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Structure and Chirooptical Properties of Bis[(*S*)-methylbutyl]silylene–Dipentylsilylene Copolymers

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ABSTRACT: Copolymers have been derived from poly(di-*n*-pentylsilylene) by incorporation of bis[(*S*)-2-methylbutyl]silylene units. Copolymers with 5–50% chiral comonomers were investigated with respect to their structures and chirooptical properties in solution, in the crystalline state, and in the columnar mesophase. Electron and X-ray diffraction showed that the 7/3 helical structure of PDPS was mainly retained. Only higher fractions of the branched chiral units hindered crystallization and caused disappearance of the mesomorphic transition. Circular dichroism (CD) spectroscopy revealed weak, temperature-dependent circular dichroism in cyclohexane solution correlated to the (σ–σ^*) backbone absorption. Remarkably strong CD couplet bands with an exciton-splitting shape were observed in THF as well as for thin spin-cast films, indicating enantioselective ordering in solution as well as in the solid. Transformation of the copolymers into the columnar, conformationally disordered mesophase led to a decrease of the strong CD bands.

Polysilylenes have been studied with respect to their photophysical properties[1–3] in the solid state as well as in solution. Due to the σ-delocalization along the catena-Si chain, the polymers show intense UV absorption, thermo- as well as piezochromism[4] and photoconductivity.[5] The band-gap energy and related charge-transport properties of poly(di-*n*-alkylsilylene)s are determined by the backbone conformation.[1,6] In the solid state, small variations of the substituents can be employed to control the backbone conformation.[7–13] Applications in the areas of microlithography,[14] nonlinear optics,[15] electrophotography,[16] and data storage[17] have been discussed.

Symmetrically substituted poly(di-*n*-alkylsilylene)s cannot only crystallize but do also form a mesophase[18] at elevated temperature. In this state, the long axes of the molecules retain their order, but the macromolecules are conformationally disordered. Segmental mobility results in a dynamic conformational equilibrium. Similar mesophases have been described for polyphosphazenes[19] and polysiloxanes.[20] Recently, it has been shown that also particular polysilylene copolymers can crystallize and form a columnar mesophase.[7]

Poly(di-*n*-pentylsilylene) (PDPS) is known to crystallize in a 7/3 helical structure and to undergo disordering to a conformationally irregular, columnarlike liquid-crystalline phase at 71°C.[21] Thus, the mesophase transition is characterized by helical disordering, and, provided it might be possible to give rise to enantioselective helical ordering, peculiar chirooptical properties can be expected.

Enantioselective helical ordering is well-known for biopolymers and has been described also for synthetic polymers consisting of stereoregular building units. It was studied for stereoregular poly(1-alkenes),[22,23] polyisocyanates,[24,25] and polyisocyanides.[26,27] Enantioselective helix formation in solution is only observed if the macromolecules form rigid helices. For flexible polymers like isotactic chiral poly(1-alkenes), e.g., poly[(*S*)-3-methyl-1-pentene],[28] crystalline packing is essential for an ordered helix formation.

Copolymers of poly(di-*n*-pentylsilylene) may crystallize with a prevalent helical sense, if a small fraction of *n*-pentyl side chains is replaced by structurally compatible chiral units, i.e., the chiral substituents might induce secondary structure chirality.[22,29] In a recent paper, we have described the synthesis, physical characterization, and solution behavior of two series of optically active polysilylene copolymers derived from poly(di-*n*-pentylsilylene).[30] In this study, the following questions are addressed regarding the solid state: (i) How large may the fraction of chiral, branched side chains be without impeding the formation of a regular crystal structure? (ii) Will the copolymers form a columnar mesophase similar to that of the homopolymer PDPS? (iii) Can the combination of chirality and mesomorphic disordering in the solid result in temperature-dependent macromolecular asymmetry?

Experimental Section

Synthesis. Monomer preparation and polymerization via the Wurtz-type coupling as well as the resulting molecular weights (M_w for all samples > 100 000) have been reported in detail before.[30]

Optical activities of polymer solutions were measured by means of a Perkin-Elmer polarimeter at 365 and 589 nm.

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Measurements were performed at two different concentrations (1 and 0.1 mmol/L) to exclude concentration effects. All solutions were filtered via Spartan 13/20 0.45-μm disposable microfilters (Schleicher & Schuell) before measuring.

CD and UV Spectroscopy. A Jasco JL-600 spectrometer, equipped with temperature control for solution cells and films, was used to determine circular dichroism of thin films and solutions. All solutions were filtered via a 0.45-m disposable Spartan 13/20 microfilter twice to remove dust and larger particles. Solid-state CD experiments were performed on thin films. Quartz disks were spin-coated by a particular polysilylene sample (film thickness 60 nm to 20 μm) using toluene or cyclohexane solutions of different concentration. An assessment of film thickness was made by comparison of the absorption spectra of spun films with that of a solution with known concentration. In the case of thicker films, the values were confirmed by weighing. Due to the possible difference between ϵ_{max} in films and solutions, the inaccuracy of the film thickness is estimated to be ±20%. None of the films appeared birefringent when inspected between crossed polarizers. The plate-supported films were rotated around the axes parallel and perpendicular to the beam in order to check for effects of linear dichroism or local film thickness variations. The CD is given as molar ellipticity, i.e., [deg·cm²/dmol]. Since UV spectra were not recorded together with CD spectra, a UVIKON 930 UV/Vis spectrometer was employed to measure UV spectra of films and solutions.

Calorimetry. A Perkin-Elmer DSC-7 was employed to monitor thermal transitions of the samples. The instrument was calibrated with high-purity samples of indium and cyclohexane. Transition temperatures were recorded with a heating rate of 10 K/min (sample amount 3−7 mg). Transition enthalpies are given as measured in the first heating run.

Electron Diffraction. The copolymers were crystallized on highly oriented (PTFE) on glass according to the method described by Wittmann and Smith.[31] This procedure yielded highly oriented films, as described elsewhere.[32] Subsequently, the films were shadowed with carbon as a support, and the polysilylene/PTFE sandwich was floated off the glass. A Philips CM 12 transmission electron microscope (operated at 120 kV) was employed to obtain the diffraction patterns. The camera length was varied between 270 and 1100 mm.

Wide-angle X-ray diffraction studies have been performed using Ni-filtered Cu Kα radiation. Samples were prepared by slow crystallization from cyclohexanol solution (cooling rate 40/h). Powder patterns were obtained with a flat-plate pinhole camera with a sample−film distance of 45 mm; the diameter of the primary beam was 0.3 mm; the exposure time was 5 h. Temperature-dependent diffractograms have been recorded on a circular film with a radius of 57.3 mm, using a Guinier−Simon camera. In order to detect the scattering intensity at scattering angles as low as 1.5° (2θ), a slight adjustment of the beam stop has been made. The samples were cooled by means of a constant flow of cold nitrogen gas, and the temperature was controlled by means of a thermocouple introduced into the nozzle in the direct vicinity of the specimen. The temperature variation in the sample compartment was checked with an additional thermocouple and was found to be ±2 K. Exposure times were approximately 3 h. Optical density data were collected from the photographically obtained patterns using a linear microdensitometer LS20 (Delft Instruments) controlled by SCANPI software.

^{13}C Solution NMR spectra were recorded on a Bruker AC 250 spectrometer in C_6D_{12} at 62.8 MHz. Chemical shifts are referenced against TMS. Spin−lattice relaxation times were determined by the usual inversion sequence.

^{29}Si-Solid State NMR was recorded on a Bruker CXP 300 spectrometer at 59.63 MHz. A double-bearing MAS probe (Bruker), modified for variable-temperature experiments, was employed. High-power decoupling and magic-angle spinning were used to achieve line narrowing. Delay times between sampling of the FIDs and cross-polarization times were chosen to yield optimum signal intensities. Thus, relative intensities in the spectra do not reflect the molecular fractions correctly. The spinning rate was 3000 Hz. ^{29}Si chemical shifts were referenced to TMS as described before.[7] The absolute accuracy of the chemical shifts was about 1 ppm, and the relative accuracy for spectra at the same temperature was about 0.1 ppm.

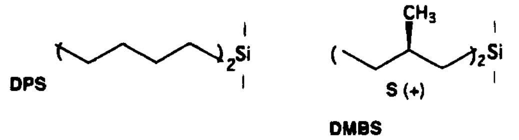

Figure 1. Building units of the chiral polysilylene copolymers; DPS = di-n-pentylsilylene; DMBS = bis[(S)-2-methylbutyl]-silylene.

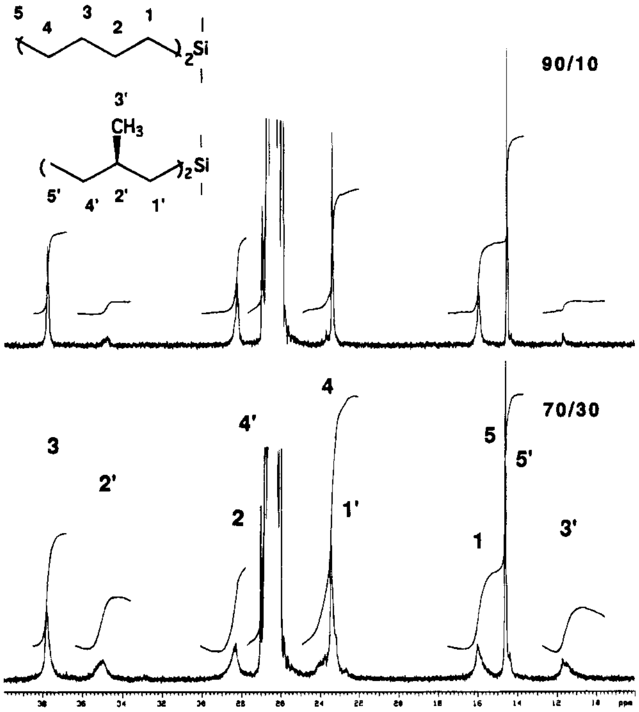

Figure 2. (a,b) Comparison of the ^{13}C-NMR spectra of the symmetrical 90/10 P(DPS/DMBS) and 70/30 P(DPS/DMBS) copolymers (26−27 ppm: cyclohexane-d_{12}).

Results and Discussion

1. Molecular Characterization. Copolymers with 5−50% symmetrically substituted chiral comonomers have been prepared. As an example for the denotation used in the ensuing text, 90/10 P(DPS/DMBS) is a polysilylene random copolymer, prepared from a 90/10 monomer mixture of di-n-pentyldichlorosilane and symmetrical bis[(S)-methylbutyl]dichlorosilane. DPS designates di-n-pentylsilylene units and DMBS the bis[(S)-methylbutyl]silylene units (Figure 1).

Parts a and b of Figure 2 depict the ^{13}C-NMR spectra of the symmetrical 90/10 P(DPS/DMBS) and 70/30 P(DPS/DMBS) copolymers. The signal assignment was made by means of "DEPT" experiments to distinguish between $-CH_3$, $-CH_2-$, and CH− groups and is consistent with the assignment of PDPS.[33] Long delay times (20 s) between sampling of the FIDs were chosen in order to ensure complete spin relaxation. Integration of the ^{13}C-NMR spectra was generally in agreement with the composition expected from the monomer feed. As usual for poly(di-n-alkylsilylene)s, the line width increased when moving from the outer carbons to the backbone, which can be explained by an increasing restriction of the segmental mobility.[33] When comparing the 70/30 and the 90/10 P(DPS/DMBS) copolymers, strong broadening of all lines is observed with increasing fraction of chiral groups. The poorly resolved

Table 1. ^{13}C T_1 Relaxation Times (s) of 70/30 P(DPS/DMBS)

C-1	0.23	C-1′	
C-2	0.36	C-2′	0.38
C-3	0.42	C-3′	0.38
C-4	0.79	C-4′	
C-5	1.79	C-5′	

splitting of the $-CH_2$ (1′) and $-CH_2$ (3′) methylbutyl group signal can be explained by the variation of the micro structure, i.e., different sequences present in the 70/30 copolymer. Thus, substantially random statistics of the copolymers has been indicated, as it should be expected because of the similar monomer structures.

Table 1 gives the ^{13}C T_1 times measured for the different carbon atoms, which are generally in good agreement with values reported before for poly(di-*n*-hexylsilylene).[33] The rather short T_1 time (0.38 s) found for the CH_3 group of the (*S*)-methylbutyl side chains and the increase in line width upon incorporation of the chiral comonomers indicate restricted mobility of the chiral branched unit caused by the dense substitution pattern. One may expect that a sterically crowded substitution would result in stiffening of the chain. This is consistent with larger values of the intrinsic viscosity observed with increasing fraction of chiral units.[30]

2. Solution Behavior. Poly(di-*n*-alkylsilylene)s exhibit thermochromic transitions in solution, which were first observed for poly(di-n-hexylsilylene) in and attributed to a coil–rod transformation.[34] However, rigid-rod-like conformations of macromolecules in solution require either a stiff main-chain structure, particular interaction forces within the chain,[35] such as H-bonding, or very strong steric constraints. Neither of these points is substantially fulfilled for poly(di-*n*-hexylsilylene), and light-scattering experiments have shown that even at concentrations below 10^{-4} mol/L the thermochromism in solution is associated with aggregation.[36,37] Accompanied by the red shift of the absorption maximum, a decrease of the coil dimensions occurs first, before aggregation takes place at low temperature. Correspondingly to poly(di-*n*-hexylsilylene), poly(di-*n*-pentylsilylene) showed a red shift of λ_{max} from 320 to 355 nm in a hexane solution at −31 °C.[21,38]

In order to study the solution behavior of the optically active polysilylene copolymers, we have carried out circular dichroism (CD) and UV measurements in cyclohexane and THF solution covering the temperature range between 0 and +60°C. While intramolecular conformational variation affects the σ-conjugation of the polysilylene chains and therefore results in changes of the UV absorption maximum, the magnitude and band shape of CD bands allow one to distinguish between mere local chiral perturbation of a macromolecule and enantioselective ordering of polymer segments.[29] In the case of prevalence of one screw sense, strong exciton coupling of the ordered array of chiral chromophores might be expected, as was reported recently for chiral polythiophenes[39,40] and as is well-known for biomolecules such as nucleic acid single strands of poly(riboadenosine).[41] Two CD bands of opposite sign, centered at the UV absorption maximum wavelength, result due to the interaction between electronic transitions of the chirally ordered, chromophoric units.[29]

In cyclohexane all chiral copolymers, which have been studied here, showed relatively weak circular dichroism (molar ellipticity $[\Theta] < 15\,000$ deg cm^2/dmol) correlated with the $\sigma-\sigma^*$ transition.[30] A slight diminution of the CD band and a variation of the correlated UV absorption intensity was observed upon raising the temperature from 3 to 30 °C. This indicated a mere local chiral perturbation of the backbone by the (*S*)-2-methylbutyl substituents. Similar weak positive CD bands have been observed in THF, which is a less good solvent for poly(dialkylsilylene)s than cyclohexane,[37] as long as the fraction of the chiral DMBS units did not exceed 20%.

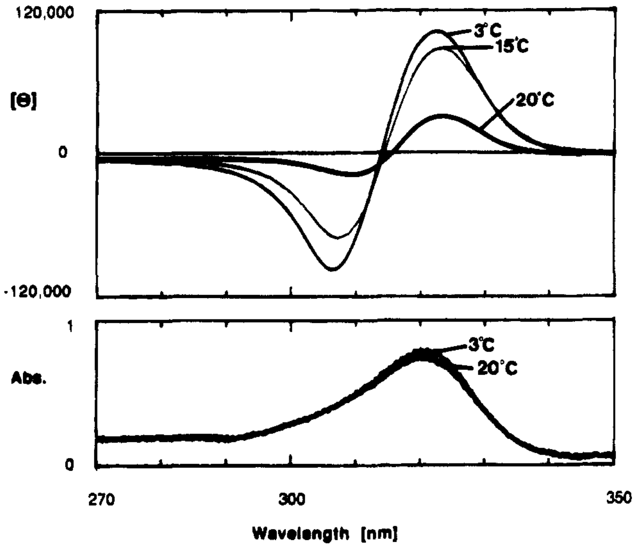

Figure 3. Variable-temperature CD and UV spectra of 80/20 P(DPS/DMBS) in THF, recorded during heating runs from 3 °C to 20 °C.

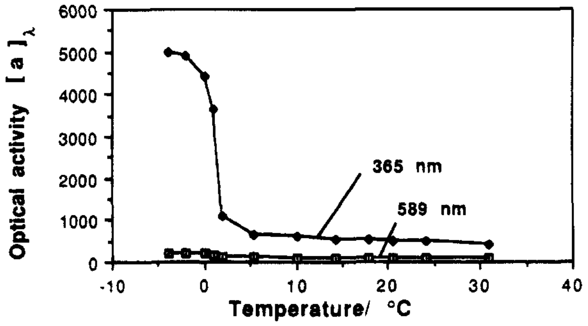

Figure 4. Optical activity of 80/20 P(DPS/DMBS) in THF, corresponding to the CD spectrum in Figure 4.

Fundamentally different behavior was observed for the 80/20 P(DPS/DMBS) polymer in THF solution (Figure 3). The UV spectrum changed almost imperceptibly, indicating that the amount of dissolved material did not vary upon the transformation. Correspondingly, no precipitation or turbidity of the solution was observed. However, the CD band was altered strongly upon cooling. Above room temperature, a weak CD band was found centered at 320 nm similarly as in cyclohexane. When the solution was cooled to 3 °C, the CD intensity grew and the band showed two components of opposite sign. This spectrum is centered at shorter wavelength than the absorption maximum and resembles an exciton splitting.

The transition of the CD band was correlated to changes of the optical rotation. Whereas the optical rotation of the chiral copolymers in cyclohexane showed generally an almost linear temperature dependence,[30] a strong increase of $[\alpha]_{365}$ to values around 5000° was measured upon cooling THF solutions (Figure 4). A similarly strong increase of the optical activity has been described upon cooling, e.g., chirally substituted polyisocyanates.[42]

The transition was thermoreversible with a hysteresis of 7–10°C. The transition temperature CD band shape

Table 2. Disordering Transitions of Optically Active Copolymers As Determined by DSC

copolymer	T_{dis}	ΔH_{dis}(kJ/mol)
PDPS	73	2.0[6]
95/5 P(DPS/DMBS)	72	1.7
90/10 P(DPS/DMBS)	73	1.2
85/15 P(DPS/DMBS)	60	0.5
80/20 P(DPS/DMBS)	64	0.4
70/30 P(DPS/DMBS)		
50/50 P(DPS/DMBS)		

were not affected by variation of the polymer concentration within the range of 10^{-3}−10^{-4} mol/L.

So far, occurrence of the exciton couplet CD band in the region of the electronic transition and the optical rotation indicates clearly that the chromophoric backbone segments became enantioselectively organized upon cooling. However, these segments must be rather short as the unchanged UV absorption evidences that the Si chain contains similar gauche−trans sequences like in the randomly coiled state.

It cannot be excluded that helix formation is accompanied by aggregation (or vice versa). Incorporation of the chiral comonomer units decreased the solubility, i.e., copolymers containing more than 30% of the symmetrical chiral units were insoluble in THF and $CDCl_3$ at room temperature. Thus, aggregation might well occur already at room temperature. After quenching the solution from Figure 3 to 3 °C, the CD band grew slightly in time to its final value, which may be interpreted in terms of noninteracting, growing helical segments as well as in terms of an increasing degree of aggregation in combination with enantioselective secondary structure formation.

3. Solid-State Structure. The formation of ordered, crystalline phases for copolymers depends on the degree of isomorphism of the building units, i.e., to which extent foreign units fit into the crystal lattice formed by the main building units.[43] Furthermore, the micro structure of the polymer is of crucial importance. If the comonomers are distributed randomly in the chains, they are less likely to be expelled from the crystalline phase than in blocky copolymers. Generally, helical polymer structures can accommodate a certain fraction of structural defects without complete loss of the structure.[40] Based on the experience with poly(di-*n*-hexyldi-*n*-pentyl) and poly(di-*n*-pentyldi-*n*-butyl) copolymers[7,44] and the random composition suggested from NMR, rather good crystallization compatibility has been expected for the poly(di-*n*-pentysilylene)s with chiral co-units.

Calorimetric data of the chiral silylene copolymers are listed in Table 2. The data were obtained for the polymers as precipitated (first heating). Copolymers with a low content of chiral units (<10%) showed a PDPS-like thermal behavior. Whereas the disordering temperature remained relatively constant, the disordering enthalpy decreased with increasing fraction of the chiral comonomers.[45]

The question arises as to whether the mesomorphic transition disappears upon incorporation of an increasing fraction of chiral comonomers because the polymers cannot crystallize but still form the less ordered mesophase or whether the copolymers do not form the mesophase and the crystals transform directly to the isotropic melt. The first case is suggested by the less regular structure of the copolymers. The second case might be expected because of the bulkiness of the chiral substituents and the fact that segmental flexibility is a major prerequisite for the formation of conformationally disordered phases.[46]

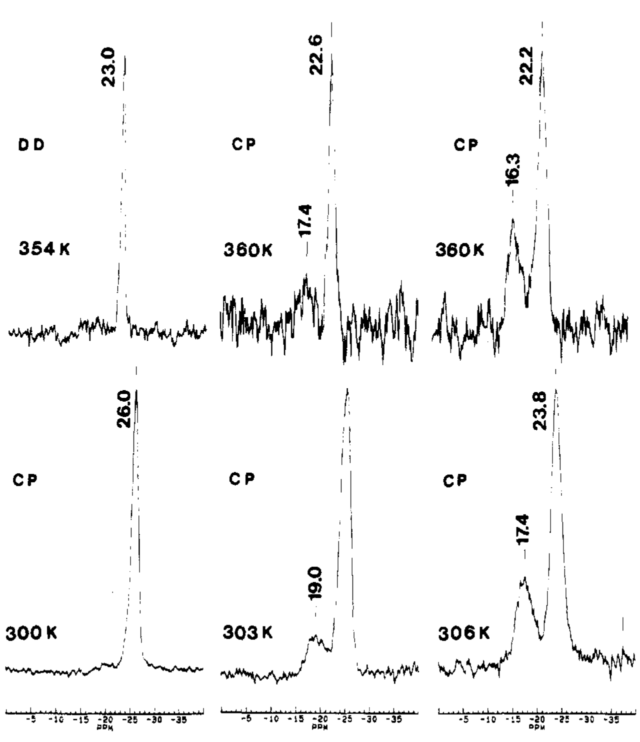

Figure 5. ^{29}Si-MAS solid-state NMR spectra of the symmetrical chiral copolymers P(DPS/DMBS) with 5% (left), 20% (middle), and 50% (right) DMBS units. CP: cross-polarization, DD: dipolar decoupling, numbers at the peaks give negative chemical shifts with respect to TMS.

Magic-angle-spinning (MAS) ^{29}Si-NMR has been employed to obtain some insight into the structure and dynamics of the polysilylene segments in the solid.[21] The 7/3 helical structure of PDPS yielded a chemical shift of −26 ppm at 300 K, whereas the conformationally disordered mesophase displayed a narrow motionally averaged signal at −23 ppm (350 K). Spin−lattice relaxation times for the Si nuclei in the crystalline and the disordered phase of poly(di-*n*-alkylsilylene) homopolymers differed considerably.[47] Thus, the mobile, conformationally disordered mesophase could be probed selectively by recording the spectra without cross-polarization (CP), while cross-polarization MAS spectra yielded the isotropic chemical shifts of the nuclei in the crystalline phase.

Figure 5 gives a comparison of the MAS ^{29}Si-NMR spectra for three (DPS/DMBS) copolymers with different composition. The 95/5 copolymer showed the same chemical shifts for a more rigid component at low temperature and a more mobile component at high temperature as found for PDPS, and also the temperature variation corresponded to the mesophase transition observed by DSC.

The ^{29}Si-NMR signals where slightly shifted toward lower field when the content of DMBS units was raised to 20%. The CP spectrum recorded at ambient temperature yielded a signal at −25 ppm, still indicating segmental helical ordering, and the spectrum at 360 K was dominated by a peak at −22.6 ppm comparable to the signal for the conformational disordered mesophase of PDPS. However, an increase of the T_1 relaxation time at high temperature was observed compared to the PDPS homopolymer which allowed us to record the 360 K spectrum with cross-polarization and which can be seen as an indication for some stiffening of the chain. Additionally, a broad peak was observed around −19 and −17 ppm in the low- and high-temperature spectra, respectively. According to its chemical shift, this signal can be assigned to the Si nuclei of the DMBS units.

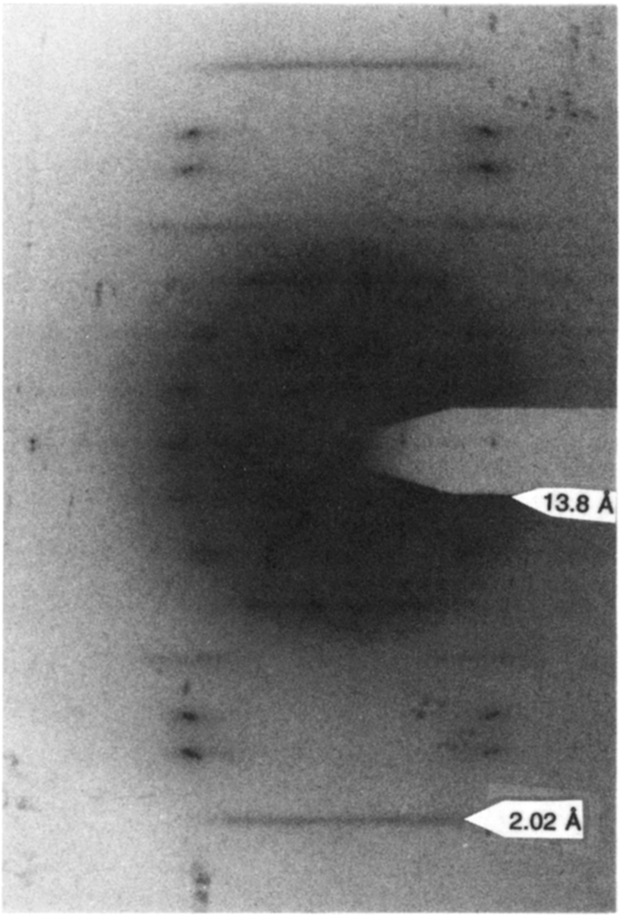

Figure 6. Electron diffraction pattern of the 90/10 P(DPS/DMBS) copolymer oriented on PTFE.

Upon increasing the DMBS content to 50%, the spectrum at 306 K depicted a main signal at −23.8 ppm and a second peak of minor intensity at −17.4 ppm. At 360 K, both signals shifted downfield by less than 1 ppm which evidences that the chain conformation does not change as much as observed for PDPS. Incorporation of the branched side chains resulted in a significant increase of the spin−lattice relaxation time at high temperature which allowed us to record the spectrum efficiently with cross-polarization even at 390 K (not shown here).

It can be concluded that incorporation of large amounts (20%) of the DMBS units inhibited the helix disordering transition which is observed for poly(dipentylsilylene). It cannot be decided from the spectra whether the −24/−23 ppm signal for the 50/50 P(DPS/DMBS) sample represents conformational disordered segments or a more or less regular helical structure, in which case the ^{29}Si signal is shifted downfield compared to PDPS because of the different substitution of the catened silicon.

Electron diffraction patterns from oriented copolymers and X-ray powder diffractograms have been measured in order to compare the crystalline packing of the chiral copolymers.

As we reported before, oriented thin films of polysilylenes can be prepared by crystallization on highly oriented PTFE.[32] The fiber pattern of the 90/10 P(DPS/DMBS) copolymer is depicted in Figure 6. The sharp meridional reflection corresponding to an interplanar distance *d* of 1.3 Å and the equatorial reflection with *d* = 7.3 Å origin from the PTFE substrate can be used as an internal standard for a precise determination of the camera length.

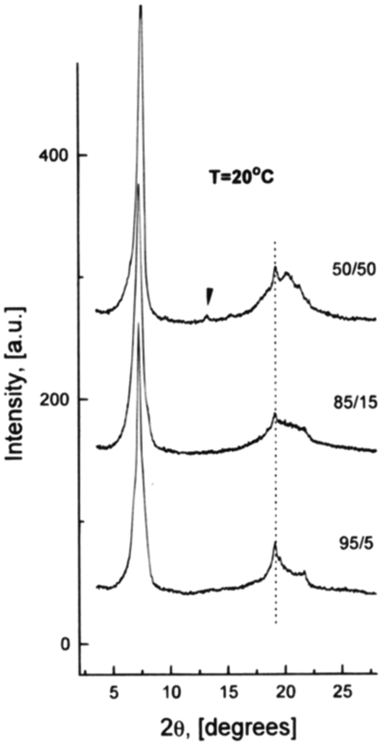

Figure 7. X-ray diffractograms for 95/5 P(DPS/DMBS) (bottom), 85/15 P(DPS/DMBS) (middle), and 50/50 P(DPS/DMBS) (top).

The diffraction pattern of the 90/10 copolymer is well resolved and exhibits reflections without significant arcing which indicates a high perfection of molecular alignment. Observation of only a few equatorial reflections suggests poor structural interchain correlation in the *ab* plane. Different than in the case of all-trans planar poly(dihexylsilylene), this is typical for PDPS.[48] Diffractograms recorded with longer camera length than in the case of of Figure 6 depicted two main equatorial reflections with *d* = 12.8 and 12.0 Å. These interplanar distances do not coincide with those found for oriented bulk PDPS.[48] However, the intermolecular spacing is observed to be rather sensitive to the sample preparation.

Layer lines are displayed up to the seventh one. Consistent with a 7/3 helix structure of the backbone, the third and the seventh exhibit meridional reflections which correspond to *d* = 4.6 Å and *d* = 2.03 Å, respectively. An identity period along the main chain of 13.8 Å can be derived which agrees with the data reported for helical PDPS and PDBS.[21,48]

In order to elucidate structural changes upon heating, X-ray powder diffractograms were recorded at ambient and elevated temperatures for solution crystallized copolymers with 5, 15, and 50% DMBS units. Figure 7 compares the results at room temperature. Up to 15% DMBS units, the diffractograms are dominated by a strong reflection, with its maximum corresponding to *d* = 12.15 Å and exhibiting a hardly resolved fine structure. Assigning this reflection to the intermolecular scattering (see the electron diffraction data and refs 21 and 48), it can be concluded that the packing of the main-chain axis remains nearly the same upon increasing the DMBS content.

A principally different sacttering pattern was observed for the 50/50 sample. The reflections listed in Table 3 and their *d*-spacings and intensities indicate that this copolymer is packed into a three-dimensional unit cell with *a* = *b* = 13.3 Å and *c* = 13.8 Å. Another

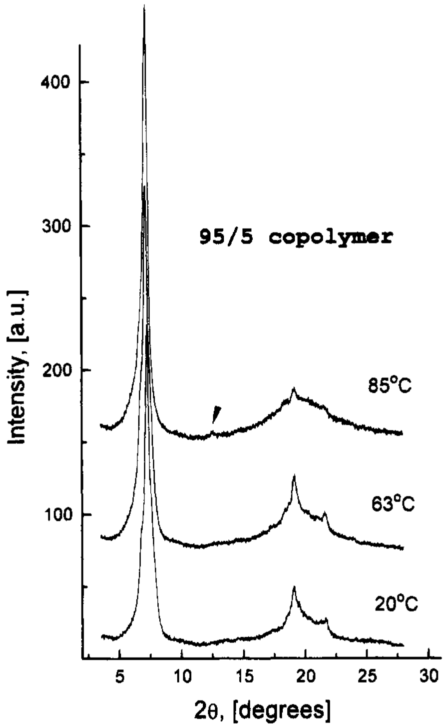

Figure 8. Temperature dependence of the X-ray diffractogram of the 95/5 P(DPS/DMBS) copolymer. The diagram in the top shows clearly a small reflection at 2Θ = 13°.

Table 3. List of X-ray Reflections for 50/50 P(DPS/DMBS) Given as Bragg Distances (±0.03 Å) with *hkl* Indices

11.5 Å, strong	100	5.75 Å, weak	200
6.63 Å, weak	110	4.6 Å, strong	003
4.34 Å, medium	210 + 013		

point to note is the unchanged position of the strong reflection for 4.6 Å, with *hkl* 003 indicating that the 7/3 helix structure remains the same despite the increase of the chiral comonomer content.

The changes of the diffractograms upon heating are illustrated in Figures 8–10. The transformation of PDPS to a quasihexagonal dense packing has been reported in the literature.[21,48] The copolymer with 5% DMBS units undergoes the same transition according to the small peak marked by the arrow in Figure 8. In contrast to this, the diffractogram of the 85/15 copolymer above the DSC transition does not display the characteristic 110 reflection for the columnar phase.

In the case of the 50/50 copolymer, heating led to a gradual decrease of the three-dimensional ordering and the regularity of the 7/3 helix accompanied by thermal expansion. As the hexagonal symmetry of the unit is not changed, there is clearly no phase transition like in the case of PDPS and the 95/5 copolymer.

In summary the diffraction data indicate that a small amount up to 15% of the chiral comonomer does not change the crystal structre of poly(dipentylsilylene). The structure distorted within the *ab* plane, but the 7/3 helix of the backbone was preserved. In particular, when only small fractions of the DMBS units were built into the chain, the material transforms from the crystalline phase to the columnar mesophase. When larger fractions of branched side chains were incorporated into the PDPS chain, the material lost its ability to undergo helix disordering, yielding a columnar mesophase at elevated temperatures.

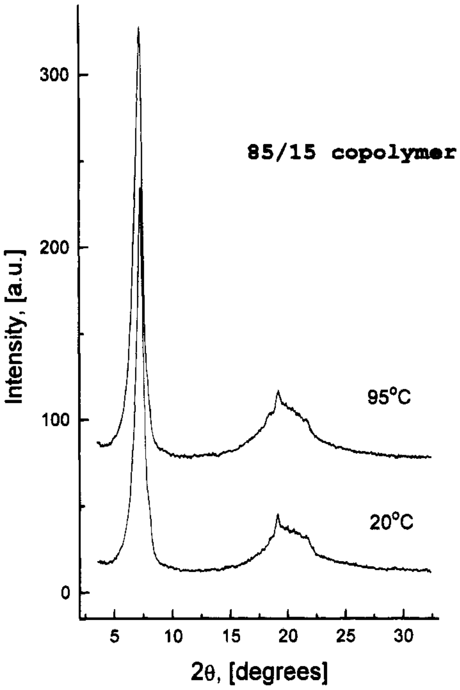

Figure 9. Temperature dependence of the X-ray diffractogram of the 85/15 P(DPS/DMBS) copolymer, below (20 °C) and above (92 °C) the mesophase transition of PDPS.

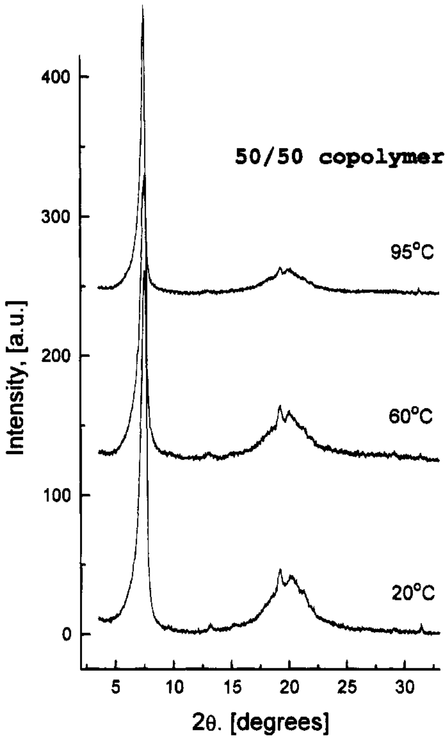

Figure 10. Temperature dependence of the X-ray diffractogram of the 50/50 P(DPS/DMBS) copolymer.

Apparently, the more bulky, branched side chains favor a helical segment conformation and prevent at higher concentration formation of the conformationally disordered mesophase. This is consistent with the MAS ^{29}Si-NMR data reported above indicating some stiffening of the backbone and the DSC studies showing that the transition vanishes gradually upon incorporation of increasing amounts of chiral comonomers.

4. Solid-State Chirooptical Properties. The results on the crystallization of the polysilylenes demonstrate that essential conditions are fulfilled to realize enantioselective helical ordering in the solid state and to expect temperature dependent optical asymmetry as, in the case of a small fraction of chiral comonomers, the helical crystal structure gets disordered by formation

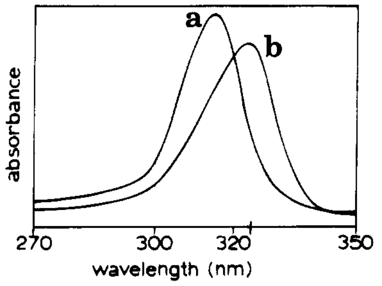

Figure 11. UV spectra of films of PDPS (a) and the 50/50 P(DPS/DMBS) (b).

of the columnar mesophase. Characterization of the molecular optical activity, optical rotatory dispersion (ORD), or CD of crystalline materials, however, is hampered by interference of birefringence and scattering effects. Molecular optical rotation, CD, and ORD can only be measured directly if the sample is isotropic with respect to the axis of observation so that birefringence is absent.[49] Fast rotation of thin film samples or suspending small crystallites in a liquid has been used in order to generate optical isotropy and to characterize ORD and CD of crystalline materials.[50,51]

Anisotropy and scattering can also be neglected in the case of a thin polycrystalline film of crystallites which are smaller than the wavelength of light and which are arranged in axial symmetry. Such thin films of polysilylene copolymers could be prepared by spin casting on quartz discs.[52] While simple casting led to rather big variations in the crystallite sizes and film thickness, the fast solvent evaporation during spin casting yielded films which did not reveal spherulitic structures (Maltese cross patterns) even when they were annealed in the mesophase for extended time.

Reproducible formation of ultrasmall crystallites was demonstrated by the pronounced UV thermochromism correlated to the thermal transitions, which is discussed below, and scanning force microscopy.[53] At the same time, the polysilylene chains were aligned in the radial direction due to the strong centrifugal forces during the spin-casting procedure. This orientation of the polysilylene backbone in the plane parallel to the quartz surface was indicated by grazing angle FT-IR spectroscopy.[53,54] As a result, axial symmetry was achieved when the CD experiments were performed on a center spot of the spin-coated quartz disks and no effect on CD intensity and shape was observed for all spectra reported here when the films were rotated around the axes parallel and perpendicular to the light beam. A precise assessment of crystallinity has not been made.

Figure 11 depicts the UV/Vis spectrum of a spin-cast film of the 50/50 P(DPS/DMBS) copolymer. As has been reported for solutions, incorporation of the chiral counits shifted the absorption maximum $\lambda_{\max}$ to 326 nm compared to 316 nm for mesomorphic or dissolved PDPS.[30] As discussed above, this is consistent with stiffening of the chain backbone and partial helical ordering.

Figure 12 compares thin film CD and UV spectra of the copolymers with 10% and 50% of symmetrical chiral building units (the circular dichroism is normalized with respect to the film thickness). Very strong CD bands were observed, which exhibit a shape with two components of opposite sign, typical for excitonic coupling of chiral chromophores.[29,55-57] The center of the CD signal did not coincide precisely with the UV/vis absorption maximum. The shape of the CD band is almost identical with the signal observed in a THF solution upon cooling, but the intensity is higher by a factor of 2. For chiral, isotactic poly(1-alkenes), it has been demonstrated that the same CD bands result for the solid as observed in solution.[58]

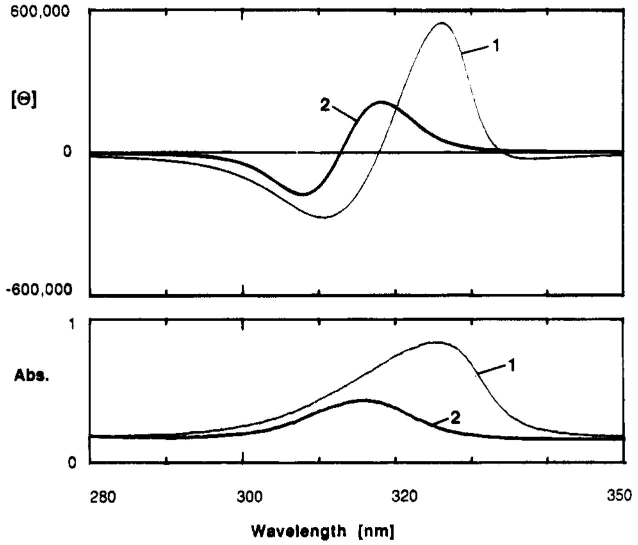

Figure 12. Comparison of the film CD and UV spectra of the 50/50 P(DPS/DMBS) (1) and 90/10 P(DPS/DMBS) (2). Both spectra have been normalized with respect to film thickness.

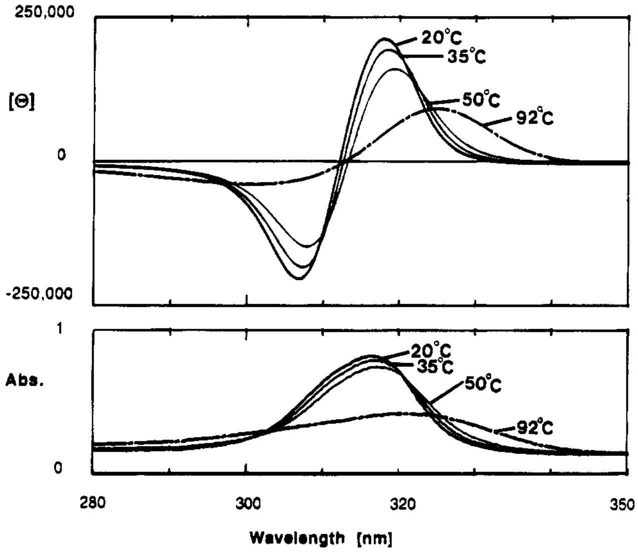

Figure 13. Temperature dependence of CD (top) and corresponding UV spectra (bottom) of a spin-cast film of 90/10 P(DPS/DMBS) (d = 0.17 μm).

In the solid, such strong CD couplets were observed for all DMBS copolymers with the same change in sign (±). Helical ordering with a preferential screw sense is clearly indicated by the magnitude of the CD and the fact that the effect is correlated to the σ–σ^* transition of the catena silicon backbone. Consistent with experimental observation, this can be expected to be the same for all (S)-2-methylbutylsilylene copolymers investigated here, because the change of sign of the exciton splitting is known to depend on the screw sense of the helix.[2] The observation that the change in sign did not coincide with the absorption maximum can be explained by variations in the contributions to the CD and the UV absorption by polymer segments which differ in conformation and length.

Variable-temperature CD and UV experiments were performed in order to study the effect of conformational disordering. Figure 13 shows the temperature dependence (first heating run) of the CD and the correlated UV spectra of a thin film of the 90/10 P(DPS/DMBS)

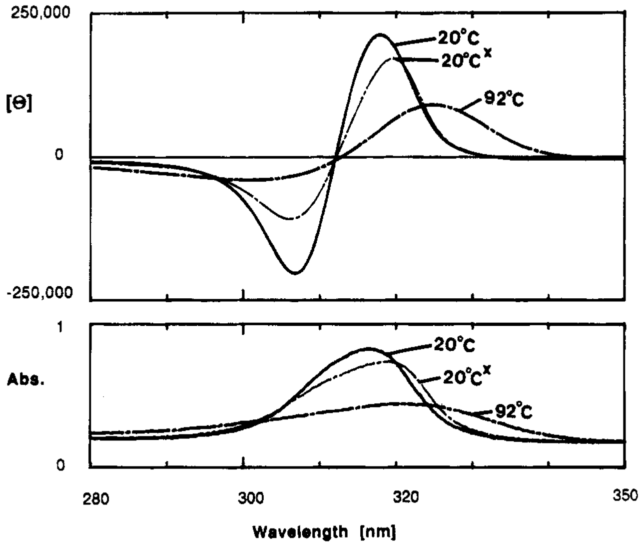

Figure 14. Comparison of CD and UV spectra of thin film of 90/10 copolymer before the first heating run, in the mesophase (92 °C) and after cooling (20 °C) marked by x.

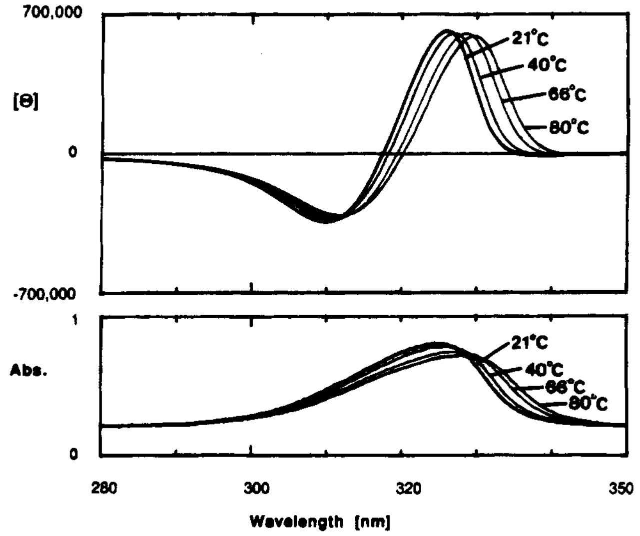

Figure 15. CD and corresponding UV spectra of a film of the 50/50 P(DPS/DMBS) recorded at variable temperature (film thickness $d = 0.12$ μm).

sample. This material exhibited a crystal to mesophase transformation, and, correspondingly, also the solid-state thermochromism known for PDPS[21] was observed by a broadening of the UV absorption above 70°C. In agreement with the concept of conformational disordering, the CD effect decreased upon this transformation and only a relatively weak CD remained in the mesophase at longer wavelength. A significant decrease of the CD upon approaching the transition from lower temperature can be explained by the strong disturbance of the helical ordering by still small defect fractions which are inevitable upon the onset of mobility before the actual phase transition.

When the film of 90/10 P(DPS/DMBS) was afterwards cooled down from the mesophase, the change of the CD was not completely reversible. Only part of the initial CD intensity was recovered (Figure 14), and also the corresponding UV spectrum differed from that of the virgin spin-casted film.

As has been discussed below, an increasing fraction of chiral comonomers inhibited formation of a highly ordered crystal phase, while, at the same time, the bulky side groups favored helix formation at higher temperatures. Consistent with a lesser temperature dependence of the backbone conformation, Figure 15 demonstrates a much smaller temperature dependence of the CD band and UV absorption for a spin-casted 50/50 P(DPS/DMBS) film than was observed for the copolymers with less chiral co-units. A band shift by 3–4 nm to longer wavelengths was noted in the CD spectrum upon heating. An isosbestic point and a pronounced shift of $\lambda_{\max}$ in the UV absorption may indicate a rather well-defined equilibrium between two (helical) backbone conformations.

Conclusions

It has been shown that (*S*)-2-methylbutyl side chains can be incorporated into poly(dipentylsilylene) in order to cause enantioselective conformational ordering. Solistate NMR, X-ray, and electron diffraction demonstrated for the crystalline state that the helical ordering is not obstructed by small amounts of the chiral co-units. As a result, strong circular dichroism couplets have been observed for spin-cast films. The CD spectra are in qualitative agreement with the spectra in THF solution, evidencing the molecular origin of the effect. The explanation by enantioselective formation of a secondary structure is supported by the observation of only weak CD bands when the polymers were dissolved in cyclohexane, which is a better solvent than THF. Clearly, the chiral perturbation of the catena Si backbone is much more localized in this case.

Correlated to the crystal mesophase transformation, i.e., the onset of conformational disorder, a temperature-dependent decrease of the solid-state circular dichroism was observed. For copolymers with a low fraction of chiral units, this effect was reversible and almost the full initial CD intensity was recovered upon cooling. Copolymers with more than 20% of chiral, branched side chains exhibit high-intensity CD bands, but only a minor fraction of the material became mobile upon heating. Stiffening of the molecular backbone and stabilization of the helix structure by branched and chiral substituents is also consistent with recent reports on chirally substituted polysilanes in solution by Fujiki.[59]

Quantitative evaluation of CD spectra of optically active polymers has been proposed by Tinoco.[55–57] This theory uses the Frenkel exciton model. The exciton model for a helix composed of identical interacting residues predicts three different contributions to the circular dichroism, namely, (i) the optical activity induced into each chromophore by the chirality of the isolated residue (if present), (ii) the "non conservative" contribution resulting from the interaction among transitions of different energy (interband interaction), and (iii) the "conservative" contribution, which stems from the interactions among transitions of the same energy in identical residues, which gives rise to the couplet band. In the case of the chiral copolymers, the components i and ii are small, whereas iii is large and determines mainly the shape of the CD bands observed.

In contrast to optically active polymers with side-chain chromophores,[24–29] the electronic transitions of the chiral polysilylenes are directly due to the backbone structure (σ–σ^* transition) and depend on the conformational regularity. Although we lack therefore essential information on the nature of the excitons in the case of polysilylenes, we have attempted to fit the observed CD bands with two different band components, one Gaussian line for contributions i and ii and one Gaussian derivative line for iii. In this manner, a reasonable fit could be obtained.

It is intriguing to address some consequences of the crystallization of polysilylenes with predominance for one helical sense. In addition to the "thermochirality", also pressure dependence of the optical activity can be expected. Asymmetric ordering of polysilylenes raises the question about their nonlinear optics. Furthermore, this work might contribute to a better general understanding of other polymers with chromophoric, intrinsically conductive backbone and chiral side chains, which are the subjects of current research activities.[60-62]

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