Polyarylenes and Poly(arylenevinylene)s. 12.[1] Synthesis and Chemical Modification of Two Novel Poly(naphthylene)s Carrying Solubilizing Pendant Groups

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ABSTRACT: Two novel alkyl-substituted poly(naphthylene)s were synthesized by a transition-metal-catalyzed coupling of aryl bromides and aromatic boronic acids. Their solubility and substitution pattern make the title structures 3 and 6 suitable for polymer-analogous reactions. Anionic and cationic cyclizations lead to polymers containing two-dimensionally fused substructures (rylene units) of perylene, terrylene, and quaterrylene. Depending on the type of substitution, rylene incorporation ranging from 39 to 78 wt % is achieved. The cyclized materials are promising candidates for charge storage.

Introduction

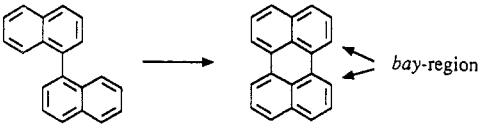
Linear π-conjugated polymers such as polyacetylene,[2] poly(*p*-phenylene),[3] polypyrrole,[4] and polythiophene[5] have attracted attention from the viewpoints of basic research and practical applications. The main drawback of such electroactive polymers is their intractability, which prevents a thorough characterization. One possibility to solve this problem is to attach solubilizing alkyl groups to the polymer backbone, as demonstrated in the syntheses, for instance, of soluble polythiophenes[6] and poly(*p*-phenylene)s.[7]

The synthesis of soluble polynaphthylenes has stirred our interest because appropriate polymer-analogous cyclizations could lead to naphthylene–rylene copolymers containing different, highly electroactive subunits in their main chain. "Rylenes" are oligomers of the peri-condensed naphthylenes.[8] The lowest member of the series, perylene (1; Scheme I), has been the subject of numerous investigations due to, e.g., its fluorescence properties,[9] photoconductivity,[10] and electrical conductivity in the doped state.[11] 1 can be synthesized by an alkali-metal-induced cyclization of 1,1′-binaphthyl.[12]

In principle, this type of cyclization reaction should be applicable to higher oligomers or polymers. Indeed, we have recently shown that oligomers up to the pentanaphthyl can be cyclized to the corresponding oligo(rylene)s by means of a sequence of an anionic cyclization with potassium or lithium, followed by a cationic cyclization under very mild conditions. Thus, rylene oligomers carrying either solubilizing *n*-alkyl groups in the sterically crowded bay-region of the molecule[13] or *tert*-butyl substituents in the terminal naphthalene units were prepared[14] (cf. **13** and **15**, Scheme IV).

In a previous paper, we presented the synthesis of a soluble poly(3,7-di-*tert*-butyl-1,5-naphthylene),[15] in which *each* repeat unit is substituted with *tert*-butyl groups. The steric requirement of the *tert*-butyl group prevents a ring closure to a rylene-containing polymer. Here, we present the synthesis of two soluble poly(naphthylene)s which can be subjected to polymer-analogous cyclizations. In the statistical copolymer **3**, consisting of di-*tert*-butyl-substituted and unsubstituted naphthalene units, the solubility can be controlled by the stoichiometry of the two monomers, and ring closure can take place due to the reduced number of *tert*-butyl groups. The cyclization leads to a copolymer with unsubstituted rylene and *tert*-butyl-substituted naphthalene units in the main chain. The alternating copolymers **6** are substituted with sterically

Scheme I



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less demanding *n*-alkyl groups, which should allow a ring-closure reaction leading to both substituted and unsubstituted rylene units. In the following, the polymer-analogous cyclizations of **3** and **6** are described. Naphthalene–rylene copolymers containing perylene (**1**), terrylene (**15a**, R = H), and quaterrylene (**15b**, R = H) subunits in the main chain are produced.

Results and Discussion

Synthesis of Monomers and Polymers. **3** and **6** (Scheme II) are synthesized by means of the palladium-catalyzed coupling of arylboronic acids with aryl bromides according to Suzuki.[16] From our own experience, this method has proven effective for the coupling of AB-type[15] as well as of AA- and BB-type[17] monomers.

The synthesis of the AB-type monomer **2a** is described in ref 15; **2b** can be synthesized from tetralin in two steps. Fourfold allylic bromination, followed by spontaneous hydrogen bromide evolution leads to 1,4-dibromonaphthalene,[18] which can be converted into **2b** by monolithiation and subsequent reaction with triisopropoxyborane. Palladium-catalyzed coupling of **2a** and **2b** affords **3** in 80% yield. Extraction with boiling toluene leads to a soluble polymeric fraction in a yield of 71%. In spite of the reduced number of alkyl groups, the solubility of this fraction is quite high in common organic solvents (ca. 40 g/L in THF or $CHCl_3$ at room temperature). GPC analysis reveals a mean molecular weight (M_n) of 9200 against polystyrene standards (see Table I). Using the calibration curve obtained earlier,[15] which is based upon the obvious resolution of oligomers in a lower molecular weight fraction and the inclusion of a reference compound, a degree of polymerization for the soluble fraction of **3** is determined as $P_{n+m} = 40$. A thermal analysis (TGA) of **3** reflects its high thermal stability. Between 400 and 600 °C a weight loss of 27% indicates the thermal cleavage of the *tert*-butyl groups.

The synthesis of dibromides **4** is described elsewhere.[13] Coupling of dibromides **4** with 1,4-bis(dihydroxyboryl)-naphthalene (**11**) merely leads to oligomers of low mo-

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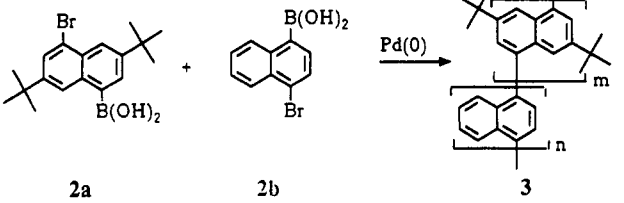
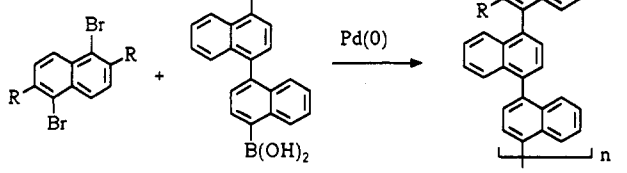
Table I
Soluble Samples of 3, 6a, and 6b and Their Molecular Weights

polymer	M_n	M_w/M_n	polymer	M_n	M_w/M_n	polymer	M_n	M_n/M_w
3	9200	1.9	6a	3700	1.7	6b	5900	1.8
7	7200	2.4	9a	3500	2.1	9b	6200	1.9
8	6900	2.5	10a	3600	2.2	10b	6000	2.2

Scheme II



2a 2b 3



4a: R=C_6H_{13}
4b: R=$C_{12}H_{25}$

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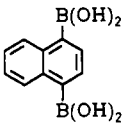
6a: R=C_6H_{13}
6b: R=$C_{12}H_{13}$



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lecular weight. NMR end-group analysis reveals deboronation as the chain-terminating reaction. Apparently, the instability of the diboronic acid in the reaction medium results in the low degree of conversion. In **5**, the functional groups are isolated electronically, thus increasing the stability of the monomer. Treatment of 4,4′-dibromo-1,1′-binaphthyl[19] with *tert*-butyllithium and subsequent reaction with triisopropoxyborane yields the BB-type monomer **5** in 34% yield. Polymerization of **4a** and **5** in a 1:1 molar ratio is carried out as described above. Extraction and precipitation from acetone lead to **6a** in 65% yield. **6a** is not completely soluble in THF. GPC analysis is therefore carried out in *o*-dichlorobenzene. A mean molecular weight (M_n) of 3700 is obtained for this fraction. A GPC analysis of the lower molecular weight THF-soluble fraction 1 leads to a M_n against polystyrene of 2300. Using the resolution of the oligomers in the GPC elugram of fraction 1 of **2a**, as well as the inclusion of a di-*n*-hexylated trinaphthyl (**16**), an average degree of polymerization P_n of 6–7 (18–21 naphthalene units) is determined for the *o*-dichlorobenzene-soluble fraction.

6a precipitates during the polymerization, suggesting that the solubility of the growing chain is the molecular-weight limiting factor. By using the dodecylated monomer **4b**, the solubility of the growing polymer chain is increased; reaction of **4b** and **5** affords a polymer (**6b**) of higher molecular weight. Extraction with boiling toluene and fractionation from acetone leads to 69% of a soluble fraction. Molecular weight determination by GPC shows

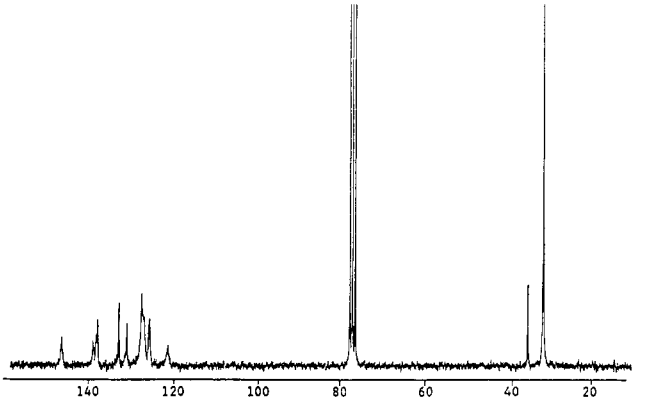


Figure 1. ^{13}C NMR spectrum of polymer **3**.

a M_n of 5900 against polystyrene. Assuming a hydrodynamic volume similar to that of **6a**, the degree of polymerization should be about $P_n = 10$; that is, a polymer chain consisting of ca. 30 naphthalene units is obtained.

The polymers **6** are also thermally quite stable. Between 420 and 550 °C, cleavage of the *n*-alkyl groups is observed.

An X-ray analysis of **6b** with long alkyl side chains shows a sharp peak in the small-angle region, characteristic of a parallel arrangement of the rigid polymer chains via side-chain crystallization. Not surprisingly, the *tert*-butylated species (**3**) and the alternating polymer carrying the shorter *n*-hexyl substituents (**6a**) are amorphous.

Structure Elucidation. The Pd(0)-induced coupling of arylboronic acids with aryl bromides allows a regioselective coupling without side reactions that lead to structural irregularities.[1,7,15,20] The molecular structures of polymers **3**, **6a**, and **6b** are investigated by NMR spectroscopy. In all samples, the ^1H NMR spectra appear broad and unstructured, and no signals stemming from dihydroxyboryl end groups are present. Likewise, no bromine end group was found by elemental analysis. The ^{13}C NMR spectrum of the statistical polymer **3** exhibits seven absorptions in the aromatic region (Figure 1).

The observed splitting of the signals is apparently due not only to the statistical distribution of the *tert*-butylated and unsubstituted repeating units but also to the presence of different diastereomeric subunits. A similar duplication of signals is found in poly(3,7-di-*tert*-butyl-1,5-naphthylene).[15] As expected, the ^{13}C NMR spectra of the alternating polymers **6a** and **6b** are similar in appearance. The spectra of the polymers (**6b**, Figure 2a; **6a**, Figure 2b) exhibit the same signals as that of the model compound **16** (Figure 2c). In the spectroscopic analysis, no indications of side reactions are found.

Polymer-Analogous Reactions. With the synthesis of **3** and **6** two different types of polymers are created, which can serve as starting materials for a rylene-containing polymer. Due to the steric requirement of the *tert*-butyl group, alkali-metal-induced cyclization of **3** can take place only between nonalkylated repeating units. Thus, few perylene units will be incorporated into **7** (Scheme III). Using the cationic conditions developed by Kovacic,[21] in which a mixture of Lewis acid and oxidizing agent is employed, cyclization can proceed with concurrent Lewis acid-induced dealkylation. This approach leads to

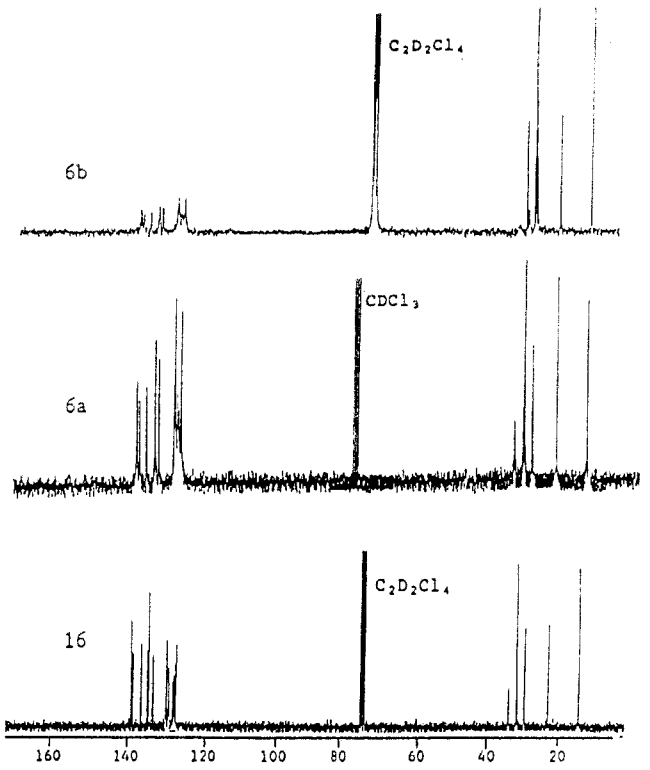
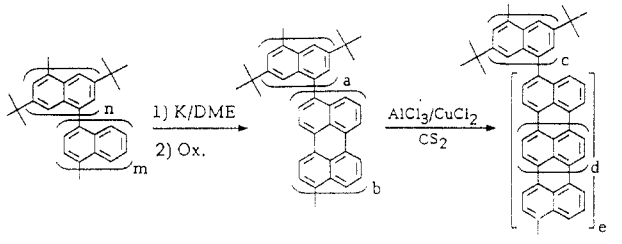


Figure 2. ^{13}C NMR spectra of (a) polymer **6b**, (b) polymer **6a**, and (c) model compound **16**.

Scheme III



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a rylene-containing polymer of low solubility, which is a prerequisite for some applications, e.g., for use in polymer batteries.

To obtain the perylene–naphthalene copolymer **7**, **3** is reduced with potassium in dry 1,2-dimethoxyethane (DME). Upon reduction, cyclization of individual binaphthyl units within the polymer chain of **3** takes place spontaneously. After reoxidation, the product is isolated in 89% yield. Surprisingly, the solubility does not decrease markedly when going from **3** to **7**. The formation of perylene units is immediately seen by the yellow color and strong blue fluorescence of a toluene solution of **7**. To determine the degree of conversion, UV spectroscopy is employed (see Figure 3a). By comparing the extinction coefficient (ϵ) in L kg^{-1} cm^{-1} of **7** with that of naphthylperylene **14**[14] (Chart I), the number of perylene units in **7** can be estimated. The extinction coefficient of **7** is determined to be 21 800 L kg^{-1} cm^{-1}. Using the value of the naphthyl–perylene **14** (ϵ = 40 400 L mol^{-1} cm^{-1} = 67 100 L kg^{-1} cm^{-1}), a perylene content of 21 wt % is estimated for **7**. It should be emphasized that in this consideration changes in ϵ caused by the inclusion of the chromophore in a polymer backbone cannot be taken into consideration. For instance, the conjugative effect brought about by the inclusion of the perylene chromophore in a polymer is expressed by a slight bathochromic shift of 10 nm of the longest-wavelength absorption (λ_{max} = 444 nm for **14** and

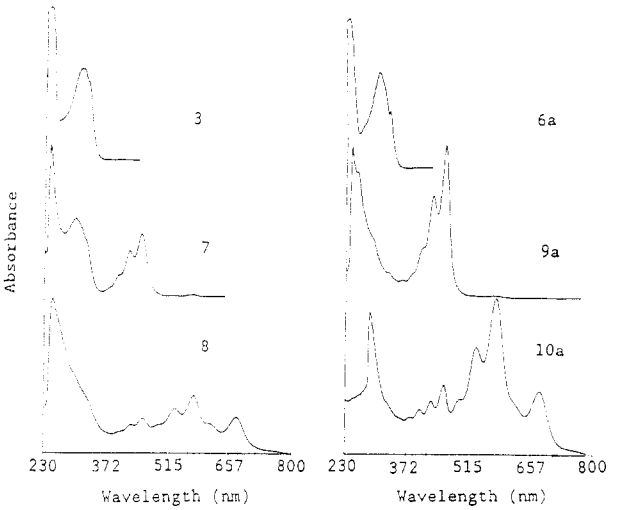
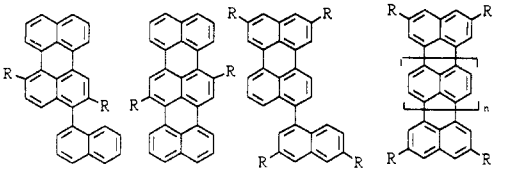


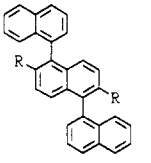
Figure 3. Polymer-analogous cyclizations of (a) **3** and (b) **6a** under UV spectroscopic control.

Chart I

Model Compounds used



12: R=C_6H_{13} **13**: R=C_6H_{13} **14**: R=$C(CH_3)_3$ **15a**: n=1;R=$C(CH_3)_3$
15b: n=2; R=$C(CH_3)_3$



16: R=C_6H_{13}

456 for **7**), as well as by a broadening of the vibrational structure of the absorption bands. The cyclization takes place without chain scission (see Table I).

Formation of terrylene chromophores is not observed in the anionic cyclization of **3**. To arrive at a polymer-containing higher rylene subunits, the cationic cyclization conditions reported earlier are employed.[14] Treatment of **7** with a mixture of anhydrous aluminum trichloride and copper(II) chloride leads to **8** in 90% yield. Continuous extraction with boiling toluene, followed by precipitation from acetone affords 15% of a soluble blue–purple fraction containing perylene, terrylene, and quaterrylene units. As for **7**, a determination of the degree of conversion is conducted by UV spectroscopy (see Figure 3a). Including the extinction coefficients of the terrylene **15a**[14] and quaterrylene **15b**,[14] the degree of rylene incorporation is calculated to be 13 wt % perylene, 19 wt % terrylene, and 7 wt % quaterrylene (see Table II and Figure 3a). Due to the conjugation along the polymer chain, a bathochromic shift of 10–15 nm of each chromophore is observed compared with the model compounds. The characteristic shape of the absorption bands, however, remains the same. Again, the cyclization takes place without chain scission (see Table I).

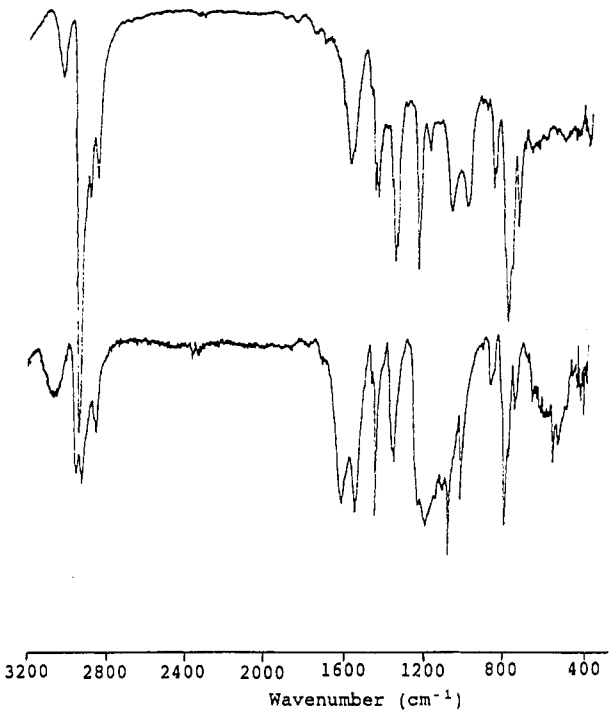


Figure 4. IR spectra of (a) a soluble fraction of 8 and (b) an insoluble fraction of 8.

Table II
Determination of the Amount of Rylene Incorporation in 8, 10a, and 10b

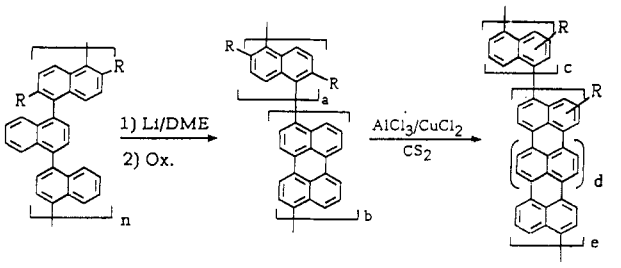
	chromophore	λ_{max} (nm)	ϵ (L kg^{-1} cm^{-1})	inclusion in polymer (wt %)
8	perylene	457	13 700	13
	terrylene	574	21 800	19
	quaterrylene	673	14 200	7
10a	perylene	457	15 800	31
	terrylene	575	34 200	28
	quaterrylene	676	14 400	8
10b	perylene	458	19 300	38
	terylene	574	40 500	33
	quaterrylene	662	12 700	7

The main fraction of 8 (75%) is completely insoluble in organic solvents. A comparison of the IR spectra of soluble and insoluble fractions of 8 shows a drastic reduction of the number of alkyl substituents in the insoluble fraction (see Figure 4). Although dealkylation appears to be the primary reason for the decrease in solubility, other factors, such as a higher degree of cyclization or cross-linking, cannot be ruled out.

Model cyclization reactions of the *n*-alkylated oligomer **16** have shown that, even under the mild conditions used, cyclization is not impeded by the *n*-alkyl group.[13] As expected, alkali-metal-induced cyclization of **6** leads to a much higher degree of conversion.

In a first cyclization step, **6a** and **6b** (Scheme IV) are reacted with lithium powder in DME at elevated temperature. Lithium is used instead of potassium, because the latter induces side reactions such as deprotonation and solvent inclusion at the benzylic positions.[13] After oxidation with oxygen and removal of the reducing agent, **9a** and **9b** are isolated in 85 and 87% yield, respectively. The cyclizations take place without chain scission (see Table I). A UV spectroscopic analysis reveals a perylene content of ca. 66 wt % for **9a** and 70 wt % for **9b** (see Figure 3b). Di-*n*-hexylated naphthylperylene **12**[13] (ϵ = 33 000 L kg^{-1} cm^{-1}) is used as the model compound for the determination of the degree of conversion. For example, 66% conversion in a polymer chain of 21 naphthalene

Scheme IV



6a: R=C_6H_{13} 9a: R=C_6H_{13} 10a: R=C_6H_{13}
6b: R=$C_{12}H_{25}$ 9b: R=$C_{12}H_{25}$ 10b:R=$C_{12}H_{25}$

repeating units results in a polymer containing 7 perylene and 7 naphthalene units. The slightly higher degree of conversion in **9b** may be the result of the better solubility of **6b** in DME compared with **9a**. While **12** is a good model for **9a**, the longer alkyl chains in **9b** should decrease the extinction coefficients of the rylene chromophore (in L kg^{-1} cm^{-1}); thus, the actual amount of perylene incorporation should be somewhat higher than the value calculated using **12** as a model. **9a** is completely soluble in THF and toluene. If the naphthylene–perylene copolymer is subjected to a second alkali-metal-induced cyclization in an attempt to increase the perylene content, a sharp reduction of the mean molecular weight from M_n = 6200 to M_n = 640 is observed.

Cyclization of **9a** with a mixture of aluminum trichloride and copper(II) chloride leads to **10a** and **10b**. As in the *tert*-butylated polynaphthylene, solubility becomes a problem at this stage. The yields of toluene-soluble **10** are about 30%, irrespective of the length of the alkyl group. In **10a** and **10b**, the extent of perylene (31 and 38 wt %), terrylene (28 and 33 wt %), and quaterrylene (8 and 7 wt %) incorporation is larger than in the soluble fractions of **8** (see Figure 3a,b and Table II).

The main fractions of **10a** and **10b** are also insoluble in toluene (60%). By extracting this fraction with boiling 1,2,4-trichlorobenzene, small quantities (1–2%) of less soluble material are obtained. UV spectra (measured in 1,2,4-trichlorobenzene) of these fractions show a slightly increased amount of the quaterrylene chromophore. This suggests that an increasing degree of conversion during the cyclization reaction is responsible for the insolubility of the main fraction of **10a** and **10b**. Again, it cannot be determined to what extent side reactions (aryl–aryl coupling, dealkylation, etc.) also take place under the conditions employed.

The fairly high solubility in the *n*-alkyl-substituted series **6**, **9**, and **10** allows the cyclization to be monitored by ^{1}H NMR spectroscopy. Characteristically, the signals of the protons in the bay-region of a rylene appear at lowest field. In Figure 5a,b the appearance of a broad peak at lowest field $\delta \geq 7.8$ ppm is seen. Integration can only give an estimate of the degree of conversion, since the region of the bay-resonances overlaps somewhat with the region of the other aromatic protons (of the so-called peri- and β-positions). Nevertheless, the values found by integration are in good agreement with the amount of cyclization determined by UV spectroscopy. Assuming a rylene content of 67 wt % for **10a**, an integral ratio of ca. 1:2 (bay-signals: remaining aromatic signals) is calculated. The ratio found is 5:8. For **10b**, a ratio of 1.3:1 is found experimentally.

Conclusion

The solubility of polymers **3** and **6** is the prerequisite for a series of polymer-analogous cyclizations directed

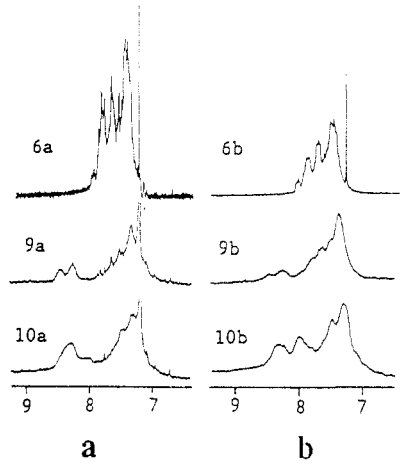


Figure 5. Polymer-analogous cyclizations of (a) **6a** and (b) **6b** under ^{1}H NMR spectroscopic control.

toward a controlled and sequential increase in the redox activity. Anionic cyclization leads to perylene–naphthalene copolymers. A subsequent cationic treatment results in the incorporation of rylene units up to the quaterrylene. An investigation of the charge–storage properties of the polymers is under way.

Experimental Part

General Procedures. The solvents were used in commercial p.a. quality; DME was distilled from potassium. ^{1}H NMR: Varian Gemini 200 (200 MHz), Bruker AM 300 (300 MHz). ^{13}C NMR: Varian Gemini 200 (50.32 MHz), Bruker AM 300 (75.48 MHz). UV–vis: Perkin-Elmer Lambda 9. Melting points (uncorrected): Büchi melting point apparatus. GPC analyses were performed with PL-gel columns (10^3- and 10^4-Å pore widths) connected to a UV–vis detector. The calibration was based on polystyrene standards with narrow weight distribution. Calibrations with oligomers are performed in THF using a 10^3- and 10^4-Å column set. The values in Table I are obtained in *o*-dichlorobenzene using a 500-, 10^4-, and 10^5-Å column set. M_n values determined on both columns are in good agreement. TGA analyses were performed on a Mettler 500 thermogravimetric analyzer. All measurements were carried out under a purified nitrogen atmosphere. 1,4-Dibromonaphthalene,[18] 4,4′-dibromo-1,1′-binaphthyl,[19] and compounds **2a**,[15] **4**,[13] **12**,[13] **13**,[13] **14**,[14] **15a**,[14] **16**,[13] and **15b**[14] were prepared according to literature procedures.

1-Bromo-4-(dihydroxyboryl)naphthalene (2b). To a solution of 1,4-dibromonaphthalene (20 g, 70 mmol) in 200 mL of dry diethyl ether was added at −78 °C 43 mL of a 1.6 N solution of *n*-butyllithium in hexane. After stirring for 1 h, the reaction mixture was allowed to warm to room temperature. The white suspension was then transferred to a dropping funnel and added to a stirred solution of 26.32 g of triisopropoxyborane in 200 mL of dry diethyl ether at −78 °C. The reaction mixture was allowed to warm to room temperature and hydrolyzed with 250 mL of a 2 N aqueous HCl solution. The layers were separated, the organic layer was dried over magnesium sulfate and filtered, and the solvent was evaporated. The residue was dissolved in low-boiling petroleum ether, and ca. 2 mL water was added. **2** precipitated as fine colorless crystals: yield 12.60 g (72%); mp 245–259 °C; ^{1}H NMR (acetone-d_6, 200 MHz) δ 8.58 (m, 2 H), 8.29 (m, 2 H), 7.80 (m, 2 H), 7.64 (m, 2 H), 7.53 (s, 2 H); ^{13}C NMR (acetone-d_6, 50 MHz) δ 134.2, 132.8, 130.8, 130.5, 128.2, 128.1, 127.8, 125.6, 108.4, 102.5; MS (70 eV) *m/z* 250 (75%, M^+), 232 (35%, $M^+ - H_2O$), 206 (16%, $M^+ - H_2O_2$), 172 (100%, $M^+ - Br$).

4,4′-Bis(dihydroxyboryl)-1,1′-binaphthyl (5). 4,4′-Dibromo-1,1′-binaphthyl (4.5 g, 11 mmol) was suspended in 250 mL of dry tetrahydrofuran at −40 °C. To this was added slowly (1 h) 26 mL of a 1.6 N solution of *tert*-butyllithium. The resulting solution was allowed to stir at this temperature and was then transferred through a cannula to a cooled solution (−78 °C) of 12.41 g (66 mmol) of triisopropoxyborane in 150 mL of dry tetrahydrofuran. After stirring for 8 h, the gray suspension was hydrolyzed with 250 mL of aqueous 2 N HCl. The precipitate was filtered off and collected. It was extracted several times with boiling water, the remaining solid was dissolved in 50 mL of acetone at room temperature, and 10 mL of aqueous 2 N HCl was added. The product crystallized as fine colorless needles: yield 1.26 g (34%); mp >250 °C; ^{1}H NMR (acetone-d_6, 200 MHz) δ 8.71 (d, 2 H), 8.01 (d 2 H), 7.48 (s, 4 H), 7.43 (m, 4 H), 7.27 (m, 4 H); ^{13}C NMR (acetone-d_6, 50 MHz) δ 220.6, 140.9, 137.6, 137.5, 136.7, 134.1, 133.9, 132.6, 130.9, 130.2, 129.7, 128.4, 128.2, 127.9, 127.3, 127.1, 126.9, 124.5.

Poly(3,7-di-*tert*-butyl-1,5:1,1′,5,4′-naphthyl)naphthylene (3). 2a (5.08 g, 14 mmol), **2b** (3.51 g, 14 mmol), and 400 mg of tetrakis(triphenylphosphane)palladium(0) were refluxed under a nitrogen atmosphere in 45 mL of toluene, 30 mL of *n*-butanol, and 45 mL of aqueous 2 N K_2CO_3. After cooling, the solution was poured into 400 mL of methanol, washed with water, and dried. The solid was collected and extracted with boiling toluene for 24 h. The volume of the toluene solution was reduced to 50 mL, and the polymer was fractionated by adding this solution dropwise to 400 mL of acetone: yield 7.36 g (71%). The insoluble fraction was repeatedly boiled with dilute aqueous HCl and dried: yield 0.93 g (9%). The insoluble fraction has an IR spectrum identical to that of the fraction precipitated from acetone: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.17–7.30 (broad absorption), 1,48 (s); ^{13}C NMR ($CCDCl_3$, 50 MHz) δ 138.9, 138.8, 138.7, 133.8, 133.7, 133.6, 131.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 126.6, 126.5, 126.4, 126.2, 126.1, 35.5, 35.4, 32.3, 31.7, 31.6; UV (cyclohexane) λ_{max} = 317 nm; IR (KBr) 2982, 2908, 2869, 1476, 1373, 1362, 1245, 887, 746 cm^{-1}.

Poly(2,6-di-*n*-hexyl-1,1′:4′,1″-ternaphthyl-1,4″-diylnaphthylene) (6a). 4a (1.062 g, 3 mmol), **5** (1.306 g, 3 mmol), and 80 mg of the catalyst were allowed to react as described above. Extraction with toluene and precipitation from acetone yielded 1.06 g (65%) of **6b** as a slightly gray powder. The insoluble fraction amounts to 150 mg (10%): ^{1}H NMR ($CDCl_3$, 50 MHz) δ 8.03–7.32 (m), 2.79 (CH_2), 2.50 (CH_2), 1.58 (CH_2), 1.27 (CH_2), 1.19 (CH_2), 0.93 (CH_3), 0.82 (CH_3); ^{13}C NMR ($CCDCl_3$, 50 MHz) δ 140.0, 138.9, 138.7, 138.6, 138.1, 136.1, 133.9, 133.7, 133.6, 132.7, 128.2, 128.0, 127.8, 127.7, 127.5, 127.4, 127.3, 127.1, 127.0, 126.8, 126.7, 126.4, 36.4, 34.3, 32.3, 31.9, 31.8, 31.7, 31.6, 29.7, 29.6, 29.6, 23.1, 22.9, 14.4; UV (cyclohexane) λ_{max} = 329 nm; IR (KBr) 2954, 2925, 2855, 1410, 1371, 1025, 764 cm^{-1}.

Poly(2,6-di-*n*-dodecyl-1,1′:4′,1″-ternaphthyl-1,4″-diylnaphthylene) (6b). 4b (1.462 g, 3.16 mmol), **5** (1.080 g, 3.16 mmol), and 120 mg of the catalyst were allowed to react as described above. Extraction with toluene and precipitation from acetone yielded 1.55 g (69%) of **6b** as a slightly gray powder. The insoluble fraction amounts to 330 mg (15%): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.15–7.30 (broad absorption), 2.56 (CH_2), 1.82 (CH_2), 1.30 (CH_2), 0.86 (CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.7, 138.3, 137.7, 135.8, 133.6, 132.4, 128.2, 127.1, 126.3, 32.2, 31.6, 29.9, 29.6, 23.0, 14.5; UV (cyclohexane) λ_{max} = 328 nm; IR (KBr) 2954, 2925, 2855, 1410, 1371, 1025, 764 cm^{-1}.

Anionic Cyclization of 3 (Synthesis of 7). The entire reaction was carried out under an argon atmosphere and with rigorous exclusion of moisture. **3** (2 g) was placed into a Schlenk reaction flask and dissolved in dry 1,2-dimethoxyethane. Potassium (2 g), which had been freed from its oxide layer, was cut into small pieces and added to the solution in an argon counterflow. The flask was closed and the mixture was stirred at room temperature for 3 days. Then the metal was removed in an argon counterflow, and 1.5 g of anhydrous cadmium chloride was added to the reaction mixture. To ensure complete reoxidation, the mixture was stirred overnight. The solvent was removed, and the solid was extracted for 12 h with boiling toluene. The volume of the solution was reduced to 50 mL, and the product was precipitated from acetone and collected by filtration: yield 1.78 g (89%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.80–7.31 (broad absorption), 1.8–1.2 (CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.1, 139.3, 138.4, 134.2, 131.0, 129.0, 127.5, 127.1, 125.7, 120.4, 119.9, 34.9, 31.2, 28.8, 27.6; UV (dioxane) λ_{max} = 456 nm; IR (KBr) 3250, 3244, 3226, 3195, 2963, 1632, 1261, 1099, 1026, 763 cm^{-1}.

Polymer-Analogous Cyclization of 6a (Synthesis of 9a). The entire reaction was carried out under a purified argon atmosphere and with rigorous exclusion of moisture. **6a** (200 mg) and pyrophoric lithium powder (−325 mesh; 250 mg) were

placed in a Schlenk reaction flask. After the addition of dry 1,2-dimethoxyethane, a reflux condenser was connected to the flask. The vigorously stirred mixture was heated to 60–70 °C. After 5 h, the deep-colored solution was cooled to room temperature and oxidized with oxygen. The suspension was filtered to remove excess lithium, and the metal was washed repeatedly with toluene. The extracts were combined, their volume was reduced to 20 mL, and the polymer was precipitated from acetone: yield 171 mg (85%) of **9a** as a yellow powder; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.70–8.15 (broad absorption), 7.91–7.01 (aromatic H), 3.10–2.91 (CH_2), 2.83–2.65 (CH_2), 2.60–2.32 (CH_2), 1.8–0.6 (CH_2, CH_3); UV (dioxane) λ_{max} = 457 nm; IR (KBr) 3193, 3167, 2950, 2853, 1656, 1632, 1619, 1594, 1037, 1028, 764, 418 cm^{-1}.

Polymer-Analogous Cyclization of 6b (Synthesis of 9b). **6b** (1.2 g) and pyrophoric lithium powder (−325 mesh; 1.5 g) were allowed to react as described above. Precipitation from acetone yielded 887 mg (65%) of **9b** as a yellow powder: ^{1}H NMR ($CDCl_3$) 8.1–7.1 (broad absorption), 2.6–2.2 (CH_2), 1.7–0.9 (CH_2), 0.9–0.7 (CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz) 139.8, 138.6, 138.4, 138.0, 137.8, 137.6, 135.8, 135.7, 135.5, 134.9, 134.6, 133.8, 133.7, 133.6, 133.4, 132.9, 132.5, 132.4, 132.3, 129.8, 129.6, 129.3, 128.8, 128.4, 128.2, 128.1, 127.9, 127.8, 127.4, 127.3, 127.2, 126.8, 126.7, 126.2, 126.0, 123.8, 120.8, 120.7, 120.6, 120.4, 34.1, 32.2, 31.5, 29.9, 20.3, 15.0; UV (dioxane) λ_{max} = 454 nm; IR (KBr) 3183, 3147, 2950, 2923, 2856, 1656, 1632, 1619, 1594, 1037, 1027, 764, 418 cm^{-1}.

Polymer-Analogous Cyclization of 7 (Synthesis of 8). **7** (1.00 g) was dissolved in 120 mL of CS_2. To the resulting solution were added 1.00 g of $AlCl_3$ and 1.00 g of $CuCl_2$, and the mixture was stirred under argon at room temperature. After 72 h, the solvent was distilled off at room temperature, and the remaining charge-transfer complex was hydrolyzed with dilute aqueous ammonia. The solid was collected, dried, and extracted with boiling toluene for 24 h. The volume of the toluene solution was reduced to 15 mL, and the polymer was precipitated by dropwise addition to acetone: yield 150 mg (15%). The insoluble fraction was boiled in dilute aqueous HCl, filtered, washed with water, and dried: yield 750 mg (75%): ^{1}H NMR ($C_2D_4H_2$, 200 MHz) δ 8.9–7.4 (broad absorption), 1.9–1.1 (CH_3); ^{13}C NMR ($C_2D_4H_2$, 50 MHz) δ 147.5, 139.1, 134.6, 133.3, 131.2, 129.3, 128.5, 128.1, 127.0, 124.0, 12.0, 121.7, 35.1, 34.0, 27.9, 21.6; UV (dioxane) λ_{max} = 673 nm; IR (KBr) 3175, 2960, 2906, 2868, 1598, 1478, 1463, 1393, 1377, 1259, 1096, 1020, 1013, 886, 786 cm^{-1}.

Polymer-Analogous Cyclization of 9a (Synthesis of 10a). **9a** (100 mg), $AlCl_3$ (100 mg), and $CuCl_2$ (100 mg) were allowed to react as described above. Precipitation from acetone gave 32 mg (32%) of a soluble fraction. The yield of the insoluble fraction was 60 mg (60%): ^{1}H NMR (C_6D_6, 200 MHz) δ 8.35–8.01 (broad absorption), 7.95–7.13 (broad absorption), 3.40–2.23 (CH_2), 2.10–0.63 (CH_2, CH_3); UV (benzene) λ_{max} = 676 nm; IR (KBr) 2960, 2906, 2868, 1598, 1478, 1463, 1393, 1377, 1259, 1096, 1020, 1013, 886, 786 cm^{-1}.

Polymer-Analogous Cyclization of 9b (Synthesis of 10b). **9b** (800 mg), $AlCl_3$ (800 mg), and $CuCl_2$ (800 mg) were allowed to react as described above. Precipitation from acetone gave 240 mg (30%) of a soluble fraction. The yield of the insoluble fraction was 496 mg (62%): ^{1}H NMR ($C_2D_2Cl_4$, 200 MHz) δ 8.6–7.0 (broad absoprtion), 3.6–0.8 (m, CH_2CH_3); UV (benzene) λ_{max} = 662 nm; IR (KBr) 2960, 2906, 2868, 1598, 1478, 1463, 1393, 1377, 1259, 1096, 1020, 1013, 886, 786 cm^{-1}.

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