Synthesis of α,ω-Difunctionalized Oligo- and Poly(*p*-phenyleneethynylene)s

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Received September 29, 1997; Revised Manuscript Received January 20, 1998

ABSTRACT: The synthesis and characterization of soluble rodlike oligo- and poly(1,4-phenyleneethynylene)s end-capped with various functional groups were achieved. The molecular weights were estimated by GPC and ^{1}H NMR spectroscopy. The possibility of quantitatively introducing different or identical functional groups at the chain ends was demonstrated by the synthesis of donor- and acceptor-substituited oligo(1,4-phenyleneethynylene)s and of poly(1,4-phenyleneethynylene)s functionalized with protected thiol moieties. The latter polymers can, after deprotection of the thiol functions, possibly serve as molecular wires and allow the bridging of a small gap between two gold nanoelectrodes.

1. Introduction

Within the last two decades new rigid rodlike polymers have been introduced that are composed of arylene and ethynylene units.[1] The most common example is poly(*p*-phenyleneethynylene) (PPE). The synthetic access to PPEs was made possible by the efficient Pd-catalyzed coupling of bis(alkynyl)arenes with dihaloarenes;[2] however, initial attempts to synthesize PPEs resulted only in low-molecular-weight oligomers with poor solubility.[1a−c] Recently, an increase in solubility and molecular weight of such rigid-rod polymers was achieved by the use of long-chain alkyl- or alkoxy-substituted arenes as monomers.[3]

Less attention has been given to the nature of the polymer end groups. Previous reports have indicated the detection of only halogen end groups.[1a−d,i] Even if AB-monomers were used to avoid stoichiometry imbalances, no evidence for acetylenic end groups was found by ^{1}H NMR spectroscopy.[1c,i] Several explanations have been proposed to account for these results. One likely reason may be that metal-catalyzed bond-opening reactions of the alkynes[4] occur, which can lead to branched or even cross-linked polymers. However, this side reaction should only occur at high temperatures (>80 °C). Another possible reason is the oxidative coupling of two terminal alkynes, which leads to the formation of butadiyne structures. This reaction is caused by the influence of oxygen and copper[5] and the nature of the catalyst. Furthermore, Heck[2a] and Moore[6] argued that Pd(II) catalysts are reduced to the active Pd(0) catalysts before entering the catalytic cycle. This initial step is accomplished by oxidative coupling of two alkyne monomers. Thus, a stoichiometric imbalance is created during initiation, causing low molecular weight polymers possessing only halogen end groups. The existence of copper acetylide end groups can also explain the failure of detecting terminal alkynes by ^{1}H NMR spectroscopy. The formation of copper acetylides is due to the strong affinity of the copper(I) salts toward terminal alkynes;[7] however, this reaction does not cause an interruption of the chain growth. Yamamoto et al. predicted that the formation of the acetylide is an intermediate step in the catalytic cycle that is followed by the transmetalation of the acetylide ligand to the Pd complex.[8]

However, if one considers specific functionalization at the ends of the oligomer or polymer, side reactions need to be reduced to a minimum. Some authors avoid the problems of side reactions by synthesizing difunctionalized oligomers in a stepwise[9] or an iterative divergent/convergent[10,11] manner, including purification of each intermediate compound. However, these approaches are tedious when increasing the oligomer length. Swager et al. synthesized difunctionalized poly(aryleneethynylene)s by copolymerization of a diiodoarylene with a slight excess of a diethynylenearylene and a small amount of a monoiodoarylene end group.[12] In this approach, however, it is not possible to introduce two different end groups at the chain ends.

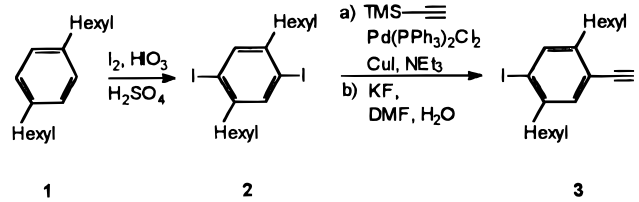
In this paper, a simple procedure for the synthesis of α,ω-difunctionalized oligo- and poly(*p*-phenyleneethynylene)s with identical or different end groups is described. One aim was to synthesize conjugated polymers with thiol end groups to serve as "molecular alligator clips".[10] These polymers may be used to bridge a gap of about 25 nm between two gold nanoelectrodes,[13] which are fabricated by electron-beam lithography on thermally oxidized Si wafers. Another aim was the synthesis of oligo(*p*-phenyleneethynylene)s with one donor and one acceptor end group. The interaction of these end groups was examined as a function of the chain length of the conjugated bridge.

2. Results and Discussion

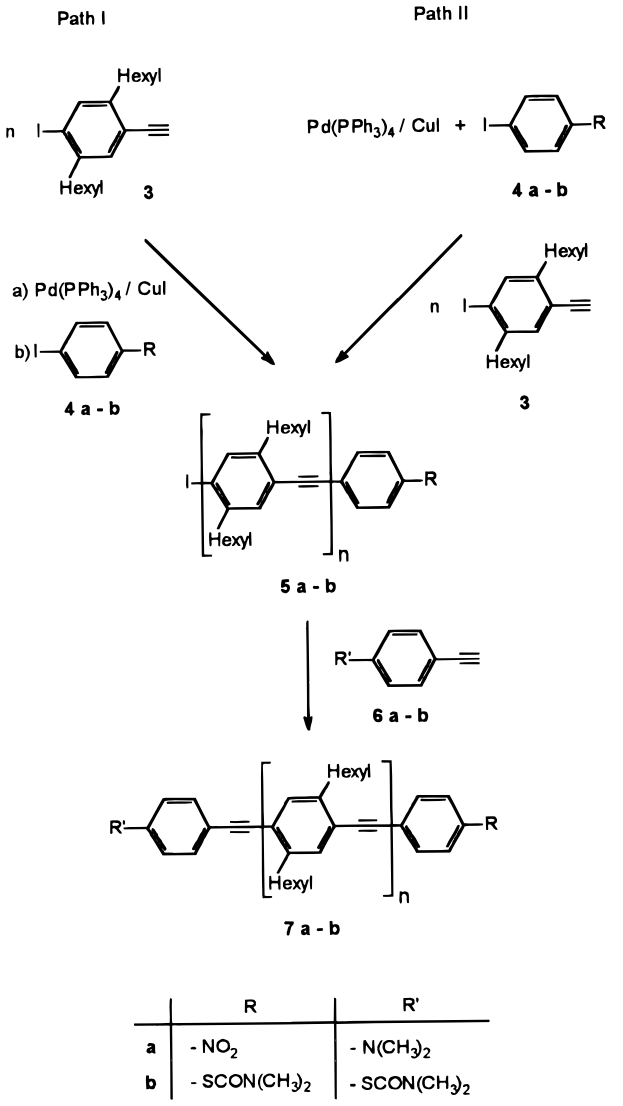
2.1. Synthetic Methods. Two important aspects of the synthesis of α,ω-difunctionalized oligo- and poly(*p*-phenyleneethynylene)s are the use of a Pd(0)-catalyst, i.e., $Pd(PPh_3)_4$, together with copper iodide as cocatalyst and of an AB-monomer to prevent imbalanced stoichiometry. 4-Ethynyl-2,5-dihexyliodobenzene (**3**) was used as the AB-monomer (Scheme 1). **3** was prepared by halogenation of 1,4-dihexylbenzene (**1**),[14,15] leading to 1,4-dihexyl-2,5-diiodobenzene (**2**). Treatment of **2** with an equimolar amount of (trimethylsilyl)acetylene under $PdCl_2(PPh_3)_2$/CuI catalysis gave 2,5-dihexyl-4-[(trimethylsilyl)ethynyl]iodobenzene and after removal of the protecting group 4-ethynyl-2,5-dihexyliodobenzene (**3**). The alkyl substituents ensure good solubility and can also lead to highly ordered supramolecular architectures of the polymers. This self-organization is often described for rigid-rod-like polymers as, for example,

S0024-9297(97)01429-0 CCC: $15.00
Published on Web 03/24/1998

Scheme 1. Synthesis of 4-Ethynyl-2,5-dihexyliodobenzene (3)



Scheme 2. Synthetic Approaches to the α,ω-Difunctionalized Oligo- and Poly[(2,5-dihexylphenylene-1,4)ethynylene]s 7a and 7b



	R	R'
a	- NO_2	- $N(CH_3)_2$
b	- $SCON(CH_3)_2$	- $SCON(CH_3)_2$

polyamides and polyesters,[16] oligothiophenes,[17] and poly(*p*-phenylene)s.[18]

Two different procedures for synthesizing the phenyleneethynylenes discussed here were examined (Scheme 2). In both cases the end-capping reagent, which should react with the acetylenic end group, was added before the workup procedure to prevent oxidative coupling of the alkynes. In path I the AB-monomer **3** was polymerized for a certain time, followed by the addition of an excess of the functionalized iodobenzene **4** to the reaction mixture. After the workup procedure, which was necessary to remove the excess of the end-capping reagent, the resulting poly(1,4-phenyleneethynylene) **5** was converted with the functionalized ethynylbenzene **6** into the difunctionalized polymer **7**. In path II end-capping reagent **4** was mixed with an equimolar amount of catalyst and heated for 15 min in order to enable the oxidative addition of **4** to the catalyst. Subsequently, a predetermined amount of the AB-monomer **3** was added to the mixture. In this case, the reaction stopped after consumption of the acetylenic groups. An addition of an excess of **6** completed the synthesis of oligomers without previous workup of the intermediate product. For the synthesis of polymers, an excess of **4** was added after the first step to ensure that every acetylenic end group was capped. Therefore, a workup of the intermediate product was necessary and the further procedure was analogous to path I. In path II the average molecular weight can be regulated by the ratio of the monomer to the end-capping reagent. An increase of this ratio leads to higher values of the average molecular weight, which is shown by two examples in section 2.3.

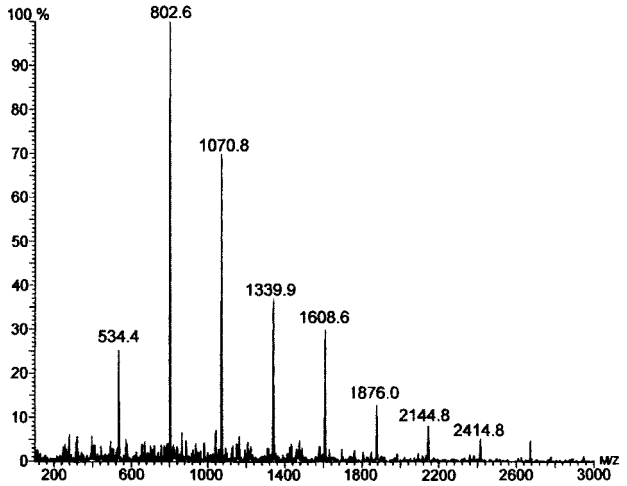
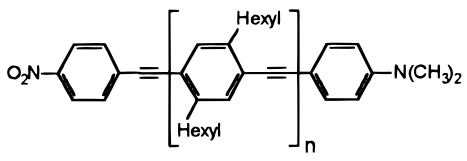


Figure 1. FD mass spectrum of α-[(4-nitrophenyl)ethynyl]-ω-[4-(*N*,*N*-dimethylamino)phenyl]oligo[(2,5-dihexylphenylene-1,4)ethynylene]s (**7a**).

To demonstrate the feasibility of the described synthetic approaches, oligomers with one donor (dimethylamino) and one acceptor (nitro) end group (section 2.2) as well as polymers with two (*N*,*N*-dimethyl(carbamoyl)-thio end groups (section 2.3) were synthesized.

2.2. Synthesis of Donor- and Acceptor-Substituted Oligomers. For the synthesis of donor- and acceptor-substituted oligomers, the coupling reaction according to path II was applied. The reaction was initiated with 4-ethynyl-2,5-dihexyliodobenzene (**3**) and 4-iodonitrobenzene (**4a**) in a ratio of 3:1, followed by addition of an excess of 4-ethynyl-*N*,*N*-dimethylaniline (**6a**)[19] after 16 h. The overall yield of the α-[(4-nitrophenyl)ethynyl]-ω-[4-(*N*,*N*-dimethylamino)phenyl]-oligo[(2,5-dihexylphenylene-1,4)ethynylene]s (**7a**) was 97%. The mixture of the oligomers was investigated by FD mass spectrometry.



7a

The FD mass spectrum indicates equidistant signals for the oligomers **7a** with $n = 1-9$ (Figure 1). No

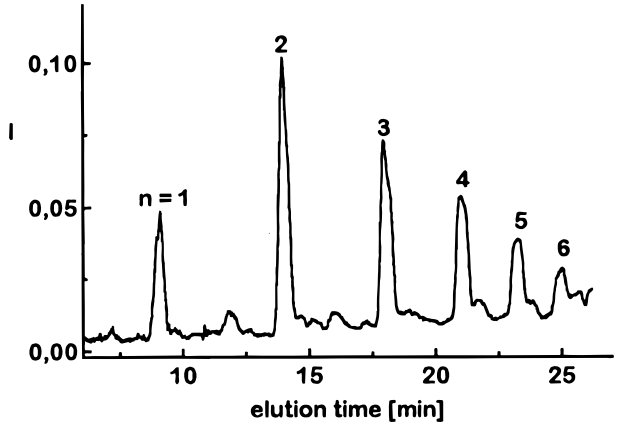


Figure 2. HPLC trace of α-[(4-nitrophenyl)ethynyl]-ω-[4-(*N*,*N*-dimethylamino)phenyl]oligo[(2,5-dihexylphenylene-1,4)-ethynylene]s (**7a**).

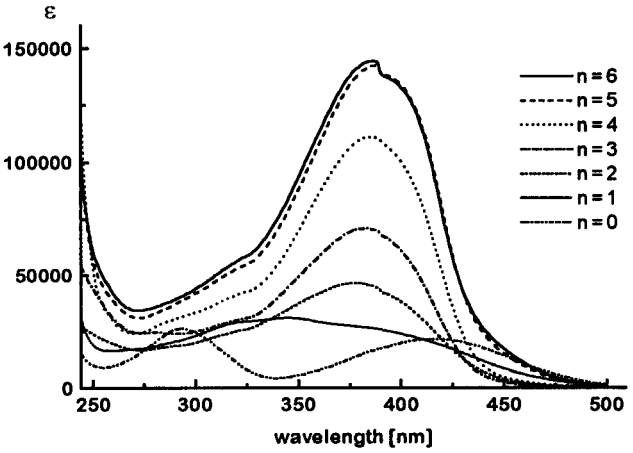


Figure 3. Absorption spectra of α-[(4-nitrophenyl)ethynyl]-ω-[4-(*N*,*N*-dimethylamino)phenyl]oligo[(2,5-dihexylphenylene-1,4)ethynylene]s (**7a**) with $n = 0-6$ in $CHCl_3$.

Table 1. Yields of the Monodisperse Oligomers 7a with $n = 1-6$, Separated by HPLC

	1	2	3	4	5	6
yield (%)	10.1	10.8	7.9	6.5	5.2	2.9

evidence of byproducts was found. Oligomers with $n = 1-6$ were separated by preparative HPLC using a reversed-phase column with an acetonitrile/chloroform gradient as eluent (Figure 3). Larger oligomers could not be isolated, due to their low yields and the small differences in their elution volumes. The yields of the isolated oligomers amounted to 44%. The single yields of the separated oligomers are shown in Table 1. These values indicate the influence of the end-capping reagent **4a** mixed with the monomer at the beginning of the coupling reaction. The reaction was terminated at an oligomeric stage because of the presence of **4a**. Due to the small ratio of 3:1 of monomer **3** to **4a**, the formation of molecules with $n = 1$ and 2 was preferred. An increase of this ratio favored larger oligomers.

2.2.1. Characterization of the Oligomers. The structure and purity of the isolated oligomers **7a** were proven by FD mass spectrometry and NMR spectroscopy. The ^{1}H NMR spectra of the oligomers **7a** confirm clearly the expected substitution pattern. The doublets centered at $\delta = 8.22$, 7.63, 7.39, and 6.66 ppm are assigned to the AA′BB′ systems of the nitrophenyl and (*N*,*N*-dimethylamino)phenyl end groups. The singlets at $\delta = 7.36$ and 7.33 ppm are due to the aromatic

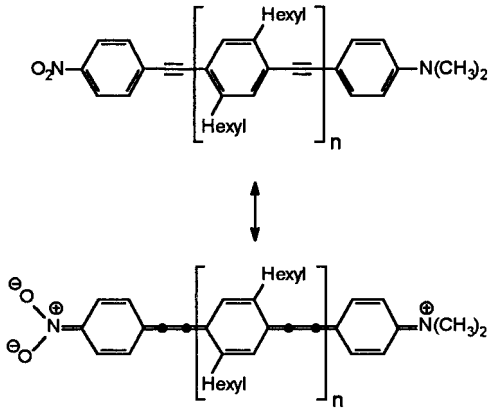


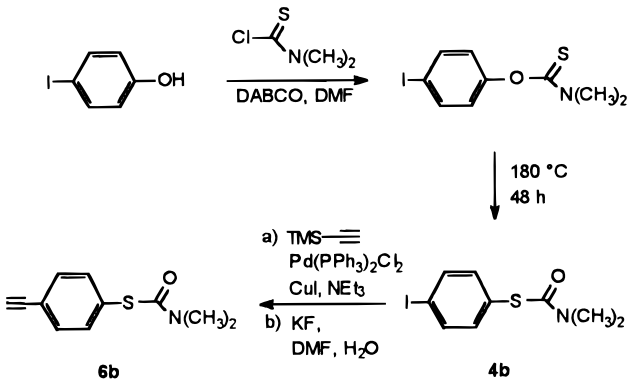
Figure 4. Neutral and charge-separated resonance structure ofα-[(4-nitrophenyl)ethynyl]-ω-[4-(*N*,*N*-dimethylamino)phenyl]-oligo[(2,5-dihexylphenylene-1,4)ethynylene]s (**7a**).

protons of the main chain. In the aliphatic region, the spectra show a singlet at $\delta = 3.00$ ppm for the dimethylamino group and the signals for the hexyl side chains. In the ^{13}C NMR spectra it is not possible to detect all signals for the aromatic and acetylenic carbon atoms because of partial overlap of the resonances. However, the signals at $\delta = 150.2$ ppm (C−NO_2), 147.0 ppm (C−$N(CH_3)_2$), and 40.2 ppm ($N(CH_3)_2$) indicate the presence of the two different end groups.

2.2.2. UV−Vis Spectroscopy. As expected from their conjugated structure, the longest wavelength absorption maxima of the oligomers **7a** show a bathochromic shift with increasing chain length and reach the convergence limit of $\lambda = 387$ nm for $n = 5$ (Figure 3). This convergence of the absorption maxima defines the value of the so-called "effective conjugation length".[20] It describes the size of the π-system, which is necessary to reach size-independent optical and electronic properties of the macromolecules. In comparison with the corresponding unfunctionalized 1,4-phenyleneethynylenes,[10b,21] **7a** shows a similar absorption behavior and size of the conjugation length, but the longest wavelength absorptions of the oligomers **7a** are shifted bathochromically. The observed absorptions are assigned to $\pi-\pi^*$ transitions. No intramolecular charge-transfer transitions (ICT) can be observed for the oligomers **7a** with $n > 1$, whereas the corresponding molecule with $n = 0$ shows a transition ($\lambda = 415$ nm)[22] of this kind. The broad absorption band for $n = 1$ possibly can be explained by partial overlap of the $\pi-\pi^*$ and the ICT band. It seems that the ICT band shifts hypsochromically with increasing chain length and is therefore covered by the $\pi-\pi^*$ band for the higher oligomers. In contrast to this result the energy and intensity of the ICT transition of donor- and acceptor-substituted oligo(1,4-phenylenevinylene)s and α,ω-diphenylpolyynes are nearly independent of the conjugated linker length.[23] The reason for this observation is probably that the charge-separated cumulenic resonance structure in the phenyleneethynylene system (Figure 4) is high in energy and therefore energetically unfavorable in the ground state. The high energy of this resonance structure is due to the loss of aromaticity of the benzene rings.

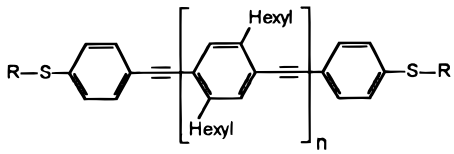
2.3. Synthesis of Polymers with (*N*,*N*-Dimethylcarbamoyl)thio End Groups. The method of α,ω-difunctionalization was also applied to polymers. Intended was the synthesis of a polymer that can be used to bridge a gap between two gold nanoelectrodes.[13] For

Scheme 3. Synthesis of the End-Capping Reagents 4b and 6b



this purpose the molecules have to meet several requirements: (i) They should have a conjugated rigid-rod structure. (ii) Functional end groups are needed, which allow the adhesion to the gold electrodes. (iii) The average length should correspond to the width of the gap between the electrodes. (iv) The molecules should be capable of self-organization on substrates, for example, mica or SiO_2. One candidate exhibiting these properties could be the α,ω-dithiol-functionalized poly(*p*-phenyleneethynylene) **8**. In contrast to Schumm et al.[10b] the synthesis of polydisperse molecules was the objective because the size of the gaps between our nanoelectrodes varies between 20 and 30 nm. For this reason the polymers require an average length of about 25 nm, which corresponds to a DP of about 35.

In this paper a simple synthesis of poly(*p*-phenyleneethynylene)s with (*N*,*N*-dimethylcarbamoyl)thio end groups **7b**, which is the protected form of **8**, is described.



7b : R = $CON(CH_3)_2$
8 : R = H

The end-capping reagents **4b** and **6b** were synthesized as shown in Scheme 3. Reaction of 4-iodophenol with *N*,*N*-dimethylthiocarbamoyl chloride, followed by a Newman−Kwart rearrangement,[24] led to 4-[(*N*,*N*-dimethylcarbamoyl)thio]iodobenzene (**4b**). Then, **4b** was converted into 4-ethynyl-[(*N*,*N*-dimethylcarbamoyl)-thio]benzene (**6b)** by reaction with (trimethylsilyl)-acetylene and deprotection with potassium fluoride.

In the first approach, according to path I in Scheme 2, the AB-monomer **1** was polymerized for 3 days followed by addition of an excess of **4b**. After the workup procedure, the resulting monofunctionalized polymer α-iodo-ω-[4-[(*N*,*N*-dimethylcarbamoyl)thio]phenyl]poly[(2,5-dihexylphenylene-1,4)ethynylene] (**5b**) was coupled with an excess of **6b** to the difunctionalized polymer α-[4-[(*N*,*N*-dimethylcarbamoyl)thio]phenyl]-ethynyl]-ω-[(4-*N*,*N*-dimethylcarbamoyl)thio]phenyl]poly-[(2,5-dihexylphenylene-1,4)ethynylene)] (**7b**). For polymer characterization see section 2.3.1. Polymer **7b** was also synthesized according to path II. Using this approach ratios of 35:1 and 20:1, respectively, of monomer **3** to end-capping reagent **4b** were chosen. After 3 days, an excess amount of **4b** was added, after which the remaining procedure followed path I. The characterization of the polymers is described in the following chapter.

Table 2. Molecular Weights and Degrees of Polymerization (DPs) of Polymer 7b

				DP	
path[a]	M_n[b]	M_w[b]	M_w/M_n[b]	GPC[b]	NMR[c]
I	18198 (27496)	149753 (442576)	8.23 (16.11)	66 (100)	42
II[d]	12767 (17917)	33225 (63481)	2.80 (3.54)	46 (65)	30
II[e]	7264 (9602)	14104 (22595)	1.94 (2.35)	25 (34)	20

[a] Synthesized according to paths I and II, respectively. [b] Determined by GPC analysis with poly(*p*-phenylene)[22] as standard, with values for polystyrene as standard in parentheses. [c] Calculated by integration of the ^{1}H NMR signals. [d] Initial ratio of monomer **3**/end-capping reagent **4b** = 35:1. [e] Initial ratio of monomer **3**/end-capping reagent **4b** = 20:1.

2.3.1. Polymer Characterization. The average degrees of polymerization, DP, of the resulting polymers were estimated by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy (Table 2).

The GPC method is especially sensitive to the calibration standards used. Since a polystyrene calibration is not suitable for the evaluation of the elugrams of rigid-rod polymers, a substituted poly(*p*-phenylene) (PPP) with known molecular weights was used for the calibration.[25] Polymer **7b**, synthesized according to path I, showed a DP of 66 determined by GPC (PPP calibration), whereas the polymers synthesized according to path II indicate DPs of 46 and 25 (Table 2). In the elugrams of the polymers **7b**, a low-intensity tailing of the molecular weight distribution curve to higher values is observed, which drastically increases the polydispersity but has only little effect on the number-average molecular weight. Possibly, the tailing is caused by aggregation of the rigid π-conjugated polymers.[12,26] Analogous to the observations of Swager et al.,[12] solutions of polymer **7b** form stable gels upon standing, which can be redissolved by heating. This observation indicates that only weak physical cross-links are responsible for the gelation. However, after removal of the solvent, only a small amount of **7b** redissolves. In addition, the intensity of the tailing increases with the age of the sample. It seems that the protected thiol end groups of the polymer have an influence on the aggregation behavior as well. Compared to the molecular weight distribution curve of unfunctionalized poly(*p*-phenyleneethynylene)s, the curve of **7b** indicates a stronger tailing.

Polymer **7b** was also examined by ^{1}H NMR spectroscopy in order to prove the existence of the end groups. The ^{1}H NMR spectrum of **7b** (Figure 5) points toward a complete functionalization of the polymer ends within the experimental error. The aromatic protons of the end groups appear as a singlet at $\delta = 7.48$ ppm (b), and the aromatic protons of the main chain, as a broad singlet at $\delta = 7.36$ ppm (c). The signal at $\delta = 3.02$ ppm (a) is assigned to the (dimethylcarbamoyl)thio group, and the other signals in the aliphatic area are caused by the hexyl groups. Signals for molecules with iodine end groups that appear at $\delta = 7.69$ and 7.30 ppm cannot be detected. Since polymer **7b** is quantitatively α,ω-functionalized, ^{1}H NMR spectroscopy provides a convenient method for determining the average number of repeat units or DP. The DP can be determined by straightforward integration of the end group and main-chain signals. By this method a DP of 42 was found for path I as well as DPs of 30 and 20, respectively,

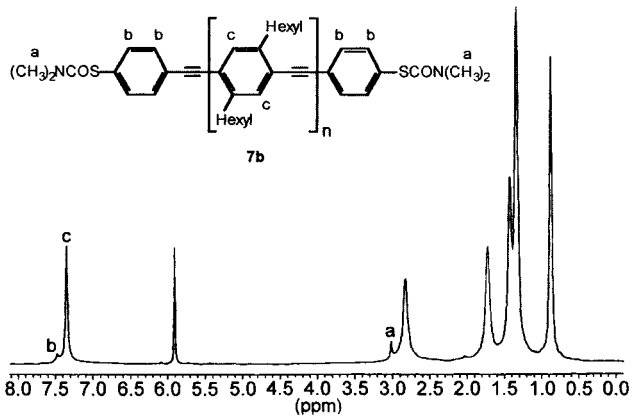


Figure 5. ^{1}H NMR (500 MHz) spectrum of polymer **7b** in tetrachloroethane-d_2.

according to path II. The values calculated by ^{1}H NMR differ from values determined by GPC (Table 2). One reason for these deviations results from errors in signal integration of the ^{1}H NMR spectra due to the partial overlap of the main-chain and end group signals. An additional error comes from the calibration standards used for GPC. The poly(*p*-phenylene) standards discussed above do not describe the elution behavior of the polymers **7b** adequately.

Despite the difficulties concerning the determination of the exact DPs, the lengths of synthesized α,ω-functionalized polymers are in range of the gap width of the nanostructures. A sufficient length to bridge a gap of 20−30 nm means DPs between 28 and 43. It is possible to synthesize α,ω-functionalized polymers with these DPs by following either path I or path II (Table 2). The research into self-organization behavior and the possibility of molecular wire conduction is in progress.

Conclusion

In summary, it is clear from our results that the Pd-catalyzed coupling of iodoarenes with alkynearenes can be used to synthesize oligo- and poly(phenyleneethynylene)s with defined end groups. In comparison with other approaches leading to such molecules, our approach is very simple and straightforward. It is possible to vary the average molecular weight of the polymers and to introduce two different end groups at the chain ends. Since our α,ω-bis(carbamoylthio)-substituted PPEs **7b** fulfill the predetermined requirements for a potential molecular wire, we are now able to investigate their self-organization behavior and, after deprotection, their capability of electron conduction between the nanoelectrodes.

The easy access to the α,ω-difunctionalized PPEs opens a variety of interesting applications. For example, it should be possible to copolymerize PPEs, functionalized with carboxy or hydroxy end groups, with common, functionalized polymers such as polystyrene. These copolymers will probably show unusual morphologies, due to the combination of incompatible polymers.[27]

Experimental Section

All starting materials were obtained from commercial suppliers and used without further purification. The reaction apparatus was predried, and the reactions were carried out under an argon atmosphere. Triethylamine was distilled over KOH before use. THF was distilled over potassium and kept under argon. ^{1}H and ^{13}C NMR chemical shifts were obtained using Varian Gemini 200 and Bruker AMX 500 spectrometers and expressed in parts per million (δ) with residual H atoms in the deuterated solvent as the internal standard. Mass spectra were obtained using a VG Trio 2000 (EI, 70 eV) and a VG Instruments ZAB2-SE-FPD (FD). Gel permeation analyses were performed with polystyrene-gel columns (two columns, 8 mm × 600 mm, 5 μm, pore widths 10^3 and 10^4 Å) and $CHCl_3$ as the solvent connected to a UV−vis detector. IR were recorded using a Nicolet FT-IR 320. The UV−vis absorption spectra were measured with a Perkin-Elmer Lambda 9.

1,4-Dihexyl-2,5-diiodobenzene (2). 1,4-Dihexylbenzene (**1**) (24 g, 0.1 mol), iodine (22.9 g, 0.09 mol), H_2SO_4 (30%, 30 mL), acetic acid (concentrated, 180 mL) and CCl_4 were mixed and stirred at 75 °C for 3 h. After cooling to 0 °C, the precipitate was filtered off and washed with an excess of methanol. The crude material was recrystallized from ethanol and dried in vacuo to yield 31.8 g (64%) of colorless needles; mp 56 °C. ^{1}H NMR (200 MHz, chloroform-*d*): δ = 7.60 (s, 2 H) 2.60 (t, J = 15.7 Hz, 4 H), 1.56 (m, 4 H), 1.35 (m, 12 H), 0.91 (t, J = 13.1 Hz, 6 H). ^{13}C NMR (50 MHz, chloroform-*d*): δ = 145.3, 139.8, 100.8, 40.3, 32.1, 30.6, 29.4, 23.0, 14.5. IR (KBr): ν/cm^{-1} = 2956, 2937, 2922, 2867, 2856, 2847, 1464. MS (EI): m/z = 498 (M^+). Anal. Calcd: C, 43.39; H, 5.66; I, 50.94. Found: C, 43.25; H, 5.78; I, 50.90.

2,5-Dihexyl-4-[(trimethysilyl)ethynyl]iodobenzene. To a solution of **2** (4.98 g, 10 mmol), CuI (48 mg, 2,5 mmol), and $Pd(PPh_3)_2Cl_2$ (351 mg, 0.5 mmol) in 80 mL of triethylamine was added (trimethylsilyl)acetylene (0.98 g, 10 mmol). The mixture was stirred at room temperature for 15 h. After removal of the solvent in vacuo, **3** was separated from starting material and byproduct by column chromatography using silica gel with pentane as eluent to yield 2.34 g (50%) of a colorless oil. ^{1}H NMR (200 MHz, chloroform-*d*): δ = 7.63 (s, 1 H), 7.50 (s, 1 H), 2.63 (m, 4 H), 1.57 (m, 4 H), 1.34 (m, 12 H), 0.91 (m, 6 H), 0.26 (s, 9 H). ^{13}C NMR (50 MHz, chloroform-*d*): δ = 145.1, 143.1, 139.8, 132.9, 123.1, 103.9, 101.6, 98.9, 40.7, 34.4, 32.2, 31.0, 30.7, 29.7, 29.5, 23.1, 14.5, 0.4. IR (KBr): ν/cm^{-1} = 2957, 2927, 2871, 2857, 2154, 1656, 1649, 1642, 1590, 1474, 1467, 1460. MS (EI): m/z = 468 (M^+), 73 (TMS, 100%). Anal. Calcd: C, 58.96; H, 7.96; I, 27.08. Found: C, 59.03; H, 7.89; I, 27.15.

4-Ethynyl-2,5-dihexyliodobenzene (3). 2,5-Dihexyl-4-[(trimethysilyl)ethynyl]iodobenzene (2 g, 4.27 mmol) was dissolved in 10 mL of DMF. To the solution was added KF (0.37 mg, 6.40 mmol) and 1 mL of water, and the mixture was stirred for 2 h at room temperature under exclusion of light. After addition of 10 mL of water, the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with water four times and then dried with $MgSO_4$. The solvent was removed in vacuo, and the crude material was purified by column chromatography using silica gel with pentane as eluent to yield 1.66 g (98%) of a colorless oil. ^{1}H NMR (200 MHz, chloroform-*d*): δ = 7.67 (s, 1 H), 7.28 (s, 1 H), 3.26 (s, 1 H), 2.65 (m, 4 H), 1.58 (m, 4 H), 1.35 (m, 12 H), 0.91 (m, 6 H). ^{13}C NMR (50 MHz, chloroform-*d*): δ = 145.1, 143.2, 139.9, 133.9, 133.4, 122.1, 102.0, 82.4, 81.6, 40.6, 34.0, 32.1, 30.9, 30.6, 29.6, 29.5, 23.1, 14.5. IR (KBr): ν/cm^{-1} = 3311, 3298, 2956, 2927, 2857, 1588, 1474, 1467, 1460. MS (EI): m/z = 396 (M^+). Anal. Calcd: C, 60.57; H, 7.37; I, 32.06. Found: C, 60.42; H, 7.48; I, 32.02.

α-[(4-Nitrophenyl)ethynyl]-ω-[4-(*N*,*N*-dimethylamino)-phenyl]oligo[(2,5-dihexylphenylene-1,4)ethynylene] (7a). 4-Iodonitrobenzene (**4a**) (249 mg, 1 mmol), $Pd(PPh_3)_4$ (1.16 g, 1 mmol), CuI (190 mg, 1 mmol), and 30 mL of piperidine were stirred and heated to 60 °C. After 15 min, 4-ethynyl-2,5-dihexyliodobenzene (**3**) (1.19 g, 3 mmol) was added and the mixture stirred for 16 h. 4-Ethynyl-*N*,*N*-dimethylaniline (**6a**) (174 mg, 1.2 mmol) was added, and the solution was stirred for an additional 2 days at 60 °C. The solvent was evaporated, the residue was dissolved in CH_2Cl_2 and filtered using a short column filled with silica gel. The solvent was removed in vacuo, and the oligomer mixture (1.06 g, 98%) was subjected to column chromatography using an RP_{18}-HPLC column with chloroform/acetonitrile as eluent. This procedure yielded

monodisperse oligomers. To give an overview of their characteristics, data for the oligomers with $n = 1$, 4, and 6 are reported.

$n = 1$: 54 mg (10.1%) of a yellow product: mp 85 °C; ^{1}H NMR (200 MHz, chloroform-*d*): δ = 8.20, 761 (AA′BB′, 2 H each), 7.38, 6.65 (AA′BB′, 2 H each), 7.34 (s, 1 H), 7.33 (s, 1 H), 2.98 (s, 6 H), 2.85−2.70 (m, 4 H), 1.75−1.50 (m, 4 H), 1.45−1.30 (m, 12 H), 0.95−0.75 (m, 6 H); ^{13}C NMR (50 MHz, chloroform-*d*): δ = 150.2, 146.8, 142.5, 141.9, 132.6, 132.5, 132.0, 132.0, 130.6, 124.8, 123.7, 120.2, 111.8, 110.0, 96.2, 94.4, 91.6, 86.3, 40.2, 34.2, 34.1, 31.8, 31.7, 30.7, 30.5, 29.3, 29.2, 22.6, 22.6, 14.1, 14.1; IR (NaCl): ν/cm^{-1} = 2954, 2926, 2856, 2359, 2339, 2332, 2198, 1610, 1592, 1558, 1548, 1521, 1498, 1485, 1465, 1457, 1446; UV ($CHCl_3$): λ_{max} = 345 nm (ϵ = 31 245); MS (FD): m/z = 534.6 (M^+). Anal. Calcd: C, 80.85; H, 7.92; N, 5.24. Found: C, 76.73; H, 7.99; N, 4.70.

$n = 4$: 86 mg (6.5%) of a yellow solid; mp 109 °C; ^{1}H NMR (200 MHz, chloroform-*d*) δ = 8.22, 7.63 (AA′BB′, 2 H each), 7.39, 6.66 (AA′BB′, 2 H each), 7.36 (s, 6 H), 7.33 (s, 2 H), 3.00 (s, 6 H), 2.90−2.70 (m, 16 H), 1.80−1.55 (m, 16 H), 1.50−1.20 (m, 48 H), 0.95−0.75 (m, 24 H); ^{13}C NMR (50 MHz, chloroform-*d*) δ = 150.0, 147.0, 142.7, 142.1, 141.9, 141.8, 141.8, 132.6, 132.5, 132.4, 132.0, 131.9, 131.8, 130.5, 124.0, 123.8, 123.5, 123.0, 122.9, 122.7, 122.6, 122.5, 121.8, 121.7, 121.2, 112.0, 95.4, 94.0, 93.7, 93.4, 93.2, 93.0, 92.7, 92.6, 92.0, 86.6, 40.2, 34.2, 31.8, 31.8, 31.7, 30.7, 30.6, 29.7, 29.3, 22.7, 14.1; IR (NaCl) ν/cm^{-1} = 2955, 2924, 2871, 2855, 2360, 2342, 2333, 1610, 1594, 1539, 1521, 1505, 1490, 1463, 1457, 1447; UV ($CHCl_3$) λ_{max} = 385 nm (ϵ = 110 994); MS (FD) m/z = 1340.3 (M^+). Anal. Calcd: C, 86.03; H, 9.48; N, 2.09. Found: C, 85.26; H, 9.68; N, 2.23.

$n = 6$: 54 mg (2.9%) of a yellow product; mp 125 °C; ^{1}H NMR (200 MHz, chloroform-*d*) δ = 8.22, 7.64 (AA′BB′, 2 H each), 7.39, 6.67 (AA′BB′, 2 H each), 7.38−7.36 (m, 10 H), 7.33 (s, 2 H), 2.99 (s, 6 H), 2.90−2.70 (m, 24 H), 1.80−1.55 (m, 24 H), 1.50−1.20 (m, 72 H), 0.95−0.75 (m, 36 H); ^{13}C NMR (50 MHz, chloroform-*d*) δ = 150.2, 147.0, 142.7, 141.9, 141.8, 141.8, 133.3, 132.6, 132.4, 132.4, 132.1, 131.9, 131.8, 127.5, 125.9, 123.7, 123.6, 123.0, 122.9, 122.8, 122.6, 122.5, 121.8, 111.9, 110.4, 95.4, 93.4, 93.2, 93.0, 92.8, 92.6, 92.0, 86.5, 40.2, 34.2, 31.8, 30.7, 30.6, 29.7, 29.3, 22.7, 14.1; IR (NaCl) ν/cm^{-1} = 2956, 2925, 2871, 2855, 2360, 2342, 1610, 1595, 1521, 1506, 1464, 1457; MS (FD) m/z = 1876.6 (M^+); UV ($CHCl_3$) λ_{max} = 387 nm (ϵ = 144 338). Anal. Calcd: C, 87.02; H, 9.78; N, 1.49. Found: C, 84.17; H, 9.86; N, 2.17.

4-[(*N*,*N*-Dimethylthiocarbamoyl)oxy]iodobenzene. DABCO (15.3 g, 136.4 mmol) and *N*,*N*-dimethylthiocarbamoyl chloride (12.6 g, 101.9 mmol) were added to a solution of 4-iodophenol (15.0 g, 68.2 mmol) in 150 mL of DMF. The mixture was stirred for 30 min at 35 °C and for an additional hour at 75 °C. After cooling to room temperature, the mixture was poured into 250 mL of water and the precipitate was collected by filtration. The crude material was recrystallized from ethanol/toluene (4:1) and dried in vacuo to yield 17.5 g (84%) of colorless product; mp 102 °C. ^{1}H NMR (200 MHz, chloroform-*d*): δ = 7.66 (d, J = 8.8 Hz, 2 H), 6.81 (d, J = 8.8 Hz, 2 H), 3.42 (s, 3 H), 3.30 (s, 3 H). ^{13}C NMR (50 MHz, chloroform-*d*): δ = 186.2, 153.8, 138.2, 125.0, 90.1, 43.3, 38.7. IR (NaCl): ν/cm^{-1} = 3340, 3082, 3062, 3058, 2941, 1538, 1532, 1479. MS (EI): m/z = 307.0 (M^+, 10%), 203.0 (M^+ − OCSN(CH_3)$_2$, 2%), 88.1 (CSN(CH_3)$_2$, 89%), 72.2 (OCN(CH_3)$_2$, 100%). Anal. Calcd: C, 35.17; H, 3.28; N, 4.56; S, 10.42. Found: C, 35.19; H, 3.32; N, 4.56; S, 10.39.

4-[(*N*,*N*-Dimethylcarbamoyl)thio]iodobenzene (4b). 4-[(*N*,*N*-Dimethylthiocarbamoyl)oxy]iodobenzene (16 g, 52.1 mmol) was heated to 180 °C for 24 h in a 50 mL Schlenk tube. The crude product was purified by column chromatography on silica gel, using CH_2Cl_2 as eluent to yield 8.4 g (53%) of pure product; mp 83 °C. ^{1}H NMR (200 MHz, chloroform-*d*): δ = 7.68 (d, J = 8.5 Hz, 2 H), 7.19 (d, J = 8.5 Hz, 2 H), 3.03 (s, 6 H). ^{13}C NMR (50 MHz, chloroform-*d*): δ = 166.0, 138.0, 137.1, 128.8, 95.6, 36.9. IR (NaCl): ν/cm^{-1} = 2942, 2933, 2453, 1653, 1620, 1489, 1484, 1470, 1457, 1430, 1401. MS (FD): m/z = 307.1 (M^+). Anal. Calcd: C, 35.17; H, 3.28; N, 4.56; S, 10.42. Found: C, 35.53; H, 3.25; N, 4.34; S, 10.48.

4-[(Trimethylsilyl)ethynyl][(*N*,*N*-dimethylcarbamoyl)thio]benzene. To a solution of compound **4b** (1.23 g, 4.0 mmol), CuI (19 mg, 0.1 mmol), and $Pd(PPh_3)_2Cl_2$ (141 mg, 0.2 mmol) in 40 mL of triethylamine was added (trimethylsilyl)acetylene (450 mg, 4.6 mmol). The mixture was stirred at room temperature for 15 h. After removal of the solvent in vacuo, the residue was purified by column chromatography using silica gel with CH_2Cl_2 as eluent to yield 790 mg (71%) of product; mp 62 °C. ^{1}H NMR (200 MHz, chloroform-*d*): δ = 7.41 (s, 4 H), 3.03 (s, 6 H), 0.23 (s, 9 H). ^{13}C NMR (50 MHz, chloroform-*d*): δ = 166.2, 135.1, 132.1, 129.3, 123.9, 104.4, 95.8, 36.8, −0.1. IR (NaCl): ν/cm^{-1} = 2959, 2454, 2158, 1674, 1484. MS (FD): m/z = 277.3 (M^+). Anal. Calcd: C, 60.60; H, 6.91; N, 5.05; S, 11.54. Found: C, 58.78; H, 6.67; N, 4.29; S, 10.36.

4-Ethynyl[(*N*,*N*-dimethylcarbamoyl)thio]benzene (6b). 4-[(Trimethylsilyl)ethynyl][(*N*,*N*-dimethylcarbamoyl)thio]benzene (4b) (655 mg, 2.36 mmol) was dissolved in 6 mL of DMF. To the solution was added KF (206 mg, 3.55 mmol) and 0.5 mL of water, and the mixture was stirred for 2 h at room temperature under exclusion of light. After addition of 5 mL of water the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with water four times and then dried with $MgSO_4$. The solvent was removed in vacuo, and the crude material was purified by column chromatography using silica gel with ethyl acetate/light petroleum (7:3) as eluent to yield 450 mg (93%) of a yellow product. ^{1}H NMR (200 MHz, chloroform-*d*): δ = 7.48 (d, J = 8.8 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 2 H), 3.11 (s, 1 H), 3.03 (s, 6 H). ^{13}C NMR (50 MHz, chloroform-*d*): δ = 166.0, 135.2, 132.3, 129.8, 122.9, 83.0, 78.5, 36.8. IR (NaCl): ν/cm^{-1} = 3294, 3226, 2936, 2104, 1720, 1662, 1505,1483, 1443. MS (EI): m/z = 204.9 (M^+, 13.4%), 72.5 (OCN(CH_3)$_2$, 100%). Anal. Calcd: C, 64.36; H, 5.41; N, 6.83; S, 15.60. Found: C, 65.14; H, 5.53; N, 6.81; S, 16.36.

α-Iodo-ω-[4-[(*N*,*N*-dimethylcarbamoyl)thio]phenyl]poly[(2,5-dihexylphenylene-1,4)ethynylene] (5b). Path I. A predried Schlenk tube was charged with 4-ethynyl-2,5-dihexyliodobenzene (**3**) (396.4 mg, 1.00 mmol), 15 mL of triethylamine, and 20 mL of THF. The resulting solution was degassed three times by briefly applying a vacuum, after which $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) and CuI (19.0 mg, 0.10 mmol) were added. The mixture was heated and stirred for 3 days at 60 °C. End-capping reagent **4b** (150.0 mg, 0.5 mmol) was added, and the mixture was stirred for an additional 3 days at 60 °C. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in as little THF as possible. The polymer was precipitated first in 400 mL of methanol and then in 400 mL of acetone. The precipitated polymer **5b** was filtered off and dried in vacuo to yield 256 mg (93%) of pure product.

Path II. A solution of end-capping reagent **4b** (8.8 mg, 2.86 × 10^{-2} mmol) in 15 mL of triethylamine and 20 mL of THF was degassed three times. $Pd(PPh_3)_4$ (57.8 mg, 0.08 mmol) and CuI (19.0 mg, 0.01 mmol) were added, and the mixture was stirred for 20 min at 60 °C. 4-Ethynyl-2,5-dihexyliodobenzene (**3**) (396.4 mg, 1.00 mmol) was added slowly over 2 h, and the resulting solution was stirred for 3 days at 60 °C. After adding an excess of **4b** (150 mg, 0.5 mmol), the mixture was stirred for an additional 24 h at 60 °C. The solvent was removed in vacuo, and the residue was dissolved in as little THF as possible. The polymer was precipitated first in 400 mL of methanol and then in 400 mL of acetone. The precipitated polymer **5b** was filtered off and dried in vacuo to yield 251 mg (91%) of product.

^{1}H NMR (500 Hz, tetrachloroethane-d_2): δ = 7.69 (s, end group), 7.50 (bs, end group), 7.38 (bs, main chain), 7.30 (bs, end group), 3.04 (s, N(CH_3)$_2$), 2.87 (bs), 1.76 (bs), 1.47 (bs), 1.37 (bs), 0.91 (bs). ^{13}C NMR (125 Hz, tetrachloroethane-d_2): δ = 142.3, 135.5, 132.8, 132.0, 123.4, 93.8, 37.4, 34.5, 31.9, 30.8, 29.5, 22.9, 14.18. IR (NaCl): ν/cm^{-1} = 2955, 2925, 2871, 2856, 2190, 1503, 1466, 1459. UV (THF): λ_{max} = 386 nm.

α-[[4-[(*N*,*N*-Dimethylcarbamoyl)thio]phenyl]ethynyl]-ω-[4-[(*N*,*N*-dimethylcarbamoyl)thio]phenyl]poly[(2,5-dihexylphenylene-1,4)ethynylene] (7b). Polymer **5b** (230.4 mg) was dissolved in 20 mL of THF. Then 10 mL of triethy-

lamine, $Pd(PPh_3)_4$ (14.0 mg, 0.01 mmol), and CuI (4.7 mg, 0.02 mmol) were added, and the mixture was stirred and heated to 60 °C. Afterward, the end-capping reagent **6b** was added and the solution was stirred for 3 days at 60 °C. The solvent was removed in vacuo, and the residue was dissolved in a minimal amount of THF. The polymer was precipitated first in 300 mL of methanol and then in 300 mL of acetone. The precipitate was filtered off and dried in vacuo to yield 207 mg (90%) of the polymer. ^{1}H NMR (500 MHz, tetrachloroethane-d_2): δ = 7.48 (s, end group), 7.36 (bs, main chain), 3.02 (bs, $N(CH_3)_2$), 2.83 (bs), 1.73 (bs), 1.43 (bs), 1.34 (bs), 0.88 (bs). ^{13}C NMR (125 MHz, tetrachloroethane-d_2): δ = 166.2, 142.3, 135.5, 132.7, 131.9, 128.7, 123.3, 122.9, 93.7, 37.3, 34.5, 31.9, 30.8, 29.5, 22.8, 14.2. IR (NaCl): ν/cm^{-1} = 2960, 2925, 2867, 2857, 2202, 1728, 1654, 1648, 1644, 1460. UV (THF): λ_{max} = 385 nm. Anal. Calcd for DP = 35 ($C_{720}H_{1000}N_2O_2S_2$): C, 88.41; H, 10.31; N, 0.29; S, 0.65. Found: C, 86.87; H, 10.48; N, 0.35; S, 0.63.

Acknowledgment. Financial support by a grant from the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie are gratefully acknowledged.

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MA971429M