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Hybrid silarylene polysiloxanes incorporating chiral BINOL entities: a new class of polymer with main chain chirality

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Abstract—We describe the synthesis of four new chiral silylated (*R*)-BINOL precursors by coupling of lithiated BINOL intermediates with chlorosilanes. These chiral precursors were submitted to different polycondensation procedures to give silarylene polysiloxanes **A**–**D** with main chain chirality: either by hydrolysis–polycondensation of the bis-chlorosilane precursor **I** or by Pd-catalyzed cross-dehydrocoupling of bis-hydrosilanes **II**, **III** and **IV**. Both monomers and polymers were characterized by NMR, FT-IR, circular dichroism and polarimetry. Polymers with molecular weights of up to 30,200 $gmol^{-1}$ were obtained.

1. Introduction

Functional polymers bearing chiral moieties have attracted considerable interest during the past decade.[1] The enantiodifferentiation properties of such macromolecules give rise to multiple applications in the fields of asymmetric catalysis and molecular recognition. In particular, the elaboration of polymers with main chain chirality is a field of intense research activity.[2] In this kind of polymer, multiple chiral units are linked together to form a chiral polymer backbone. Control of the tacticity of polyolefins, which has been achieved elegantly by stereospecific polymerisation using chiral metallocene catalysts has attracted particular interest.[3] In contrast to asymmetric polymerisation reactions, a large variety of chiral main chain polyamides, polyureas,[4] polyesters,[5] and polypeptides[6] have been obtained by polycondensation reactions from chiral monomers. Polymers with main chain chirality have been used successfully as chiral auxiliaries in asymmetric catalysis[7–9] and for molecular recognition.[10] Polymers containing C_2-symmetric binaphthyl units have been investigated.[11] 2,2′-Dihydroxy-1,1′-binaphthol (BINOL) often serves as the starting material for obtaining chiral binaphthyl compounds, as the 2,2′-hydroxyl groups of BINOL can be easily converted into other functional groups (ethers, esters, etc.) and the 3,3′-, 4,4′- and 6,6′-positions of BINOL can selectively be functionalized, leading to a variety of binaphthyl derivatives bearing polymerisable groups. This approach gives rise to BINOL-derived polymers with unique structures and properties. Besides the excellent chiral induction in asymmetric catalysis and enantiorecognition properties, these polymers have been shown to be interesting materials for applications in the fields of optical nonlinearity and polarized luminescence.[11b] Furthermore, chiral binaphthyl-based main chain polymers offer the possibility to control the secondary structure of the macromolecule. Thus, chiral binaphthyl units have been shown to induce a helicoidal secondary structure in linear polymers.[12]

As part of our continuing interest in polymers and materials with defined architecture at the nano- and mesoscopic scale,[13] we focused on the synthesis of linear polymers with controlled secondary structure. In the present work, we investigated the synthesis of silarylene polysiloxanes [(O-$(Me)_2$Si-Ar-Si)$_n$] ('hybrid silicones', polycarbosiloxanes) incorporating chiral BINOL units in the main chain. Hybrid silicones exhibit interesting properties due to the direct linkage between the organic and siloxane (–Si–O–Si–) segments in the polymer backbone and are useful materials for the elaboration of elastomers, membranes and coatings.[14–16] We believe that silarylene polysiloxanes are also promising candidates for the synthesis of linear

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polymers with controlled secondary structure as they allow the direct catenation of rigid chiral BINOL units by flexible siloxane linkages. In view of a controlled supramolecular arrangement of the polymer chain, the intramolecular interactions can be adjusted by multiple possibilities of functionalisation either on the siloxane bridges or on the BINOL units, e.g. with long aliphatic chains. Herein, we first investigated convenient synthetic methods for hybrid silicones with main chain chirality by the polycondensation of several BINOL precursors.

2. Results and discussion

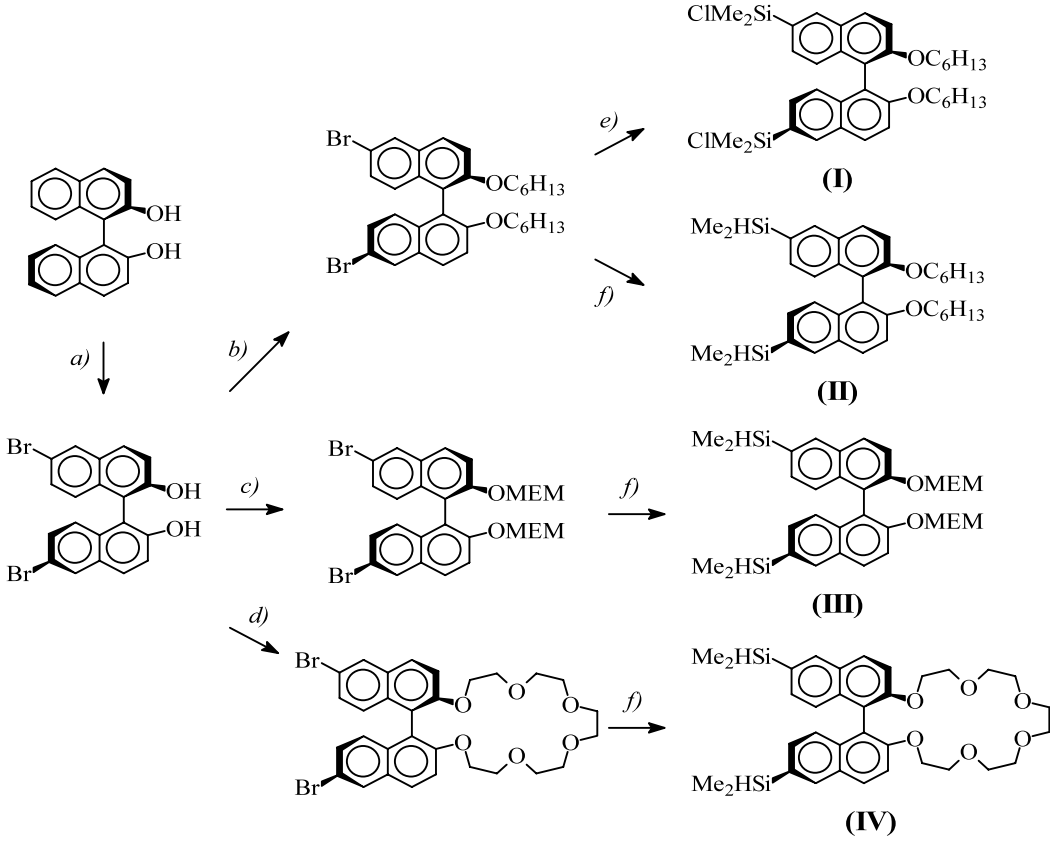
For the synthesis of hybrid silicones incorporating chiral BINOL entities, we first prepared four new silylated bis-6,6′-substituted BINOL precursors by a lithiation–chlorosilane coupling procedure,[17] among them a new silylated (*R*)-2,2′-binaphtho-20-crown-6 precursor, which is particularly suitable for applications in molecular recognition.[18] The polymers were prepared either by hydrolysis/polycondensation in aqueous basic medium[19] or by Pd-catalyzed cross-dehydrocoupling of bis-silanes.[14]

2.1. Monomer synthesis

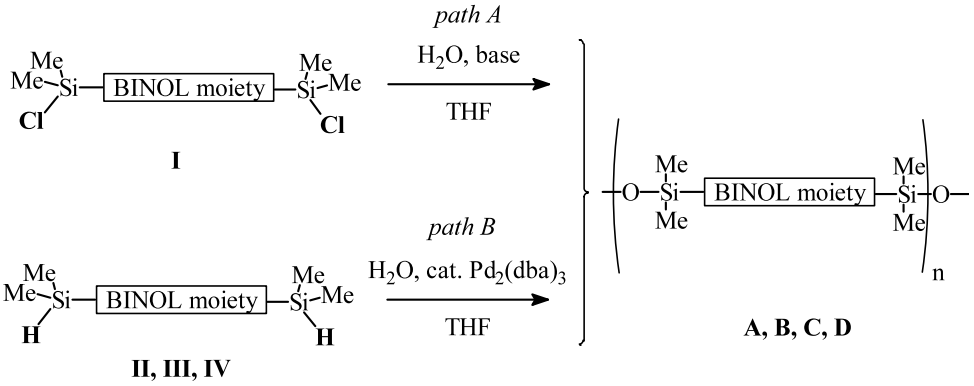
The monomers were prepared in a three-step synthesis starting from (*R*)-BINOL (Scheme 1). In all cases, (*R*)-(+)-BINOL was brominated in dichloromethane at −78°C leading to the corresponding (*R*)-(−)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl.[1e] The hydroxyl groups were then protected either by reaction with 1-bromohexane,[11c] with methoxyethoxymethyl chloride (MEM-Cl)[20] or by coupling with pentaethyleneglycol-ditosylate.[21] Treatment of the formed 6,6′-dibromo-2,2′-alkoxy-1,1′-binaphthyls with two molar equivalents of *n*-BuLi then allowed metallation of these intermediates by lithium–bromide exchange at the 6- and 6′-positions.[17] The lithiated intermediates were silylated by coupling with dichlorodimethylsilane to afford **I** or with chlorodimethylsilane to give **II**, **III** and **IV** in nearly quantitative yields.

2.2. Polymer syntheses

Polymerization of the monomers was achieved either by hydrolysis/polycondensation of the bis-chlorosilane **I** in aqueous basic solution (Scheme 2, path A) or Pd-catalyzed cross-dehydrocoupling of the bis-hydrosilanes **II**–



Scheme 1. Synthesis of BINOL-derived silylated monomers **I**–**IV**. *Reactions and conditions*: (a) Br_2, CH_2Cl_2, −80°C→rt; (b) Br-C_6H_{13}, K_2CO_3, acetone, reflux; (c) NaH, Cl-MEM, THF, 0°C→rt; (d) $TsO(CH_2CH_2O)_5Ts$, KOH, THF, reflux; (e) *n*-BuLi, Et_2O, −80→0°C, then Cl_2SiMe_2, −80°C–rt; (f) *n*-BuLi, THF, −80→0°C, then $ClHSiMe_2$, −80°C→rt.



Scheme 2. Synthesis of silarylene polysiloxanes **A**, **B**, **C** and **D** by hydrolysis/polycondensation of bis-chlorosilanes (path A) or by Pd-catalysed cross-dehydrocoupling of bis-hydrosilanes (path B).

IV with water (Scheme 2, path B). The hydrolysis–polycondensation of the precursor **I** and the cross-dehydrocoupling of **II** led to the structurally identical polymers **A** and **B** and permits the direct comparison of the two polymerization methods via the characterization the formed materials.

2.2.1. Hydrolysis/condensation. Silarylene polysiloxanes can be synthesized by hydrolysis–polycondensation of bis-chlorosilanes.[19] We applied this synthetic method for the polymerisation of precursor **I**. The polycondensation reactions were carried out at room temperature in a 1 M THF solution using ammonia as the base. A precipitate was formed immediately after the addition of water due to the hydrolysis of the bis-chlorosilane and the formation of ammonium chloride. After isolation by repeated precipitation from THF/methanol, polymer **A** was characterized by IR and NMR spectroscopy, elemental analysis, polarimetry and circular dichroism. The molecular weights were determined by gel permeation chromatography (GPC) using polystyrene standards.

The IR spectra of the polymer revealed the complete hydrolysis of the Si–Cl groups, as the Si–Cl bond vibration (492 cm^{-1}) in the infrared spectrum of the precursor molecule completely disappeared in the spectra of the polymerization products. Furthermore, the IR spectra of the polymers showed only weak OH absorption (3300 cm^{-1}) indicating near complete condensation of Si–OH groups and formation of siloxane (Si–O–Si) bridges.

The GPC curves of the polymers showed the formation of low molecular weight polymers ($M_w/M_n = 6000/4000$). Heating of the polymerization mixture did not result in an increase of the molecular weight of the formed macromolecules, but higher polymers were obtained by curing the prepolymers at 100°C for 18 h under vacuum. The resulting material shows a molecular weight of $M_w/M_n = 30{,}200/12{,}100$, but also a considerably increased polydispersity (Fig. 1).

Characterization of the polymers by ^1H NMR spectroscopy allowed the determination of the molecular weight of the polymer via determination of the end groups. Whereas polymeric Si–O–Si($\underline{CH_3}$)$_2$– groups show a signal at 0.35 ppm, the corresponding silanol end groups HO–Si(CH_3)$_2$– show an absorption at 0.5 ppm. The integration ratio of these two peaks directly gives the average degree of polymerization (Dp). The results obtained by the quantitative determination of the end groups by ^1H NMR spectroscopy (Dp = 7.8; $M = 4530$ $gmol^{-1}$ for the prepolymer and Dp = 35.5; $M = 20{,}800$ $gmol^{-1}$ for the cured polymer) are consistent with the molecular weight values obtained from GPC analyses.

These results indicate the complete hydrolysis of bis-chlorosilanes to give bis-silanol derivatives in basic medium. These silanols can be coupled in basic solution to form low molecular weight silarylene polysiloxanes. Curing of these prepolymers affords polymers with higher molecular weights.

2.2.2. Polycondensation by Pd-catalyzed cross-dehydrocoupling. Pd-catalyzed cross-dehydrocoupling has been shown to be a convenient route for the preparation of hybrid silicones under very mild conditions.[14] We applied the optimized polycondensation conditions using $Pd_2(dba)_3{\cdot}CHCl_3$ as a polycondensation catalyst. Hydrolysis of the hydrosilanes **II**, **III** and **IV** in the presence of a Pd catalyst occurred immediately after the addition of a stoichiometric amount of water, as indicated by vigorous hydrogen evolution. After the polycondensation reaction the formed polymers **B**, **C** and **D** were isolated by precipitation in MeOH and characterised by infrared and NMR spectroscopy, GPC and circular dichroism.

As above in the case of the polymerization of bis-chlorosilanes, comparison of the spectroscopic properties of monomers and polymers gives information about the polymerization reaction. The IR spectra of the precursors **II**–**IV** show the characteristic absorption of the Si–H bond at 2120 cm^{-1}. This signal completely disappeared after the polycondensation reaction in the spectra of the polymers **B**, **C** and **D**. The ^1H NMR spectra of the polymers nicely show the expected substitution pattern for a 1,2,6-trisubstituted binaphthyl derivative with one singlet and two AB systems. In the

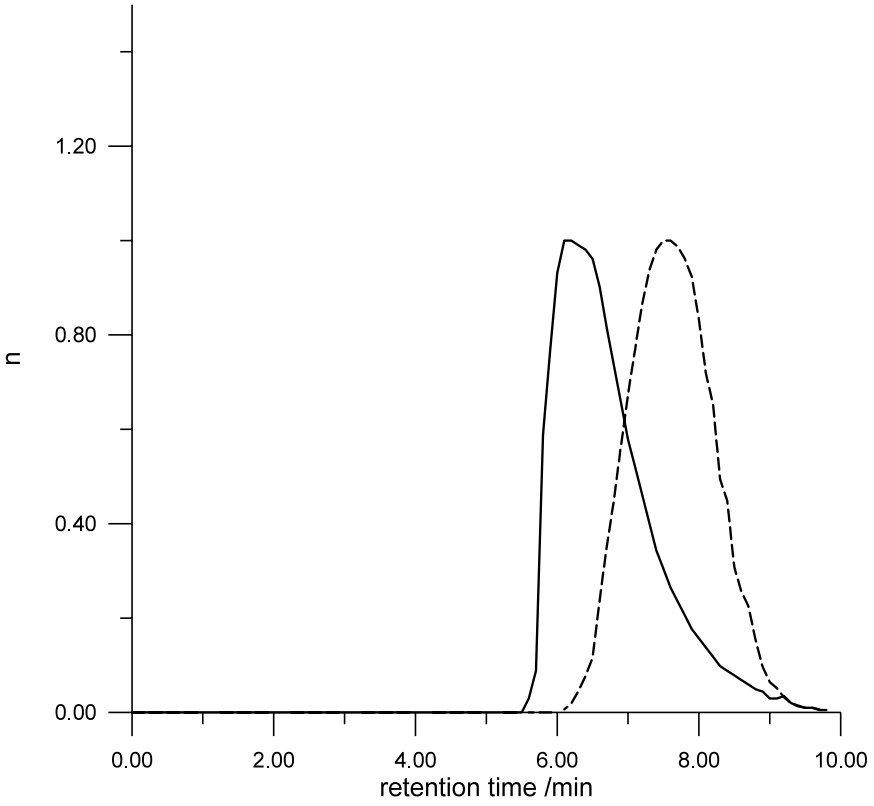


Figure 1. GPC curves of the polymer **A** before (- - -) and after curing (——).

^{29}Si NMR of the polymers, one signal at $\delta = -0.7$ ppm was observed, whereas the signal of the hydrosilane precursors ($\delta = -16.8$ ppm) completely disappeared. GPC curves indicate the formation of polymers of a molecular weight $M_w/M_n = 7300/5300$ (polymer **B**), $M_w/M_n = 15{,}800/8500$ (polymer **C**) and $M_w/M_n = 10{,}100/6300$ (polymer **D**). The GPC chromatograms reveal no significative formation of low molecular weight compounds.

We studied the circular dichroism spectra of the monomers and polymers in order to detect a change of the chiral environment of the chromophores and a supramolecular arrangement in the polymers. Fig. 2 shows the CD spectra of the crown ether precursor **IV** and the corresponding polymer **D**. As no change in the CD spectra can be observed, no supramolecular arrangement of the chromophores in the polymers can be concluded. Similar results were observed for the less rigid linear hexyloxy- and OMEM- (methoxyethoxymethyl-) functionalised precursors **II** and **III** and the corresponding polymers **B** and **C**. These results indicate no significative influence of the rigidity of the 2,2′-binaphthyl substituents on the polymer conformation.

3. Conclusions

Four new chiral silylated BINOL-derived precursors **I**–**IV** were prepared by coupling lithiated BINOL derivatives with chlorosilanes. The bis-hydrosilane (Si–H) precursors **II**, **III** and **IV** are easier to handle (synthesis, purification and storage) than the moisture-sensitive and hydrolysable bis-chlorosilane **I**. These precursors were submitted to different polycondensation procedures to give silarylene polysiloxanes: either by hydrolysis–polycondensation of the bis-chlorosilane precursor **I** or by Pd-catalyzed cross-dehydrocoupling of bis-hydrosilanes **II**, **III** and **IV**. Both polymerization methods give rise to hybrid silicones with main chain chirality. The cross-dehydrocoupling of bis-hydrosilanes resulted in polymers showing a monomodal polydispersity with molecular weights of up to $M_w/M_n = 15{,}800/8500$ gmol^{-1}. The hydrolysis–polycondensation method leads to polymers with slightly lower molecular weight. However, hybrid silicones with higher molecular weight can be prepared by curing these prepolymers in vacuo. Comparison of the CD spectroscopic properties of monomers and polymers indicated no supramolecular arrangement of the binaphthyl moieties in the polymers. The synthesis of hybrid silicones with controlled secondary structure is under further investigation.

4. Experimental

All reactions were performed under a nitrogen or argon atmosphere using Schlenk tube techniques. ^{1}H, ^{13}C and ^{29}Si NMR spectra in solution were recorded on Bruker AC-200 and AC-250 spectrometers. Deuterated chloroform was used as NMR solvent and chemical shifts are reported as δ values in parts per million relative to tetramethylsilane. J-values are in Hz. IR spectra were determined with a Perkin–Elmer SPECTRUM 1000 FT-IR spectrometer. Mass spectra were measured on a

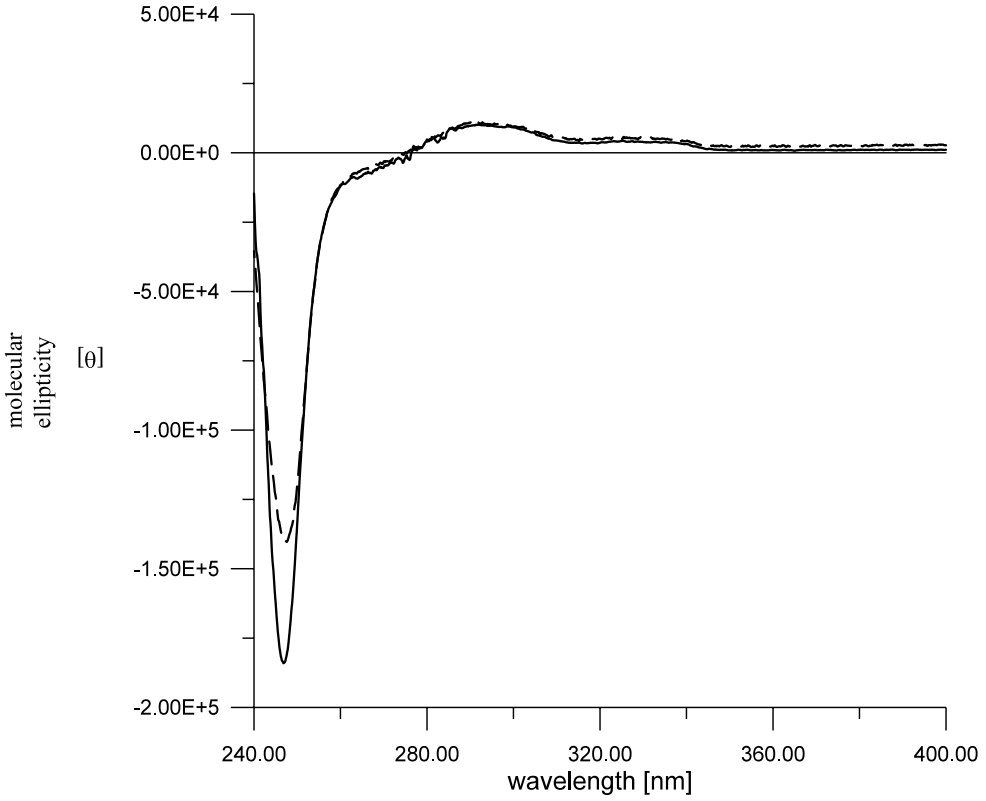


Figure 2. Circular dichroism spectra of crown-ether precursor IV (—) and the corresponding polymer D (---).

JEOL MS-DX 300 mass spectrometer. Optical rotations were measured on a Perkin–Elmer polarimeter 241. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS" at Vernaison (France). Molecular weights were determined by gel permeation chromatography in THF as solvent and are relative to polystyrene standards. All reagents were obtained from commercial sources and used without purification. In experiments requiring dry solvents, THF, toluene and diethyl ether were distilled from sodium-benzophenone, DMF was distilled from CaH_2, dichloromethane was distilled from P_2O_5 and alcohols were distilled from Mg.

The preparation of (*R*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl,[1e] (*R*)-6,6′-dibromo-2,2′-dihexyloxy-1,1′-binaphthyl,[11c] (*R*)-6,6′-dibromo-2,2′-di(methoxyethoxymethoxy)-1,1′-binaphthyl,[20] and (*R*)-6,6′-dibromo-2,2′-binaphtho-20-crown-6[21] were carried out as described in the literature.

4.1. Monomer syntheses

4.1.1. General procedure for the silylation of BINOL derivatives: synthesis of the monomers I, II, III and IV. In a schlenk tube under an inert atmosphere, (*R*)-6,6′-dibromo-2,2′-di(alkoxy)-1,1′-binaphthyl (11.6 g, 18.7 mmol) was dissolved in THF. To this solution cooled to −80°C, was added dropwise *n*-BuLi (1.6 M in hexane, 2.5 equiv.). The mixture was stirred at this temperature for 1 h and then added dropwise to a solution cooled to −80°C of 4 equiv. of degassed chlorosilane [dichlorodimethylsilane for **I**/chlorodimethylsilane for **II**, **III** and **IV**] in THF. The reaction mixture was stirred for 30 min at −80°C and then allowed to warm to room temperature and stirred overnight. After removal of the solvent in vacuo, the residue was extracted with diethyl ether and filtered under a nitrogen atmosphere. After evaporation of the solvent under reduced pressure and drying under vacuum, the products **I**, **II**, **III** and **IV** were isolated as viscous products.

4.1.2. (*R*)-6,6′-Bis(chlorodimethylsilyl)-2,2′-di(hexyloxy)-1,1′-binaphthyl I. ^{1}H NMR ($CDCl_3$): δ 0.70–0.76 (m, 18H), 0.86–1.07 (m, 12H), 1.34–1.44 (m, 4H), 3.90–4.01 (m, 4H), 7.15 (d, $J=8.5$ Hz, 2H), 7.38 (dd, $J=8.5$ and 1.3 Hz, 2H), 7.43 (d, $J=9$ Hz, 2H), 7.97 (d, $J=9$ Hz, 2H), 8.14 (bs, 2H); ^{13}C NMR ($CDCl_3$) δ 2.2, 13.9, 22.5, 25.3, 29.3, 31.3, 69.5, 115.7, 120.0, 125.0, 128.5, 129.0, 129.8, 130.3, 134.4, 135.1, 155.6; ^{29}Si NMR ($CDCl_3$) δ +20.87 (s); ν_{max} (KBr)/cm^{-1} 3058, 2931, 2871, 1616, 1463, 1253, 1114, 1098, 1048, 905, 808, 492; $[\alpha]_D^{25}=+37.8$ ($c=1.08$, CH_2Cl_2). Anal. calcd for $C_{36}H_{48}Cl_2O_2Si_2$: C, 67.58; H, 7.56. Found: C, 67.70; H, 7.55%.

4.1.3. (*R*)-6,6′-Bis(dimethylsilyl)-2,2′-di(hexyloxy)-1,1′-binaphthyl II. ^{1}H NMR ($CDCl_3$): δ 0.38 (d, $J=3.7$ Hz, 12H), 0.73 (t, 6H, $J=6.5$ Hz), 0.80–1.20 (m, 12H), 1.40 ('q', 4H, $J=6.4$ Hz), 3.94 (m, 4H), 4.50 (sept, $J=3.7$ Hz, 2H), 7.13 (d, $J=8.4$ Hz, 2H), 7.31 (dd, $J_1=8.4$, $J_2=1.1$ Hz, 2H), 7.40 (d, $J=8.8$ Hz, 2H), 7.93 (d,

$J=8.7$ Hz, 2H), 8.05 (s, $J=1.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.7, 13.9, 22.4, 25.3, 29.4, 31.3, 69.7, 115.7, 120.4, 124.7, 128.8, 129.2, 130.4, 131.5, 134.7, 134.8, 155.0; ^{29}Si NMR ($CDCl_3$) δ −16.82 (s); ν_{max} (KBr)/cm^{-1} 3056, 3014, 2956, 2922, 2117, 1615, 1584, 1463, 1326, 1248, 1144, 1112, 1096, 1048, 874; $[\alpha]_D^{25}=-2.1$ (THF, $c=1.35$). Anal. calcd for $C_{36}H_{50}O_2Si_2$: C, 75.73; H, 8.83. Found: C, 75.99; H, 8.95%.

4.1.4. (*R*)-6,6′-Bis(dimethylsilyl)-2,2′-di(methoxyethoxymethyloxy)-1,1′-binaphthyl III. ^{1}H NMR ($CDCl_3$): δ 0.39 (d, $J=3.7$ Hz, 12H), 3.18–3.63 (m, 14H), 4.50 (sept, $J=3.7$ Hz, 2H), 5.14 (2d, $J=6.9$ Hz, 4H), 7.13 (d, $J=8.4$ Hz, 2H), 7.34 (dd, $J_1=8.4$, $J_2=1.1$ Hz, 2H), 7.62 (d, $J=9$ Hz, 2H), 7.96 (d, $J=8.9$ Hz, 2H), 8.08 (d, $J=1.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.7, 58.9, 67.5, 71.4, 94.3, 117.5, 121.1, 124.8, 129.5, 129.6, 130.7, 132.6, 134.4, 134.8, 153.2; ^{29}Si NMR ($CDCl_3$) δ −16.75 (s); ν_{max} (KBr)/cm^{-1} 3056, 2957, 2922, 2116, 1616, 1472, 1248, 1232, 1107, 1021, 875; $[\alpha]_D^{25}=+1.9$ (THF, $c=$ 0.57). Anal. calcd for $C_{32}H_{42}O_6Si_2$: C, 66.40; H, 7.31. Found: C, 66.82; H, 7.37%.

4.1.5. (*R*)-6,6′-Bis(dimethylsilyl)-2,2′-binaphtho-20-crown-6 IV. ^{1}H NMR ($CDCl_3$): δ 0.39 (d, $J=3.7$ Hz, 12H), 3.40–3.69 (m, 16H), 4.00–4.27 (m, 4H), 4.53 (sept, $J=3.7$ Hz, 2H), 7.13 (d, $J=8.4$ Hz, 2H), 7.34 (d, $J=8.4$, 2H), 7.48 (d, $J=9$ Hz, 2H), 7.96 (d, $J=8.9$ Hz, 2H), 8.07 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −3.7, 69.7, 69.8, 70.6, 70.7, 116.0, 120.3, 124.7, 129.0, 129.5, 130.7, 131.9, 134.6, 134.8, 155.0; ^{29}Si NMR ($CDCl_3$) δ −16.84 (s); ν_{max} (KBr)/cm^{-1} 3057, 2957, 2868, 2111, 1616, 1467, 1325, 1249, 1111, 870; $[\alpha]_D^{25}=-5.2$ (THF, $c=0.46$). Anal. calcd for $C_{34}H_{44}O_6Si_2$: C, 67.51; H, 7.33. Found: C, 66.38; H, 7.19%.

4.2. Polymer syntheses

4.2.1. Method a: hydrolysis–polycondensation of bischlorosilane I with water, synthesis of polymer A. (*R*)-6,6′-Bis(chlorodimethylsilyl)-2,2′-di(hexyloxy)-1,1′-binaphthyl **I** (470 mg, 0.74 mmol) was dissolved in THF (0.74 mL) and a 28% aqueous NH_3 solution (140 μL) was added. A white precipitate formed immediately. This heterogeneous solution was stirred for 18 h at room temperature. The reaction mixture was poured onto acidic methanol and filtered. The precipitate was dissolved in THF and reprecipitated in acidic methanol. After drying, the polymer was isolated as an off-white glassy solid (240 mg, 56%). ^{1}H NMR ($CDCl_3$): δ 0.39 (s, 12H), 0.73 (t, 6H, $J=6.8$ Hz), 0.98 (m, 12H), 1.40 (m, 4H), 3.95 (m, 4H), 7.19 (d, $J=8.4$ Hz, 2H), 7.40 (m, 4H), 7.90 (d, $J=9.0$ Hz, 2H), 8.08 (s, 2H), several small signals due to end groups at 0.50 ppm and in the aromatic region; ^{13}C NMR ($CDCl_3$) δ 1.1, 13.9, 22.5, 25.3, 29.4, 31.3, 69.8, 115.7, 120.6, 124.6, 128.8, 129.5, 129.6, 133.9, 134.1, 134.8, 155.0; ^{29}Si NMR ($CDCl_3$) δ −0.81 (s); $[\alpha]_D^{25}=+6.7$ (THF, $c=1.05$); ν_{max} (KBr)/cm^{-1} 3057, 2957, 2868, 2111, 1616, 1467, 1325, 1249, 1111, 870. Anal. calcd for $C_{36}H_{48}O_7Si_2$: C, 73.92; H, 8.27. Found: C, 72.88; H, 8.32%.

The material was cured at 100°C/6 mbar for 18 h. The resulting polymer showed identical spectroscopic properties, except for the signals due to end groups which disappeared. GPC: $M_w/M_n=30{,}200/12{,}100$; ^{29}Si NMR ($CDCl_3$) δ −0.82 (s); $[\alpha]_D^{25}=+5.7$ (THF, $c=1.04$).

4.2.2. Method b: Pd-catalzed cross-dehydrocoupling of hydrosilanes II, III and IV, synthesis of polymers B, C and D. Polymer **B**: (*R*)-6,6′-Bis(dimethylsilyl)-2,2′-di(hexyloxy)-1,1′-binaphthyl **II** (619.8 mg, 1.086 mmol) and polymerisation catalyst $Pd_2(dba)_3{\cdot}CHCl_3$ (2.3 mg, 2.2×10^{-3} mmol) were dissolved in THF (3 mL). The reaction mixture was cooled in a ice-water bath. After addition of water (39 μL, 2.2 mmol), a vigorous evolution of hydrogen was observed. After 60 min at 0°C, the reaction mixture was allowed to warm to rt and was stirred for 18 h. The catalyst was removed by filtration over a short column (silica gel/THF). Reprecipitation of the concentrated polymer solution in acidic methanol gave polymer **B** as an off-white solid. Yield: 410 mg (65%). GPC: $M_w/M_n=7300/5300$; ^{1}H NMR ($CDCl_3$): δ 0.35 (d, 12H), 0.69 (t, 6H, $J=6.8$ Hz), 0.95 (m, 12H), 1.37 (m, 4H), 3.92 (m, 4H), 7.15 (d, $J=8.4$ Hz, 2H), 7.46 (m, 4H), 7.86 (d, $J=9.0$ Hz, 2H), 8.04 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.1, 13.9, 22.5, 25.3, 29.4, 31.4, 69.8, 115.7, 120.6, 124.6, 128.8, 129.5, 129.6, 133.9, 134.1, 134.8, 155.0; ^{29}Si NMR ($CDCl_3$) δ −0.82 (s); $[\alpha]_D^{25}=+6.9$ (THF, $c=1.01$). ν_{max} (KBr)/cm^{-1} 3057, 2954, 1615, 1473, 1255, 1018, 913, 791. Anal. calcd for $C_{36}H_{48}O_7Si_2$: C, 73.92; H, 8.27. Found: C, 72.75; H, 8.31%.

Polymer **C** was prepared by a similar experimental procedure starting from (*R*)-6,6′-bis(dimethylsilyl)-2,2′-di(methoxyethoxymethyloxy)-1,1′-binaphthyl **III** (566.6 mg, 0.979 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (2.9 mg, 2.8×10^{-3} mmol), THF (2 mL) and water (35.3 μL, 1.96 mmol). Yield: 237 mg (68%). GPC: $M_w/M_n=15{,}800/8500$; ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 12H), 3.25–3.51 (m, 14H), 5.08 (d, $J=6.8$ Hz, 2H), 5.21 (d, $J=6.8$ Hz, 2H), 7.16 (d, $J=8.3$ Hz, 2H), 7.41 (d, $J=8.4$, 2H), 7.61 (d, $J=9$ Hz, 2H), 7.93 (d, $J=8.9$ Hz, 2H), 8.09 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.1, 58.8, 67.5, 71.4, 94.1, 117.2, 120.9, 124.7, 129.3, 129.8 (two signals), 133.9, 134.5, 135.0, 153.1; ^{29}Si NMR ($CDCl_3$) δ −0.70 (s); ν_{max} (KBr)/cm^{-1} 3057, 2954, 1615, 1473, 1255, 1018, 913, 791; $[\alpha]_D^{25}=+19.1$ (THF, $c=0.317$). Anal. calcd for $C_{32}H_{40}O_7Si_2$: C, 64.83; H, 6.80. Found: C, 64.94; H, 6.80%.

Polymer **D** was prepared by a similar experimental procedure starting from (*R*)-6,6′-bis(dimethylsilyl)-2,2′-binaphtho-20-crown-6 **IV** (340 mg, 0.562 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (1.5 mg, 1.5×10^{-3} mmol), THF (2 mL) and water (20.2 μL, 1.124 mmol). Yield: 220 mg (63%). GPC: $M_w/M_n=10{,}100/6300$; ^{1}H NMR ($CDCl_3$): δ 0.35 (s, 12H), 3.37–3.75 (m, 16H), 4.04 (m, 2H), 4.18 (m, 2H), 7.13 (d, $J=7.8$ Hz, 2H), 7.34–7.45 (m, 4H), 7.89 (d, $J=8.1$ Hz, 2H), 8.04 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.0, 69.8, 70.5, 70., 70.8, 115.9, 120.3, 124.5, 128.8, 129.6, 129.7, 133.8, 134.5, 134.6, 154.9; ^{29}Si NMR ($CDCl_3$) δ −0.71 (s); ν_{max} (KBr)/cm^{-1} 2956, 2868, 1616, 1468, 1326, 1253, 1114, 1046, 792; $[\alpha]_D^{25}=+19.2$ (THF, $c=0.449$). Anal. calcd for $C_{34}H_{42}O_7Si_2$: C, 65.99; H, 6.84. Found: C, 63.80; H, 6.61%.

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