Liquid Crystalline Compounds in the Thiophene Series, Part 12

Synthesis and Characterization of Side Chain Polysiloxanes with Low Transition Temperatures

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Liquid Crystalline Thiophene Compounds, Liquid Crystalline Polysiloxanes, Bithiophene Derivatives, Liquid Crystalline Side Chain Polymers

Polysiloxanes as side chain polymers containing the 2.2'-bithiophene unit, hexyl and octyl terminal groups and spacer units with 3, 5, 6 and 10 methylene groups were prepared and characterized. These polymers have monotropic liquid crystalline phases with transition temperatures below 0 °C (e. g. for polymer 6p: isotropic — liquid crystalline transition: – 20 °C; liquid crystalline — solid transition: – 43 °C). Polymers with a trimethylene spacer group must contain an octyl terminal group for forming liquid crystalline phase; a hexyl group does not form such a phase.

Introduction

Liquid crystalline side chain polymers with polysiloxane “backbones” have been prepared by several authors [ 1–10 ]. The mesogenic groups are mostly aromatic units and only few papers deal with polysiloxanes bearing heteroaromatic units as mesogenic groups [ 11–13 ]. Polymers with thiophene derivatives as mesogenic groups were also prepared [14, 15 ]. In this paper, we present our studies on polysiloxanes with bithiophene units as mesogenic groups.

Results and Discussion

Synthesis

The polysiloxanes were synthesized according to Scheme 1.

Starting with 2,2'-bithiophene the two 5-acyl-2,2'-bithiophenes 1a and 1b were formed by a Friedel Crafts acylation. Huang Minlon reduction yielded the corresponding 5-alkyl-2,2'-bithiophene derivatives 2a and 2b. Friedel Crafts acetylation of 2a and 2b gave the 5'-acetyl-5-alkyl-2,2'-bithiophene compounds 3a and 3b, which were converted by haloform reaction to the 5-alkyl-2,2'-bithiophene-5'-carboxylic acids 4a and 4b, which were then esterificated by ω-unsaturated alcohols (allylalcohol, 4-penten-l-ol, 5-hexen-l-ol, 9-decen-1-ol) to the ω-alkenyl 5-alkyl-2,2'-bithiophene-5'-carboxylates 5a to 5h. The polysiloxanes 6a to 6p were prepared by a polyhydrosilylation reaction of poly(hydrogenmethylsiloxane) with the ω-alkenyl 5-alkyl-2,2'-bithiophene-5'-carboxylates 5a to 5h.

The low molecular weight compounds and the polymers were characterized by ¹H NMR and IR spectroscopy, the low molecular weight compounds were analyzed additionally by mass spectra and elemental analyses. These data and their interpretation are given in the experimental part.

Phase transitions

In contrast to the compounds 1a, 1b, 2a, 2b, 3a and 3b, the carboxylic acids 4a and 4b, the ω-unsaturated esters 5a to 5h and the polymers 6a to 6p show liquid crystalline phases, mostly nematic, as found by DSC and seen by their textures during microscopic inspection under polarized light (see Tables I and II).

The dimeric carboxylic acids 4a and 4b have enantiotropic nematic phases.

The monomeric ω-unsaturated esters 5a to 5h show differentiated behaviour. The allyl esters 5a and 5e have no liquid crystalline phases. The pentenyl and hexenyl esters 5b, 5c, 5f and 5g show...
monotropic liquid crystalline phases of an unknown type. Only the decenyl esters 5d and 5h have enantiotropic liquid crystalline phases of an unknown type. In both cases, two different liquid crystalline phases can be seen during the microscopic inspection under polarized light. These textures are pronounced, but not comparable to the wellknown textures given in literature [16].

With the exception of the polymers 6a and 6b, the remaining polymers have liquid crystalline phases showing pronounced “sand like” textures. Enantiotropic liquid crystalline behaviour could not be recognized, only monotropic liquid crystalline behaviour was found. As awaited, all the liquid crystalline phases were in a temperature range lower than room temperature. No remarkable difference was noted for the polysiloxanes containing 10 or 40 Si atoms in average. The same influence of the chain length was discovered by H. Stevens et al. [17].

From Table II, with the phase transition temperatures, one can see that the transition temperatures are lower with an increasing length of the spacer group and the alkyl terminal group. The width of the liquid crystalline phases increases in this order. For example, the lowest transition temperature for 6o and 6p were found to be \(-20 \, ^\circ\text{C}\) for the I \(\rightarrow\) LC transition and \(-43 \, ^\circ\text{C}\) for the LC \(\rightarrow\) S transition (Fig. 1).
One remarkable result should be pointed out: the polymers 6a and 6b with the trimethylene spacer and the hexyl terminal group have no liquid crystalline phase, whereas the polymers 6i and 6j with trimethylene spacer groups, but octyl terminal groups, have a liquid crystalline phase demonstrating the minimum length of the flexible units in the molecular structure required in order to stabilize liquid crystalline phases.

**Experimental**

The \(^1\)H NMR spectra were recorded on a Bruker WH-270 at 270 MHz: the chemical shifts given are relative to tetramethylsilane (TMS). The

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**Table I. Phase transitions of the low molecular weight compounds 4a, 4b, 5a to 5h.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>t(_{th}) [°C]</th>
<th>t(_{tc}) [°C]</th>
<th>(\Delta H_c) [kJ/mol]</th>
<th>(\Delta S_c) [kJ/K·mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>C 112 N</td>
<td>I 152 N</td>
<td>0.9</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>N 90 C</td>
<td>10.9</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>C 108 N</td>
<td>N 144 I</td>
<td>1.6</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>N 88 C</td>
<td>11.3</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>C -5 I</td>
<td>I -6 C</td>
<td>10.4</td>
<td>38.8</td>
</tr>
<tr>
<td>5b</td>
<td>C -15 I</td>
<td>I -16 LC</td>
<td>2.2</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>LC -26 C</td>
<td>4.3</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>5c</td>
<td>C -20 I</td>
<td>I -21 LC</td>
<td>5.2</td>
<td>20.6</td>
</tr>
<tr>
<td></td>
<td>LC -40 C</td>
<td>4.7</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>5d</td>
<td>C -35 LC(_1)</td>
<td>I -10 LC(_1)</td>
<td>1.1</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>LC(_1) -17 LC(_2)</td>
<td>4.4</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC(_2) -2 I</td>
<td>5.0</td>
<td>23.6</td>
<td></td>
</tr>
<tr>
<td>5e</td>
<td>C -6 I</td>
<td>I -7 C</td>
<td>15.7</td>
<td>59.0</td>
</tr>
<tr>
<td>5f</td>
<td>C -17 I</td>
<td>I -17 LC</td>
<td>2.1</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>LC -37 C</td>
<td>5.2</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>5g</td>
<td>C -18 I</td>
<td>I -18 LC</td>
<td>3.9</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>LC -44 C</td>
<td>6.7</td>
<td>29.2</td>
<td></td>
</tr>
<tr>
<td>5h</td>
<td>C -36 LC(_1)</td>
<td>I -5 LC(_2)</td>
<td>1.1</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>LC(_1) -10 LC(_2)</td>
<td>3.9</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC(_2) -3 I</td>
<td>5.7</td>
<td>28.1</td>
<td></td>
</tr>
</tbody>
</table>

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**Experimental**

The \(^1\)H NMR spectra were recorded on a Bruker WH-270 at 270 MHz: the chemical shifts given are relative to tetramethylsilane (TMS). The
infrared spectra were determined with a Perkin-Elmer-580 B-spectrometer. Mass spectra were measured on a Varian MAT-112-S. Elemental analyses were performed with a Perkin-Elmer-Recorder 56. The thermal properties of the low molecular weight compounds and the polymers were checked by DSC (Netzsch) using a scanning speed of either 10 °C/min or 20 °C/min for heating and cooling runs. Optical investigations were carried out on a Zeiss polarization microscope (Linkam THM 600 and TMS 90) fitted with a programmable heating stage.

5-Hexanoyl-2,2'-bithiophene (1a)

126.96 g (1.093 mol) hexanoic acid and 194.99 g (1.639 mol) thionyl chloride were refluxed for 2 h. The excess of thionyl chloride was removed and the hexanoyl chloride purified by vacuum distillation [18]; yield: 133.90 g (91%). Analogous to K. E. Miller et al. [19], 225.70 g (0.866 mol) anhydrous stannic chloride in 300 ml absolute dichloroethane were added dropwise (under stirring and cooling by an ice bath) to 102.03 g (0.758 mol) hexanoyl chloride. While cooling, 120.00 g (0.722 mol) 2,2'-bithiophene in 250 ml absolute dichloroethane were added carefully, bringing the temperature of the reaction mixture to about 20 °C. The mixture was stirred for an additional 12 h at room temperature in order to complete the reaction. Decomposition of the reaction mixture was accomplished by the addition of 10% hydrochloric acid. After separation, the organic layer was washed with water, with 2% NaOH and water again, then dried over calcium chloride. Removal of the dichloroethane and unchanged 2,2'-bithiophene as well as the purification of the residue by vacuum distillation produced the desired ketone; yield: 83.82 g (44%); m. p.: 73 °C; yellow crystals.

\[
C_{14}H_{16}OS_2 \quad \text{(264.4)}
\]

Calcd C 63.60 H 6.10%,

Found C 63.93 H 6.21%.

\(^1\)H NMR (CDCl\(_3\)): \(\delta\) (ppm) 7.54 (d, 1H), 7.28 (d, 2H), 7.12 (d, 1H), 7.00 (t, 1H) (bithiophene); 2.88 (t, 2H, -CO-CH\(_2\)-); 1.76 (quint, 2H, -CH\(_2\)-CH\(_2\)-CH\(_3\)); 1.34 (m, 4H, -CH\(_2\)(CH\(_2\)_2-CH\(_2\)-); 0.92 (t, 3H, -CH\(_3\)).

MS: \(m/e\) 264 (C\(_{14}\)H\(_{16}\)OS\(_2\)) M\(^+\) (32); 208 (M-C\(_6\)H\(_5\))^+ (100); 193 (M-C\(_6\)H\(_{11}\))^+ (71); 166 (208-C\(_2\)H\(_2\)O) (10); 121 (166-CHS) (40).
IR (KBr): (cm⁻¹) 3120 (w), 3080 (w) ν(=C-H); 2946 (s), 2937 (s), 2864 (s) ν(C-H); 1660 (vs) ν(C=O); 1500 (s), 1467 (s), 1452 (vs), 1422 (s), 1410 (s) ν(C=C), 1361 (m), 1319 (s) δ(C-H); 1232 (m), 1205 (m) δ(C-H); 1079 (s), 1036 (m) δas(C-H); 887 (w), 838 (s), 818 (s), 795 (vs), 725 (m), 690 (vs) δas(C-H). - These absorptions are also typical for 2b.

5-Octanoyl-2,2′-bithiophene (1b) [20]

From 24.05 g (0.148 mol) octanoyl chloride, prepared by 31.02 g (0.215 mol) octanoic acid, 38.38 g (0.323 mol) thionyl chloride, 44.08 g (0.169 mol) anhydrous stannic chloride and 23.45 g (0.141 mol) anhydrous stannic chloride, and 23.45 g (0.141 mol) anhydrous stannic chloride; yield: 27.18 g (66%); m.p.: 28 °C (20) 83 °C); light yellow crystals.

C₁₆H₁₆O₅S₂ (292.5)
Calcd C 65.70 H 6.89%.
Found C 65.62 H 6.85%.

1H NMR (CDCl₃): δ (ppm) 7.58 (d, 1H), 7.32 (d, 2H), 7.14 (d, 1H), 7.00 (t, 1H) (bithiophene); 2.86 (t, 2H, -CO-CH₂-); 1.76 (quint, 2H, -CH₂(CH₂)₂-CH₃); 1.30 (m, 8H, -CH₂(CH₂)₄-CH₂-); 0.90 (t, 3H, -CH₃).

MS: m/e 292 (C₁₆H₁₆O₅S₂) M⁺ (26); 208 (M-C₇H₁₃)⁺ (100); 193 (M-C₇H₁₃)⁺ (48); 166 (208-C₂H₅O) (9); 121 (166-CHS) (24).

5-Hexyl-2,2′-bithiophene (2a)

Once more, analogous to K. E. Miller [19] from 30.44 g (0.950 mol) 99% hydrazine hydrate and 14.40 g (0.360 mol) KOH in 300 ml triethylene glycol analogously to the synthesis of 2a; yield: 19.87 g (79%); m.p.: 28 °C (20) 83 °C); light yellow crystals.

C₁₆H₁₈S₂ (278.5)
Calcd C 69.00 H 7.96%.
Found C 68.91 H 7.88%.

1H NMR (CDCl₃): δ (ppm) 7.15 (d, 1H), 7.06 (d, 1H), 6.94 (m, 2H), 6.63 (d, 1H) (bithiophene); 2.74 (t, 2H, bithiophene-CH₂-); 1.66 (quint, 2H, -CH₂-CH₂(CH₂)₃-CH₃); 1.20 (m, 10 H, -CH₂-(CH₂)₃-CH₃); 0.90 (t, 3H, -CH₃).

MS: m/e 278 (C₁₆H₁₈S₂) M⁺ (29); 179 (M-C₇H₁₅) (56); 166 (M-C₆H₁₆) (100); 121 (M-CHS) (17).

5′-Acetyl-5-hexyl-2,2′-bithiophene (3a)

From 62.13 g (0.239 mol) anhydrous stannic chloride, 13.13 g (0.167 mol) acetyl chloride and 39.89 g (0.159 mol) anhydrous stannic chloride; yield: 26.65 g (57%); m.p.: 62 °C; light beige coloured crystals.

C₁₆H₂₀O₂S₂ (279.5)
Calcd C 65.70 H 6.89%.
Found C 65.66 H 6.79%.

1H NMR (CDCl₃): δ (ppm) 7.67 (d, 1H), 7.09 (d, 1H), 7.03 (d, 1H), 6.70 (d, 1H) (bithiophene); 2.82 (t, 2H, bithiophene-CH₂-); 2.56 (s, 3H, -CO-CH₃); 1.70 (quint, 2H, -CH₂(CH₂)₃-CH₃); 1.34 (m, 6H, -CH₂-(CH₂)₃-CH₃); 0.92 (t, 3H, -CH₃).

MS: m/e 292 (C₁₆H₂₀O₂S₂) M⁺ (60); 221 (M-C₇H₁₅) (100); 208 (221-CH₃) (38); 193 (208-CH₃) (35); 165 (193-CO) (3); 121 (165-CS) (19).

IR (KBr): (cm⁻¹) 3086 (w), 3056 (w) ν(=C-H); 2952 (s), 2926 (s), 2873 (m), 2855 (s) ν(C-H); 1653 (vs) ν(C=O); 1477 (s), 1441 (s), 1360 (s), 1304 (m) ν(C≡C); 1275 (vs), 1223 (w), 1205 (w) δ(=C-H); 1076 (m), 1030 (m) δas(C-H); 804 (s), 786 (s), 725 (w) δas(C-H). - These absorptions are also typical for 3b.
5'-Acetyl-5-octyl-2,2'-bithiophene (3b)

From 21.57 g (0.083 mol) anhydrous stannic chloride, 5.69 g (0.073 mol) acetyl chloride and 19.29 g (0.069 mol) 2b im 300 ml dichloroethane analogous to the synthesis of 3a; yield: 15.54 g (70%); m. p.: 47 °C; light beige crystals.

C_{19}H_{22}O_2S_2 (322.5)
Calcd C 67.24 H 7.39%.
Found C 67.24 H 7.39%.

1^H NMR (CDCl_3): δ (ppm) 7.59 (d, 1H), 7.12 (d, 1H), 7.06 (d, 1H), 6.72 (d, 1H) (bithiophene); 2.79 (t, 2H, bithiophene-CH_2-); 2.56 (s, 3H, -CO-CH_3); 1.72 (quint, 2H, -CH_2-CH_3); 1.28 (m, 10H -CH_2-(CH_2)_5-CH_2-); 1.10 (s, 6H, -CH(CH_3)_2); 0.88 (t, 3H, -CH_3).

MS: m/e 320 (C_{19}H_{22}O_2S_2) M^+ (80); 221 (M-C_6H_5) (100); 193 (208-CH_3) (46); 165 (193-CO) (4); 121 (165-CS) (15).

5-Hexyl-2,2'-bithiophene-5'-carboxylic acid (4a)

While stirring and cooling with an ice bath, 43.63 g (0.273 mol) bromine were dropped into 2.79 (t, 2H, bithiophene-CH_2-); 2.56 (s, 3H, -CO-CH_3); 1.72 (quint, 2H, -CH_2-CH_3); 1.28 (m, 10H -CH_2-(CH_2)_5-CH_2-); 1.10 (s, 6H, -CH(CH_3)_2); 0.88 (t, 3H, -CH_3).

The product was recrystallized from hexane; yield: 16.00 g (60%); m. p.: 112 °C; beige coloured crystals.

C_{15}H_{18}O_2S_2 (294.4)
Calcd C 61.20 H 6.16%.
Found C 61.01 H 6.22%.

1^H NMR (DMSO-d_6): δ (ppm) 13.08 (s, 1H, -COOH); 7.72 (d, 1H), 7.26 (d, 1H), 7.08 (d, 1H), 6.86 (d, 1H) (bithiophene); 2.86 (t, 2H, bithiophene-CH_2-); 1.66 (quint, 2H, CH_2-CH_2-CH_3); 1.30 (m, 6H, -CH_2-(CH_2)_2-CH_2-); 1.05 (m, 6H, -CH(CH_3)_2); 0.91 (t, 3H, -CH_3).

MS: m/e 294 (C_{15}H_{18}O_2S_2) M^+ (44); 250 (M-CO_2) (1); 223 (M-C_6H_5) (100); 179 (223-CO_2) (4); 147 (179-S) (2); 134 (147-CH) (2); 121 (134-CH) (2).

IR (KBr): (cm⁻¹) 3105 (w), 3057 (m) ν(-=C-H); 2957 (s), 2923 (vs), 2872 (s) ν(C-H); 2655 (s), 2609 (s), 2546 (s), 2517 (s) ν(O-H), 1678 (vs) ν(C=O); 1525 (m), 1474 (vs), 1442 (vs), 1414 (s) ν(C=C); 1331 (s) δ(O-H); 1293 (vs) ν(C=O); 1265 (s), 1241 (m), 1218 (m), 1201 (m) δ(-=C-H); 1105 (s), 1037 (m) δ_as (C-H); 805 (vs) δ_o,p (C-H). - These absorptions are also typical for 4b.

5-Octyl-2,2'-bithiophene-5'-carboxylic acid (4b)

From 21.60 g (0.540 mol) NaOH in 200 ml water and 25.89 g (0.162 mol) bromine and 15.04 g (0.054 mol) 3b in 100 ml dioxane analogous to the synthesis of 4a; yield: 12.86 g (74%); m. p.: 108 °C; beige coloured crystals.

C_{17}H_{22}O_2S_2 (322.5)
Calcd C 63.31 H 6.88%.
Found C 63.59 H 7.12%.

1^H NMR (DMSO-d_6): δ (ppm) 13.08 (s, 1H, -COOH); 7.62 (d, 1H), 7.28 (d, 1H), 7.06 (d, 1H), 6.90 (d, 1H) (bithiophene); 2.86 (t, 2H, bithiophene-CH_2-); 1.62 (quint, 2H, -CH_2-CH_2-CH_3); 1.25 (m, 10H, -CH_2-(CH_2)_5-CH_2-); 0.90 (t, 3H, -CH_3).

MS: m/e 322 (C_{17}H_{22}O_2S_2) M^+ (20); 258 (M-CO_2) (28); 223 (M-C_6H_5) (100); 179 (223-CO_2) (45); 147 (179-S) (12); 134 (147-CH) (8); 121 (134-CH).

General synthesis of the o-alkenyl 5-alkyl-2,2'-bithiophene-5'-carboxylates 5a to 5h

0.014 mol 5-Alkyl-2,2'-bithiophene-5'-carbonic acid (4a, 4b) and 0.168 mol thionyl chloride were refluxed for 4h until no more gas was developed. Then the excess of thionyl chloride was removed by vacuum distillation [18]. The esterification was performed, while heating a mixture of 0.014 mol carbonoyl chloride in 100 ml absolute dichloromethane and 0.014 mol allyl alcohol or 4-penten-1-ol or 5-hexen-1-ol or 9-decen-1-ol in 70 ml absolute pyridine to 40 °C for 10 min. Then the reaction mixture was stirred for additional 12h at room temperature [21]. At last the solution was poured onto ice and 30 ml HCl were added. After extraction with dichloromethane the product was washed with water and a solution of 2% NaOH. The product was purified by column chromatography [neutral Al_2O_3-Merck, dichloromethane/ethyl acetate (3:1)].

Allyl 5-hexyl-2,2'-bithiophene-5'-carboxylate (5a)

From 3.98 g (0.014 mol) 4a, 20.00 g (0.168 mol) thionyl chloride in 100 ml absolute dichloromethane and 0.81 g (0.014 mol) allyl alcohol in 70 ml absolute pyridine; yield: 2.99 g (64%); m. p.: -5 °C; orange coloured oil.
C_{18}H_{22}O_2S_2 (334.5)  
Calcd  C 64.63 H 6.63%,  
Found  C 64.25 H 6.78%.  

1H NMR (CDCl_3): δ (ppm) 7.73 (d, 1H), 7.08 (d, 1H), 7.04 (d, 1H), 6.72 (d, 1H) (bithiophene); 6.00 (d, 2H, -(CH_2)-OOC-); 2.81 (t, 2H, bithiophene-CH_2-); 1.60 (quint, 2H, -CH_2-CH_3); 1.30 (m, 6H, -CH_2-(CH_2)_3-CH_2-); 0.88 (t, 3H, -CH_3). - This spectrum is similar to those of 5a-5h.

MS: m/e 334 (C_{18}H_{22}O_2S_2) M+ (88); 294 (M-C_3H_4)+ (12); 223 (263-C_3H_4)+ (15); 205 (223-H_2O) (4); 179 (223-CO_2) (6).

IR (KBr): (cm⁻¹) 3073 (m) ν (=C-H); 2955 (s) v(CH_3); 2929 (vs) v(CH_2); 2870 (s) v (C-H); 1710 (vs) ν(C =O); 1648 (m), 1556 (w), 1456 (s), 1441 (vs), 1377 (s), 1275 (vs) ν(C-O-C); 1257 ν(C-O); 1090 (vs), 1043 (s) δ(C-H); 994 (s), 915 (m), 843 (m) δ(CH2); 747 δ(C-H). - These absorptions are also typical for those of 5a-5h.

\[
\text{cu-Pentenyl 5-hexyl-2,2'-bithiophene-5'-carboxylate (5b)}
\]

From 3.98 g (0.014 mol) 4a and 20.00 g (0.168 mol) thionyl chloride in 100 ml absolute dichloromethane and 1.21 (0.014 mol) 4-penten-1-ol in 70 ml absolute pyridine; yield: 3.35 g (66%); m. p.: -15 °C; orange coloured oil.

C_{20}H_{26}O_2S_2 (362.6)  
Calcd  C 66.25 H 7.23%,  
Found  C 66.50 H 7.27%.  

MS: m/e 362 (C_{20}H_{26}O_2S_2) M+ (91); 322 (M-C_3H_4)+ (12); 263 (M-C_5H_11)+ (75); 223 (291-C_5H_8)+ (64); 205 (223-H_2O) (5); 179 (223-CO_2) (5).

\[
\text{co-Hexenyl 5-hexyl-2,2'-bithiophene-5'-carboxylate (5c)}
\]

From 3.98 g (0.014 mol) 4a and 20.00 g (0.168 mol) thionyl chloride in 100 ml absolute dichloromethane and 1.40 g (0.014 mol) 5-hexen-1-ol in 70 ml absolute pyridine; yield: 2.95g (56%); m. p.: -20 °C; orange coloured oil.

C_{21}H_{28}O_2S_2 (376.6)  
Calcd  C 67.00 H 7.49%,  
Found  C 66.99 H 7.44%.  

MS: m/e 376 (C_{21}H_{28}O_2S_2) M+ (100); 305 (M-C_5H_11) (55); 294 (M-C_6H_{10}) (17); 277 (294-OH)+ (14); 223 (305-C_6H_{10}) (63); 205 (223-H_2O) (6); 179 (223-CO_2) (5).

\[
\text{doc-Decenyl 5-hexyl-2,2'-bithiophene-5'-carboxylate (5d)}
\]

From 3.98 g (0.014 mol) 4a and 20.00 g (0.168 mol) thionyl chloride in 100 ml absolute dichloromethane and 2.19 g (0.014 mol) 9-decan-1-ol in 70 ml absolute pyridine; yield: 3.64 g (60%); m. p.: -35 °C; orange colored oil.

C_{25}H_{36}O_2S_2 (432.7)  
Calcd  C 67.00 H 7.49%,  
Found  C 66.99 H 7.44%.

MS: m/e 432 (C_{25}H_{36}O_2S_2) M+ (100); 361 (M-C_5H_8)+ (55); 294 (M-C_10H_{18}) (17); 277 (294-OH) (9); 223 (263-C_10H_{18}) (33); 205 (223-H_2O) (3); 179 (223-CO_2) (3).

\[
\text{Allyl 5-octyl-2,2'-bithiophene-5'-carboxylate (5e)}
\]

From 3.00 g (0.009 mol) 4b and 20.00 g (0.168 mol) thionyl chloride in 100 ml absolute dichloromethane and 0.54 g (0.009 mol) allyl alcohol in 70 ml absolute pyridine; yield: 2.06 g (61%); m. p.: -6 °C; orange coloured oil.

C_{20}H_{26}O_2S_2 (362.6)  
Calcd  C 66.25 H 7.23%,  
Found  C 66.08 H 7.25%.  

MS: m/e 362 (C_{20}H_{26}O_2S_2) M+ (91); 322 (M-C_3H_4)+ (12); 263 (M-C_5H_11)+ (75); 223 (291-C_5H_8)+ (64); 205 (223-H_2O) (5); 179 (223-CO_2) (5).

\[
\text{co-Pentenyl 5-octyl-2,2'-bithiophene-5'-carboxylate (5f)}
\]

From 3.00 g (0.009 mol) 4b and 20.00 g (0.168 mol) thionyl chloride in 100 ml absolute dichloromethane and 0.80 g (0.009 mol) 4-penten-1-ol in 70 ml absolute pyridine; yield: 2.55g (70%); m. p.: -17 °C; orange coloured oil.

C_{22}H_{30}O_2S_2 (390.7)  
Calcd  C 67.63 H 7.74%,  
Found  C 67.55 H 7.69%.

MS: m/e 390 (C_{22}H_{30}O_2S_2) M+ (91); 322 (M-C_5H_8)+ (11); 305 (322-OH)+ (12); 291 (M-C_5H_{15}) (61); 223 (291-C_5H_{12}) (56); 205 (223-H_2O) (7); 179 (223-CO_2) (6).

\[
\text{co-Decenyl 5-octyl-2,2'-bithiophene-5'-carboxylate (5g)}
\]

From 3.00 g (0.009 mol) 4b and 20.00 g (0.168 mol) thionyl chloride in 100 ml absolute dichloro-
methane and 0.93 g (0.009 mol) 5-hexen-1-ol in 70 ml absolute pyridine; yield: 2.56 g (68%); m. p.: -26 °C; orange coloured oil.

C_{23}H_{32}O_2S_2 (404.7)
- Cacld C 68.26 H 7.97% ,
- Found C 68.10 H 7.69% .
- MS: m/e 404 (C_{23}H_{32}O_2S_2) M^+ (100); 322 (M-C_{6}H_{10}) (22); 305 (M-C_{7}H_{15}) (64); 277 (294-OH) (33); 223 (305-C_{6}H_{10})^+ (96); 205 (223-H_2O) (6); 179 (223-CO_2) (12).

ω-Decenyl 5-octyl-2,2′-bithiophene-5′-carboxylate (5h)

From 3.00 g (0.009 mol) 4b and 20.00 g (0.168 mol) thionyl chloride in 100 ml absolute dichloromethane and 1.45 g (0.009 mol) 9-decen-1-ol in 70 ml absolute pyridine; yield: 2.90 g (66%); m. p.: -36 °C; orange coloured oil.

C_{27}H_{40}O_2S_2 (460.8)
- Cacld C 70.38 H 8.75% ,
- Found C 70.09 H 8.55% .
- MS: m/e 460 (C_{27}H_{40}O_2S_2) M^+ (100); 361 (M-C_{10}H_{18}) (27); 322 (M-C_{10}H_{18})^+ (14); 305 (322-OH) (12); 223 (361-C_{10}H_{18})^+ (51); 205 (223-H_2O) (13); 179 (223-CO_2) (18).

General synthesis of the polysiloxanes 6a to 6p

According to G. Nestor et al. [22] a mixture of 0.16 g (0.21 mmol) poly(hydrogenmethylsiloxane) (x = ca. 10; Baysilonoil MH4*) and 2.5 mmol of the appropriate ω-alkenyl 5-alkyl-2,2′-bithiophene-5′-carboxylates 5a-5h respectively 0.13 g (0.05 mmol) poly(hydrogenmethylsiloxane) (x = ca. 40; Baysilonoil MH15*) and 2.5 mmol of the compounds 5a to 5h in 9 ml absolute toluene were heated up to 80 °C under stirring in a dry nitrogen atmosphere. 0.1 mol of a 2% (wt/v) ethanolic H_2PtCl_6-solution was added, and the mixture was heated to 80 °C for one more hour. Then it was refluxed for 30 h. The solvent was evaporated and the residue was dissolved in dichloromethane. The product was precipitated with cold ethanol and isolated by centrifugation until it was free from ω-alkenyl carboxylates analogous to G. Nestor et al. [22] by DC (CH_2Cl_2 eluent, silica gel). The polymers were dissolved in dichloromethane and filtered to remove any particulate impurities. The solvent was evaporated and the polymers dried in vacuum at 40 °C; yield: in all cases about 40%; brown coloured oils. Melting and clearing point see Table II.

Because of their viscous consistency no elemental analyses could be carried out. However, the results of the IR and the 1H NMR spectroscopy confirm the structures of the polymers.

No Si-H absorption by 2160 cm⁻¹ was detectable at IR spectroscopy. No peak for Si-H by the chemical shift of 4.75 ppm and no peak for the protons of vinylene were found by 1H NMR spectroscopy. In the 1H NMR spectra of the polymers additional to the signals of the compounds 5a to 5h one finds the signals for CH_3 (directly bound to the Si atom) at 0.1 ppm and CH_3 (at the end of the alkyl substituent) at 0.9 ppm, a complex signal for CH_2 (in the alkyl terminal group and in the spacer group) in the expected quantity at 1.1 to 1.8 ppm, and especially the CH_2 (directly bound to the Si atom) at 0.5 ppm and the CH_2 (directly bound to the O atom) at 4.2 ppm.

IR (KBr) of the polymers: (cm⁻¹) 3073 (w) ν(=CH-H); 2956 (m) ν(CH_3); 2871 (m) ν(C-H); 1710 (vs) ν(C=O); 1556 (w), 1441 (vs), 1377 (s), 1343 (m) ν(C=C); 1474 (vs) δ(C-H); 1275 (vs) ν(C-O-C); 1258 (vs) ν(C-O); 1101 (vs) ν(Si-O); 1090 (vs), 1043 (m) δ(=CH_2); 1056 (vs) ν(Si-O); 994 (m), 915 (m), 895 (m) δ(=CH_2); 799 (s) δ(=C-H); 747 (s) δ(C-H).

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