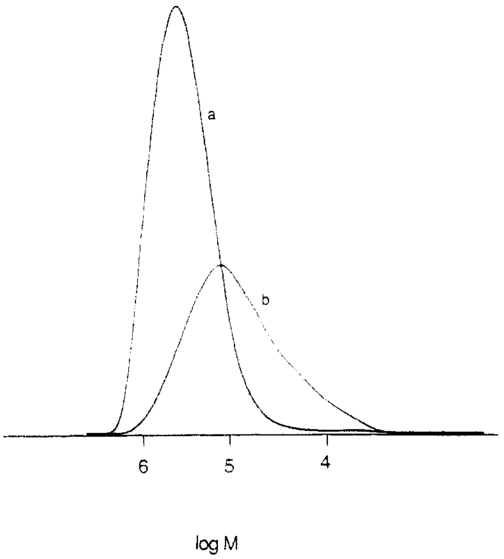


Figure 2. GPC traces of PDEPS before (a) and after (b) melting.

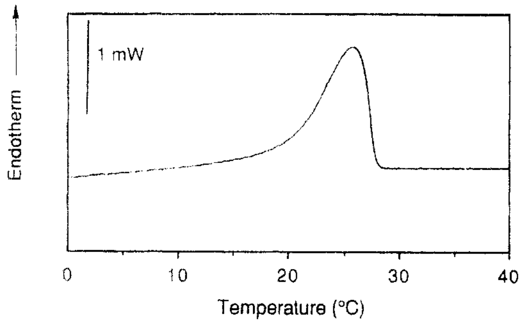


Figure 3. DSC thermogram of PDEPS (heating rate 3 K/min).

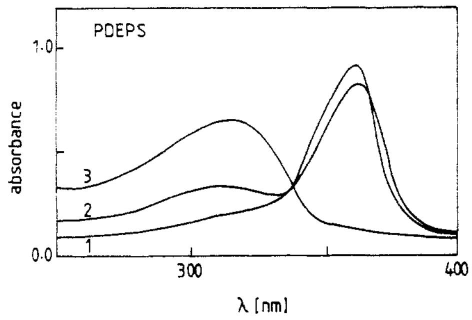


Figure 4. Solid-state UV thermochromism of cast PDEPS film. Temperatures: 1, −20 °C; 2, 16 °C; 3, 30 °C.

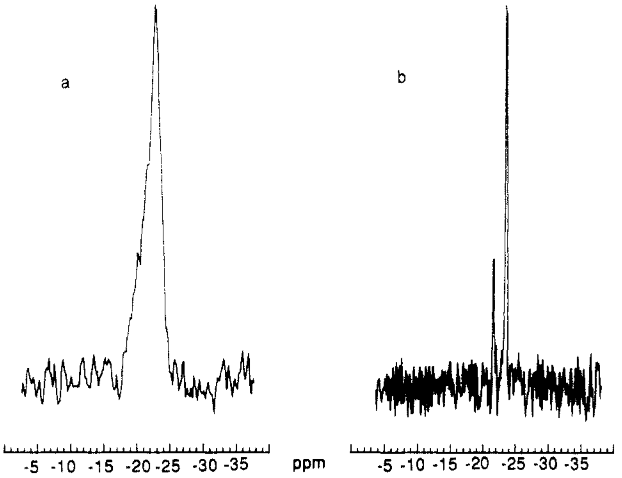


Figure 5. 59.63-MHz solid-state ^{29}Si NMR MAS spectra of PDEPS at 290 K recorded with cross polarization (a) and at 300 K recorded without cross-polarization (b). (Smaller signal at −22 ppm: reference signal.)

It must be noted, however, that the thermal stability of PDEPS in air is considerably lower than that of PDHS. Longer exposure of PDEPS to temperatures above 100 °C in air resulted in decomposition.

The mesophase transition of PDEPS was studied by DSC, temperature-dependent UV spectroscopy, and temperature-dependent ^{29}Si NMR spectroscopy. The DSC diagram, given in Figure 3, shows a reversible first-order-like transition with a transition enthalpy of $\Delta H_{\text{trans}} = 10$ kJ/mol. The onset temperature of the disordering transition was 19 °C and the peak temperature 25 °C. The transformation temperatures and transition enthalpies (10–11 kJ/mol) varied only slightly with molecular weight for the three PDEPS samples listed in Table I. A thermal hysteresis of almost 20 °C was found upon cooling the polymers from above the transition, similar to that observed for PDHS. The isotropization could not be detected by DSC. However, this result has also been reported both for poly(diethylsiloxane)[7] and various polyphosphazenes,[8] and it has been suggested by Wunderlich[10] that conformationally disordered mesophases might gradually become isotropic.

Figure 4 shows the UV thermochromism of bulk PDEPS, as determined by heating thin films slowly from the crystalline phase. The hypsochromic shift of the absorption is explained by the phase transition observed in DSC. Whereas the crystalline, low-temperature phase absorbs light at 362 nm (−20 °C), the mesophase is characterized by a broad absorption maximum at 315 nm. As described for PDHS and polysilylenes with longer *n*-alkyl side chains,[15] the all-trans backbone structure leads to an absorption maximum between 370 and 380 nm. However, there are examples, e.g., poly(di-*n*-propylsilylene)[11] and a number of polysilylene copolymers,[13] where the all-trans planar structure is slightly perturbed and the polysilylenes absorb at shorter wavelengths. Absorption maxima at 360 nm have been reported.[13] An absorption maximum at 362 nm can therefore be viewed as an indication of an all-trans-like backbone structure in the crystalline phase of PDEPS. The broad absorption at 315 nm at 30 °C is typical for the columnar mesophase and demonstrates a loss of σ-conjugation above the disordering transition.

Further information on the structure and dynamics of the Si backbone in the solid can be attained by solid-state ^{29}Si NMR.[25,28] The chemical shifts in MAS-CP spectra depend on the conformational structure of the backbone and side chains. The mobility affects the relaxation and thus also to some extent the line widths in MAS spectra. Figure 5 shows the MAS-CP spectrum for PDEPS at 290 K in comparison to the dipolar-decoupled MAS spectrum at 300 K, above the disordering transition. The signal for the crystalline, low-temperature phase at −22.7 ppm is asymmetric in shape, and the line width is considerably larger than for PDHS.[25] A chemical shift observed between −19 and −23 ppm for the low-temperature phase of PDEPS is a further indication of an all-trans backbone structure with certain conformational variety.

Above 27 °C, the broad signal for the low-temperature phase has disappeared and the mesophase signal is observed at −24 ppm. The relaxation behavior demonstrates high segmental mobility. The location of the mesophase signal at −24 ppm is typical for all poly(di-*n*-alkylsilylene)s in the columnar liquid crystalline state. Compared to PDHS, the signal is much narrower, indicating more efficient motional averaging of the molecular conformation.

The disordering of the side chains during the mesomorphic transition can be monitored by ^{13}C MAS solid-

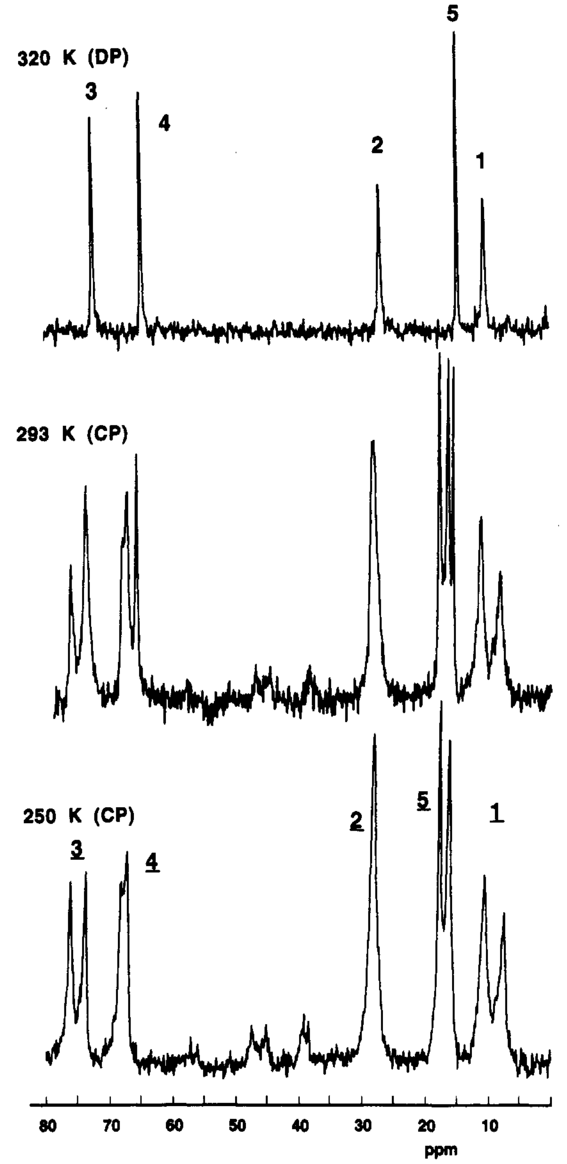


Figure 6. Variable-temperature ^{13}C MAS solid-state NMR spectra of PDEPS, recorded at 250 K (CP), 293 K (CP), and 320 K (DP). The spectra were recorded upon heating from 250 K. The chemical shifts refer to TMS.

state NMR. Figure 6 shows the ^{13}C solid-state NMR spectrum of PDEPS at 250 K (bottom), 293 K, and 320 K (top). At 320 K, the spectrum (dipolar decoupling) resembles the spectrum measured in solution. Relatively narrow lines for all carbons are observed, and the spectrum exhibits a similar increase in line width when moving from C5 closer to the main chain. This has been discussed before in the context of the solution spectrum. The resonances of the ordered phase (phase I) observed at lower temperature are completely absent. Also at 320 K, no signals are observed under cross-polarization conditions, which evidences that all methylene units are present in a highly mobile, conformationally disordered state.

^{13}C NMR spectra recorded at 250 K (phase I) with cross polarization (CP) show relatively broad resonances, which are split for each of the constitutionally different carbons; i.e., the respective carbons exist in two equally population conformations in the low-temperature state. As has been reported for PDHS,[28] this may be attributed either to the presence of two crystal modifications or variations of the packing of the side chains within the same crystal lattice.

At 293 K the ordered and disordered phases can be observed simultaneously under cross-polarization conditions. Clearly, a fraction of C3, C4, and C5 is already present in the mobile, disordered state. As described for PDHS,[25] the disordering starts at the outer carbon atoms, which undergo enhanced rotational motion first, followed by the sterically more constrained carbons closer to the silicon backbone. Generally, the resonances of the mobile phase appear at higher field, as has also been observed for PDHS.[25,28] In summary, the solid-state NMR data indicate that the disordering of PDEPS occurs in a way similar to that reported for PDHS.

Table II. Copolymers P(DHS/DEPS)

monomer feed[a]	copolymer[c] compos.	yield (%)	$M_w \times 10^{-3}$ [b]	M_w/M_n[b]
90/10	88/12	7	820	3
80/20	94/6	12	18	1.7
50/50	79/21	18	6	1.6
20/80	57/43	nd	14	1.6

[a] Di-*n*-hexylsilylene (DHS)/bis(γ-ethoxypropyl)silylene (DEPS). [b] As obtained from GPC based on polystyrene calibration. [c] From ^{1}H NMR; spectra were recorded in C_6D_6 except for the 90/10 P(DHS/DEPS) ($CDCl_3$).

Copolymers. In the course of this work, a number of copolymers of di-*n*-hexyl-substituted units and bis(γ-ethoxypropyl) units (termed P(DHS/DEPS)) were also synthesized. As the mixture of cyclic and oligomeric products displayed a continuous spectrum of polarity and solubility, separation of high molecular weight polymer from cyclics and oligomers was difficult. Each copolymer had to be worked up by a modified procedure depending on the fraction of γ-ethoxypropyl side chains. The composition of the isolated copolymers and the separated oligomer fraction was analyzed by ^{1}H NMR and is reported in Table II together with the corresponding yields and apparent molecular weights. It is evident that in almost all cases fewer ether units are incorporated into the high molecular weight products than employed in the monomer feed. The respective oligomeric fractions showed considerably higher contents of ether side chains, i.e., 75% and 49% for the 20/80 and 50/50 copolymerizations, respectively. One might conclude that the presence of ether moieties in the side chains leads to a higher probability of cyclization or termination at an early stage of the reaction. This is also consistent with a lower yield of high polymer as compared to the synthesis of poly(di-*n*-alkylsilylene)s. Different reactivity of the monomers could also affect the microstructure of the copolymers. However, from the ^{1}H NMR spectra of the copolymers, there is no evidence for long blocks or incorporation of the monomers in different polymer chains. The splitting pattern of the C6-methyl group of the *n*-hexyl side chain shows distinct variations with composition, as also observed for other poly(di-*n*-alkylsilylene) copolymers.[27] This is a strong indication that no blocklike structures or mixtures of different homopolymers have been formed. Whether the microstructure is truly random and the extent to which the microstructure might depend on the polymerization conditions have not yet been evaluated.

Data on the thermal behavior of the P(DHS/DEPS) copolymers are summarized in Table III.

The copolymers with a DEPS content between 10 and 22% showed disordering transitions. The transition temperatures, as well as the transition enthalpies, decreased with increasing content of DEPS. The relatively large values of the transition enthalpies might still be regarded as typical for the disordering of an all-trans structure. Heterogeneity was indicated in the case of the 90/10 P(DHS/DEPS), where the transition showed a shoulder at 35 °C in the thermograms.

Table III. Copolymers

copolymer[a]	T_{dis} (°C)	ΔH_{dis} (kJ/mol)	λ_{max}(cryst) (nm)
90/10	45/35	13.7[b]	373
80/20	43	13.8	370
50/50	26	7.8	360
20/80	22	10.5	346

[a] Based on monomer feed ratios; for actual compositions, see Table II. [b] Total value.

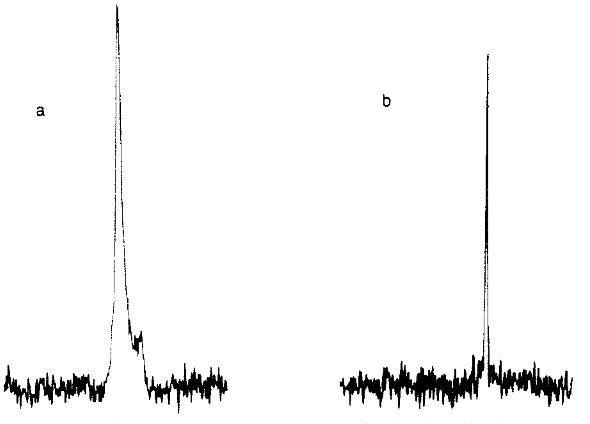


Figure 7. ^{29}Si MAS solid-state NMR spectra of 90/10 P(DHS/DEPS) copolymer at 300 K with cross polarization (a) and at 330 K without cross polarization (b).

All of the copolymers were thermochromic. In thin films, the UV absorption maxima of the crystalline, low-temperature phase varied between 362 and 373 nm. This observation supports a slightly disturbed all-trans structure, with decreased σ-conjugation length. In the mesophase, all copolymers absorbed between 314 and 318 nm.

The 90/10 P(DHS/DEPS) copolymer was studied by ^{29}Si MAS solid-state NMR spectroscopy and the behavior is comparable to PDHS. Below the transformation, at 300 K the typical signal for the all-trans phase is observed at −20.9 ppm; at 330 K the narrow mesophase signal is found at −23.9 ppm (Figure 7). In the crystalline phase at 300 K, a small amount of the disordered phase is already present.

Conclusions. Hydrosilylation proved to be an efficient route for the preparation of bis(γ-ethoxypropyl)dichlorosilane. The compound can be polymerized to yield cyclic products and monomodal high molecular weight poly[bis(γ-ethoxypropyl)silylene] (PDEPS). The comparison of PDEPS and and PDHS shows that the incorporation of an ether functionality leads to significantly altered solubility properties; i.e., the newly synthesized PDEPS is an alcohol- and acetone-soluble material. Besides the homopolymer, copolymers with di-*n*-hexylsilylene units could also be prepared. These polymers may also be of interest because the ethoxy or corresponding methoxy functionalities can provide a basis for grafting reactions or other functional modifications.

The transition enthalpy, wavelength of the absorption maximum, and ^{29}Si MAS CP solid-state NMR data support the conclusion that PDEPS crystallizes in an all-trans-like structure and transforms to a highly mobile columnarlike mesophase similar to that of poly(di-*n*-alkylsilylene)s. The lower transition temperature and a decreased transition enthalpy are interpreted as a consequence of perturbed side-chain interaction. As for PDHS, a distinct blue shift of λ_{max} from 362 to 315 nm is correlated with the mesomorphic transition. These spectral properties also support the picture of a perturbed all-trans-like structure for the low-temperature state.

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References and Notes

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