

Synthesis and Structural Characterization of Alkyl-substituted Oligo(thio-1,4-phenylene)s

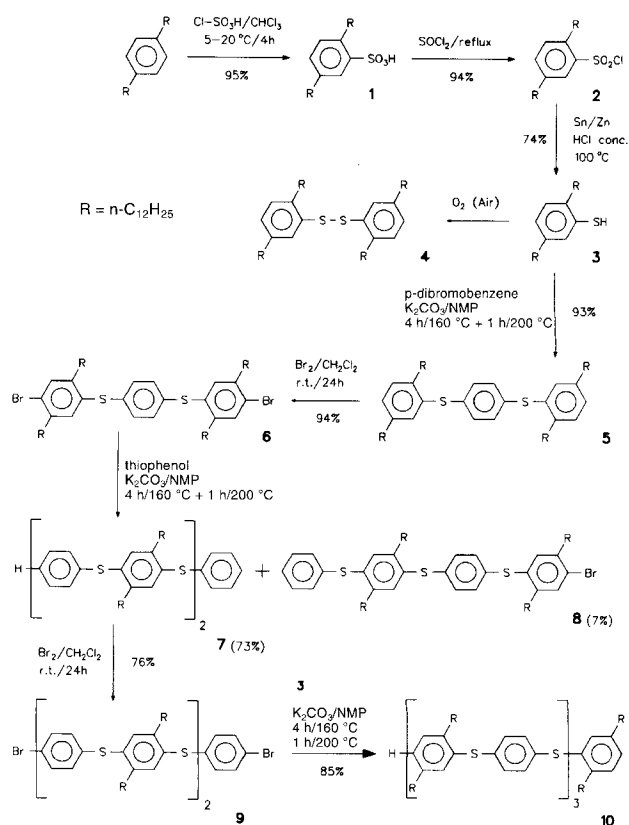
Gerhard Kühn and Jürgen Kelm

Berlin, Federal Institute for Materials Research and Testing (BAM)

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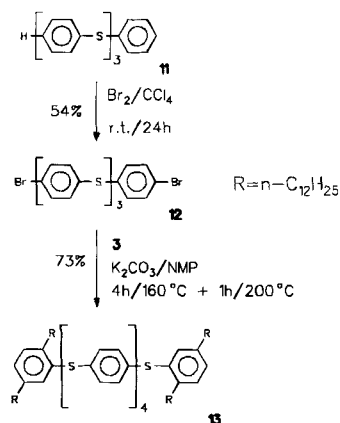
Poly(thio-1,4-phenylene) better known as poly(p-phenylenesulfide) is one of the most important high performance engineering thermoplastic polymers [1–4]. For model investigations of interface problems in connection with its use as matrix material in carbon fiber enhanced composites defined oligo(thio-1,4-phenylene)s are needed. Solubility of these oligomers in organic solvents, however, drops drastically with increasing chain length. Better solubility at room temperature in organic solvents may be achieved by introducing flexible alkyl side chains into the aromatic rings well-known from other classes of compounds [5–7]. But not so much is known about alkyl-substituted poly(thio-1,4-phenylene)s [8–12]. It was our aim to produce defined oligo(thio-1,4-phenylene)s which are soluble in organic solvents at room temperature by introducing alkyl groups into the aromatic rings. The strategy of preparing alkyl-substituted oligo(thio-1,4-phenylene)s is outlined in Scheme 1. The starting material 1,4-di-*n*-dodecylbenzene, prepared by the Kumada reaction [13, 14], reacts in CHCl₃ with chlorosulfonic acid [15] only to the sulfonic acid **1**, and not to the sulfonyl chloride **2**, even when the chlorosulfonic acid was used in an excess. The reason for this behaviour could possibly be the poor solubility of **1** in CHCl₃. By boiling **1** for several hours with an excess of thionyl chloride, it was nevertheless converted into **2** [15]. The following reduction [16] of **2** yielded 2,5-di-*n*-dodecylbenzenethiol **3**, which was kept and processed under nitrogen since it would otherwise oxidize to the corresponding disulfide **4**. The reaction of **3** with 1,4-dibromobenzene to **5** was carried out in *N*-methylpyrrolidone (NMP) in the presence of K₂CO₃ at temperatures of 160–200 °C [17]. Bromination of **5** to **6** took place under rigorous exclusion of light to avoid bromination of alkyl chains. The following reaction of **6** with thiophenol led to compound **7**. Also small amounts of **8** were isolated by the purification of **7** using flash chromatography. Analogously, **9** and **10** were obtained exploiting the same techniques as used for **6** and **5**. Compound **11** was synthesized as described in [18] and brominated to **12** as shown in Scheme 2. The same procedure, which led to **5** or **10**, can be used to produce **13**.

The prepared alkyl-substituted oligo(thio-1,4-phenylene)s are soluble at room temperature in organic solvents as for



Scheme 1

instance toluene, *n*-hexane, dichloromethane and tetrahydrofuran whereas the unsubstituted compounds are only dissolved in boiling solvents as *N,N*-dimethylformamide. The melting points are decreased drastically in relation to the unsubstituted oligo(thio-1,4-phenylene)s, for instance **10** melts at 65–66 °C whereas the unsubstituted compound melts at 195 °C [18].



Scheme 2

We thank Mrs. R. Decker for the purification of compounds by flash chromatography and Mrs. I. Metasch for measuring the NMR and IR spectra.

Experimental

All reagents were purchased from Merck and used without further purification. The solvents were dried by standard methods. All reactions with thiols were carried out under dry nitrogen. The purification was carried out in most cases by flash chromatography on a silica gel (Merck SiO₂-60; 40–63 μm) filled column (length: 80 cm; diameter: 4 cm). A prepurification using a short silica gel (Merck SiO₂-60; 0.2–0.5 mm) filled column (length: 20 cm; diameter: 1.8 cm) was appropriate for the work-up of the in NMP prepared substances. The melting points of all synthesized compounds were determined by Büchi 530 and are uncorrected. IR spectra were recorded as KBr pellet using a Nicolet 800 FTIR spectrometer. The MALDI-MS spectra were performed using a Kratos Kompact MALDI-3 mass spectrometer (Shimadzu) in reflectron mode. Samples were prepared in a matrix of dithranol (10 mg/ml THF) at a concentration of 0.5 mg/ml THF. Sample ions were created by laser desorption at 337 nm with a 3 ns pulse width and accelerated through 20 kV in the positive ion mode. ¹H- and ¹³C NMR spectra were obtained on a Varian XL-200 (200 MHz). Definition of δ-scale was carried out by standard adjustment for the respective solvent.

2,5-Di-*n*-dodecylbenzenesulfonic acid (1)

23.3 g (0.2 mol) of freshly distilled chlorosulfonic acid was added dropwise, over 1 h, to a stirred and ice-cooled solution of 41.4 g (0.1 mol) 1,4-di-*n*-dodecylbenzene dissolved in 300 ml CHCl₃, and the formation of a white precipitate began immediately. After adding of chlorosulfonic acid the reaction mixture was stirred at room temperature for 3 h. The resulting mixture was then carefully poured in 500 ml ice-water, CHCl₃ was evaporated *in vacuo* and produced acid **1** was extracted with 3 × 100 ml diethyl ether. Combined organic layers were washed with 3 × 100 ml water and dried over anhydrous sodium

sulfate. 47.0 g (95%) **1** was yielded as a white waxlike substance after evaporation of diethyl ether. – IR: ν/cm^{-1} = 2955 (m, CH), 2922 (s, CH), 2852 (s, CH), 1489, 1467, 1221, 1162 (s, SO₃H), 1090, 1021 (s, SO₃H), 721, 621 (s, SO₃H). – ¹H NMR (CDCl₃): δ/ppm = 0.89 (t, 6H, CH₃), 1.26 (m, 36H, CH₂), 1.57 (br m, 4H, CH₂), 2.52 (t, 2H, CH₂), 2.94 (t, 2H, CH₂), 7.23 (m, 2H, H_{arom}), 7.74 (m, 1H, H_{arom}), 11.12 (s, 1H, SO₃H). – ¹³C NMR (CDCl₃): δ/ppm = 14.09 (q), 22.69 (t), 29.37–29.70 (t), 31.14 (t), 31.21 (t), 31.93 (t), 32.54 (t), 35.26 (t), 128.00 (d), 130.96 (d), 132.81 (d), 136.45 (s), 139.39 (s), 140.85 (s). – MALDI-MS: Calcd. for C₃₀H₅₄O₃S: 494.4. Found: 494.6.

2,5-Di-*n*-dodecylbenzenesulfonyl chloride (2)

44.5 g (90 mmol) of sulfonic acid **1** and 80 ml SOCl₂ were refluxed until no further generation of SO₂ could be observed. After evaporation of excess thionyl chloride *in vacuo* at 30 °C a brownish oil was obtained, which slowly solidified. Recrystallization from a small amount of *n*-hexane yielded 43.3 g (94%) **2** as almost white crystals, *m.p.* 51–52 °C. – IR: ν/cm^{-1} = 2954 (m, CH), 2918 (s, CH), 2850 (s, CH), 1380 (s, SO₂Cl), 1174 (s, SO₂Cl). – ¹H NMR (CDCl₃): δ/ppm = 0.87 (t, 6H, CH₃), 1.26 (m, 36H, CH₂), 1.64 (br m, 4H, CH₂), 2.65 (t, 2H, CH₂), 3.07 (t, 2H, CH₂), 7.40 (m, 2H, H_{arom}), 7.85 (m, 1H, H_{arom}). – ¹³C NMR (CDCl₃): δ/ppm = 14.07 (q), 22.64 (t), 29.15–29.60 (t), 31.06 (t), 31.88 (t), 32.33 (t), 35.20 (t), 128.38 (d), 132.10 (d), 135.17 (d), 140.04 (s), 141.84 (s), 142.54 (s). – MALDI-MS: Calcd. for C₃₀H₅₃ClO₂S: 512.3. Found: 512.6 (linear mode and indole-2-carboxylic acid as matrix was used).

2,5-Di-*n*-dodecylbenzenethiol (3)

41 g (80 mmol) of **2**, 10 g granulated tin, 30 g zinc turnings and 150 ml conc. hydrochloric acid were stirred at 100 °C. The reaction process was controlled by TLC on precoated SiO₂-60 F₂₅₄ gel plates (Merck) with *n*-hexane as mobile phase. After about 3 to 4 h **2** was no longer evident. The reaction mixture was cooled and crude **3** floated as an oily layer on aqueous solution, which was extracted with 3 × 50 ml diethyl ether. Organic layers were combined, washed with 3 × 50 ml water, and dried over anhydrous sodium sulfate. After evaporation of solvent a yellow oil was obtained, which gradually crystallized. Pure **3** was obtained by flash chromatography of 8 portions with *n*-hexane as eluent. First small amounts of disulfide **4** generated by oxidation of **3** were obtained after evaporation of solvent as yellow crystals, *m.p.* 40 °C. Afterwards 26.4 g (74%) main product **3** was eluted as pale yellow crystals, *m.p.* 45 °C. – Data for **3**: IR: ν/cm^{-1} = 2953 (m, CH), 2917 (s, CH), 2849 (s, CH), 2565 (w, SH), 1603, 1491, 1465, 722. – ¹H NMR (CDCl₃): δ/ppm = 0.91 (t, 6H, CH₃), 1.29 (m, 36H, CH₂), 1.59 (br m, 4H, CH₂), 2.53 (t, 2H, CH₂), 2.64 (t, 2H, CH₂), 3.26 (s, 1H, SH), 6.99 (m, 2H, H_{arom}), 7.10 (m, 1H, H_{arom}). – ¹³C NMR (CDCl₃): δ/ppm = 14.12 (q), 22.71 (t), 29.37–29.69 (t), 29.81 (t), 31.39 (t), 31.94 (t), 34.25 (t), 35.32 (t), 126.15 (d), 129.32 (d), 129.74 (s), 130.56 (d), 137.98 (s), 141.16 (s). – MALDI-MS: Calcd. for C₃₀H₅₄S: 446.4. Found: 446.0 (indole-2-carboxylic acid as matrix was used). Calcd.: C, 80.64; H, 12.18; S, 7.18. Found: C, 80.67; H, 12.44; S, 7.14.

Data for **4**: $^1\text{H NMR}$ (CDCl_3): $\delta/\text{ppm} = 0.89$ (t, 12H, CH_3), 1.27 (m, 72H, CH_2), 1.53 (br m, 8H, CH_2), 2.50 (t, 4H, CH_2), 2.71 (t, 4H, CH_2), 7.00 (m, 4H, H_{arom}), 7.38 (m, 2H, H_{arom}). – $^{13}\text{C NMR}$ (CDCl_3): $\delta/\text{ppm} = 14.12$ (q), 22.71 (t), 29.32–29.72 (t), 31.02 (t), 31.31 (t), 31.95 (t), 33.42 (t), 35.43 (t), 127.76 (d), 129.19 (d), 130.01 (d), 135.12 (s), 139.88 (s), 141.24 (s). – MALDI-MS: Calcd. for $\text{C}_{60}\text{H}_{106}\text{S}_2$: 890.8. Found: 890.7 (indole-2-carboxylic acid as matrix was used). Calcd.: C, 80.83; H, 11.98; S, 7.19. Found: C, 80.86; H, 12.10; S, 7.11.

1,4-Bis(2,5-di-*n*-dodecylphenylthio)benzene (**5**)

11.15 g (25 mmol) of **3**, 2.36 g (10 mmol) of *p*-dibromobenzene, 4.15 g (30 mmol) of anhydrous K_2CO_3 were stirred in 30 ml NMP at 160 °C for 4 h and at 200 °C for 1 h. The solution turned dark in the course of the reaction. After extensive removal of NMP *in vacuo* at 80 °C a dark mushy residue was left over, which was suspended in *n*-hexane, and a prepurification by chromatography on a short silica gel filled column with *n*-hexane yielded a nearly colourless eluat. Flash chromatography on silica gel with *n*-hexane produced 9.0 g (93%) of pure **5** as white crystals, *m.p.* 53–54 °C. – $^1\text{H NMR}$ (CDCl_3): $\delta/\text{ppm} = 0.89$ (t, 12H, CH_3), 1.26 (m, 72H, CH_2), 1.55 (br m, 8H, CH_2), 2.51 (t, 4H, CH_2), 2.71 (t, 4H, CH_2), 7.05 (s, 4H, H_{arom}), 7.10 (m, 4H, H_{arom}), 7.15 (m, 2H, H_{arom}). – $^{13}\text{C NMR}$ (CDCl_3): $\delta/\text{ppm} = 14.13$ (q), 22.71 (t), 29.27–29.69 (t), 30.95 (t), 31.32 (t), 31.95 (t), 33.81 (t), 35.28 (t), 128.40 (d), 129.59 (d), 129.67 (d), 132.34 (s), 133.92 (d), 135.24 (s), 141.45 (s), 142.13 (s). – MALDI-MS: Calcd. for $\text{C}_{66}\text{H}_{110}\text{S}_2$: 966.8. Found: 967.3. Calcd.: C, 81.92; H, 11.46; S, 6.62. Found: C, 82.02; H, 11.70; S, 6.71.

1,4-Bis(4-bromo-2,5-di-*n*-dodecylphenylthio)benzene (**6**)

2.96 g (18.5 mmol) of bromine was added quickly to a stirred solution of 8.7 g (9 mmol) of **5** and 10 mg of iodine in 100 ml CH_2Cl_2 at room temperature, and stirred under rigorous exclusion of light for 1 d. 20% aq. KOH was added to the obtained dark yellow suspension until the colour of the solution disappeared. CH_2Cl_2 and water were removed *in vacuo*, the residue was suspended in toluene and prepurified by chromatography on a short silica gel filled column with toluene. After complete evaporation of toluene recrystallization from *n*-hexane yielded 9.5 g (94%) of **6** as white crystals, *m.p.* 72–73 °C. – $^1\text{H NMR}$ (CDCl_3): $\delta/\text{ppm} = 0.88$ (t, 12H, CH_3), 1.25 (m, 72H, CH_2), 1.52 (br m, 8H, CH_2), 2.62 (m, 8H, CH_2), 7.03 (s, 4H, H_{arom}), 7.14 (s, 2H, H_{arom}), 7.40 (s, 2H, H_{arom}). – $^{13}\text{C NMR}$ (CDCl_3): $\delta/\text{ppm} = 14.12$ (q), 22.70 (t), 29.29–29.66 (t), 29.75 (t), 30.67 (t), 31.93 (t), 33.55 (t), 35.59 (t), 124.51 (s), 129.71 (d), 131.91 (s), 133.65 (d), 134.96 (s), 135.38 (d), 140.51 (s), 144.14 (s). – MALDI-MS: Calcd. for $\text{C}_{66}\text{H}_{108}\text{Br}_2\text{S}_2$: 1122.6, 1124.6, 1126.6. Found: 1123.2, 1125.2, 1127.2. Calcd.: C, 70.43; H, 9.67; S, 5.70; Br, 14.20. Found: C, 70.21; H, 9.89; S, 5.49; Br, 14.35.

1,4-Bis(4-phenylthio-2,5-di-*n*-dodecylphenylthio)benzene (**7**)

9.0 g (8 mmol) of **6**, 2.2 g (20 mmol) of thiophenol, 3.4 g (24 mmol) of anhydrous K_2CO_3 were heated in 80 ml NMP according to the procedure described for **5**. Solvent was evaporated *in vacuo* at 80 °C, the dark residue was suspended

in toluene and prepurified by chromatography on a short silica gel filled column with toluene. After removing of toluene a yellowish crystal mush remained, from which by flash chromatography in two runs, the first run using *n*-hexane-toluene (14/1 v/v) as eluent and the second one using *n*-hexane- CH_2Cl_2 (10/1 v/v) as eluent, 6.9 g (73%) of pure **7** was separated as white crystals, *m.p.* 52–54 °C. 0.65 g (7%) of white crystals of **8** (*m.p.* 39–40 °C) could also be isolated, which were generated by exchanging only one bromine atom through thiophenol. – Data for **7**: $^1\text{H NMR}$ (CDCl_3): $\delta/\text{ppm} = 0.93$ (t, 12H, CH_3), 1.30 (m, 72H, CH_2), 1.53 (br m, 8H, CH_2), 2.67 (m, 8H, CH_2), 7.16 (s, 4H, H_{arom}), 7.18 (s, 2H, H_{arom}), 7.20 (s, 2H, H_{arom}), 7.29 (m, 10H, H_{arom}). – $^{13}\text{C NMR}$ (CDCl_3): $\delta/\text{ppm} = 14.20$ (q), 22.77 (t), 29.38–29.74 (t), 30.52 (t), 32.01 (t), 33.58 (t), 33.63 (t), 126.52 (d), 129.14 (d), 129.96 (d), 130.23 (d), 132.67 (s), 133.68 (s), 134.10 (d), 134.30 (d), 135.00 (s), 136.50 (s), 142.53 (s), 142.66 (s). – MALDI-MS: Calcd. for $\text{C}_{78}\text{H}_{118}\text{S}_4$: 1182.8. Found: 1183.2. Calcd.: C, 79.12; H, 10.05; S, 10.83. Found: C, 79.27; H, 10.27; S, 10.63.

Data for **8**: $^1\text{H NMR}$ (CDCl_3): $\delta/\text{ppm} = 0.91$ (t, 12H, CH_3), 1.28 (m, 72H, CH_2), 1.52 (br m, 8H, CH_2), 2.65 (m, 8H, CH_2), 7.10 (m, 4H, H_{arom}), 7.15 (s, 1H, H_{arom}), 7.16 (s, 1H, H_{arom}), 7.18 (s, 1H, H_{arom}), 7.21 (m, 5H, H_{arom}), 7.44 (s, 1H, H_{arom}). – $^{13}\text{C NMR}$ (CDCl_3): $\delta/\text{ppm} = 14.17$ (q), 22.75 (t), 29.35–29.71 (t), 29.75 (t), 30.50 (t), 30.71 (t), 31.98 (t), 33.55 (t), 33.60 (t), 35.63 (t), 124.56 (s), 126.50 (d), 129.12 (d), 129.73 (d), 129.93 (d), 130.21 (d), 131.97 (s), 132.63 (s), 133.63 (s), 133.68 (d), 134.09 (d), 134.25 (d), 134.84 (s), 135.14 (s), 135.43 (d), 136.48 (s), 140.54 (s), 142.51 (s), 142.62 (s), 144.18 (s). – MALDI-MS: Calcd. for $\text{C}_{72}\text{H}_{113}\text{BrS}_3$: 1152.7, 1154.7. Found: 1152.4, 1154.4. Calcd.: C, 74.89; H, 9.86; S, 8.33; Br, 6.92. Found: C, 74.78; H, 10.05; S, 8.30; Br, 7.05.

1,4-Bis[4-(4-bromophenylthio)-2,5-di-*n*-dodecylphenylthio]benzene (**9**)

1.73 g (10.8 mmol) of bromine was added to a solution containing 6.15 g (5.2 mmol) of **7**, 10 mg of iodine and 60 ml CH_2Cl_2 . The reaction conditions and the work-up were carried out as described for the synthesis of **6**. After removing of CH_2Cl_2 a yellow oil was obtained. Applying two flash chromatographic runs eluent *n*-hexane- CH_2Cl_2 (10/1 v/v) yielded 5.3 g (76%) of **9** as white crystals, *m.p.* 55.5–56.5 °C. – $^1\text{H NMR}$ (CDCl_3): $\delta/\text{ppm} = 0.91$ (t, 12H, CH_3), 1.28 (m, 72H, CH_2), 1.52 (br m, 8H, CH_2), 2.66 (m, 8H, CH_2), 7.17 (s+s, 6H, H_{arom}), 7.19 (s, 2H, H_{arom}), 7.24 (m, 8H, H_{arom}). – $^{13}\text{C NMR}$ (CDCl_3): $\delta/\text{ppm} = 14.19$ (q), 22.76 (t), 29.43–29.73 (t), 30.50 (t), 30.62 (t), 31.99 (t), 33.57 (t), 33.65 (t), 120.20 (s), 130.57 (d), 130.81 (d), 132.16 (d), 132.37 (s), 133.70 (s), 134.11 (d), 134.70 (d), 134.85 (s), 136.25 (s), 142.65 (s), 143.00 (s). – MALDI-MS: Calcd. for $\text{C}_{78}\text{H}_{116}\text{Br}_2\text{S}_4$: 1338.6, 1340.6, 1342.6. Found: 1338.7, 1340.7, 1342.7. Calcd.: C, 69.82; H, 8.71; S, 9.56; Br, 11.91. Found: C, 69.94; H, 9.10; S, 9.65; Br, 12.11.

1,4-Bis[4-(4-2,5-di-*n*-dodecylphenylthiophenylthio)-2,5-di-*n*-dodecylphenylthio]benzene (**10**)

3.08 g (2.3 mmol) of **9**, 0.96 g (6.9 mmol) of **3** and 1.0 g (7 mmol) of anhydrous K_2CO_3 were given to 50 ml NMP and heated in an analogous manner as for **5**. After evaporation of

solvent *in vacuo* at 80 °C the dark residue was suspended in *n*-hexane and prepurified by chromatography on a short silica gel filled column with *n*-hexane. The final purification was carried out by two flash chromatographic runs with *n*-hexane as eluent. 4.05 g (85%) of **10** was obtained as colourless oil after removing of solvent, which slowly solidified. The white crystals softened at 53–55 °C and gave a clear molten mass at 65–66 °C. – ¹H NMR (CDCl₃): δ/ppm = 0.89 (t, 24H, CH₃), 1.27 (m, 144H, CH₂), 1.53 (br m, 16H, CH₂), 2.63 (m, 16H, CH₂), 7.04–7.20 (m, 22H, H_{arom}). – ¹³C NMR (CDCl₃): δ/ppm = 14.13 (q), 22.72 (t), 29.28–29.71 (t), 30.46 (t), 30.54 (t), 31.02 (t), 31.34 (t), 31.96 (t), 33.56 (t), 33.84 (t), 35.28 (t), 128.70 (d), 129.28 (d), 129.77 (d), 130.20 (d), 130.71 (d), 131.85 (s), 132.56 (s), 133.48 (s), 133.63 (d), 133.71 (s), 134.22 (d), 134.39 (d), 134.93 (s), 136.62 (s), 141.53 (s), 142.22 (s), 142.49 (s), 142.63 (s). – MALDI-MS: Calcd. for C₁₃₈H₂₂₂S₆: 2071.6. Found: 2072.4. Calcd.: C, 79.93; H, 10.79; S, 9.28. Found: C, 79.96; H, 11.01; S, 9.08.

4,4'-Bis(4-bromophenylthio)diphenylthioether (**12**)

A solution 6.4 g (40 mmol) of bromine dissolved in 10 ml CCl₄ was dropped into a ice-cooled suspension of 8.0 g (20 mmol) of 4,4'-bis(phenylthio)diphenylthioether (**11**) [19] and 30 mg of iron powder in 50 ml CCl₄. Then the mixture was stirred at room temperature for 24 h. The reaction mixture was neutralized with 5% aq. Na₂CO₃, the precipitate collected, washed with water and dried. Repeated recrystallization from toluene/*i*-propanol (1/1 v/v) yielded 6.1 g (54 %) of **12**, *m.p.* 186–187 °C; [19]: 187 °C. – ¹H NMR (THF-d₈): δ/ppm = 7.29 (s, 8H, H_{arom}), 7.34 (m, 8H, H_{arom}). – ¹³C NMR (THF-d₈): δ/ppm = 122.52 (s), 132.83 (d), 132.93 (d), 133.66 (d), 134.08 (d), 136.05 (s). – MALDI-MS: Calcd. for C₂₄H₁₆Br₂S₃: 557.9, 559.9, 561.9. Found: 557.6, 559.6, 561.6.

4,4'-Bis[4-(2,5-di-*n*-dodecylphenylthio)phenylthio]diphenylthioether (**13**)

2.8 g (5 mmol) of **12**, 5.6 g (12.5 mmol) of **3** and 2.14 g (15 mmol) of anhydrous K₂CO₃ were heated in 50 ml NMP according to the procedure described to **5**. Solvent was evaporated by heating *in vacuo* and by flash chromatography in two runs, the first one using *n*-hexane as eluent and the second one using *n*-hexane-toluene (9/1 v/v) as eluent, 4.7 g (73%) of **13** was separated as a colourless viscous liquid, which then solidified to a white waxlike mass after several weeks, *m.p.* 32–33 °C. – ¹H NMR (CDCl₃): δ/ppm = 0.89 (t, 12H, CH₃), 1.26 (m, 72H, CH₂), 1.56 (br m, 8H, CH₂), 2.54 (t, 4H, CH₂), 2.72 (t, 4H, CH₂), 7.04–7.26 (m, 22H, H_{arom}). – ¹³C NMR (CDCl₃): δ/ppm = 14.09 (q), 22.68 (t), 29.23–29.65 (t), 31.05 (t), 31.26 (t), 31.92 (t), 33.86 (t), 35.23 (t), 128.84 (d), 129.05 (d), 129.86 (d), 130.58 (d), 131.23 (s), 131.43 (s), 131.55 (d), 132.44 (d), 133.97 (s), 134.97 (d), 135.86 (s),

138.45 (s), 141.64 (s), 142.94 (s). – MALDI-MS: Calcd. for C₈₄H₁₂₂S₅: 1290.8. Found: 1291.1. Calcd.: C, 78.08; H, 9.52; S, 12.40. Found: C, 77.99; H, 9.70; S, 12.13.

References

- [1] P. Cebe, *Polymers & Polymer Composites* **3** (1995) 239
- [2] K. Kohlhepp, *Kunststoffe* **83** (1993) 791
- [3] L. C. Lopez, G. L. Wilkes, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **C29** (1989) 83
- [4] H. Cherdron, F. Herold, A. Schneller, *Chem. unserer Zeit* **23** (1989) 181
- [5] M. Ballauf, *Angew. Chem., Int. Ed. Engl.* **28** (1989) 253 and references therein
- [6] M. Rehahn, A.–D. Schlüter, W. J. Feast, G. Wegner, *Polymer* **30** (1989) 1060
- [7] P. Bäuerle, F. Pfau, H. Schlupp, F. Würthner, K.–U. Gaudl, M. B. Caro, P. Fischer, *J. Chem. Soc., Perkin Trans. 2* **1993**, 489
- [8] R. F. Wright, M. C. Yu, US 5189121 A; *Chem. Abstr.* **118** (1993) 236067h
- [9] E. Tsuchida, K. Yamamoto, H. Nishide, *J. Macromol. Sci., Chem.* **A27** (1990) 1119
- [10] K. Yamamoto, S. Yoshida, H. Nishide, E. Tsuchida, *Bull. Chem. Soc. Jpn.* **62** (1989) 3655
- [11] E. Tsuchida, K. Yamamoto, M. Jikei, H. Nishide, *Macromolecules* **22** (1989) 4138
- [12] W. Heitz, W. Koch, DE 3421608 A1 and DE 3421610 A1, 1985; *Chem. Abstr.* **105** (1986) 24817j and 43567u
- [13] M. Kumada, K. Tamao, K. Sumitani, *Org. Synth.* **58** (1978) 127
- [14] M. Rehahn, A.–D. Schlüter, W. J. Feast, *Synthesis* **1988**, 386
- [15] *Organikum, Autorenkollektiv*. VEB Deutscher Verlag der Wissenschaften, Berlin 1986, p. 310 and p. 423
- [16] L. Gattermann, Th. Wieland, *Die Praxis des organischen Chemikers*, Walter de Gruyter & Co., Berlin 1961, 177
- [17] F. P. Glatz, R. Mülhaupt, *Polymer Bull.* **31** (1993) 129
- [18] W. Koch, W. Heitz, *Makromol. Chem.* **184** (1983) 779
- [19] V. A. Sergeev, V. I. Nedel'kin, A. V. Astankov, A. V. Nikiforov, E. M. Alov, Yu. A. Moskvichev, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 854

Address for correspondence:

Dr. G. Kühn
 Bundesanstalt für Materialforschung und -prüfung
 Unter den Eichen 87
 D-12205 Berlin