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Side-Chain Liquid-Crystalline Polysiloxanes via Anionic Polymerization: (*n*-Undecyloxy)arenecarboxylic Acid Mesogens Linked to Poly(dimethylsiloxane-*co*-methylvinylsiloxane)

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ABSTRACT: A novel, anionic route to well-defined side-chain liquid-crystalline polysiloxanes is described. The usual cationic approach to these polymers leads to polydisperse materials with uncontrolled microstructures. Ring-opening polymerization of pentamethylvinylcyclotrisiloxane yielded a poly(dimethylsiloxane-*co*-methylvinylsiloxane) with a low polydispersity ($\bar{M}_w/\bar{M}_n = 1.16$), a controlled molar mass, and a uniform distribution of pendant vinyl groups along the chain. Vinyl-containing mesogenic molecules could be attached to the polysiloxane vinyl groups in a two-step hydrosilylation reaction by means of the coupling agent 1,1,3,3-tetramethyldisiloxane, yielding polymers with regularly spaced side groups. The flexible disiloxane link increases the mobility of the mesogenic moieties. In this study, 4-(*n*-undecyloxy)benzoic acid and the novel side group 4′-(*n*-undecyloxy)-4-biphenylcarboxylic acid were used as mesogens. The thermal behavior of the side-chain liquid-crystalline polymers was investigated by means of differential scanning calorimetry and optical microscopy.

Introduction

Side-chain liquid-crystalline polymers (SCLCPs) have attracted much attention in the last 2 decades because they combine the anisotropy of liquid crystals[1] with the viscoelastic properties of polymers.[2] This combination allows SCLCPs to be used in, for example, laser-writable optical recording devices,[3] as nonlinear optical materials,[4] and, when cross-linked to liquid-crystalline elastomers,[5] as stress sensors.[6] The most widely studied SCLCPs have polyacrylate, methacrylate, or siloxane main chains. Siloxane polymers[7] have many useful characteristics such as high chain flexibility, low-temperature elasticity, transparency, high oxidative and thermal stability, and excellent resistance to radiation. Many of these features render siloxanes very attractive as backbones in SCLCPs.

Since their discovery in 1980,[8] the approach to SCLC polysiloxanes has been to prepare a SiH-containing backbone onto which vinyl-containing mesogenic molecules were attached by means of a hydrosilylation reaction[7−9] (Figure 1a). The main chain is usually prepared by acid-catalyzed equilibrium polymerizations[7,10] of 1,3,5,7-tetramethylcyclotetrasiloxane, or mixtures of this tetramer and octamethylcyclotetrasiloxane, yielding poly(methylsiloxane) or poly(dimethylsiloxane-*co*-methylsiloxane), respectively. However, this approach has the disadvantage of causing broad molar mass distributions ($\bar{M}_w/\bar{M}_n \sim 2-3$)[10−12] and the formation of cyclic oligomers, which are not readily separated from the desired linear polymer. In the case of the widely used copolymers, a nonstatistical distribution of SiH groups may occur, causing block instead of random sequences, which has an influence on the thermal properties.[13] Commercially available SiH-containing polysiloxanes also have the above-mentioned broad molar mass distributions and variations in microstructure.

For both academic and industrial reasons, it is of interest to produce well-defined materials with controlled properties that do not vary from batch to batch.[12] This implies control over molecular weight, over the molecular weight distribution, and over the distribution of mesogens along the polymer main chain. These requirements prompted us to develop a route to well-defined SCLC polysiloxanes.

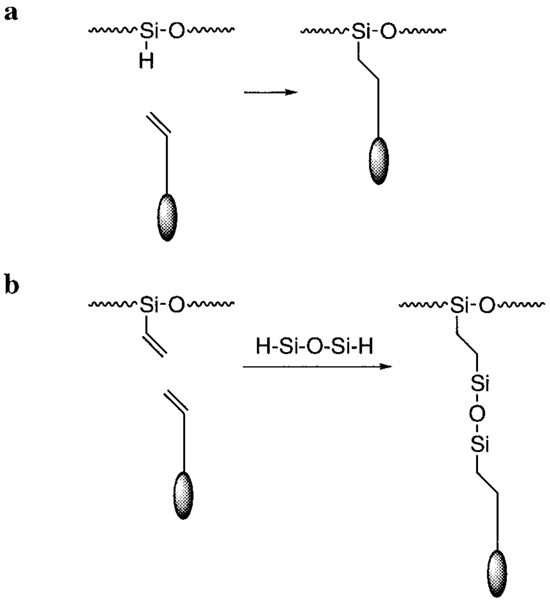

Figure 1. SCLC polysiloxanes from a SiH (a) and a $SiCH{=}CH_2$ (b) containing backbone.

In this study, 4-(*n*-undecyloxy)benzoic acid[14,15] and 4′-(*n*-undecyloxy)-4-biphenylcarboxylic acid[16,17] were used as mesogenic groups. The first SCLC polysiloxanes with alkoxybenzoic acid mesogens were reported only recently,[18] even though the mesomorphic properties of these molecules have been known since 1953.[14] Mesogenic molecules that have carboxylic acid moieties undergo dimerization as a result of reciprocal hydrogen bonding of the acid groups. The hydrogen bonds contribute greatly to the mesophase stability of low molar mass and polymer-linked (alkyloxy)arenecarboxylic acids.

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Experimental Section

Materials. Ethyl 4-hydroxybenzoate, 4′-hydroxy-4-biphenylcarboxylic acid, 4-methoxybenzyl alcohol, 4-methoxybenzyl chloride, ω-undecylenyl alcohol, sodium hydride (60% dispersion in mineral oil), lithium trimethylsilanolate (1.0 M in CH_2Cl_2), *tert*-butyldimethylsilyl chloride, dichloromethylvinylsilane, 1,1,3,3-tetramethyldisiloxane, and THF-d_8 were obtained from Aldrich. Palladium on carbon (10% Pd), silica gel 60 (70−230 mesh), *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), $CDCl_3$, and all solvents (pa grade) were obtained from Merck. Pentamethyldisiloxane and platinum−cyclovinylmethylsiloxane catalyst PC085 (3−3.5 wt % Pt) were obtained from ABCR Karlsruhe. *N*,*N*-Dimethylformamide (DMF) was dried over molecular sieves (3 Å), and tetrahydrofuran (THF) and toluene were distilled from potassium−benzophenone under argon.

Equipment. GPC measurements were carried out in THF using microstyragel columns with pore sizes of 10^5, 10^4, 10^3, and 10^6 Å (Waters), a dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502). A calibration line was made with this setup, using narrow polystyrene reference standards in THF, and the molar mass (g/mol) of polysiloxane **4** was referenced to this line. A Perkin-Elmer DSC-7 equipped with a PE-7700 computer and TAS-7 software was used to monitor thermal transitions. Scan rates between 5 and 10 K/min were utilized in the DSC experiments, using sample masses of 10−20 mg. The transition temperatures represent the onset of the endotherms during the second or third heating cycle. Optical polarizing microscopy was performed on a Leitz Ortholux II Pol BK Microscope equipped with a Mettler FP82 hot stage. ^1H NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.1 MHz and on a Varian Unity 400WB spectrometer at 400 MHz. ^{29}Si NMR spectra were measured by the same spectrometer at 79.5 MHz, using proton noise decoupling, $CDCl_3$ as an internal lock, and $Cr(AcAc)_3$ as a relaxation agent.

Ethyl 4-(10-Undecenyloxy)benzoate (1a). Under a N_2 atmosphere, NaH (4.10 g, 102 mmol) was washed with pentane to remove mineral oil. DMF (25 mL) and THF (75 mL) were added. Ethyl 4-hydroxybenzoate (16.6 g, 0.1 mol) was added in portions. The mixture was stirred for 1 h, and then 10-undecenyl tosylate[19] (32.4 g, 0.1 mol) was added. After refluxing overnight, THF was evaporated and the residue was dissolved in diethyl ether and washed with water (3 × 500 mL). Concentration of the organic layer yielded **1a**, which was obtained in quantitative yield. Anal. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.5; O, 15.07. Found: C, 75.28; H, 9.58; O, 15.14.

4-(10-Undecenyloxy)benzoic Acid (1b). Crude **1a** (30.0 g, 94.2 mmol) was saponified with KOH (11.2 g, 0.2 mol) in $MeOH/H_2O$ (100/100 mL) by refluxing overnight. The mixture was acidified with dilute HCl. The product was isolated and recrystallized from acetic acid. Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02; O, 16.53. Found: C, 74.36; H, 9.23; O, 16.41.

***p*-Methoxybenzyl 4-(10-Undecenyloxy)benzoate (1c).** A solution of DCC (20.0 g, 97 mmol) in THF (20 mL) was added dropwise to a mixture of **1b** (25.5 g, 88 mmol), 4-methoxybenzyl alcohol (12.13 g, 88 mmol), and DMAP (1.0 g, 8.2 mmol) in THF (100 mL). The mixture was stirred for 48 h, filtered, and concentrated. The residue was purified by means of column chromatography (SiO_2−toluene), yielding 23.1 g of **1c** (64%): mp 47 °C. Anal. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35; O, 15.59. Found: C, 75.95; H, 8.47; O, 15.58.

***p*-Methoxybenzyl 4-((11-(1,1,3,3-Tetramethyldisiloxane)undecanyl)oxy)benzoate (1d).** See the procedure for **1e**. ^1H NMR ($CDCl_3$) $\delta = 0.00$ (s, 6H, $SiMe_2$), 0.096 (d, 6H, $J = 2.7$ Hz, $HSiMe_2$), 0.47 (m, 2H, 11-CH_2), 1.22−1.39 (m, 16H, 3- + 4- + 5- + 6- + 7- + 8- + 9- + 10-CH_2), 1.72 (m, 2H, 2-CH_2), 3.74 (s, 3H, MeO), 3.92 (t, 2H, 1-CH_2), 4.62 (m, 1H, SiH), 5.20 (s, 2H, benzyl-CH_2), 6.80−6.86 (m, 4H, 3- + 5-H and 3- + 5-H (MeObenzyl)), 7.31 (d, 2H, 2- + 6-H (MeObenzyl)), 7.93 (d, 2H, 2- + 6-H).

Side Chain Polysiloxane 1e. The hydrosilylation reactions were performed in a magnetically stirred flask, under argon. Pt catalyst PC085 (2 droplets, 3−3.5 wt % solution) was added to a solution of **1c** (5.52 g, 13.4 mmol) in dry toluene (20 mL, distilled under N_2 from K−benzophenone) and 1,1,3,3-tetramethyldisiloxane (50 mL, 0.28 mol) under argon. The mixture was stirred for 40 h at room temperature. Complete conversion to **1d** was achieved (^1H NMR). While being stirred, the excess 1,1,3,3-tetramethyldisiloxane and toluene were removed under vacuum or by flushing with argon. Dry toluene (10 mL) was added to the oily residue, and was again removed by a stream of argon in order to ensure the complete removal of disiloxane. A solution of **4** (2.4 g, 10.2 mmol vinyl) in toluene (20 mL) was added to **1d**. Pt catalyst (2 droplets of PC085 solution) was added and the mixture was stirred at room temperature (90 h). After complete conversion (^1H NMR), the solution was concentrated. Excess **1d** was removed by column chromatography (SiO_2−toluene), and the polymer was subsequently eluted with Et_2O. **1e** was precipitated twice in MeOH (400 mL) and isolated: yield: 80−90%; ^1H NMR ($CDCl_3$) $\delta =$ 0.00 (s, SiMe), 0.06 (s, SiMe), 0.34−0.47 (m, 11-CH_2-Si + $SiCH_2CH_2Si$), 0.84 (s, Si-*t*-Bu), 1.16−1.41 (m, 3- + 4- + 5- + 6- + 7- + 8- + 9- + 10-CH_2), 1.74 (m, 2-CH_2), 3.94 (m, 1-CH_2), 5.22 (s, benzyl-CH_2), 6.82−6.88 (m, 3- + 5-H and 3- + 5-H (MeObenzyl)), 7.33 (d, 2- + 6-H (MeObenzyl)), 7.95 (d, 2- + 6-H).

SCLC Polysiloxane 1. Nitrogen was passed through a solution of polymer **1e** (1.22 g, 1.56 mmol methoxybenzyl ester) in THF (10 mL) and EtOH (25 mL) for 30 min. Pd/C (200 mg) was added, and the suspension was purged with N_2 for another 15 min. After this, a slow stream of H_2 was led through the suspension for 20 h. The catalyst was removed by filtration over Celite. The solvent was evaporated, and the residue was precipitated twice in pentane (200 mL) in order to remove 4-methoxytoluene. Polymer **1** (0.93 g) was obtained in 90% yield: ^1H NMR (THF-d_8) $\delta = 0.00$ (s, SiMe), 0.06 (s, SiMe), 0.43−0.44 (m, 11-CH_2-Si + $SiCH_2CH_2Si$), 0.84 (s, Si-*t*-Bu), 1.26−1.41 (m, 3- + 4- + 5- + 6- + 7- + 8- + 9- + 10-CH_2), 1.72 (m, 2-CH_2), 3.94 (t, 1-CH_2), 6.84 (d, 3- + 5-H), 7.87 (d, 2- + 6-H).

***p*-Methoxybenzyl 4′-Hydroxy-4-biphenylcarboxylate (2b).** A mixture of 4′-hydroxy-4-biphenylcarboxylic acid (**2a**) (4.73 g, 22 mmol), $NaHCO_3$ (3.7 g, 44 mmol), and 4-methoxybenzyl chloride (3.5 g, 22 mmol) in DMF (40 mL) was stirred for 24 h at 65 °C. The solvent was evaporated and the residue was purified (SiO_2−$CHCl_3$), yielding 5.9 g of **2b** (80%): mp 153.5 °C. Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43; O, 19.14. Found: C, 75.10; H, 5.32; O, 19.58.

***p*-Methoxybenzyl 4′-(10-Undecenyloxy)-4-biphenylcarboxylate (2c).** Ccompound **2b** (4.85 g, 14.5 mmol) was added in portions to a stirred mixture of THF (40 mL), DMF (15 mL) and NaH dispersion (0.59 g, 14.7 mmol) under N_2. Stirring was continued for 30 min. The temperature was raised to 60 °C and 10-undecenyl tosylate (4.7 g, 14.5 mmol) was added. After 12 h, the solvents were evaporated, and the residue was dissolved in CH_2Cl_2 and washed with H_2O. The organic layer was dried on Na_2SO_4 and concentrated. Column chromatography (SiO_2−toluene) yielded 6.4 g (91%) of **2c**. The product was recrystallized from *n*-heptane: mp 77.5 °C. Anal. Calcd for $C_{32}H_{38}O_4$: C, 78.98; H, 7.87; O, 13.15. Found: C, 78.71; H, 7.81; O, 13.48.

***p*-Methoxybenzyl 4′-((11-(1,1,3,3-Tetramethyldisiloxane)undecanyl)oxy)-4-biphenylcarboxylate (2d).** See the procedure for **1e**.

Side Chain Polysiloxane 2e. See the procedure for **1e**. Compound **2c** (3.6 g, 7.4 mmol) was hydrosilylated in dry toluene (30 mL) with 1,1,3,3-tetramethyldisiloxane (27 mL). After removal of excess disiloxane, a solution of **4** (1.48 g, 0.85 equiv) in toluene (15 mL) was added, and stirring was continued until complete conversion was achieved.

SCLC Polysiloxane 2. SC polysiloxane **2e** (225 mg, 0.26 mmol ester) in phenol (2 g, 21 mmol) was stirred at 70 °C for 72 h. The mixture was taken up in THF (5 mL) and precipitated in MeOH (200 mL). After several precipitations, polymer **2** was obtained in 80−90% yield: ^1H NMR (THF-d_8) $\delta = 0.00$ (s, SiMe), 0.06 (s, SiMe), 0.44−0.49 (m, 11-CH_2-Si + $SiCH_2CH_2Si$), 0.84 (s, Si-*t*-Bu), 1.26−1.42 (m, 3- + 4- + 5- + 6- + 7- + 8- + 9- + 10-CH_2), 1.66 (m, 2-CH_2), 3.92 (t, 1-CH_2), 6.90 (d, 3′- + 5′-H), 7.53 (d, 2′- + 6′-H), 7.58 (d, 2- + 6-H), 7.97 (d, 3- + 5-H).

Pentamethylvinylcyclotrisiloxane (3). 1,1,3,3-Tetramethyldisiloxane was converted to tetramethyldisiloxane-1,3-diol,[21] using Pd/C as catalyst. The product was recrystallized in pentane, yielding pure disiloxanediol (74%). A solution of this diol (37.8 g, 0.227 mol) in Et_3N (46 g, 0.45 mol) and Et_2O (total volume of mixture 500 mL) and a solution of dichloromethylvinylsilane (32.1 g, 0.227 mol) in Et_2O (total volume 500 mL) were dropped simultaneously into a stirred mixture of Et_3N (4.6 g, 45 mmol) in Et_2O (100 mL) at 0 °C under N_2. After this, the mixture was stirred for 4 h at 0 °C, filtered in order to remove $Et_3N{\cdot}HCl$, and then concentrated. The residue was distilled (bp 45−50 °C, 14 mmHg). The yield of **3**, based on the diol, was 26.7 g (50%). ^1H NMR ($CDCl_3$) $\delta = 0.00$ (s, 12H, 3- + 3- + 5- + 5-Me), 0.06 (s, 3H, 1-Me), 5.64−5.90 (m, 3H, 1-vinyl).

Poly(dimethylsiloxane-*co*-methylvinylsiloxane) (4). Compound **3** (26.5 g, 0.113 mol) in dry THF (20 mL) was added to a solution of lithium trimethylsilanolate (2.83 mmol) in dry THF (20 mL) at 0 °C under an argon atmosphere. The mixture was stirred in an ice bath for 24 h. DMF (5 mL) and *tert*-butyldimethylsilyl chloride (0.85 g, 5.64 mmol) were then added, and the ice bath was removed. After stirring for 24 h, the solution was concentrated and the polymer was precipitated in MeOH (200 mL) containing Et_3N (5 mL) and then twice in MeOH and dried *in vacuo*. ^1H NMR ($CDCl_3$) $\delta = 0.00$ (s, $SiMe_2$), 0.06 (s, *Me*SiVi), 0.79 (s, Si-*t*-Bu), 5.66−6.00 (m, MeSi*Vi*). Anal. Calcd for $C_7H_{18}O_3Si_3$: C, 35.86; H, 7.74. Found: C, 35.89; H, 7.78.

***p*-Methoxybenzyl 4-((11-(Pentamethyldisiloxanyl)undecanyl)oxy)benzoate (1f).** Compound **1c** was quantitatively converted to **1f** through a Pt-catalyzed (1 drop of PC085 solution) hydrosilylation of **1c** (1.0 g, 2.4 mmol) with pentamethydisiloxane (1.0 mL, ca. 3 equiv) in dry toluene (10 mL) under argon at room temperature, in several days. Compound **1f** was purified by passing it through a short column of SiO_2−toluene. Anal. Calcd for $C_{31}H_{50}O_5Si_2$: C, 66.62; H, 9.02. Found: C, 66.93; H, 9.30.

4-((11-(Pentamethyldisiloxanyl)undecanyloxy)benzoic Acid (1g). Hydrogenolysis of **1f** in THF (10 mL) and EtOH (20 mL) with H_2-Pd/C (200 mg) at room temperature for 20 h, followed by filtration over Celite, evaporation of the solvents, and repeated precipitation in pentane (100 mL), yielded **1g**: ^1H NMR (THF-d_8) $\delta = 0.00$ (m, 15H, $SiMe_2$-$OSiMe_3$), 0.49 (m, 2H, 11-CH_2), 1.27−1.43 (m, 16H, 3- + 4- + 5- + 6- + 7- + 8- + 9- + 10-CH_2), 1.73 (m, 2H, 2-CH_2), 3.96 (t, 2H, 1-CH_2), 6.86 (d, 2H, 3- + 5-H), 7.88 (d, 2H, 2- + 6-H).

***p*-Methoxybenzyl 4′-(11-(Pentamethyldisiloxanyl)undecanyl)oxy)-4-biphenylcarboxylate (2f).** See the procedure for **1f**. Mp 64.0 °C.

4′-((11-(Pentamethyldisiloxanyl)undecanyl)oxy)-4-biphenylcarboxylic Acid (2g). See the procedure for **1g**. ^1H NMR (THF-d_8) $\delta = 0.00$ (m, 15H, $SiMe_2OSiMe_3$), 0.47 (m, 2H, 11-CH_2), 1.26−1.44 (m, 16H, 3- + 4- + 5- + 6- + 7- + 8- + 9- + 10-CH_2), 1.72 (m, 2H, 2-CH_2), 3.93 (t, 2H, 1-CH_2), 6.91 (d, 2H, 3′- + 5′-H), 7.54 (d, 2H, 2′- + 6′-H), 7.59 (d, 2H, 2- + 6-H), 7.97 (d, 2H, 3- + 5-H).

Supplementary ^1H NMR data of compounds **1a**−**g** and **2b**−**g** are available as Supporting Information.

Results

Synthesis of the Backbone and the Mesogens.

Pentamethylvinylcyclotrisiloxane **3** was prepared by heterofunctional condensation[20] of tetramethyldisiloxane-1,3-diol[21] and dichloromethylvinylsilane. Anionic polymerization of **3** in THF, using lithium trimethylsilanolate as initiator, yielded living poly(dimethylsiloxane-*co*-methylvinylsiloxane) chains which were endcapped by adding *tert*-butyldimethylsilyl chloride (Scheme 1). The latter reaction, which produced **4**, proceeded quantitatively in the presence of *N*,*N*-dimethylformamide.

Vinyl-containing alkyloxybenzoic acid-type mesogenic molecules were attached to the pendant vinyl groups of **4** by means of a two-step hydrosilylation reaction (Figure 1b). During hydrosilylation reactions, the carboxylic acid moieties of the mesogens must be protected, for instance by converting them into *p*-methoxybenzyl esters. In general, benzyl groups are readily removed through hydrogenolysis.[22] *p*-Methoxybenzyl esters were employed here because they can be converted into carboxylic acids through hydrogenolysis or, alternatively, by heating them in phenol.[23] Both methods usually allow high, if not quantitative, conversions under neutral conditions. This is important because conventional base-catalyzed saponification of the esters could damage the polysiloxane chain.

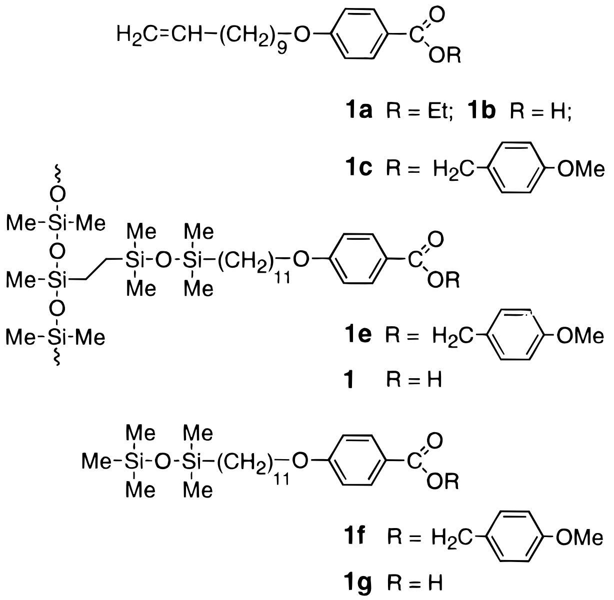
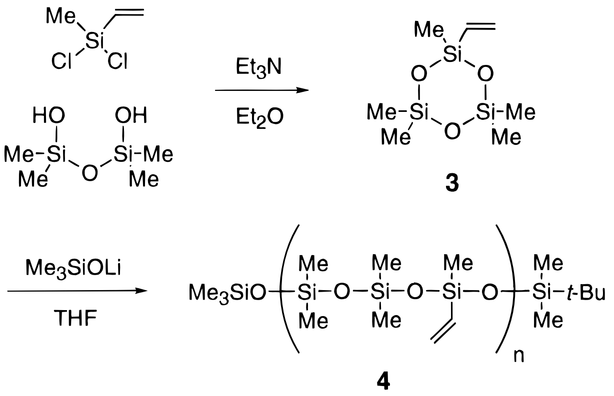


Figure 2.

Scheme 1

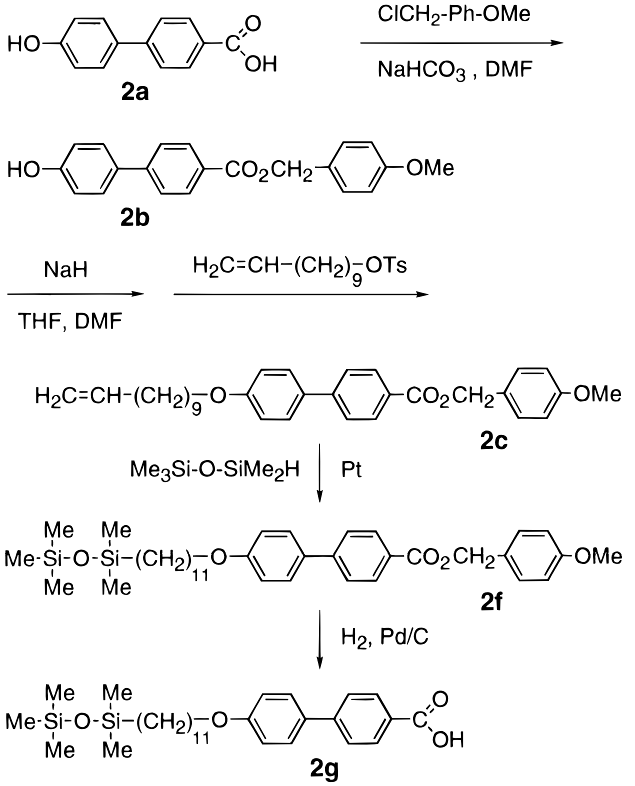


The protected *p*-methoxybenzyl 4-(10-undecenyloxy)benzoate (**1c**) was prepared as follows: alkylation of ethyl 4-hydroxybenzoate with 10-undecenyl tosylate and NaH in THF−DMF (3:1) yielded ethyl 4-(10-undecenyloxy)benzoate (**1a**), which was saponified to 4-(10-undecenyloxy)benzoic acid (**1b**). Esterification with 4-methoxybenzyl alcohol, DCC, and DMAP produced *p*-methoxybenzyl ester **1c**. The benzoic acid derivatives **1a**−**g** are shown in Figure 2.

Compound **2c** was obtained by starting with 4′-hydroxy-4-biphenylcarboxylic acid (**2a**), which was converted into its *p*-methoxybenzyl ester **2b** by alkylation of the carboxylate ion with 4-methoxybenzyl chloride in DMF. Alkylation of the 4′-hydroxyl group with 10-undecenyl tosylate yielded compound **2c** (Scheme 2).

The way in which **2c** was linked to the polysiloxane backbone **4** is outlined in Scheme 3. In a Pt-catalyzed hydrosilylation, the vinyl group of **2c** (**1c**) was allowed to react with an excess of 1,1,3,3-tetramethyldisiloxane,

Scheme 2



which was subsequently removed. Next, polysiloxane **4** was added to the SiH-terminal compound **2d** (**1d**) and further Pt-catalyzed hydrosilylation resulted in the graft polymer **2e** (**1e**). Hydrogenolysis of the *p*-methoxybenzyl groups of **1e** with H_2 and Pd/C led to SCLC polysiloxane **1**. A week was required for the complete deprotection of polymer **2e** by hydrogenolysis, but the heating of **2e** in phenol[23] at 70 °C yielded the SCLC polysiloxane **2** in 72 h.

Mesogens **1g** and **2g** were prepared (Scheme 2) in order to obtain information on the influence of the disiloxane linker on the thermal behavior of the SCLC polysiloxanes **1** and **2**.

Characterization of the backbone and the SCLCPs 1 and 2. Polysiloxane **4** was characterized by means of gel permeation chromatography (GPC) and ^{1}H NMR (Table 1). The ratio of *tert*-butyl to vinyl signal was used to determine $\overline{DP}$. The GPC and NMR results agree with the expected molecular weight based on the used ratio of monomer to initiator ($\overline{DP}$ = 120, $\bar{M}_n$ = 9400).

Table 1. Characteristics of the Polysiloxane Backbone 4[a]

GPC[b]			^{1}H NMR[c]	
$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\overline{DP}$
10770	9054	1.16	10900	140

[a] Based on the ratio of monomer to initiator, a number-average degree of polymerization $\overline{DP}$ = 120 was expected. [b] GPC measurements in tetrahydrofuran, polystyrene-effective weight-average and number-average molar masses. [c] $\overline{DP}$ based on the ratio of the vinyl to *tert*-butyl integral in the ^{1}H NMR spectrum.

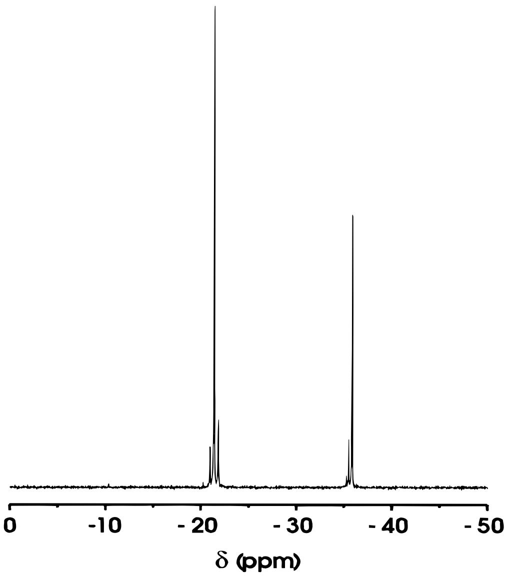


Figure 3. 79.5 MHz ^{29}Si NMR ($CDCl_3$) of **4**.

In addition, polymer **4** was characterized by means of ^{29}Si NMR (Figure 3) in order to obtain information on the microstructure.[24] The chemical shift of a given Si atom is affected by the type of first neighbor groups. As a result, characteristic triplet splittings in the ^{29}Si NMR spectra can reveal the triad microstructure of

Scheme 3

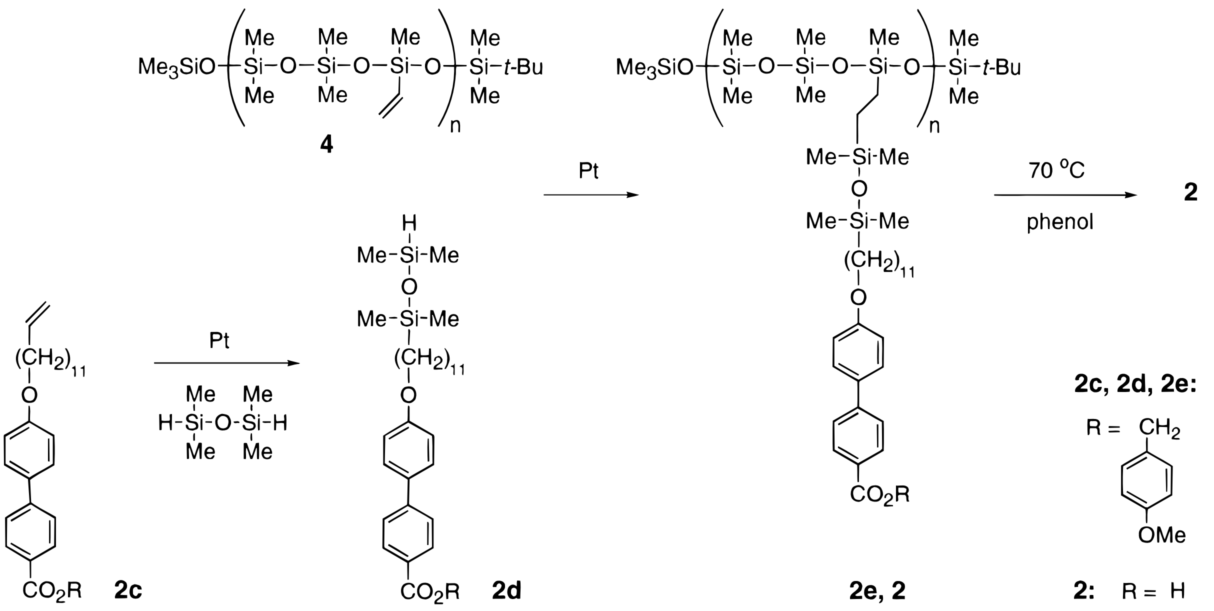


Table 2. Relative Triad Intensities (%) in 4

sequence[a]	δ (ppm)[b]	calculated intensity[c]	measured intensity[d]
$\mathrm{d\underline{d}d}$	−21.8	14.8	9.2
$\mathrm{d\underline{d}v}$	−21.3	44.4	53.5
$\mathrm{v\underline{d}v}$	−20.9	7.4	4.5
$\mathrm{v\underline{v}v}$	−35.0	0	0
$\mathrm{v\underline{v}d}$	−35.4	7.4	5.2
$\mathrm{d\underline{v}d}$	−35.8	25.9	27.7

[a] d = Me_2SiO, v = MeViSiO. [b] Figure 3 and ref 22. [c] Assuming equal reactivity for each Si atom in **3**. [d] From ^{29}Si NMR integrals.

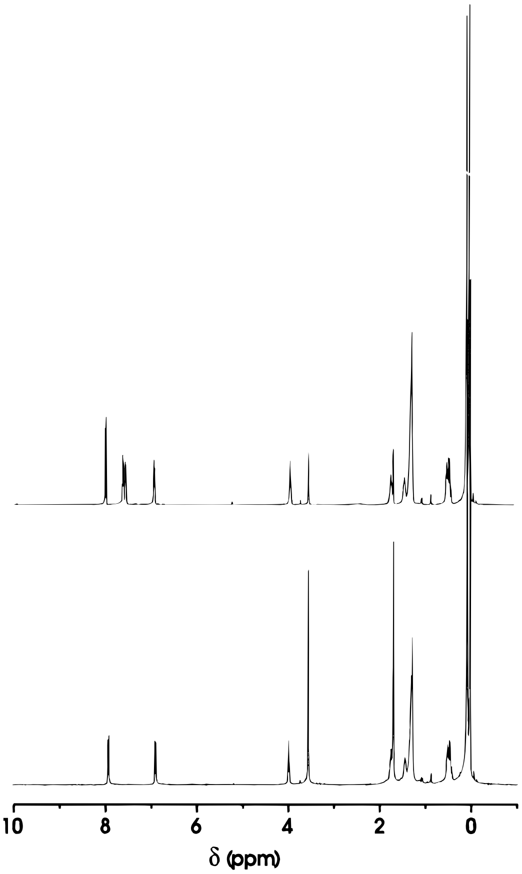


Figure 4. 400 MHz ^{1}H NMR (THF-d_8) of SCLC polysiloxanes **1** and **2** (top).

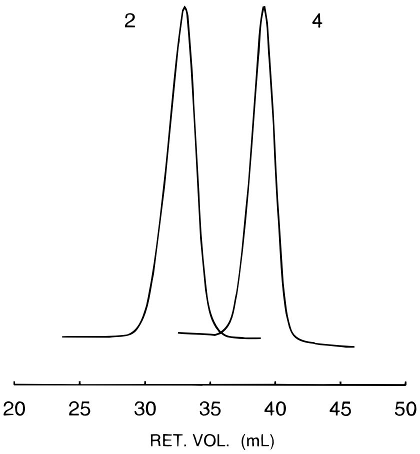


Figure 5. GPC traces (THF) of SCLC polysiloxane **2** and backbone **4**.

siloxane copolymers. Calculated intensities, based on the assumption that each Si atom in **3** has the same probability to react with the living chain end, and measured intensities of the various triads are given in Table 2. From these relative intensities, the run number *R* (the average number of like repeat unit sequences in a copolymer per 100 repeat units) can be calculated. *R* can be obtained from dimethylsiloxane (d) and methylvinylsiloxane (v) repeat units: $R_{\mathrm{d,meas}} = \mathrm{v\underline{d}v} + 1/2\ \mathrm{d\underline{d}v} = 31.3$; $R_{\mathrm{v,meas}} = \mathrm{d\underline{v}d} + 1/2\ \mathrm{v\underline{v}d} = 30.3$; $R_{\mathrm{avg,meas}} = 30.8$; $R_{\mathrm{calc}} = 29.6$. The run numbers for alternating and random copolymers with a composition of 33.3% v and 66.7% d are $R_{\mathrm{alt}} = 33.3$ and $R_{\mathrm{rnd}} = 22.2$, respectively. From the measured triad intensities and the run numbers, one can conclude that the microstructure of **4** is predominantly head-to-tail.

The completion of the grafting and deprotection reactions was ensured by means of 250 MHz ^{1}H NMR spectrometry measurements. In addition, 400 MHz ^{1}H NMR spectrometry was used to characterize the side-chain polysiloxanes **1** and **2** (Figure 4). GPC measurements showed that **1** and **2** (Figure 5) have an equally low molar mass distribution ($\bar{M}_w/\bar{M}_n = 1.12-1.16$) as the backbone **4**. The thermal behavior of **1** and **2** and of the disiloxane mesogens **1g** and **2g** was studied by means of differential scanning calorimetry (Table 3, Figure 6). Under crossed polarizers, **1** and **2** showed the sanded textures typical of aromatic carboxylic acids.[25]

Discussion

The approach described here provides a general route to well-defined siloxane polymers with functional groups attached nearly uniformly along the chain. The number of Me_2SiO repeat units between the pendant vinyl groups in the poly(dimethylsiloxane-*co*-methylvinylsiloxane) (**4**) main chain, and thus between functional groups, is expected to vary only between zero and four. ^{29}Si NMR measurements on **4** support this and give evidence of predominant head-to-tail addition. In spite of the large amount of work done on anionic polymerization of cyclotrisiloxanes,[7] no detailed report on the anionic polymerization of **3** and on the microstructure of the resulting polysiloxane has appeared in the literature. 1,1,3,3-Tetramethyldisiloxane has, to our knowledge, not been used earlier as a coupling reagent between functional groups and polymer chains. Many functional groups tolerate the hydrosilylation reactions required to couple them to the main chain. For some sensitive cases such as the esters used here, reactions were carried out at room temperature, but normally higher temperatures can be employed,[9] thus reducing the time for complete conversion. Complete coupling of 4-(ω-alkenyloxy)-4′-cyanobiphenyl mesogenic molecules to **4** was, for instance, achieved after 20 h at 50 °C.[26]

The disiloxane unit has only occasionally been used as a flexible link between mesogenic side groups and polymer backbones,[27,28] but its introduction into SCLCPs differed from the method described here. In the cases where polybutadienes and polymethacrylates served as main chains, the disiloxane link was found to lower the glass transition and the isotropization temperatures T_g and T_i.

The influence of the disiloxane link on the thermal properties of SCLC polysiloxanes **1** and **2** can be estimated by comparing the thermal properties of 4-(*n*-undecyloxy)benzoic acid (UB) and **1g**, and 4′-(*n*-undecyloxy)-4-biphenylcarboxylic acid (UBi) and **2g** (Table 3, Figure 6). UB has a smectic C−nematic transition at 129 °C[15] and a low enthalpy of isotropization ($\Delta H_i = 2.5$ kJ/mol), typical of nematics.[29] Compound **1g**, however, shows one liquid-crystalline phase (83−130 °C)

Table 3. Thermal transitions (°C) and Enthalpy Changes [kJ/mol of mesogen] of Mesogens 1g and 2g and the SCLC polysiloxanes 1 and 2[a]

compd[d]	$T_{\text{solid-s}}$	$T_{\text{s-n}}$	$T_{\text{n-i}}$	$T_{\text{s-i}}$	T_g	T_m	$T_{\text{s-i}}$
UB[b]	96 [40.1]	129 [2.1]	140 [2.5]				
1g	83 [10.5]			130 [19.3]			
UBi[c]	164 [11.0]			253 [17.4]			
2g	134 [9.5]			223 [14.4]			
1					−14	49 [6.1]	91 [5.0]
2					0	114 [4.2]	221 [11.0]

[a] Transition temperatures (DSC) represent the onset of the endotherms upon heating. [b] Reference 15. [c] Reference 16. [d] **UB**, $C_{11}H_{23}O$-$PhCO_2H$; **UBi**, $C_{11}H_{23}O$-$PhPhCO_2H$; **1g**, $Me_3SiOSiMe_2$-$C_{11}H_{22}O$-$PhCO_2H$; **2g**, $Me_3SiOSiMe_2$-$C_{11}H_{22}O$-$PhPhCO_2H$.

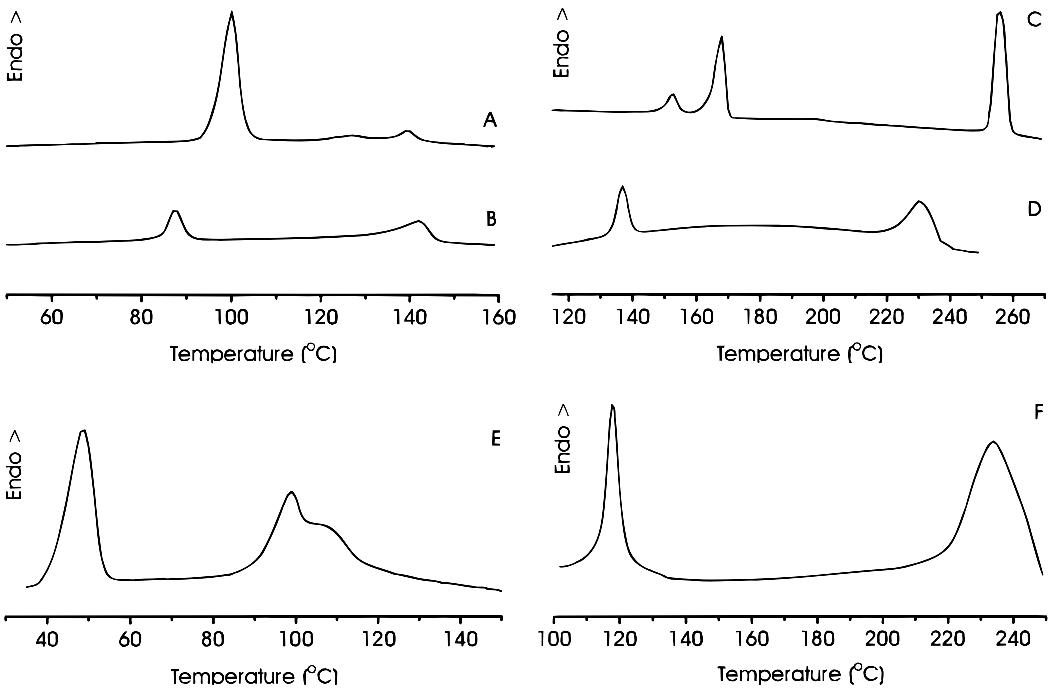


Figure 6. DSC thermograms of 4-(*n*-undecyloxy)benzoic acid (A), $Me_3SiOSiMe_2$-$C_{11}H_{22}O$-$PhCO_2H$ (**1g**) (B), 4′-(*n*-undecyloxy)-4-biphenylcarboxylic acid (C), and $Me_3SiOSiMe_2$-$C_{11}H_{22}O$-$PhPhCO_2H$ (**2g**) (D), and the SCLC polysiloxanes **1** (E) and **2** (F).

and a much larger ΔH_i (19.3 kJ/mol), indicating[29] smectic order. This behavior can be explained by looking at the homologous series of 4-*n*-alkyloxybenzoic acids.[15] The lower members show a nematic mesophase, the intermediate members display nematic and smectic phases, and the higher members, starting with 4-*n*-tetradecyloxybenzoic acid, only exhibit a smectic mesophase.

A similar dependence of mesophase structure on alkyl chain length exists for 4′-(*n*-alkyloxy)-4-biphenylcarboxylic acids. The even members display exclusively smectic order from dodecyl on.[16,17] We found a large ΔH_i (17.4 kJ/mol) for 4′-(*n*-undecyloxy)-4-biphenylcarboxylic acid (UBi) (Table 3), which indicates that UBi was the lowest of the uneven members to display a smectic mesophase until isotropization. On the basis of these considerations, it may be concluded that both **1g** and **2g** have smectic mesophases. Extending UB and UBi with a disiloxane unit lowers the solid−smectic and isotropization temperatures somewhat more strongly than is known to be caused by an increase in alkyl chain length. A further reduction of the transition temperatures is observed upon going from **1g** and **2g** to the siloxane polymers **1** and **2**, as a result of mesogen dilution by the backbone.[13] This effect is more pronounced in the case of **1**, probably because its side groups, with their smaller axial ratio, form a less stable mesophase. If, however, these materials are compared with UB and UBi, it is clear that the disiloxane link does not decrease the liquid-crystalline phase length.

In view of the high enthalpies of isotropization (ΔH_i), it can be concluded that **1** and **2** exhibit a smectic mesophase until isotropization. The sanded textures displayed by these polymers under crossed polarizers are quite similar to textures exhibited by (alkyloxy)-arenecarboxylic acids that are known to have a smectic C phase over a wide temperature range. Moreover, the mesophase of polysiloxanes with decyloxy and dodecyloxybenzoic acid side groups[18] was identified by X-ray diffraction as smectic C. It is therefore likely that **1** and **2** have a smectic C mesophase.

An interesting difference between the thermal behavior of **1** and the benzoic acid SCLC polysiloxanes[18] which was mentioned and discussed is that the latter do not display a melting transition. Side-chain crystallization is facilitated if the mesogenic molecules are decoupled more effectively from the backbone. The side-chain crystallization of **1** points at an increased mobility of the mesogenic molecules, compared to SCLCPs with all-methylene spacers. This observation is in agreement with the results of preliminary, electric field-induced orientation experiments on the above-mentioned polysiloxanes with alkyloxycyanobiphenyl mesogenic side groups that were linked to the main chain via a disiloxane unit. The cyanobiphenyl side groups could be oriented in dc electric fields within 1 min at room temperature and in seconds around 30 °C, whereas SCLCPs with all-methylene spacers between the cyanobiphenyl side groups and the polysiloxane main chain showed similar electro-optical switching times only at elevated temperatures (60−80 °C).[30,31] Both findings suggest that the disiloxane link markedly increases the mobility of side groups in SCLCPs.

In summary, a route to side-chain liquid-crystalline polysiloxanes with controlled molar mass, a low polydispersity and a homogeneous distribution of mesogenic molecules along the main chain was developed. The mesogenic side groups discussed in this paper, the relatively unexplored 4-(*n*-undecyloxy)benzoic acid and the novel 4′-(*n*-undecyloxy)-4-biphenylcarboxylic acid, were attached to the backbone via a flexible disiloxane link in a novel, one-pot hydrosilylation procedure. Well-defined SCLCPs, displaying broad smectic mesophases, were obtained. The disiloxane link was found to increase the mobility of the mesogenic groups, compared to systems with all-methylene spacers between mesogens and the polymer chain. As the polysiloxanes are prepared anionically in a living ring-opening polymerization, block copolymers with other polysiloxanes, polydienes, and polystyrene are accessible, and special architectures such as star and comb polymers with liquid-crystalline or other desired functionalities are within reach.

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Supporting Information Available: ^{1}H NMR data for **1a**−**c**,**f**,**g** and **2b**−**g** (2 pages). Ordering information is given on any current masthead page.

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