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Soluble, High Molecular Weight Ladder Polymers Possessing a Poly(phenylene sulfide) Backbone

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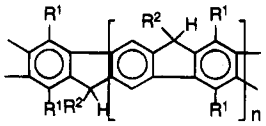
ABSTRACT: A novel route to aromatic ladder-type polymers consisting of linearly annulated six-membered rings is presented. The synthetic sequence involves a polycondensation of dithioresorcinols and aromatic dichlorodiketones to high molecular weight poly(thioether ketone)s under basic conditions. The polymer-analogous ring closure to the desired ladder structures was accomplished by reducing the keto functionalities to the corresponding secondary polyalcohols followed by a Friedel−Crafts-analogous intramolecular cyclization. The course of the polycondensation and the subsequent polymer-analogous reaction steps was studied using model dimers. A uniform formation of completely linear annulated six-membered rings was found for 2-methylated dithioresorcinol as one of the starting compounds. The novel ladder polymers are attractive precursors for the synthesis of poly(arylene methide)s and polycations of the thioxanthylium type, which are isoelectronically related to the hitherto unknown poly[*n*]acene.

1. Introduction

The synthesis of structurally defined ladder polymers is an outstanding challenge for polymer chemistry. In 1991, we reported on the first successful preparation of a fully conjugated, soluble, and structurally well-defined ladder polymer, the polyphenylene ribbon **1**.[1] The novel synthesis follows a so-called classical two-step route in which a suitably functionalized single-stranded precursor is subsequently cyclized to **1** in a polymer-analogous fashion. The type of the final ring closure reaction, a polymer-analogous Friedel−Crafts alkylation to fluorenylene building blocks, is known from the literature to proceed quantitatively.[2] The ladder-type PPP's **1** possess very attractive electronic properties, in particular a highly efficient electroluminescence when used as the active layer in light-emitting diodes (LED's).[3]



1

$R^1 = -C_6H_{13}$
$R^2 = -1,4\text{-}C_6H_4-C_{10}H_{21}$

The main advantage of the novel synthetic approach to ladder polymers like **1** and related structures is the high structural regularity of the obtained materials. This is very important, since the absence of structural defects is one of the crucial needs for an application in efficient and stable electronic devices like LED's. Furthermore, the rather simple synthesis of **1** readily provides the material on, e.g., a 10 g scale in our laboratory. The molecular weights are limited to ca. 25 000−30 000 (number average) and 50 000−60 000 (weight average), respectively. The Pd-catalyzed aryl−aryl coupling used in the formation of the polymer backbone[4] leads only to moderate degrees of polymerization (50−60 phenylene units). This is not a major drawback, however, since the molecular weights are high enough to achieve transparent, flexible, and stable thin films, e.g., for an application in electroluminescent devices.

The molecular weights are, on the other hand, too low to produce free-standing and flexible thicker films or to study the often-proposed specific mechanical and rheological properties[5,6] of stiff ladder polymers in comparison with their single-stranded analogues. Intending such studies, it is crucial to increase the lengths of the polymer chains, adapting highly efficient polycondensation principles.

It is known from the literature that Friedel−Crafts-type intramolecular cyclizations are also successful starting from aryl-substituted 2-hydroxymethyl diphenyl ether precursors under formation of 9-diarylxanthene derivatives.[2] Therefore, it was obvious to investigate the synthesis and subsequent polymer-analogous cyclization of substituted poly(phenylene oxide) and poly(phenylene sulfide) precursors in order to generate aromatic ladder polymers consisting of linearly annulated six-membered rings (ribbons with a poly(hetero-[*n*]acene) perimeter).

The high molecular weights which can be achieved in nucleophilic aromatic polycondensation reactions (e.g., in poly(phenylene sulfide) and poly(ether ketone) synthesis[7,8]) pave the way for preparing high molecular weight ladder structures. The following results should demonstrate the successful combination of nucleophilic aromatic substitution reactions for polymer backbone formation and polymer-analogous Friedel−Crafts cyclizations toward the synthesis of novel soluble, structurally defined *and* high molecular weight aromatic ladder polymers. We describe here only the synthesis of ladder polymers with a poly(phenylene *sulfide*) backbone; the generation of the corresponding phenylene *oxide* analogoues will be the subject of a later publication.

2. Results and Discussion

The preparation of ladder polymer **1** used 2,5-dihexylphenylenediboronic acid and 2,5-dibromo-1,4-bis(4-decylbenzoyl)benzene (**2a**) as condensation monomers to generate the aryl−aryl coupled backbone of the PPP-type (Suzuki coupling[9]). The ring-closure sequence involves reduction of the keto to alcohol functions of the

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Table 1

monomer (product)	T (°C) (duration, h)	monomer conc (mol/L)	M_n	M_w	yield (%)
2b/3a (4a)	100 (24)	0.477	42 000	350 000	69
2b/3a (4a)	120 (24)	0.803	128 000	380 000	72
2b/3b (4b)	100 (24)	0.605	34 500	80 000	81
2b/3b (4b)	130–140 (9)	0.590	53 000	159 000	86

primary coupling product using lithium aluminum hydride followed by a treatment with the Lewis acid boron trifloride etherate as a Friedel–Crafts catalyst to carry out the cyclization.

The synthesis of the corresponding single-stranded precursors containing a *poly(phenylene sulfide)* backbone needs a 2,5-dichloro- or 2,5-difluoro-1,4-bis(4-decylbenzoyl)benzene **2b/c** as one of the coupling monomers, since the dibromodiketone used in the aryl–aryl coupling reactions is not sufficiently reactive with respect to our nucleophilic aromatic substitutions. We therefore subjected the dichloro compound **2b** to a coupling reaction with aromatic dithiols.

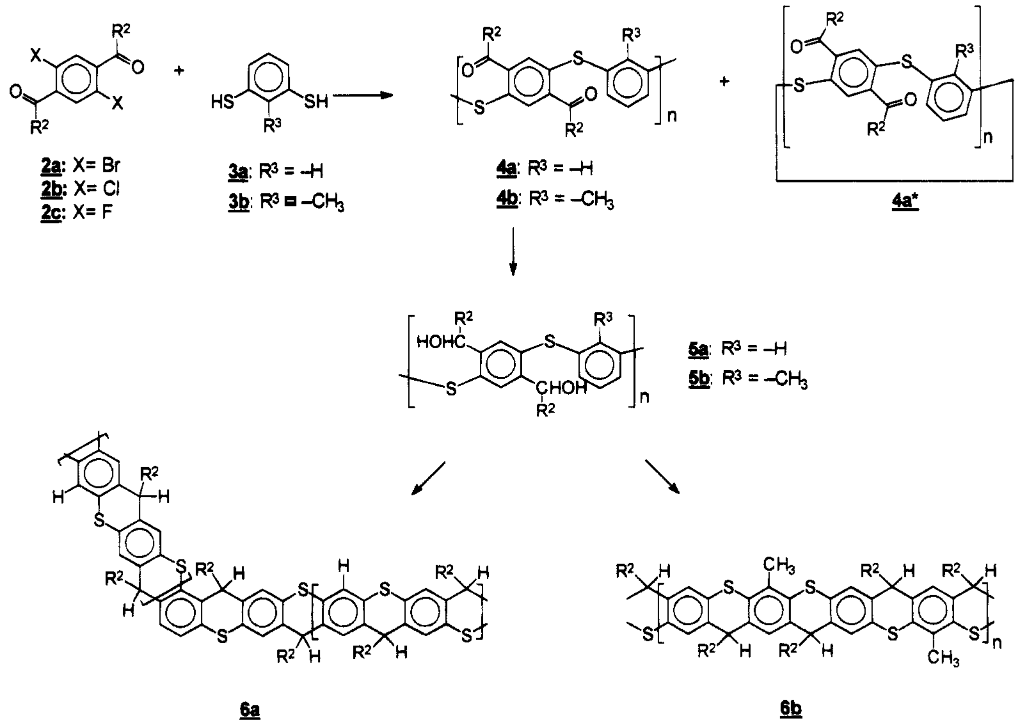
In this paper, we describe the condensation with two easily available dithioresorcinol derivatives **3a/b**. Hereby, we have conducted nucleophilic aromatic substitutions with unsubstituted dithioresorcinol (**3a**) and 2-methyldithioresorcinol (**3b**), in which the position between the two SH substituents is blocked by a methyl group to avoid unwanted cyclizations into this 2-position leading to kinks ("ortho-linkages") of the final ladder structure.

Table 1 summarizes reaction and product data (yield, molecular weight) of several coupling experiments between **2b** and **3a/b** to open-chain poly(phenylene sulfide) precursors **4a/b**. According to the experience gained in poly(ether ketone) synthesis,[10] we used dimethylacetamide as the solvent in connection with potassium carbonate as the base in all of our further polycondensation experiments.

The molecular weights of the condensation products with number-average values of 50 000–170 000 (determined by size-exclusion chromatography and membrane osmometry) corresponding to weight-average values of 100 000–380 000 (size-exclusion chromatography) are as high as needed for the preparation of extended ladder molecules suited for an investigation of mechanical and rheological properties. A comparison of the molecular weights determined by means of GPC (polystyrene calibration) to the data of membrane osmometry (MO) shows that there are no significant differences. The values of the number-average molecular weight M_n determined by MO as the absolute method are slightly increased as compared to those of size-exclusion chromatographic data.

The obtained raw materials exhibit a bimodal distribution of molecular weights in the case of **4a** (unsubstituted dithioresorcinol **3a** as monomer), originating from a small amount of low molecular weight, cyclic oligomers **4a*** present in the product mixture, as detected by FD mass spectroscopy (cyclic di- up to octamers). These oligomers can be removed by means of a reprecipitation into acetone (fractionation). In the case of the coupling products **4b**, originating from the methyl derivative **3b** and **2b** as monomers, cyclic oligomers could not be detected in the condensation product. The molecular mass distribution shows a unimodal shape, in this case. Obviously, the use of **3b** with its methyl substituent in the 2-position suppresses the formation of macrocycles and favors the generation of linear products.

To transform **4** into the final ladder structures, the keto groups of **4** were, in a first step, reduced to secondary alcohol functions using lithium aluminum hydride as the reducing agent. Then, the resulting polyalcohols **5a/b** were subjected to a Friedel–Crafts-analogous ring closure to afford the proposed ladder structures **6a/b**. Whereas zinc chloride and boron trifluoride etherate as Lewis acid catalysts do not lead to a complete cyclization, tin and titanium tetrachloride give access to fully cyclized materials. $SnCl_4$ is particularly useful, since a simple removal of the inorganic byproducts is possible after hydrolysis of the reaction mixture. Molecular weight determinations of **4–6**

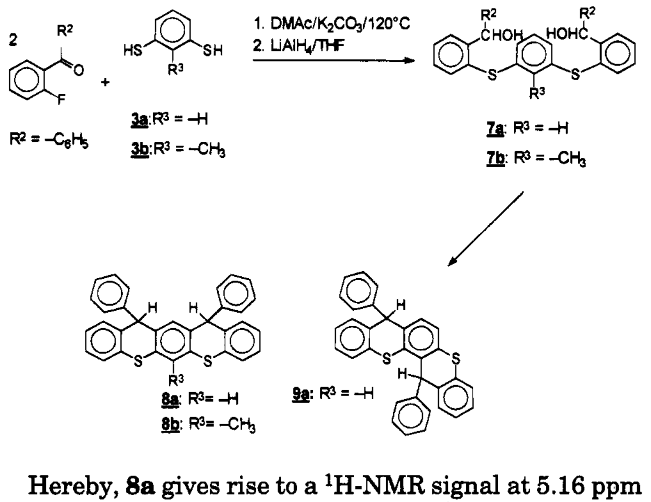


demonstrate clearly that there is no decrease in M_n or M_w during the polymer-analogous reaction steps.

By means of NMR spectroscopic investigations, the product's structure can be studied in detail. Thereby, three points are of particular interest: (i) the completeness of the cyclization; (ii) the regioselectivity of the ring closure and (iii) the tacticity of the products caused by the methylene bridge substituents. The ^{13}C-NMR spectra of the single-stranded polyalcoholic precursors **5a/b** display a signal at 72.8 ppm for the carbon of the diphenylmethanol side groups. This signal disappears completely after the cyclization step, and one or two new signals are detectable at 49.0/52.0 ppm (**6a**) and 52.9 ppm (**6b**) originating from the carbons of the methylene bridge formed during the cyclization. The ^{1}H-NMR spectra of **6a/b** show signals for the methylene bridge hydrogens at 5.25/5.95 ppm (**6a**) and 5.27 ppm (**6b**). The ^{1}H-NMR spectra of **6a/b** do not display any signals of uncyclized diphenylmethanol units in the range 6.0–6.3 ppm for **6a** and 5.8–6.3 ppm for **6b**. Therefore, the completeness of the ring-closure reaction can be assumed.

The presence of two methylene bridge hydrogen and carbon signals in the case of **6a** is in contrast to the spectroscopic behavior of **6b**, a result of the specific structure of monomer **3a**. Next to ring closures into the 4- and 6-positions of the dithioresorcinol building block, a considerable part of cyclizations are directed into the unblocked 2-position between the two thio functions of the building block, giving rise to the formation of kinks (angular annulations of the ribbon) and causing the ^{1}H-NMR signal at 5.95 ppm and the ^{13}C-NMR signal at 49.0 ppm. This interpretation is supported by detailed studies using the low molecular weight compounds **7a/b** as model systems.

The cyclization of **7a** (R = H) leads quantitatively (no uncyclized diphenylmethanol units are detectable in the product) to a mixture of two products, representing the linear and angularly annulated structures **8a** and **9a**, respectively.



Hereby, **8a** gives rise to a ^{1}H-NMR signal at 5.16 ppm and **9a** to two signals at ca. 5.40 and 6.07 ppm. The corresponding ^{13}C-NMR signals are detectable at 49.8 ppm (**8a**) and 51.0/55.0 ppm (**9a**). The cyclization of the methyl-substituted model precursor **7b** provides only one product of ring closure (**8b**), representing the linearly annulated cyclization product since the formation of angularly annulated products is impossible. The signals of the methylene bridge hydrogens and carbons are detectable at 5.52 and 53.5 ppm. Therefore, the use of **3b** as a coupling monomer secures a strict regioselectivity of the intramolecular cyclization (no kink formation!). **6b** represents a linearly annulated ladder structure, while **6a** contains kinks originating from cyclizations into the 2-position of the dithioresorcinol unit.

In the case of the model compounds **8a/b** and **9a**, the methylene bridge hydrogen gives rise to a doubling into two singlet signals due to the presence of *cis/trans* diastereomers, while the corresponding signals of the polymers **6a/b** are observed as broad signals.

The cyclization of the precursor polymer **5b** to the ladder structure **6b** is accomplished by a distinct change of the absorption spectrum. While the open-chain precursor **5b** shows a longest wavelength absorption maximum at 265 nm, the planarized ladder polymer **6b** is characterized by a sharp absorption edge with a λ_{max} of 306 nm. An absorption of very low intensity centered at 595 nm originates from a small part of dehydrogenated (benzoquinone bismethide) subunits present in the polymer (see refs 11 and 12). These substructures are formed during the ring closure and give rise to the light blue color of the products. These defects are not detectable by NMR and IR spectroscopy, and, therefore, their molar content can be estimated to be lower than 1 mol %.

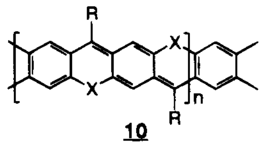
In contrast to the PPP ladder polymer **1**, the ribbons **6a** and **6b** do not exhibit an intense blue fluorescence. There is only a weak, red-colored component of fluorescence detectable, originating from the small part of benzoquinone bismethide defect structures. This fluorescence properties open up the possibility of conducting detailed light scattering studies.

The PPP-type ribbon **1** is not suited for light scattering experiments, since the molecular weights are after all not high enough (number average up to 30 000), and, furthermore, the very strong fluorescence of **1** leads to an enormous widening of the laser beam (laser wavelengths of up to 633 nm). Therefore, the ladder structures **6a** and **6b** represent better candidates for detailed light scattering studies. These investigations should quantify parameters of **6** such as the persistence length. This will be very helpful to discuss rheological and mechanical properties of ladder polymers as rigid, two-dimensional structures.

Thermogravimetric measurements using ladder polymer **6b** display a high thermal stability, since up to 350 °C no weight loss occurs. The main decomposition of **6b** (53% weight loss) is detectable in the temperature range of 400–700 °C. Hereby, the thermal stability of ladder polymer **6b** is defined by that of the side-chain decylphenylene substituents. The decomposition starts with chemical changes of these side groups; decene is detectable as one main component of the volatile decomposition products.

While the synthetic procedures to ladder polymers **6a/b** and **1** are closely related, the chemical and electronic behavior of **6** and **1** is quite different. This aspect concerns, in particular, oxidation or reduction (deprotonation/hydride abstraction) at the methylene bridges.

1 and **6** are suitable precursors to the formation of neutral poly(arylene methide)s **10** as potential low-band-



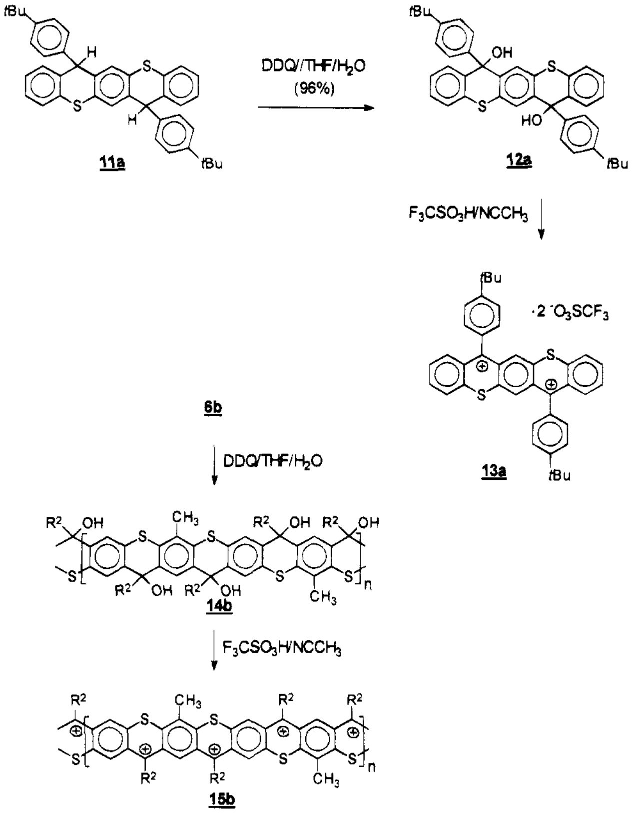
10

—X— = —, —S—

gap materials.[13] Unfortunately, a direct dehydrogenation (e.g., with dichlorodicyanobenzoquinone (DDQ)) of **1**[12] as well as of **6b**[14] leads to structurally ill-defined products as a result of the high chemical instability of the poly(arylene methide) substructures formed.

1 is characterized by a high CH acidity of the methylene bridge hydrogen, caused by the tendency to form stabilized (aromatic) cyclopentadienide (or more precisely 9-phenylfluorenyl) anionic moieties. Using butyllithium as the metallating agent, a deprotonation of more than 90% of the methylene bridge hydrogens is possible.[12] The electronic behavior of the polyanions is very similar to that of isolated 9-phenylfluorenyl anions.[5,12]

On the other hand, **6b** is a very potent precursor to the formation of (aromatically stabilized) polycations of the thioxanthylium type, formally via hydride abstraction. A suitable synthetic procedure to generate cations of this type was developed using the dimeric model **11a** as the starting compound. Oxidation of **11a** with DDQ/THF in the presence of water produces the dialcohol **12a** via hydrolysis of cationic species immediately formed. **12a** can be converted completely into the stable dication **13a** using trifluoromethanesulfonic acid in methylene chloride or acetonitrile.[15] The cation **13a** has been characterized using NMR and UV/vis spectroscopy.



13a is isoelectronic with pentacene as its neutral hydrocarbon analogue. This analogy can be impressively demonstrated by the closely related absorption spectra of **13a** and pentacene. The brownish-colored **13a** exhibits a λ_{max} of 778 nm.

The synthetic procedure to generate **13a** starting from the dimeric model compound **11a** was then used to transform the corresponding ladder polymer **6b** into the polyalcohol **14b** with DDQ/THF/water as the reagent. The absence of the methylene bridge hydrogen signal at 5.27 ppm in the ^{1}H-NMR spectrum of **14b** indicates the complete conversion of the bridge hydrogens of **6b** into hydroxyl groups. First experiments to generate the polycation **15b** in solution were unsuccessful, since the polycation is nearly insoluble in methylene chloride, chloroform, or acetonitrile. Nevertheless, treatment of a solid **14b** film with trifluoromethanesulfonic acid results, after careful washings with acetonitrile, in a deeply colored product, showing a λ_{max} of 978 nm (film), thus indicating an extended π-conjugation in the molecule.

Further investigations should now elucidate, if the cation formation is complete and if the polycation **15b**, which is isoelectronic to the hitherto unknown poly[*n*]-acene,[16] is indeed generated.

In addition, the general synthetic procedure outlined opens up the possibility of using also the corresponding meta-substituted diketones and para-substituted aromatic dithiols as coupling monomers, under the formation of other, novel topologies of the ladder-type backbone.

3. Experimental Part

Reagents. The solvents were used in commercial p.a. qualities or purified according to standard procedures. The preparation of the polymers **4a/b**, **5a/b**, **6a/b**, **14b**, and **15b** was carried out under an argon atmosphere. 2,5-Dichloro-1,4-bis(4-decylbenzoyl)benzene (**2b**) was synthesized according to the literature.[1] The synthesis of 2-methyldithioresorcinol (**3b**) and those of the model compounds **7a/b**, **8a/b**, **9a**, **11a**, **12a**, and **13a** are described in ref 17. All other chemicals are commercially available.

Poly[thio-[2,5-bis(4-decylbenzoyl)-1,4-phenylene]thio-1,3-phenylene] (4a). A 100-mL reaction flask was charged with 2,5-dichloro-1,4-bis(4-decylbenzoyl)benzene (**2b**; 10.20 g, 16.06 mmol) and dithioresorcinol (**3a**; 2.28 g, 16.06 mmol) in 20 mL of DMAc under an inert atmosphere (argon). K$_2$CO$_3$ (2.22 g, 16.09 mmol) was added to the mixture under a rapid stream of argon. The mixture was placed in an oil bath and stirred at 110−120 °C for 24 h; thereby, a highly viscous, slightly yellow-colored suspension is formed. Then, the mixture was allowed to cool and added dropwise to rapidly stirring acetic acid (500 mL, 10 wt %). The precipitate was collected and redissolved in methylene chloride (400 mL). The solution was washed thoroughly with two portions of an aqueous NaHCO$_3$ solution (5%) and water. The solution was dried (MgSO$_4$) and reprecipitated by a dropwise addition of acetone (1 L). The gel formed was isolated by centrifugation. The precipitation procedure was then repeated once more. Finally, the gel was dissolved in benzene (100 mL) and freeze dried. Yield: 8.1 g (72%) of **4a** as a lemon-colored material.

^{1}H-NMR (300 MHz, CDCl$_3$): δ 0.89 (6H, t), 1.27 (28H, s), 1.57 (4H, m), 2.58 (4H, t), 7.11−7.15 (9H, m), 7.29 (1H, s), 7.53 (4H, d). ^{13}C-NMR (75 MHz, CDCl$_3$): δ 14.07, 22.63, 29.29, 29.42, 29.56, 30.94, 31.86, 35.99, 128.56, 130.11, 131.87, 132.06, 133.74, 134.52, 135.52, 135.93, 141.15, 149.57, 194.03. UV/vis (λ, nm (ϵ)): 268 (4.59). Anal. Calcd for $(C_{46}H_{56}O_2S_2)_n$ $(703.0)_n$: C, 78.83; H, 8.03; S, 9.12. Found: C, 78.18; H, 8.31; S, 9.13. GPC (polystyrene calibration): M_n, 128 000; M_w, 380 000. Membrane osmometry: M_n, 170 000. DSC: T_g = 25 °C.

Poly[thio-[2,5-bis(4-decylbenzoyl)-1,4-phenylene]thio-(2-methyl-1,3-phenylene)] (4b). Polymer **4b** was prepared and purified in an analogous fashion to polymer **4a** only replacing 4-methyldithioresorcinol (**3b**) with dithioresorcinol (**3a**). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 0.86 (6H, t), 1.27 (28H, s), 1.55 (4H, m), 2.17 (3H, s), 2.59 (4H, m), 6.90 (3H, m), 7.12 (6H, m), 7.46 (4H, d), ^{13}C-NMR (75 MHz, CDCl$_3$): δ 14.08, 18.49, 22.65, 29.30, 29.41, 29.57, 30.97, 31.87, 36.00, 127.30, 128.48, 130.01, 131.06, 133.69, 134.47, 134.60, 140.48, 142.71, 149.23, 194.23. UV/vis (λ, nm (ϵ)): 267 (4.63). Anal. Calcd for $(C_{47}H_{58}O_2S_2)_n$ $(719.0)_n$: C, 78.51; H, 8.13; S, 8.92. Found: C, 78.38; H, 8.18; S, 8.92. GPC (polystyrene calibration): M_n, 34 500; M_w, 80 000). DSC: T_g = 27.4 °C.

Poly[thio-[2,5-bis[(4-decylphenyl)hydroxymethyl]-1,4-phenylene]thio-1,3-phenylene] (5b). A solution of the poly(phenylene sulfide) precursor **4b** (5.0 g, 6.95 mmol; M_n 34 000, M_w 80 000) in 250 mL of THF was added dropwise to a stirred suspension of $LiAlH_4$ (1.57 g, 42.0 mmol) in 200 mL of dry THF. After reacting the mixture for 6 h at room temperature, the reaction product was poured carefully onto ice (1 kg). The mixture was acidified with aqueous hydrochloric acid, and the solution formed was extracted with methylene chloride (250 mL). The organic phase was isolated, washed with water, an aqueous $NaHCO_3$ solution (5%), and water, and dried (K_2CO_3). The solution was concentrated (100 mL) and then poured into methanol (500 mL). The gel formed was isolated by centrifugation, redissolved in benzene, and freeze dried. Yield: 4.3 g (85%) of **5b** as a colorless material. ^{1}H-NMR (300 MHz, THF-d_8): δ 0.90 (6H, t), 1.30 (28H, s), 1.59 (4H, m), 2.34 (3H, b), 2.54 (4H, m), 4.85 (2H), 6.08 (2H), 6.95 (3H), 7.04 (4H, m), 7.18 (4H, m), 7.54 (2H, m). ^{13}C-NMR (75 MHz, THF-d_8): δ 14.36, 18.10, 23.44, 30.18, 30.26, 30.41, 30.50, 32.43, 32.49, 32.75, 36.40, 72.59, 72.69 (−*C*HOH−), 127.48, 127.70, 127.78, 128.67, 130.79, 131.61, 131.78, 138.78, 142.12, 142.29, 142.43, 146.39. GPC (polystyrene calibration): M_n, 45 000; M_w, 85 000). DSC: $T_g = 62.3$ °C.

Poly[thio-[2,5-bis[(4-decylphenyl)hydroxymethyl]-1,4-phenylene]thio(2-methyl-1,3-phenylene)] (5a). The reduction of polymer **4a** was carried out as described above in the case of polymer **4b**. ^{1}H-NMR (300 MHz, THF-d_8): δ 0.87 (6H, t), 1.27 (28H, s), 1.54 (4H, m), 2.50 (4H, m), 4.95 (2H), 6.10 (2H), 6.90 (3H), 7.00 (5H), 7.15 (4H), 7.65 (2H, m). ^{13}C-NMR (75 MHz, THF-d_8): δ 14.33, 23.43, 30.17, 30.27, 30.49, 32.43, 32.74, 36.40, 72.79 (−*C*HOH−), 127.79, 127.94, 125.71, 130.35, 133.00, 138.74, 142.21, 147.07. Anal. Calcd for $(C_{46}H_{60}O_2S_2)_n$ $(709.1)_n$: C, 77.91; H, 9.04; S, 8.87. Found: C, 76.36; H, 8.51; S, 9.41.

Ladder Polymer 6b. A 1-L reaction flask was charged with a solution of $SnCl_4$ (3.30 g, 12.70 mmol) in 350 mL of dry chloroform. To this solution was added dropwise under rapid stirring a solution of the polyalcohol **5b** (3.0 g, 4.15 mmol) in an additional 350 mL of chloroform. After stirring this mixture for 2.5 h methanol (50 mL) and 2 N HCl (150 mL) were added. After additional stirring for 1 h, the organic phase was isolated and washed with 2 N HCl, an aqueous $NaHCO_3$ solution (5%), and water. The solution was dried ($MgSO_4$) and concentrated (100 mL). The polymer was precipitated by adding acetone. The precipitate formed was isolated by centrifugation. This procedure was then repeated once more. The product was redissolved in benzene and freeze dried. Yield: 2.67 g (94%) of a slightly blue-colored material. ^{1}H-NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2): δ 0.86 (6H), 1.24 (28H), 1.59 (4H), 2.52 (7H), 5.23 (2H), 6.97, 7.07, 7.29, 7.53 (11H). ^{13}C-NMR (125 MHz, 1,1,2,2-tetrachloroethane-d_2): δ 14.5, 23.0, 29.6, 29.8, 29.9, 31.5, 32.2, 35.7, 52.9, 127.6, 127.9, 128.6, 131.8, 136.5, 137.8, 141.5. UV/vis (λ, nm (ϵ)): 306 (4.50), 552 (2.62), 595 (2.72). Anal. Calcd for $(C_{47}H_{58}S_2)_n$ $(687.1)_n$: C, 82.16; H, 8.51; S, 9.33. Found: C, 81.94; H, 8.51; S, 9.24. GPC (polystyrene calibration): M_n, 50 000; M_w, 100 000).

Ladder Polymer 6a. The ladder polymer **6a** was synthesized as described above in the case of polymer **6b**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.82 (6H), 1.20 (28H), 1.47 (4H), 2.44 (4H), 5.17/5.92 (2H), 6.89, 7.27, 7.41 (12H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.10, 22.66, 29.32, 29.49, 29.60, 31.32, 31.89, 35.50, 49.50, 51.96, 125.42, 127.32, 127.75, 130.20, 130.30, 131.88, 136.07, 137.13, 141.32. UV/vis (λ, nm (relative intensity)): 299 (16), 547 (0.8), 593 (1). GPC (polystyrene calibration): M_n, 67 000, M_w, 131 000.

Ladder Polymer 14b. A solution of ladder polymer **6b** (50 mg, 0.073 mmol) in 50 mL of freshly distilled THF was treated with a mixture of DDQ (35 mg, 0.154 mmol) and water (0.8 mL). The mixture was heated for 12 h at 60 °C. After 8 h, an additional portion of DDQ (35 mg, 0.154 mmol) was added. The solution was concentrated under reduced pressure (10 mL) and poured into acetone (60 mL). The precipitate was collected, redissolved in THF (5 mL), and reprecipitated (acetone). The precipitate formed was isolated by centrifugation and redissolved in THF (2 mL), and then benzene (30 mL) was added. Finally, the solution was concentrated (15 mL) and freeze dried. Yield: 48 mg (92%) of a colorless material. ^{1}H-NMR (500 MHz, THF-d_8): δ 0.88 (6H), 1.24 (28H), 1.48 (4H), 2.56 (7H), 6.02 (2H), 6.87/6.97 (8H), 8.19 (2H), 8.86 (1H). ^{13}C-NMR (125 MHz, THF-d_8): δ 14.4, 23.4, 30.2, 30.3, 30.4, 30.8, 32.3, 32.4, 32.8, 36.2, 125.8, 128.2, 130.4, 130.8, 139.9, 140.2, 141.4, 142.2, 143.1. UV/vis (λ, nm): 307. Anal. Calcd for $(C_{47}H_{58}O_2S_2)_n$ $(719.1)_n$: C, 78.50; H, 8.13; S, 8.92. Found: C, 76.82; H, 8.03; S, 9.09.

Polycation 15b. A film of **14b** on silicia was prepared by spin coating (1% of **14b** in a THF solution). The dried films (18 h, 60 °C, 0.01 Torr) were dipped into a solution of trifluoromethanesulfonic acid in acetonitrile (30 min). Then, the films were washed carefully with acetonitrile and dried under high vacuum (0.01 Torr). UV/vis (λ, nm (relative intensity)): 974 (1.0), 626 (8.2), 489 (8.4), 347 (23.3), 264 (15.2).

Measurements. ^{1}H- and ^{13}C-NMR spectral data were obtained on a Varian Gemini 200, a Bruker AC 300, and a Bruker AMX 500 spectrometer.

Gel permeation chromatographic (GPC) analysis utilized PL-gel columns (10 μm) connected with UV/vis and/or refractive index detection. All GPC analyses were performed on solutions of polymers in THF (concentration of polymer: ca. 2 g/L). Calibration was based on narrow polystyrene standards. Membrane osmometry was performed on polymer solutions in toluene using a Knauer membrane osmometer.

The UV/vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer.

The thermal analysis was carried out using a Mettler DSC 30 differential scanning calorimeter (heating rate 5 K/min) and a Mettler 500 thermogravimetric analyzer between 20 and 800 °C (under an inert atmosphere, nitrogen; heating rate 10 K/min).

The mass spectra were recorded on a Finnigan TRIO 2000 (EI) and a ZAB2-SE-FPD (FD) mass spectrometer.

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