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Polymers Containing Silicon Spiro Centers

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ABSTRACT: A novel silaspirotetraene, (*all-E*)-2,3,7,8-tetrakis[(trimethylsilyl)methylene]-5-silaspiro[4.4]-nonane (4), with orthogonal geometry was synthesized. By reaction of 4 as a bisdiene (AA type) in a repetitive Diels–Alder reaction under high pressure with a bisdienophile (BB type), a ribbon-type polymer (8) was obtained in which pentacene precursor units are separated by silicon spiro centers. To investigate possible aromatization sequences and to exclude structural defects of polymer 8, model compound 11 was synthesized. The silaspirotetraene 4 is a promising candidate for the development of structures with orthogonal subunits, resulting in polymers and model compounds with high-spin character and, perhaps, ferromagnetic couplings.

Introduction

A promising strategy for achieving ferromagnetic couplings in agreement with theoretical expectations[1] is the orthogonality of partially filled orbitals in a regular chain. The Hartree–Fock band theory predicts that the ferromagnetic state is favored over the antiferromagnetic and metallic states at the limiting case where the overlap between the interacting orbitals is truly zero (orthogonality).[2] The ionic states derived from the 9,9′-bianthryl (1) ($n = 0$), for example, and higher polyanthryls exhibit a high-spin character owing to the orthogonality of the anthryl units (Chart I).[3]

Our method of including orthogonal building blocks in a polymer is to rigidly fix the units by silicon spiro centers. Recent papers[4,8] have shown that both hetero- and carbocyclic spiro[4.4]nonane structures are highly stabilized by fusing aromatic rings, such as benzene or thiophene, in the β-positions of the spiro center. We expect this to be true for our final fully aromatized polymer, in which the silicon spiro centers are localized between pentacene units as shown in Chart II.

To build up polymers, we make use of the Diels–Alder cycloaddition, whose concerted reaction mechanism has the following advantage over other polymer-forming reactions: the two-dimensional polymer is created in a single cycloaddition step and is therefore expected to possess a defect-free structure. A two-step process, involving, e.g., a ring closure of a prepolymer, could lead to possible structural defects. Two-dimensional structures as in Chart II are expected to have a high thermostability and, with the presence of pentacene subunits in the polymer, should display attractive electronic and magnetic properties.

In principle there are two different approaches to introduce orthogonality in ladder-type polymers. First, it is possible to generate the spiro center during the actual polyaddition, as in the synthesis of the poly(spiroorthocarbonate) 2[4] or the spiroionenes 3[5] (Chart III).

We have chosen a second approach by using a Diels–Alder-active AA-type monomer which already contains the orthogonal geometry. We opted for (*all-E*)-2,3,7,8-tetrakis[(trimethylsilyl)methylene]-5-silaspiro[4.4]nonane (4) (Chart IV), because the synthesis of its spiro center is, in comparison to carbocyclic systems, considerably simpler.[6] Also the four trimethylsilyl (TMS) groups of 4 are expected to create sufficient solubility.

For the construction of polymers by means of a repetitive Diels–Alder reaction, both an AA-type monomer (bisdiene) (4) and a BB-type monomer (bisdienophile) are required. In this paper we use 1,4:5,8-diepoxy-9,10-dihexyl-1,4,5,8-tetrahydroanthracene[7] (5) as a bisdienophile, wherein the two hexyl side chains provide additional solubility for the polymer. The new model compound 11 was also synthesized to gain information on eventual structural defects and possible aromatization sequences of the polymer.

Chart I

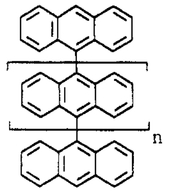
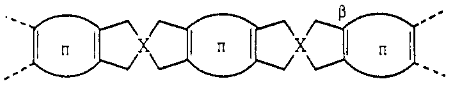
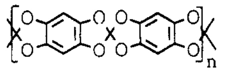


Chart II



π = Pentacene X= Si

Chart III



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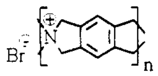
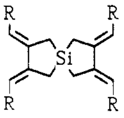
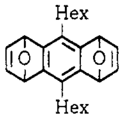


3

Chart IV



4



5

R= TMS

Hex= C_6H_{13}

Results and Discussion

In the synthesis of the silaspirotetraene 4 we refer to the known cyclization of the tetraalkyne 6[8]. Converting 3-bromo-1-(trimethylsilyl)prop-1-yne[9] into its Grignard reagent, and allowing it to react with silicon tetrachloride, tetrakis[3′-(trimethylsilyl)-2′-propynyl]silane (6) is formed. The silaspirotetraene 4 is a new compound that is obtained by acid-induced hydrolysis of the known zirconium complex 7 of the tetraalkyne 6 (Scheme I). In the isolation of compound 4, the strict absence of bases like a 10% $NaHCO_3$ solution must be ensured since otherwise an unwanted isomerization of the *all-E* form of the butadiene structure occurs, the consequences of which will be discussed later.

In a Diels–Alder reaction of 4 with 5 under normal pressure no oligomeric or polymeric material could be

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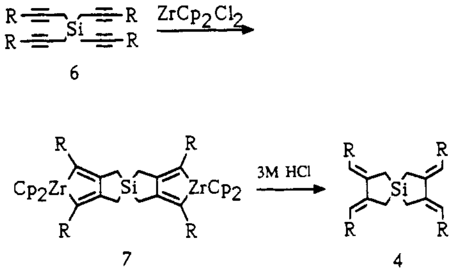
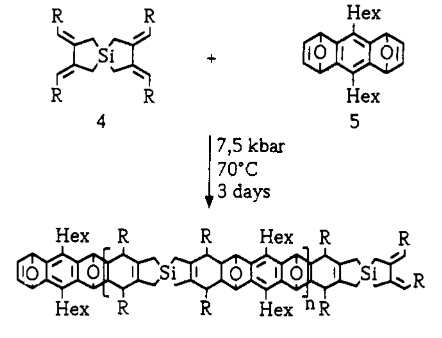
Scheme I



Scheme II



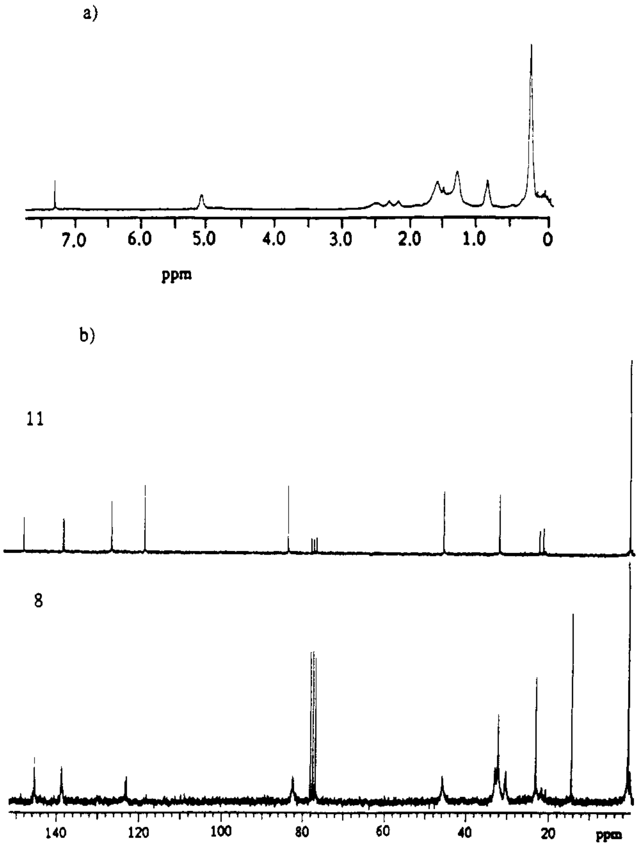
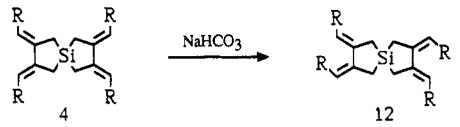


Figure 1. (a) ^{1}H NMR spectrum of polymer 8. (b) ^{13}C NMR spectra of polymer 8 and model compound 11.

isolated. Therefore, all the Diels–Alder reactions were carried out at high pressure (7–8 kbar).[10,11] At a pressure of 7.5 kbar, the reaction of 4 with 5 (3 days, 70 °C, 2-methyltetrahydrofuran (MTHF), Scheme II) leads to a clear solution of 8. After separating the high molecular weight fraction via precipitation in ethanol/ether, 3:2, a colorless polymer (8) is isolated in a yield of 79%.

Figure 1a depicts the ^{1}H NMR spectrum of the high molecular weight fraction of 8. The gel permeation chromatography (GPC) analysis shows a number-average molecular weight M_n of 11 000 which corresponds to 13 repeating units in the polymer. However, no end groups are detectable by ^{1}H and ^{13}C NMR spectroscopy. Only in the case of lower molecular weight fractions are both end groups from the tetraene 4 (protons at the exocyclic double bonds) and from the diepoxyanthracene 5 apparent in the ^{1}H NMR spectrum at 5.73 and 7.00 ppm. According to a GPC analysis, the low molecular weight fraction of 8 has a P_n of 2, whereas the integration of the end groups in the ^{1}H NMR spectrum in relation to the protons at the epoxy groups at 5.05–5.15 ppm results in a P_n of 12. Comparing the two different degrees of polymerization, it can be concluded that the GPC analysis of 8, resulting in a P_n of 13 without visible end groups in the ^{1}H NMR spectrum, reveals only the lower limit of the actual molecular weight.

Scheme III



In the repetitive Diels–Alder reaction yielding polymer 8, three effects on its molecular weight can be detected.

(a) Influence of concentration: When comparing GPC analyses of polymers under identical conditions, it can be concluded that a decrease in concentration of the starting materials from 1 to 0.7 mol/L results in a lowering of the mean molecular weight from 11 000 to about 7000. This reveals the sensitivity of the Diels–Alder reaction toward concentration.[11]

(b) Influence of solvent: In this case MTHF was the best solvent for the polymerization. The use of dichloromethane leads to a decrease of the mean molecular weight. There is no precipitation in ethanol/ether, which means that only oligomers are produced. This finding can be rationalized by the higher viscosities of the solvents at 7.5 kbar[12] (the viscosity increases by a factor of 2 when the pressure increases by 1 kbar). Quite naturally, higher viscosities will then decrease the rate constants of diffusion, whereby it is also noteworthy that the reaction mixture in the autoclave cannot be stirred.

(c) Possible reactions terminating chain growth: In the reaction of tetraene 4 with bisdienophile 5, the possibility of an Alder-ene reaction arises. Alder-ene reactions are knwon to occur only at temperatures above 150 °C,[13] and the mild reaction conditions applied here, that is 70 °C, should ensure that this reaction does not take place. There is also no analytical evidence for this side reaction, such as the appearance of new allylic protons or carbon signals in the ^{1}H and ^{13}C NMR spectra of 8.

Via the possible isomerization of the *all-E* isomer of 4 to the more stable *E,Z* form of the butadiene structure (Scheme III), a Diels–Alder reaction of 12[14] is suppressed. The steric hindrance of the TMS groups in the *E,Z*-isomerized tetraene 12 (during the ring closure) explains that even at high pressure no Diels–Alder reaction of 12 with 5 has been observed. In the ^{1}H NMR spectrum of a lower molecular weight fraction of 8, the end group of the silaspirotetraene (two protons at the exocyclic double bonds) appears at 5.73 ppm, which corresponds well to the signal position (5.65 ppm) of the exocyclic protons in the ^{1}H NMR spectrum of the isomerized tetraene 12 (instead of 5.90 ppm in the all-(*E*) form). We conclude from this observation that a thermal isomerization from the *all-E* form of 4 into the *E,Z* structure of 12 terminates

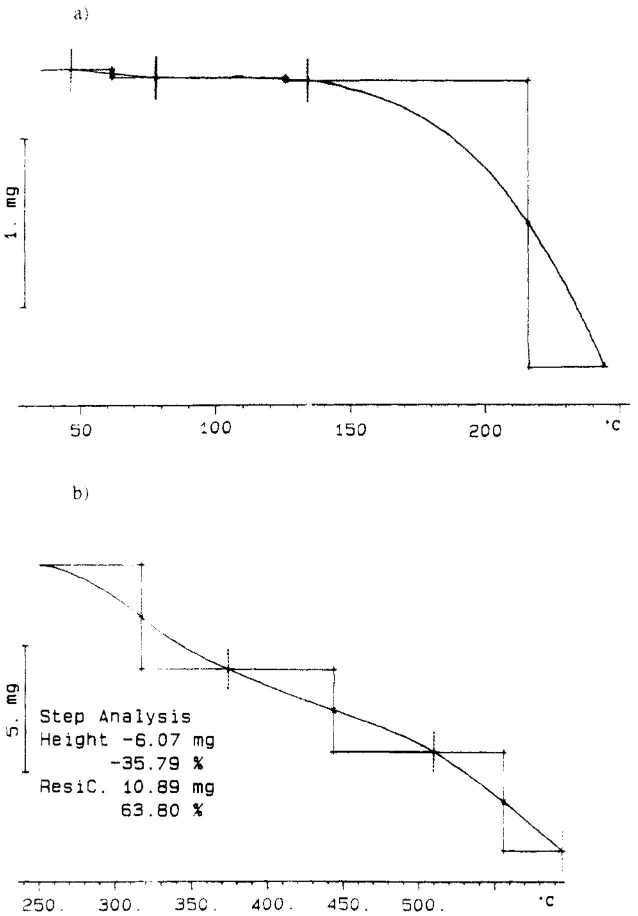
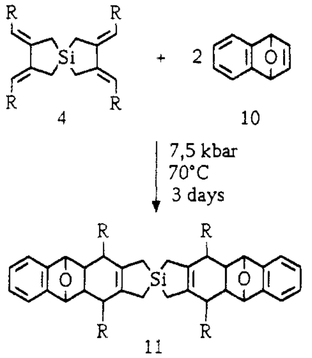


Figure 2. Thermogravimetric analysis of polymer 8.

Scheme IV



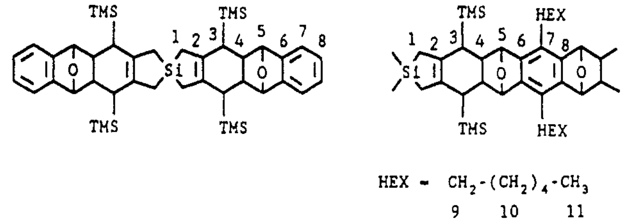
the polymerization under the formation of *E*,*Z* structures as an end group.

A thermogravimetric investigation (Figure 2) reveals a low thermostability of polymer 8 which is only stable up to 135 °C (Figure 2a). In the range of 135–350 °C (Figure 2b), the polymer loses a mass of 35.8% corresponding to that of the four TMS groups (the calculated value is 34.2%). This is not unexpected because of the lower energy of bonding (single bond, Si–C, 318 kJ/mol; C–C, 334 kJ/mol).[15] Cleavage of four spirocyclic Si–C bonds should follow at higher temperatures.

To investigate possible aromatization sequences and structural defects of the polymer, a model compound 11, representing one repeating unit of the polymer, was synthesized via the reaction of 4 with 1,4-dihydro-1,4-epoxynaphthalene (10)[16] (Scheme IV).

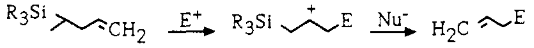
In Table I, the chemical shifts of the carbon atoms in 8 and model compound II are compared. Any structural defects of polymer 8 could safely be excluded.

Table I. ^{13}C NMR Data of Polymer 8 and Model Compound 11



model 11	ppm	polymer 8	ppm
TMS	0.1	TMS	0.1
C-1	21.4, 22.0	C-1	23.0
C-2	138.2, 138.6	C-2	138.5
C-3	32.4	C-3	32.2
C-4	46.0	C-4	46.0
C-5	84.0	C-5	82.5
C-6	148.0	C-6	145.0
C-7	118.5	C-7	123.0
C-8	126.6	C-8	145.0
		C-9	33.0
		C-10	30.0
		C-11	14.0

Scheme V



Using the model compound 11, aromatization sequences have been tested to optimize yields for future application on polymer 8. A series of known aromatization sequences were used (e.g., (TMS)Cl/NaJ/CH_3CN,[17] TMSJ/$CHCl_3$,[18] dioxane/3 M HCl,[19] Ac_2O/H_2SO_4,[20] Ac_2O/HCl,[21] etc.). All these reactions resulted in the formation of insoluble material, along with small amounts of 2,3-dimethylanthracene and 2,3-dimethyl-2,3-dihydroanthracene. It should be pointed out that, in polymer 8 as well in 11, the TMS groups and the silicon spiro center are placed in an allylic position. This leads to problems concerning the aromatization because allylsilanes[22] are known to react with electrophiles as shown in Scheme V. This problem of synthetic creation of pentacene units in the polymer is the subject of future investigations.

Conclusion

We have demonstrated the utility of an AA monomer such as 4 with its orthogonal structure to build up a ribbon-type polymer in a repetitive Diels–Alder reaction. The resulting defect-free polymer has an unconventional structure and shows excellent solubility due to the four TMS and two hexyl side chains of each repeating unit. The tetraene 4 described in this paper is a useful new synthon toward orthogonal structures. The value is illustrated in the novel synthesis of polymer 8 and its corresponding model compound 11. The present discussion has been limited to not fully aromatized structures due to the problems with creating π-systems in the polymer. The difficulties associated with the aromatization sequence of the polymer can be solved by applying arynes in a repetitive Diels–Alder reaction. Arynes applied in AB-type monomers have already been used in our group to synthesize polymers which can easily be aromatized in high yields.[23] The Diels–Alder reaction of tetraene 4 with arynes will be published elsewhere.[24]

Experimental Section

General Procedures. The solvents were used in commercial quality; tetrahydrofuran (THF) was destilled from K. The following instruments were used for NMR measurements: ^{1}H NMR, Varian Gemini 200 (200 MHz); ^{13}C NMR; Varian Gemini

200 (50.32 MHz). GPC analyses were performed with PL-gel columns (Spectra Physics PSS SDV 10^3 A 8 600, 5-μm pore widths) connected to a UV–vis detector. Thermogravimetric analysis (TGA) measurements were carried out with a Mettler (TG 50) apparatus under pure nitrogen. The high-pressure reactions were done in a Nova Swiss autoclave at 7.5 kbar.

(*all-E*)-2,3,7,8-Tetrakis[(trimethylsilyl)methylene]-5-silaspiro[4.4]nonane (4). A 20.35-mL sample of a 1.6 M solution of *n*-butyllithium in hexane (32.5 mmol) is dropped slowly to 4.76 g of zirconocene dichloride (16.3 mmol) dissolved in 50 mL of THF at −78 °C. The yellow solution is stirred at this temperature for 1 h. After that 3.5 g of tetrakis[3′-(trimethylsilyl)-2′-propynyl]silane[8] (7.4 mmol) in 20 mL of THF is added. The solution is allowed to warm to room temperature and stirred for an additional hour. The now dark red mixture is poured into 200 mL of 3 M hydrochloric acid. The aqueous phase is extracted with two 150-mL portions in *n*-pentane. The collected organic phases are washed twice with saturated NaCl solution (150 mL) and dried over $MgSO_4$. The solvent is removed and the residue is chromatographed on silica gel/pentane to give 2.5 g (73%) of 4 as a colorless oil which crystallizes in vacuo. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.15 (s, 36H, –CH_3-TMS); 1.82 (s, 8H, CH_2); 5.95 (s, 4H, CH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 0.1 (CH_3-TMS); 20.0 (CH_2); 123.1 (C-TMS); 159.9 (CH). MS (EI) (70 eV): *m/z* (rel intens) 476.6 (M^+, 34.2); 461.5 ($M^+ - CH_3$, 6.1); 73.3 (TMS^+, 100). Anal. Calcd for $C_{24}H_{48}Si_5$: C, 60.40; H, 10.14. Found: C, 60.12; H. 9.69.

Polymer (8). A 0.5-g sample of 4 (1.05 mmol) and 0.4 g of 5[7] (1.05 mmol) are dissolved in 5 mL of MTHF. The mixture is filled into a Teflon shrinking tube, which is sealed and placed in the high-pressure autoclave. The autoclave is heated to 70 °C for 3 days under 7.5 kbar of pressure. After that the clean reaction mixture is precipitated in EtOH/diethyl ether (3:2). The resulting polymer is dried in vacuo. Yield: 0.71 g (79%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.25 (br, C*H*$_3$-TMS); 0.9 (br, C*H*$_3$-hexyl); 1.30–1.80 (SiC*H*$_2$, –C*H*$_2$-hexyl, C*H*CH-TMS); 2.20–2.35 (br, C*H*-TMS); 2.55 (br, C*H*$_2$-aryl); 5.05–5.15 (br, O-C*H*). ^{13}C NMR ($CDCl_3$): all signals very broad; chemical shifts are the centers of gravity of the peaks; δ (ppm) = 0.1 (*C*H$_3$-TMS); 14.0 (*C*H$_3$-hexyl); 23.0 (*C*H-TMS); 30.0 (*C*H$_2$-hexyl); 32.3 (Si-*C*H$_2$); 33.0 (*C*H$_2$-aryl); 46.0 (*C*HCH-TMS); 82.5 (O-*C*H); 123.0 (aryl); 138.0 (*C*CH$_2$-Si); 145.0 (aryl). Anal. Calcd for $C_{50}H_{82}Si_5O_2$: C, 70.12; H, 9.70. Found: C, 69.73; H, 9.81.

Diels–Alder Adduct (11). A solution of 1.5 g of 4 (3.15 mmol) and 1.01 g of 1,4-dihydro-1,4-epoxynaphthalene[15] (6.9 mmol) in 6 mL of MTHF is prepared for the high-pressure autoclave as explained for the polymer 8. After 3 days under 7.5 kbar and 80 °C the Teflon tube is removed and the product which precipitates during the reaction is filtered off, washed with cold MTHF, and dried in vacuo to yield 1.48 g (62%) of 11 as a colorless solid. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.25 (s, TMS, 36H); 1.63 (s, $SiCH_2$), 8H); 1.70 (s, C*H*CH-TMS, 4H); 2.25 (s, C*H*-TMS, 4H); 5.10 (s, O-CH, 4H); 7.11 (AA′BB′, 8H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 0.1 (TMS); 21.4, 22.0 (Si*C*H$_2$); 32.4 (*C*H-TMS); 46.0 (*C*HCH-TMS; 84.1 (O-*C*H); 118.5 (aryl); 126.6 (aryl); 138.2, 138.6 (SiCH$_2$*C*); 148.0 (aryl). MS (EI) (70 eV): *m/z* (rel intens) 764.7 (M^+, 0.47); 73.3 (TMS^+, 100). Anal. Calcd for $C_{44}H_{64}Si_5O_2$: C, 69.02; H, 8.43. Found: C, 68.92; H, 8.51.

(*E,Z*)-2,3,7,8-Tetrakis[(trimethylsilyl)methylene]-5-silaspiro[4.4]nonane (12). The preparation and yield of 12 are similar to those for compound 4 but with one single difference. The collected organic phases were washed twice with 150-mL portions of 10% $NaHCO_3$ solution instead of being washed with saturated NaCl solution. Complete isomerization is indicated by the significant difference in the ^{1}H NMR spectra of the isomeric tetraenes as shown here for 12 compared with 4. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.01 and 0.15 (s, 18H, CH_3-TMS); 1.70 and 2.00 (s, 4H, CH_2); 5.65 (s, 4H, CH).

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