Macromolecules **1994,** *27,* 1814-1818

Chiral Poly(dipentylsilylene) Copolymers

Holger Frey[†] **and Martin Möller**[*,‡]

Chemische Technologie, Universiteit Twente, Postbus 217,
7500 AE Enschede, The Netherlands

Krzysztof Matyjaszewski

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue,
Pittsburgh, Pennsylvania 75213

Received March 26, 1993; Revised Manuscript Received December 21, 1993[⊗]

ABSTRACT: Chiral polysilylene copolymers derived from poly(di-*n*-pentylsilylene) (PDPS) with chiral (*S*)-2-methylbutyl side chains were prepared. Symmetrical bis[(*S*)-2-methylbutyl]silylene units (5–50%) as well as nonsymmetrical (*S*)-2-methylbutyl/*n*-pentylsilylene units (2–30%) were incorporated. The copolymers showed high optical activities and circular dichroism related to the $\sigma-\sigma^*$ transition in a cyclohexane solution. Increasing the degree of substitution with bulky chiral side chains resulted in narrowing of the absorption band and a blueshift of λ_{max} in solution. In the solid, copolymers with a low content of branched chiral units showed transitions to a columnarlike mesophase as known for PDPS; materials with a higher content exhibited no measurable thermal transitions.

Introduction

This paper comprises a first report on the synthesis and optical characterization of optically active polysilylenes. On the basis of the peculiar σ electron delocalization along the polymeric backbone, catenated silicon polymers possess intriguing properties such as strong UV absorptions, photoconductivity, and thermochromism.[1] The polymer backbone itself can be considered as a one-dimensional semiconductor and also as a chromophore. Potential applications in the fields of electrophotography,[2] data storage,[3] display fabrication,[4] and nonlinear optics are discussed at present.

In the fields of conductive or semiconductive polymers, growing interest has been focused upon asymmetric structures to design materials characterized as "chiral metals" or "chiral molecular wires",[5] which might be useful for applications in sensors, optical switches, and nonlinear optics. It appears especially challenging to investigate polysilylenes with chiral molecular structure because of their intriguing thermooptical properties. Poly(di-*n*-pentylsilylene) (PDPS) crystallizes in a 7/3 helical structure and undergoes a solid disordering transition at 70 °C to a conformationally disordered columnar mesophase.[6] Disordering of the helix occurs while the material remains anisotropic, as shown in Figure 1.

Several approaches have been reported to prepare helical macromolecules with dominantly one helical sense[7,8] either in solution or in the solid state. In these polymers, configurational chirality in the backbone or in the lateral chains can generate enantioselectivity in the helical backbone conformation. In such cases the optical activity of the polymers exceeds by far the pure configurational activity of the chiral moieties. Also, if only a small fraction of the side chains used is chiral (copolymers based on a nonchiral monomer unit with a small quantity of chiral comonomers), highly optically active polymers are formed,[9] as observed for polyisocyanides[10] and polyisocyanates.[11] In the latter case, the optical activity of the polymers was shown to be strongly temperature dependent.

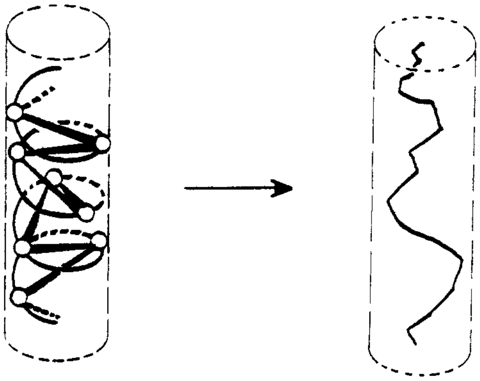


Figure 1. Schematic picture of the disordering of the 7/3 helix to the columnarlike mesophase, as expected for chiral copolymers with a low content of chiral units.

We reported before that random copolymers consisting of di-*n*-pentylsilylene units and di-*n*-hexylsilylene units crystallize and form ordered mesophases.[12] Relatively large defects can be incorporated in the crystal structure of symmetrically substituted poly(di-*n*-alkylsilylene)s without destroying crystallizability of the copolymers.[13]

In the present work, it was our approach to incorporate a minor fraction of chiral comonomer in the ordered structure of PDPS by copolymerization to study enantioselective helix formation in dependence of the phase behavior. There are two main requirements for the chiral building unit: (i) the side chains of the comonomer should possess a chiral center close to the backbone, and (ii) the chiral moiety should not impede crystallization of the polymers in the 7/3 helical conformation.

The (*S*)-2-methylbutyl group is comparable in size with the *n*-pentyl substituent and the asymmetric carbon atom is separated from the molecular backbone by only one methylene group. Two series of copolymers of di-*n*-pentylsilylene (DPS) with [(*S*)-2-methylbutyl]silylene (MBS) units have been synthesized. Symmetrical bis-[(*S*)]-2-methylbutyl]silylene (DMBS) units as well as (*S*)-2-methylbutyl/*n*-pentyl substituted units (MBPS) were incorporated within the copolymers. For the synthesis of the symmetrically substituted di-*n*-pentyldichlorosilane monomers, as an alternative to the Grignard reaction, hydrosilylation was employed. The chiral comonomers were prepared via reaction of $SiCl_4$ with the respective

---

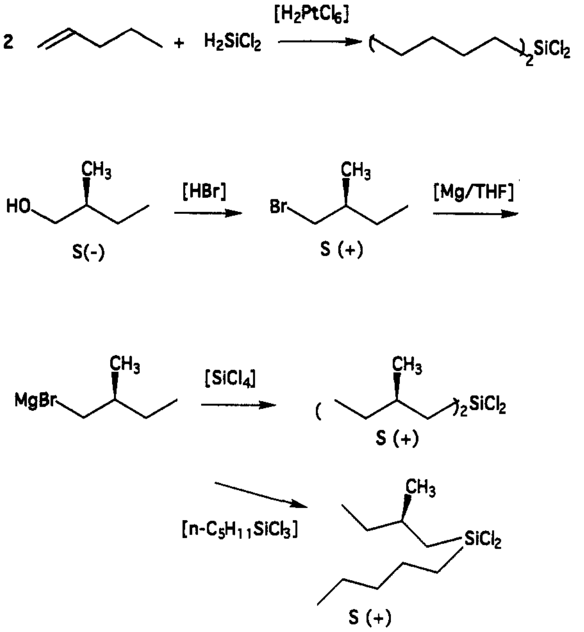
[†] Present address: Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier Strasse 31, D-79104 Freiburg, FRG.

[‡] Present address: Organische Chemie III, Makromolekulare Chemie, Universtät Ulm, Albert-Einstein Allee 11, Ulm, FRG.

[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1994.

0024-9297/94/2227-1814$04.50/0

Scheme 1. Synthesis of the Monomers



Grignard reagents. Scheme 1 shows the synthetic routes employed for the monomer synthesis.

Experimental Section

Synthesis. Di(*n*-pentyldichlorosilane). A 500-mL stainless steel vessel (pressure proof up to 400 bar), thoroughly dried and argon purged, was used for the hydrosilylation reaction. All manipulations were carried out under Ar. The reaction vessel was equipped with a needle valve and magnetic stirring bar. A total of 145 g (2.07 mol) of 1-pentene was syringed into the reaction flask. A total of 0.5 mL of a solution of H_2PtCl_6 (Speier's catalyst, 1% in anhydrous isopropyl alcohol) was then added and the reaction vessel closed, cooled to the temperature of liquid nitrogen, and evacuated. Subsequently, 101 g (1 mol) of H_2SiCl_2 (UCAR) was distilled into the steel cylinder. The cold apparatus was placed in a waterbath (0 °C) and allowed to warm up in a bunker under remote control. After 5 min under stirring, a highly exothermic reaction commenced, which lasted 2–3 min. The product mixture was allowed to cool down overnight before the reaction vessel was opened to release volatile products. The yellow liquid obtained was distilled twice [90 °C (6 mmHg)]. Finally, 214 g (87%) of di-*n*-pentyldichlorosilane was obtained [purity (GC, ^{1}H NMR) > 99%].

(*S*)-(+)-2-methylbutyl bromine was obtained by reaction of (*S*)-(−)-2-methyl-1-butanol with HBr: bp 118–121 °C, $[\alpha]_D$ = +4.4° (liquid measurement).

Bis[(*S*)-(+)-2-methylbutyl]dichlorosilane. A total of 151 g (1 mol) of (*S*)-(+)-2-methylbutyl bromide was dissolved in 250 mL of dry THF and added slowly (4 h) to 26 g of Mg (1.07 mol) in 30 mL of THF in a 1-L, three-necked flask. The reaction mixture was then stirred at 40 °C for 1 h. The dark solution of the Grignard reagent was decanted under Ar and the remaining Mg weighed in order to determine the conversion (85%).

In a 4-L, three-necked, round-bottom flask, 73 g (0.43) mol) of $SiCl_4$ was dissolved in 1.5 L of dry *n*-heptane. A total of 0.85 mol of the [(*S*)-2-methylbutyl]magnesium bromide was added slowly under strong stirring. The occurring exothermic reaction resulted in the formation of gray magnesium salts as byproducts. The salt was removed by filtration under Ar and extracted twice more with heptane. Subsequently, heptane was distilled off and the remaining yellow liquid purified by repeated distillation [87 °C (6 mmHg)] to yield 54 g of bis[(*S*)-(+)-methylbutyl]dichlorosilane (52%): purity (GC, ^{1}H NMR) > 98%; ^{13}C NMR (75.47 MHz, C_6H_6, coupled) δ 11.1 (q, CH_3, 3H), 22.2 (q, CH_3, 3H), 28.5 (t, CH_2, 2H), 31.1 (d, CH, 1H), 32.6 (t, CH_2, 2H); $[\alpha]_D$ = +20.6°.

P(DPS/DMBS) Copolymers. As an example, the synthesis of 70/30 P(DPS/DMBS) is described. Toluene and isooctane were dried over sodium benzophenone. All subsequent manipulations were carried out under dry argon. In a 50-mL Schlenk flask, under vigorous stirring a dispersion of 0.92 g (40 mmol) of freshly cut Na in 15 mL of toluene was prepared. A mixture of 3.37 g of di-*n*-pentyldichlorosilane (21 mmol) and 1.45 g of bis[(*S*)-(+)-2-methylbutyl]dichlorosilane (7 mmol) in 4 mL of isooctane was syringed into the reaction flask. After 4 h of reaction time, the viscous, purple slurry was allowed to cool to room temperature and poured into methanol. After filtration the product mixture was dissolved in warm THF, the solution filtered, and the polymer precipitated by slow addition of methanol. All polymers were reprecipitated twice in THF/methanol. (GPC results are given in Table 1.)

Table 1

polymer	yield (%)	M_w[a]	$[\eta]$ (dL/g)	M_w/M_n
Symmetrical Chiral Copolymers (DPS = Di-*n*-pentylsilylene; DMBS = bis[(*S*)-Methylbutyl]silylene)				
PDPS	30	1 280 000	1.7	1.48
95/5 P(DPS/DMBS)	29	537 000	0.6	2.13
90/10 P(DPS/DMBS)	24	392 000	0.7	2.00
85/15 P(DPS/DMBS)	23	785 000	1.8	1.42
80/20 P(DPS/DMBS)	17	298 000	0.8	3.42
70/30 P(DPS/DMBS)	13	246 000	0.9	1.88
50/50 P(DPS/DMBS)	9	512 000	2.1	2.09
Nonsymmetrical Chiral Copolymers (MBPS = [(*S*)-2-Methylbutyl/*n*-pentyl]silylene)				
98/2 P(DPS/MBPS)	25	1 470 000	2.0	1.56
95/5 P(DPS/MBPS)	17	1 330 000	2.0	1.40
92/8 P(DPS/MBPS)	14	115 000	0.3	3.40
84/16 P(DPS/MBPS)	16	576 000	1.0	2.21
70/30 P(DPS/MBPS)	10	not determined		

[a] GPC was performed in cyclohexane and referenced to a universal calibration line; for details, see the Experimental Section; $[\eta]$ was determined using an on-line viscosimeter detector.

Characterization. *GPC* was performed in cyclohexane using Waters μ-Styragel 10^5, 10^4, 10^3, and 10^6 columns (+guard column). A tunable absorbance detector (Waters 486) was employed at a wavelength of 320 nm. Simultaneously, an on-line viscosimeter–detector H-502 (Viscotek Corp.) was used to determined $[\eta]$. A universal calibration line was made with this setup, using narrow polyisoprene reference standards in cyclohexane (detector at 225 nm). The molecular weights are referenced to this universal calibration line (thus not to polystyrene standards). Using this method, absolute values for M_w, M_n, and $[\eta]$ could be obtained simultaneously.

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. The detailed results will be the subject of a subsequent paper.

UV spectra of solutions of cyclohexane (0.1–0.2 mmol/L) were measured with a Kontron UVIKON 930 spectrometer.

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

Polarimetry. A Perkin-Elmer 241 polarimeter was employed to determine optical activities at 365 and 589 nm. Measurements were performed at two concentrations (1 and 0.1 mmol/L). Due to the high dilution employed in order to exclude aggregation effects, the values could only be reproduced with an accuracy of ±10%.

Circular dichroism was studied using a Jasco J-600 spectropolarimeter. Concentrations were the same as those used for UV spectroscopy. All solutions were filtered with micropore filters (2 μm) before the measurements.

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 in closed pans with a heating rate of 10 K/min, using samples of 3–7 mg. The transition enthalpies are given as measured in the first heating scan (Table 4); little variation was observed in subsequent heating runs. Polymer samples were used as obtained after the second reprecipitation.

Results and Discussion

Copolymerization was carried out in a toluene/isooctane mixture. The composition of the monomer feed used for

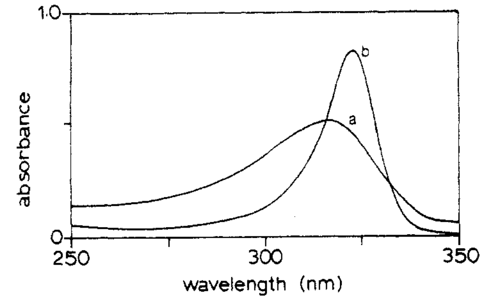


Figure 2. UV spectra of PDPS (a) and 50/50 P(DPS/DMBS) (b) in cyclohexane (concentration < 10^{-4} mol/L).

Table 2. Absorption Maxima and Extinction Coefficients (20 °C)

polymer	λ_{max} (nm)	ϵ_{max}[a]
Symmetrical Chiral Copolymers		
PDPS	317	10 600
95/5 P(DPS/DMBS)	318	12 600
90/10 P(DPS/DMBS)	319	13 300
85/15 P(DPS/DMBS)	320	16 500
80/20 P(DPS/DMBS)	320	18 500
70/30 P(DPS/DMBS)	322	22 500
50/50 P(DPS/DMBS)	323	23 500
Nonsymmetrical Chiral Copolymers		
98/2 P(DPS/MBPS)	318	11 800
95/5 P(DPS/MBPS)	319	12 100
92/8 P(DPS/MBPS)	319	12 400
84/16 P(DPS/MBPS)	319	13 700
70/30 P(DPS/MBPS)	320	17 000

[a] [ϵ_{max}] = mol^{-1} cm^{-1}, per Si–Si bond.

Table 3. Optical Activities (20 °C) in Cyclohexane[a]

polymer	$[\alpha]_{589}$	$[\alpha]_{365}$	$[\alpha]_{365}/[\alpha]_{589}$
Symmetrical Chiral Copolymers			
PDPS			
95/5 P(DPS/DMBS)	25	132	5.3
90/10 P(DPS/DMBS)	30	193	6.4
85/15 P(DPS/DMBS)	54	354	6.5
80/20 P(DPS/DMBS)	58	390	6.7
70/30 P(DPS/DMBS)	100	684	6.8
50/50 P(DPS/DMBS)	112	848	7.6
Nonsymmetrical Chiral Copolymers			
98/2 P(DPS/MBPS)	6	20	3.3
95/5 P(DPS/MBPS)	10	60	6.0
92/8 P(DPS/MBPS)	12	76	6.3
84/16 P(DPS/MBPS)	20	180	9.0
70/30 P(DPS/MBPS)	72	463	6.4

[a] Optical activities are given in deg mL/g dm.

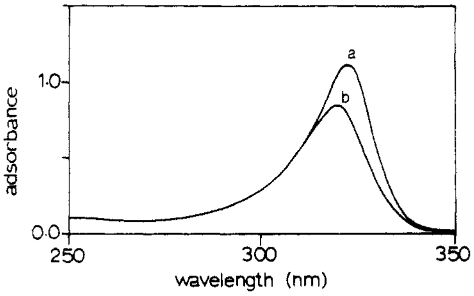


Figure 3. Comparison of UV spectra of (a) symmetrical 70/30 P(DPS/DMBS) and (b) nonsymmetrical 70/30 P(DPS/MBPS) (concentration < 10^{-4} mol/L).

copolymerization was varied from 3–30% of the nonsymmetrical chiral and 5–50% of the symmetrical chiral units as shown in Table 1. When the feed of chiral dichlorosilane in the monomer mixture was increased, the yields of high molecular weight polymer decreased, especially in the case of the symmetrically substituted chiral comonomers. Preferential formation of cyclic products was observed. An attempt to copolymerize more than 50% of the bis[(*S*)-2-methylbutyl]]-substituted monomers resulted only in a mixture of cyclic and linear oligomers. Table 1 summarizes GPC data, yields, and composition of the monomer feed of the respective copolymers. From ^{13}C NMR it resulted that for concentrations exceeding 20%, the concentration of chirally substituted building units in the copolymers was slightly lower (up to 5%) than that in the respective monomer feed.[18] Precise compositions of the copolymers are the subject of a further study.[19] From NMR spectra there is no indication that blocklike structures were present.

Properties in Solution. In order to gain insight into the backbone organization in solution, UV spectra of the chiral copolymers in cyclohexane were compared with PDPS. Cyclohexane is known to be a good solvent in the thermodynamic sense for symmetrically substituted polysilylenes.[14] The maximum of absorption of symmetrically alkyl-substituted polysilylenes in solution is determined by the organization of backbone segments consisting of approximately 30 silicon units.[15] PDPS absorbs at 317 nm at ambient[6] temperature. Figure 2 shows a comparison of the UV spectra of PDPS and the chiral copolymer 50/50 P(DPS/DMBS) with 50% symmetrical chiral side chains incorporated.

Apparently the chiral units lead to a narrowing of the absorption band and a shift λ_{max} to higher wavelengths (323 nm for 50/50; Table 2). Band shift as well as band narrowing increases gradually with the fraction of chiral side chains in all copolymers (Table 2). The variation of the absorption band may be ascribed to a preference for longer, regular backbone segment conformations caused by the bulky chiral groups in the chiral copolymers. Also the extinction coefficient ϵ_{max}, calculated per Si–Si bond, increases with the fraction of chiral side chains (Table 3). It has been shown before, in a comparison of different polysilylene homopolymers, that the position of λ_{max} in THF solution depends on the steric bulk of the substituents.[17] This is confirmed here for a series of homologous alkyl-substituted copolymers.

A comparison of the UV spectra of symmetrically and nonsymmetrically chiral substituted copolymers with the same content of chiral building units (Figure 3) shows that the band of the symmetrical copolymer is slightly more narrow and shifted to longer wavelengths. In general, nonsymmetrically substituted polysilylene homopolymers show greater line widths than symmetrically substituted materials, which has been explained by conformational broadening.[17] This confirms that the branched, chiral groups induce segmental ordering, leading to corresponding changes of the electronic structure. Due to the formation of diastereomeric sequences, this effect must be limited in the case of the MBPS copolymers.

Optical activities of the copolymers were measured at 20 °C in dilute cyclohexane solution at 589 nm as well as at 365 nm (two different concentrations in the range of 0.05–0.2 wt % polymer; Table 3). No dependence on concentration (indicating aggregation) was found at these low concentrations, as was also observed for various polysilylene polymers in light scattering experiments reported recently.[14] The optical activities are clearly related to the fraction of the chiral units built in. If the electronic structures were similar for the various copolymers, the ratio of [α] at 365 and 589 nm should be constant too. This is not the case, as indicated in Table 3, but in agreement with the conformation dependence of the electronic structure of the Si backbone (the chromophore).

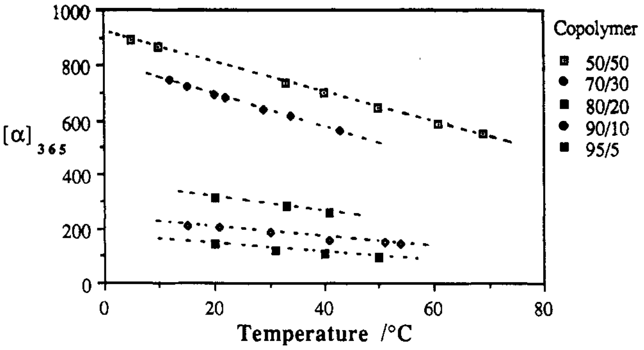


Figure 4. Temperature dependence of $[\alpha]_{365}$ of the symmetrical chiral copolymers in a cyclohexane solution (concentrations ranged between 3 and 6 mmol/L).

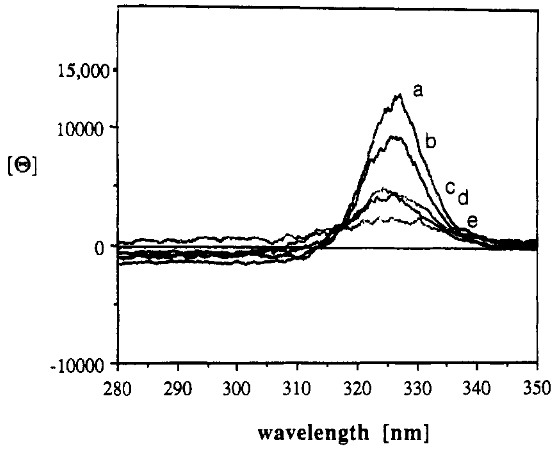


Figure 5. CD spectra of symmetrical chiral copolymers in cyclohexane at 20 °C: (a) 50/50 P(DPS/DMBS); (b) 70/30 P(DPS/DMBS); (c) 85/15 P(DPS/DMBS); (d) 90/10 P(DPS/DMBS); (e) 95/5 P(DPS/DMBS). [Θ] in deg cm^2/dmol. (Concentration used for measurements: 3–6 mmol/L).

All copolymers showed a positive optical rotation at both wavelengths. A steady increase of the ratio of $[\alpha]_{365}/[\alpha]_{589}$ for the DMBS copolymers corresponds to the observed narrowing of the UV absorption. Interestingly, the $[\alpha]_{365}/[\alpha]_{589}$ ratio runs through a maximum for the PMBS copolymers. This might be explained by an increasing importance of diastereomeric irregularities.

In agreement with the conformationally induced variation of the optical activity, a strong dependence on temperature and solvent is observed. In cyclohexane, a linear decrease of $[\alpha]_{365}$ with increasing temperature is observed for the P(DPS/DBMS) copolymers (Figure 4).

The large optical activities related to the backbone chromophore suggest either an asymmetric perturbation of the main chain or even formation of segmental enantioselective order on short length scales.

CD spectra of the chiral copolymers in cyclohexane solution (Figure 5) show weak circular dichroism for all of the symmetrical copolymers, correlated to the absorption of the σ-conjugated molecular backbone. It should be noted that the CD effects correspond to the long wavelength part of the absorption maximum, which according to the common interpretation of the UV spectra is caused by the regular (i.e., longest σ-conjugated) segments. The intensity of the circular dichroism corresponds to the fraction of chiral comonomers (Figure 6). No excitonic splitting pattern is observed in these spectra, as is usually found for neighboring, strongly interacting, chiral chromophores. This observation and the order of magnitude of the CD bands indicates that small chirally perturbed or organized polymer segments are separated by chain segments with lower (i.e., nonchiral) order in solution. Similar, but weaker, circular dichroism was also found for the nonsymmetrical copolymers in cyclohexane.

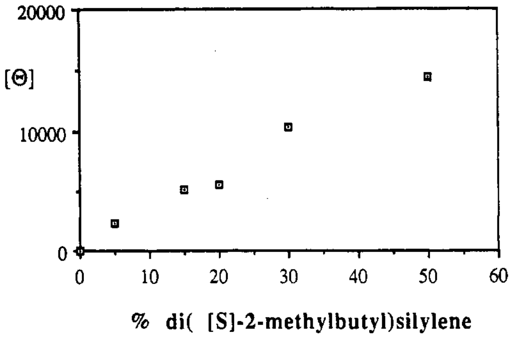


Figure 6. Intensity of the circular dichroism of the symmetrical chiral copolymers P(DPS/DMBS) vs fraction of chiral units incorporated.

Table 4. Disordering Transitions

copolymer	T_{dis}	ΔH_{dis} (kJ/mol)
Symmetrical Chiral Copolymers		
PDPS	73	2.0
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)		
Nonsymmetrical Chiral Copolymers		
98/2 P(DPS/MBPS)	63	1.9
95/5 P(DPS/MBPS)	69	1.7
92/8 P(DPS/MBPS)	69	1.0
84/16 P(DPS/MBPS)	59	0.8
70/30 P(DPS/MBPS)	79	0.3

Considerably stronger circular dichroism and correspondingly very high optical activities were found for solutions of the copolymers in THF and thin films and will be described in a forthcoming publication.[19]

Bulk Properties. It is a crucial question, whether the chiral copolymers can still crystalline and form conformationally disordered mesophases. Calorimetric (DSC) analysis of both series of chiral copolymers shows that an increase of the content of chiral units in the copolymers leads to a decrease of the transition enthalpies for the precipitated samples (Table 4, first heating scan); the transition temperatures only show small variations. We assume that in all cases the same type of conformationally disordered mesophase is formed. There are two possible explanations for the decrease of the transition enthalpies: (i) crystallization may be hindered, when an increasing fraction of chiral, bulky side chains is incorporated or (ii) the bulky side chains might impede the formation of conformationally disordered mesophases (i.e., the polymers remain in the crystalline state). Which structural picture is correct and whether this is due to kinetic reasons or an intrinsic feature of the structure cannot be decided on the basis of our first experiments. Polarizing microscopy showed that all polymers were birefringent above the expected transition temperature.

Conclusions

The synthesis of PDPS copolymers with chiral (*S*)-2-methylbutyl side chains was achieved by copolymerization of di-*n*-pentyldichlorosilane with the respective symmetrical and nonsymmetrical comonomers. The polymers showed high optical activity and circular dichroism related to the backbone absorption in cyclohexane solution. Extinction coefficients and absorption maxima depended on the fraction of the chiral moiety. Symmetrical chiral comonomers affected the spectroscopic properties stronger than nonsymmetrical building units. These results indicate a chiral perturbation of the Si-catenated backbone or even preferential helical organization on short length scales.

In the solid, copolymers with a low content of the chiral moiety crystallized and formed mesomorphic phases comparable to PDSP; increasing incorporation of the bulky side chains led to a decrease of the transition enthalpies. This may be explained either by disorder induced by the bulky side chains or by a loss of molecular flexibility, which may disable the formation of conformational disorder.

Acknowledgment. We gratefully acknowledge the valuable support of the group of Prof. Dr. de Kruyff of Department of Biochemistry, University of Utrecht, in measuring the CD spectra. H.F. acknowledges financial support by DSM. K.M. acknowledges support from the National Science Foundation.

References and Notes

(1) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
(2) Yokoyoma, K.; Yokoyoma, M. *Chem. Lett.* **1989**, 1005.
(3) Kakui, M.; Yokoyoma, K.; Tokoyoma, M. *Chem. Lett.* **1991**, 867.
(4) Kido, J.; Nagai, K.; Okamoto, Y.; Skotheim, T. *Chem. Lett.* **1991**, 1267.
(5) Garnier, F. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 513 and references cited therein.
(6) Schilling, F. C.; Lovinger, A. J.; Zeigler, J. M.; Davis, D. D.; Bovey, F. A. *Macromolecules* **1989**, *22*, 3055.
(7) Selegny, E., Ed. *Optically Active Polymers*; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1979.
(8) Wulff, G. *Angew. Chem., Int. Ed. Eng.* **1989**, *28*, 21.
(9) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Willson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452.
(10) Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, C. *Macromolecules* **1988**, *21*, 1839.
(11) Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 8850.
(12) Frey, H.; Matyjaszewski, K.; Möller, M.; Oelfin, D. *Colloid Polym. Sci.* **1991**, *269*, 442.
(13) Frey, H.; Möller, M.; Matyjaszewski, K. *Synth. Met.* **1991**, *41*, 1571.
(14) Shukla, P.; Cotts. P. M.; Miller, R. D.; Russell, T. P.; Smith, B. A.; Wallraff, G. M.; Baier, M.; Thiyagarajan, P. *Macromolecules* **1991**, *24*, 5606.
(15) Trefonas, P.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823.
(16) Frey, H.; Out, G.; Möller, M.; Greszta, D.; Matyjaszewski, K. *Macromolecules* **1993**, *26*, 6231.
(17) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601.
(18) Frey, H. Ph.D. Thesis, Universiteit Twente, Enschede, The Netherlands, 1993, ISBN 90-9006428-1.
(19) Frey, H.; Möller, M.; Lotz, B.; Matyjaszewski, K., to be submitted.