

Crystalline and disordered state of poly(dihexylsilylene) copolymers

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SUMMARY:

A systematic comparison of random copolymers, derived from poly(dihexylsilylene) (PDHS) by incorporation of monomeric units with shorter unbranched alkyl side chains, has been carried out based on calorimetry, variable temperature UV spectroscopy, and ²⁹Si MAS (magic angle spinning) solid state NMR investigations. Also, hexylmethylsilylene units and branched monomers have been copolymerized. Up to 10% comonomer with shorter linear side chains (i. e., pentyl to propyl) could be incorporated into PDHS without impeding the all-*trans* order of the crystalline phase. In this case, the UV absorption maximum of the crystalline low-temperature phase was affected only slightly according to the length and fraction of the comonomer side chains. A less ordered crystal structure ($\lambda_{\text{max}} = 345 - 355 \text{ nm}$) was observed when the content of comonomers with shorter side chains was about 20%. Yet, all these materials form conformationally disordered mesophases. A clear disordering transition and corresponding thermochromism was not observed any more when 50% of propyl side chains were incorporated. The order of the crystalline and the mesophase is also strongly perturbed if only a small fraction (4%) of the side chains are branched at C².

Introduction

Polysilylenes are σ -conjugated silicon polymers with peculiar properties¹⁾, which are of interest for applications in electrophotography²⁾, non-linear optics³⁾, data storage⁴⁾ and microlithography⁵⁾. The catenated photoconductive Si-polymers may be considered to represent one-dimensional silicon. Poly(di-*n*-alkylsilylene)s in particular combine these properties with mesomorphic behavior⁶⁾. A transformation into a

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mesophase with columnar-like packing of the macromolecules is observed at elevated temperature⁶). In this state, the side chains and the backbone are conformationally disordered⁷). The first-order-like phase transformation is accompanied by thermo- and piezochromism, and leads to altered charge transport properties⁸).

Similar conformationally disordered mesophase have been observed for various polymers with a flexible molecular backbone and symmetrical side chain substitution. Well known examples are poly(di-*n*-alkylsiloxane)s⁹), polyphosphazenes¹⁰), but also polytetrafluoroethylene¹¹) and polyethylene at elevated pressures. Flexibility of the molecular backbone is a prerequisite for the formation of conformationally disordered ("condis") phases¹²). Incompatibility between the backbone and side chains might play a role in some cases¹³), but does not seem to be a necessary condition.

Poly(di-*n*-alkylsilylene) homopolymers have been studied intensively regarding their mesomorphic transitions¹⁴⁻¹⁶). A number of nonsymmetrically substituted homopolymers, such as e.g. polybutyl(hexyl)silylene) also exhibit crystalline order and disordering transitions, even though the *n*-alkyl substituents differ in length by two methylene units¹⁷⁻¹⁹). Typically, the columnar-like mesophase is stable over a wide temperature range, i. e. in many cases up to the degradation temperature.

Reports on the structure and thermal behavior of symmetrically substituted poly(di-*n*-alkylsilylene) copolymers with side chains of different lengths²⁰⁻²⁴) have appeared only rather recently. Most of these polymers were substituted with equal fractions of different *n*-alkyl side chains. This resulted in considerable irregularity of the primary structure, as it is also the case for homopolymers of nonsymmetrically substituted homopolymers. In contrast, incorporation of a small amount of pentyl side chains into the regular structure of poly(dihexylsilylene)²⁹) may be visualized as a minor structural defect. This results, however, also in pronounced changes of the backbone conformation and the corresponding optoelectronic properties²⁰).

The present work represents a systematic study on the phase behaviour of copolymers derived from poly(di-hexylsilane) (PDHS) by incorporation of (i) comonomers with shorter side chains and (ii) an increasing fraction of these comonomers. The structural "defects" are supposed to disturb the side chain interactions and thereby affect the conformation of the backbone chromophores. The questions raised in this context are, how much disorder is tolerated in the ordered crystalline and the partially disordered mesophase and how the incorporation of structural perturbations affects the optical properties.

The minimum length of the shorter *n*-alkyl side chains was chosen as 3 methylene units (i. e., propyl substituents), in order to avoid formation of block-like structures, as observed for copolymerization of dimethyldichlorosilane with dihexyldichlorosilane²¹).

Experimental part

Monomers

Di-*n*-alkyldichlorosilanes were synthesized by Grignard reaction. All di-*n*-alkyldichlorosilanes were distilled twice prior to use (>98% purity according to gas chromatography).

Polymerization

Toluene and isooctane were distilled from CaH_2 and dried over Na/benzophenone. A dispersion of freshly cut Na in a 4 : 1 mixture of toluene/isooctane was prepared under vigorous stirring at $107 \pm 3^\circ\text{C}$. A mixture of dihexyl- and the respective di-*n*-alkyldichlorosilane was syringed into the reaction flask in 2 : 1 mole ratio of Na/monomer. After 4 h reaction time, the viscous, purple slurry was allowed to cool to room temperature, quenched and simultaneously precipitated with 2-propanol. The blue precipitate was filtered, dissolved in toluene and washed with water several times to remove NaCl. The polymer was reprecipitated in tetrahydrofuran methanol in order to separate small cyclics, dried, and the yield determined gravimetrically. Typical yields were 30–45%.

Gel permeation chromatography

A set of 10^6 , 10^5 , 10^4 , 10^3 and 500 Å Waters columns was used to perform GPC analysis. All molecular weights are referenced to narrow polystyrene standards.

NMR

Solution ^{13}C NMR spectra were recorded on a 300 MHz (GE) spectrometer in CDCl_3 . High resolution solid state ^{29}Si NMR spectra were recorded on a Bruker CXP 300 spectrometer at 75,47 MHz. A double bearing MAS probe (Bruker), which was modified for variable temperature experiments, was used. High power decoupling and magic angle sample spinning were employed to achieve line narrowing. The spinning rates were set to 1900–2400 Hz. ^{13}C as well as ^{29}Si chemical shifts are referenced to tetramethylsilane.

Calorimetry

A Perkin-Elmer DSC 7 was used to monitor the thermal transitions at scan rates in the range of $2^\circ\text{C}/\text{min}$ to $10^\circ\text{C}/\text{min}$. The instrument was calibrated with high purity samples of indium and cyclohexane. Sample weights were typically chosen between 4 and 6 mg. Transition temperatures were obtained by extrapolation to zero heating rate. The transition enthalpies determined by integration of the peaks showed variations of less than 5%. Assuming equilibrium conditions, the transition entropies have been calculated from $\Delta H_{\text{tr}} = T_{\text{tr}} \cdot \Delta S_{\text{tr}}$.

UV Spectra

Films of about 0,1–0,3 μm thickness were spincoated on quartz plates from toluene solution. After brief heating to 115°C in order to evaporate remaining solvent, UV spectra of the films on the substrate were recorded throughout several cooling/heating cycles (IBM 9430 UV-Vis spectrophotometer). A Mettler hotstage FP 5 was used, allowing temperature control in the range of -20°C to 120°C with an accuracy of $\pm 0,2^\circ\text{C}$.

Results and discussion

Molecular characterization of the copolymers

Poly(dihexylsilylene/di-*n*-alkylsilylene) copolymers with varying length of the comonomer side chains have been prepared. HS, PS, BS and PrS designate hexyl, pentyl, butyl, and propyl side chains, respectively. In the following, the copolymers are denoted by the monomer feed composition in combination with the abbreviations of the monomer units. 80/20 P(DHS/DBS), e.g., is a copolymer prepared from a monomer mixture of 80% dihexyldichlorosilane and 20% dibutyldichlorosilane.

In addition, copolymers with small fractions of hexylmethylsilylene units (HMS) and branched di(*S*)-2-methylbutyl)silylene units (DMBS) were prepared in order to study the influence of a different kind of structural defect. Tab. 1 summarizes the yields, molecular weights and polydispersities of all copolymers which are compared in this study.

Tab. 1. Polydihexylsilylene copolymers, yields and molecular weights

Copolymer	Yield	$\bar{M}_w \cdot 10^{-3}$	\bar{M}_w/\bar{M}_n
PDHS	35%	540	2,8
90/10 P(DHS/DPS)	31%	510	2,1
80/20 P(DHS/DPS)	35%	570	2,7
90/10 P(DHS/DBS)	28%	520	1,6
80/20 P(DHS/DBS)	23%	470	2,0
90/10 P(DHS/DPrS)	25%	440	1,7
80/20 P(DHS/DPrS)	21%	480	1,6
50/50 P(DHS/DPrS)	20%	1 050	2,2
95/5 P(DHS/HMS)	19%	380	2,7
90/10 P(DHS/HMS)	21%	450	1,7
96/4 P(DHS/DMBS)	24%	460	2,4

The composition and microstructure of the copolymers have been investigated by ^{13}C NMR spectra and high resolution ^1H NMR spectra (620 MHz). The synthesis was directed to copolymers with the same composition as used in the monomer feed. The side chain structures of the monomers are relatively similar and therefore the monomer reactivities should not differ significantly. Thus, the formation of extended blocks of one kind of monomer was not expected and correspondingly insoluble product fractions were formed in no case. This is also consistent with kinetic data²⁵⁾ reported by Worsfold and coworkers. Representative of all copolymers listed here, the ^{13}C NMR spectrum of the copolymer 80/20 P(DHS/DPrS) is shown in Fig. 1. The peaks of the methylene units of the side chains have been assigned using the data known for the homopolymers²⁶⁾. As it is common for poly(di-*n*-alkylsilylene)s, the line widths increase from C^6 to C^1 . C^1 is directly attached to the catenated Si backbone, and the broadening of the NMR resonance can be explained by the restricted segmental mobility of the densely substituted polymer backbone. The signal intensities indicate that the ratio of comonomer units equals the composition of the monomer feed.

High resolution ^1H NMR spectra (620 MHz) have been recorded in order to analyze the segmental composition of the copolymers. Fig. 2 displays the ^1H NMR spectrum of the 80/20 P(DHS/DBS) copolymer. Also in this case, the spectra of the corresponding homopolymers could be used to assign the resonances. Comparison of the signal intensities for C^6 and C^4 demonstrates a composition as expected from the monomer feed. Analogous spectra have been obtained for all copolymers and indicate little or small deviation of the ratio of the overall comonomer composition from the monomer feed.

Fig. 1. ^{13}C NMR spectrum of the 80/20 P(DHS/DPrS) copolymer (recorded in C_6D_6)

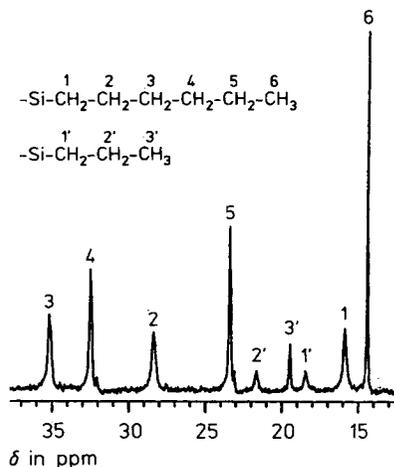
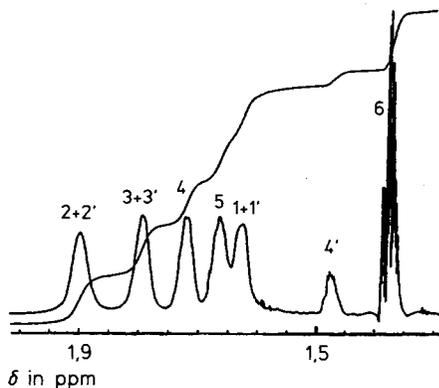


Fig. 2. ^1H NMR spectrum of 80/20 P(DHS/DPrS) copolymer with integration (in C_6D_6)



The multiplet pattern observed for C^6 is of particular interest. Whereas in PDHS only a well resolved triplet is found, multiplets have been observed for all P(DHS/DBS) as well as P(DHS/DPrS) copolymers. The multiplets can be explained as overlapping triplet signals with a small difference in chemical shift and reflect the segmental composition of the copolymers. A comparison of the C^6 splitting-pattern for the 80/20 P(DHS/DPrS) and 90/10 P(DHS/DPrS) is given in Fig. 3.

The decrease of the signal intensities on the high field side of the spectrum for the 90/10 copolymer can be attributed to the statistically lower probability of sequences containing few propyl units. For the 50/50 P(DHS/DPrS)²⁷⁾ copolymer, the multiplet splitting pattern was found to be symmetrical (not shown here). The intensities of the triplet signals which constitute the multiplet are consistent with Bernoullian statistics of the possible monomer sequences. Thus, the fine structure of the C^6 signal supports the reactivity-based assumption of a random or close to random distribution of the building units in the copolymers.

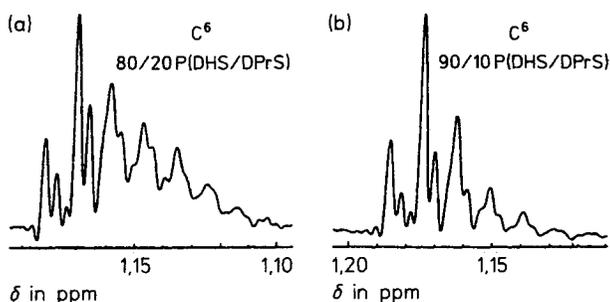


Fig. 3. Splitting pattern of C^6 in P(DHS/DPrS) copolymers, (a) 80/20; (b) 90/10

Thermal behavior

Poly(dihexylsilylene) crystallizes with a planar all-*trans* backbone structure²⁴⁾ and transforms into the columnar-like mesophase at 42 °C^{28,29)}. The transition is first-order-like with a disordering enthalpy of approximately 15 kJ/mol^{1,28)} and results in a widening of the crystal lattice. The loss of σ -conjugation in comparison to the *trans*-ordered crystalline phase causes a blueshift of the absorption maximum λ_{\max} from 373 nm to 316 nm. Corresponding disordering transitions were found for all copolymers (with the exception of the 50/50 P(DHS/DPrS)). Generally, the copolymers were birefringent below and above the transition, as observed microscopically between crossed polarizers. From this and the solid state NMR data reported below, it can be concluded that also the copolymers form ordered low-temperature and mesophases.

Dependent on the thermal behavior (*vide infra*), the copolymers were obtained as powders or plastic, deformable solids at room temperature. Connected with plasticity, the 50/50 P(DHS/DPrS) showed orientation upon shear deformation. The thermal behavior of all copolymers was studied calorimetrically.

The calorimetric data are listed in Tab. 2 together with the maximum of the respective electronic absorption of the ordered phase. A decrease of the transition temperatures and transition enthalpies is observed with increasing the fraction of the smaller comonomer units. Comparison of the transition enthalpies with the disordering of the all-*trans* planar PDHS shows that the transition enthalpies for all 90/10 copolymers are of similar magnitude. Supported by the values for λ_{\max} , which are discussed in detail below, it can be concluded that small amounts of the linear shorter comonomer units did not disturb the all-*trans* planar structure and crystallization strongly.

However, it is obvious from Tab. 2 that the disordering enthalpies and temperatures decrease with increasing fraction of comonomers with shorter side chains. Fig. 4 depicts some representative thermograms of the copolymers. A general effect, noticed in the thermograms of the copolymers, is the broadening of the transitions. A gradual onset of mobility is seen already far below the actual transformation temperature. The 90/10 P(DHS/DPrS) copolymer exhibits PDHS-like behavior. The 90/10 P(DHS/HMS) transforms into the mesophase in a similar way, but in this case a shoulder is seen at temperatures below the actual disordering. Incorporation of 10% propyl side chains or of 20% butyl side chains introduces considerable disorder as shown by broadening of the peak and decrease of the transition temperature.

Tab. 2. Disordering temperatures, enthalpies and entropies for the different poly(di-*n*-alkylsilylene) copolymers, listed together with the UV absorption maxima of the crystalline phase

Copolymer	T_{dis}/K	$\Delta H_{\text{dis}}/[\text{kJ/mol}]$	$\Delta S_{\text{dis}}/[\text{J}/(\text{K} \cdot \text{mol})]$	$\lambda_{\text{max}}/\text{nm}$
PDHS	315	15,0	48,0	372
90/10 P(DHS/DPS)	307	12,7	41,5	367
80/20 P(DHS/DPS)	283	10,3	36,6	346
90/10 P(DHS/DBS)	302	11,5	38,1	365
80/20 P(DHS/DBS))	295	6,3	21,3	354
90/10 P(DHS/DPrS)	287	7,0	24,4	362
80/20 P(DHS/DPrS)	269	3,3	12,1	348
50/50 P(DHS/DPrS)	— ^{a)}	—	—	320
95/5 P(DHS/HMS)	310	10,6	34,2	368
90/10 P(DHS/HMS)	308	10,2	33,1	366
96/4 P(DHS/DMBS)	283–308 ^{b)}	5,7	19	362

a) No transitions, but birefringent up to isotropization (230 °C).

b) Broad, not well defined endotherm, but birefringent above transition until decomposition.

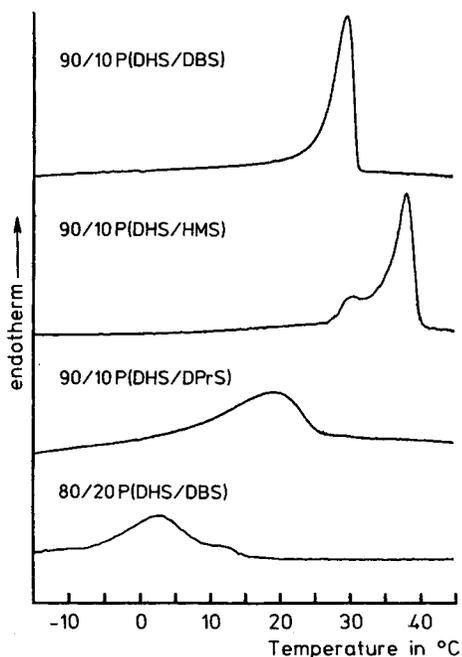


Fig. 4. Comparison of the thermograms of PDHS, 90/10 P(DHS/DBS), 80/20 P(DHS/DPrS)

The gradual onset of mobility in the copolymers upon elevation of the temperature can be explained in terms of enhanced mobility of polymer segments which contain the shorter substituents. These observations are not only valid for copolymers with shorter *n*-alkyl side chains, but also for hexylmethylsilylene copolymers.

Two of the copolymers, however, show different behavior:

No transitions could be detected calorimetrically for 50/50 P(DHS/DPrS). It is known that the 50/50 P(DHS/DPS) or 50/50 P(DPS/DBS) copolymers crystallize in a helical structure and are also capable of forming conformationally disordered mesophases^{20,24}. In 50/50 P(DHS/DPrS), the difference of the side chain length appears to be too large for the formation of an ordered crystal structure. This is not completely unexpected, as nonsymmetrically substituted poly(di-*n*-alkylsilylene)s with side chains differing by 3 methylene units show similar behaviour¹⁹. On the other hand, the 50/50 P(DHS/DPrS) was clearly anisotropic and thus not completely amorphous, as it is indicated by the birefringence observed between crossed polarizers. Within the series investigated here, the copolymer 50/50 P(DHS/DPrS) was the only material that could be molten with negligible decomposition. Upon elevation of the temperature, isotropization was observed at 230 °C.

The second exception in the series is the 96/4 P(DHS/DMBS) copolymer (MBS = (*S*)-2-methylbutylsilylene), where a small fraction of side chains was incorporated, which are branched at C². Also this material was found to form a partially disordered mesophase. Upon cooling from the mesophase, 96/4 P(DHS/DMBS) showed a single, broad transition to the crystalline phase at 278 K. However, in the subsequent heating run a very broad, multiple endotherm was observed with an onset at 278 K and extending to 308 K. Clearly, the incorporation of branched units into the ordered, planar structure of PDHS resulted in strong structural perturbation.

The chain length dependence of the transition enthalpies in Fig. 5 a, b demonstrates decreasing interaction of the side chains for pentyl-, butyl- and propyl-substituted copolymers. The diagrams show the effect of a gradual increase of the fraction and size of structural defects incorporated into PDHS. Building in 10 or 20% of shorter *n*-alkyl side chains (Fig. 5 a) leads to a significant decrease of the disordering enthalpy. The slope of the decrease depends clearly on the length of the shorter side chain, i. e. on the size of the structural defect. Fig. 5 b shows that for 90/10 and 80/20 copolymers with dipentylsilylene comonomers the disordering enthalpy decreases almost linearly with decreasing length of the shorter side chains, while shorter linear side chains lower the transition enthalpies much stronger.



Fig. 5. Transition enthalpies of the copolymers vs. composition **a** and length of side chain of comonomer **b**

^{29}Si MAS solid state NMR

MAS solid state ^{29}Si NMR allows monitoring of the structure and mobility of the catenated Si backbone^{14, 20, 21, 24, 30}. The chemical shifts and linewidths in ^{29}Si MAS cross-polarization spectra mirror variations in the backbone conformation and the related packing of the side chains. The all-*trans* order found for PDHS and poly(di-*n*-alkylsilylene)s with longer *n*-alkyl side chains results in a chemical shift of $\delta = -21$ ppm, whereas helical ordering (PDPS) results in a signal between $\delta = -27$ and -29 ppm. Thus, ^{29}Si solid state NMR spectra together with spectroscopic information allow identification of the backbone structure of the polymers. Furthermore, spin-lattice relaxation times for silicon nuclei in the crystalline and in the disordered phase differ strongly. Therefore, the conformationally disordered mesophase can be probed selectively by recording the spectra without cross-polarization (CP). In contrast, the signals obtained with CP and short delay between subsequent scans of the FID (free induction decay) represent the Si-nuclei in the ordered low-temperature phase. In the following, ^{29}Si MAS solid state NMR chemical shifts are used to distinguish different backbone structures. However, additional fiber diffraction experiments are necessary for a detailed and unambiguous assignment of the backbone structure.

Variable temperature ^{29}Si solid state NMR spectra have been recorded for all copolymers. Apart from the lowered disordering temperatures, which were confirmed by the NMR measurements, the behavior of the copolymers was similar to PDHS. Consistent with the calorimetric observations, ^{29}Si MAS NMR evidenced that the transformation to the columnar like mesophase occurred over a broader temperature range than was observed for the corresponding homopolymer, i. e. PDHS. All 90/10 copolymers P(DHS/DBS) and P(DHS/DPrS), as well as P(DHS/HMS), exhibited chemical shifts between $\delta = -20$ and $-21,5$ ppm. This indicates all-*trans* like ordering as is also suggested by the respective UV spectra discussed below. Small fractions of other modifications and minor, local structural backbone variations caused by the shorter linear side chains are not detected by NMR, although they might well be visible in the UV spectra.

A different behavior was observed for the 80/20 copolymers, which exhibited broader ^{29}Si MAS solid state peaks in the low-temperature phase, which were centered at $\delta = -23,0$ ppm.

Fig. 6a shows temperature dependent ^{29}Si NMR spectra of 80/20 P(DHS/DBS). The position of the broad resonance at low temperature (270 K) indicates that, in contrast to the 90/10 copolymers, the backbone is not all-*trans* ordered. When recording the spectrum without CP, a signal for a mobile fraction could be detected already far below the actual phase transition. The width of the CP signal at low temperature indicates a certain conformational variety. At 300 K the typical narrow mesophase signal is observed at $\delta = -25,0$ ppm.

The study of 50/50 copolymers is particularly interesting, because they resemble strongly the non-symmetrically substituted, atactic homopolymers such as poly(hexyl(propyl)silylene). At 280 K, the ^{29}Si CP MAS solid state NMR spectrum of the 50/50 P(DHS/DPrS) copolymer (Fig. 6b) shows a broad resonance ranging from $\delta = -22$ ppm up to 27 ppm. Upon elevation of the temperature, a continuous

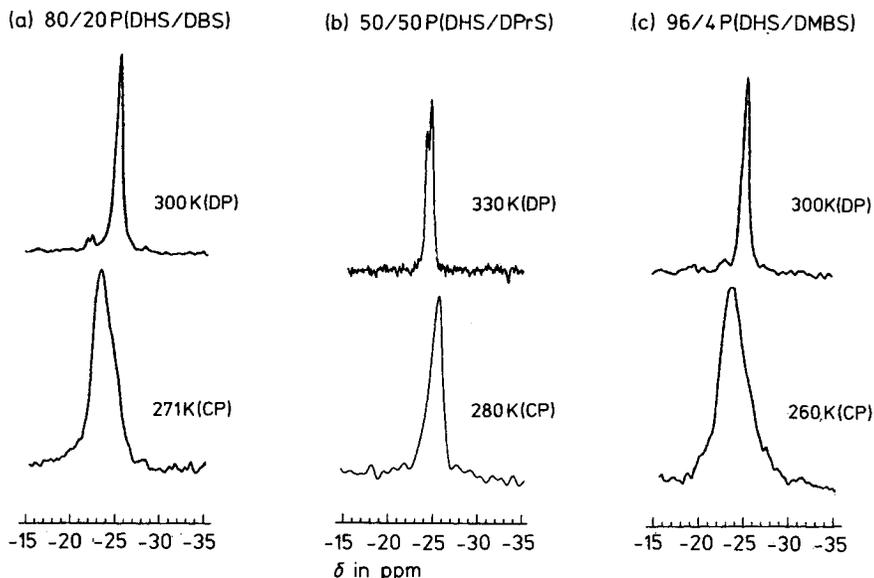


Fig. 6. ^{29}Si MAS solid state NMR spectra: (a) 80/20 P(DHS/DBS); (b) 50/50 P(DHS/DPrS); (c) 9/4 P(DHS/DMBS); CP: spectrum recorded with cross polarization, DP: spectrum recorded with polar decoupling

narrowing of the signal is observed, which can be explained by increasing segmental mobility. (The splitting of the signal at 330 K can be assigned to the different shielding of the Si-atoms in the two comonomers.) The resonance signal remains centered at the position of the mesophase at $\delta = -25$ ppm. Spectra recorded in dipolar decoupling mode without CP evidenced that the copolymer is present in a rather mobile state at 345 K. The behavior of the 50/50 P(DHS/DPrS) copolymer may be interpreted as a freezing of the mesomorphic disorder upon cooling. This explains the apparent contradiction between the low extent of order indicated by the solid state NMR spectra and the observed anisotropy.

The ^{29}Si MAS solid state NMR spectrum of the 96/4 P(DHS/DMBS) (Fig. 6c) shows a very broad resonance for the low-temperature phase, which again demonstrates conformational variety. The broad transition observed in calorimetry is confirmed by ^{29}Si solid state NMR. Already at low temperature, a fraction of the material is in the mobile state, as shown by the corresponding spectra recorded without CP in the dipolar decoupling mode. The broad resonance of the crystalline phase and the narrow motionally averaged signal of the mesophase are well resolved in the spectra. It is obvious from the data that considerable disorder is introduced into the planar structure of PDHS by the branched side chains. A large effect caused by a small fraction of branched side chains is in agreement with the fact that polysilylenes with branched side chains do not exhibit the thermo- and piezochromic behavior observed in PDHS, even if the branched moiety is 3 carbon atoms distant from the main chain^{31, 32}). In the case of the 96/4 P(DHS/DMBS) copolymer, the formation of a partially disordered

mesophase was still possible, as is obvious from ^{29}Si NMR spectra recorded at elevated temperature.

Variable temperature UV spectroscopy

PDHS shows a pronounced UV-thermochromism, when spin-cast films are heated above the transition temperature of 42°C . The UV absorption band shifts from 372 nm to 315 nm ²⁸⁾. This thermochromism is completely reversible and is ascribed to the onset of mobility and loss of the all-*trans* ordered structure of the σ -conjugated chromophores. The bathochromic shift of the UV absorption of PDHS is due to the decrease of band gap energy between σ -delocalized HOMO and LUMO for *trans*-sequences compared to *gauche* Si-Si bonds³³⁾. In the mesomorphic state, all copolymers investigated here exhibited an absorption band between 315 and 318 nm in the mesomorphic state, as expected for conformationally disordered polysilylenes. In the ordered low-temperature phase, different absorption bands were observed depending on the composition of the copolymers.

The 90/10 materials showed PDHS-like behavior. The isosbestic points in the spectra indicate coherent phase transitions (Fig. 7a/b). When comparing the variable temperature UV spectra of PDHS with the 90/10 copolymers with side chains ranging

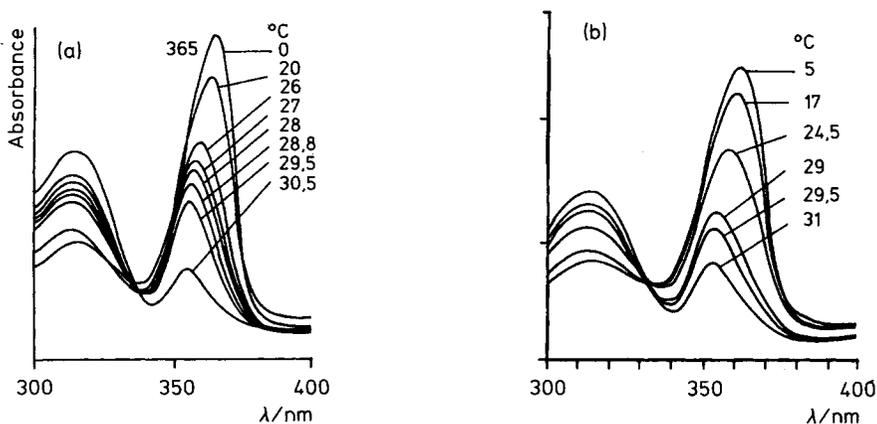


Fig. 7. Variable temperature UV spectra of film of (a) 90/10 P(DHS/DBS) and (b) 90/10 P(DHS/DPrS)

from pentyl to propyl, an important difference becomes evident: The UV-thermochromism occurs in two steps, as illustrated for the 90/10 P(DHS/DBS) copolymer in Fig. 7a. At first, a continuous redshift of λ_{max} to 355 nm is discerned, then the actual disordering to the columnar mesophase sets in. The effect is correlated to the gradual onset of mobility seen in the thermograms and is most pronounced for the material with the shortest comonomer side chains. This behavior may be explained by the

distribution of the segment composition. A second difference in comparison to the homopolymer, PDHS, is the blueshifted absorption maximum of the low-temperature phase. Whereas PDHS absorbs at 373 nm, the absorption maxima are at 367, 365, 362 nm for the copolymers with 10% pentyl, butyl, propyl side chains, respectively. This expresses a higher probability of non-*trans* conformed Si-Si bonds in these materials. Thus, the incorporation of a small percentage of shorter side chains allows a variation the σ -conjugation length of the backbone chromophores to a certain extent, however, an all-*trans* like structure is retained.

The 80/20 copolymers generally exhibited absorption maxima between 345 and 350 nm and transformed into the mesophase already around 0 °C. Representative for these materials, Fig. 8 depicts the UV spectrum of the copolymer 80/20 P(DHS/DBS). The UV-midtemperatures of the transitions are generally lower than the transition temperatures observed calorimetrically. The loss of the isosbestic point in the variable temperature UV spectra indicates that the transition does not occur from one defined state to another, but from a crystalline phase with an already disordered fraction to the mesophase.

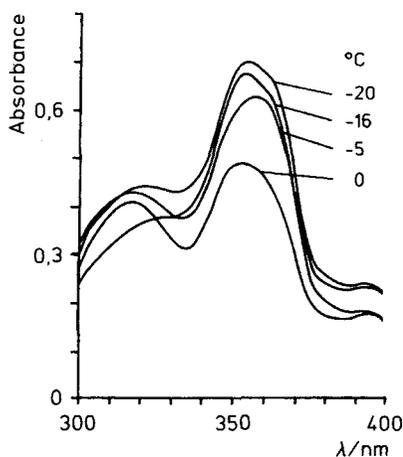


Fig. 8. Variable temperature solid state UV spectrum of 80/20 P(DHS/DBS)

The copolymer 96/4 P(DHS/DMBS) with some branched side chains built in is also ordered all-*trans* like, as evidenced by λ_{max} of 362 nm, but even at temperatures 15 °C below the phase transition, the mesophase absorption did not disappear completely, probably due to the incompatibility of a branched substituent with a planar backbone structure. The spectroscopic observations for this material are correlated to differential scanning calorimetry and ^{29}Si solid state NMR data.

Conclusions

A number of random copolymers derived from PDHS by incorporation of 10, 20 and 50% of shorter *n*-alkyl side chains has been studied. Also, nonsymmetrically hexyl-

methyl substituted units and branched side chains have been incorporated. Some structural principles for the formation of ordered crystalline and mesophases can be deduced from this study:

(i) 10% Linear, shorter side chains or non-symmetrically substituted silylene units can be incorporated into PDHS without destroying the all-*trans* order. Interruption of the all-*trans* planar order by structural defects resulted in blueshifts of the absorption maxima.

(ii) Incorporation of 20% or more of different side chains leads to a considerable decrease of side chain interaction, which results in conformational disorder already in the crystalline phase.

(iii) Branched side chains disturb the all-*trans* order of PDHS strongly, as also known for comb-like polymers in general and also impede the formation of conformational disorder.

In summary, ordered crystalline phases and mesomorphic disorder can only be expected for materials with linear side chains, with a difference in length of no more than 2 methylene units. These principles may have more general validity for polymers with inorganic backbones and linear aliphatic side chains, as indicated by recent results of the study of poly(di-*n*-alkylsiloxane)s in our laboratory³⁴.

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