Poly(arylene)s and Poly(arylenevinylene)s. 11.† A Modified Two-Step Route to Soluble Phenylene-Type Ladder Polymers

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ABSTRACT: A modified route to ladder-type poly(*p*-phenylene)s is presented to reduce the amount of chromophorically inactive alkyl side chains attached to the double-stranded macromolecules. The novel synthetic sequence involves first the Pd(0)-catalyzed coupling of 2,5-dihexyl-1,4-phenylenediboronic acid with 2,5-dibromoterephthalic dialdehyde. A polymer-analogous addition of metalloorganic species followed by subsequent ring closure with BF_3 then leads to the planar, soluble ribbon-type poly(phenylene)s.

Introduction

Recently, we described the synthesis and characterization of novel ladder-type poly(phenylene)s generated in a two-step process.[1-3] In the key step, methylene-bridged, planar poly(phenylene)s **1** are formed via ring closure of suitably substituted open-chain precursors. The first step of the synthetic sequence involves the design of the polymeric backbone by means of a Pd(0)-catalyzed polycondensation reaction according to Suzuki.[4] Hereby, a 1,4-phenylenediboronic acid[5] is reacted with a 2,5-dibromo-1,4-dibenzoylbenzene derivative. To guarantee sufficient solubility of the primary coupling product (polyketone **2**), it is necessary to introduce alkyl substituents into both starting components.[1,5]

On the other hand, the alkyl side chains are ballast, which reduces the density of the electronically active chromophores incorporated into the ribbon-type macromolecules. The molar values of parameters like the absorption coefficients are directly proportional to the amount of chromophoric substructures in the polymers. In line with this argument, we have searched for a modified route to the ladder polymers **1**, allowing a dramatic reduction of the number of alkyl side chains attached to the macromolecules.

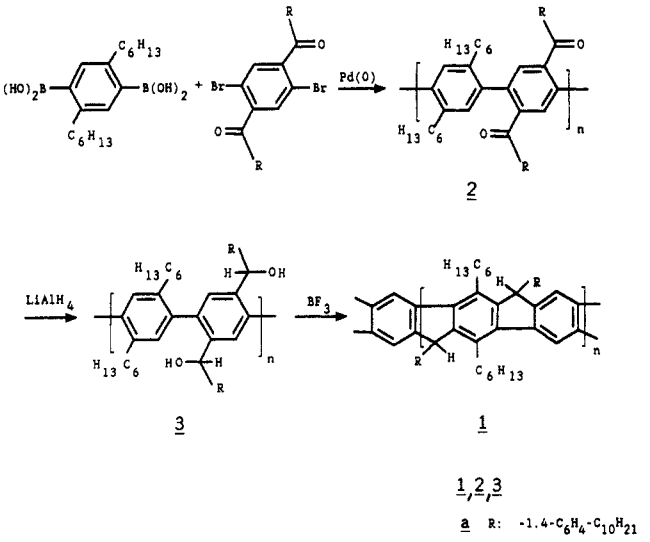
Results and Discussion

During the synthetic route described[1] (Scheme I), the least soluble species are the primary condensation products **2** of the aryl–aryl coupling, setting the limit of alkyl side chains necessary to guarantee the processibility of the polymers. That is why, following the reaction sequence shown, a reduction of the large number of solubilizing alkyl substituents incorporated into the ladder-type poly(phenylene)s is not possible.

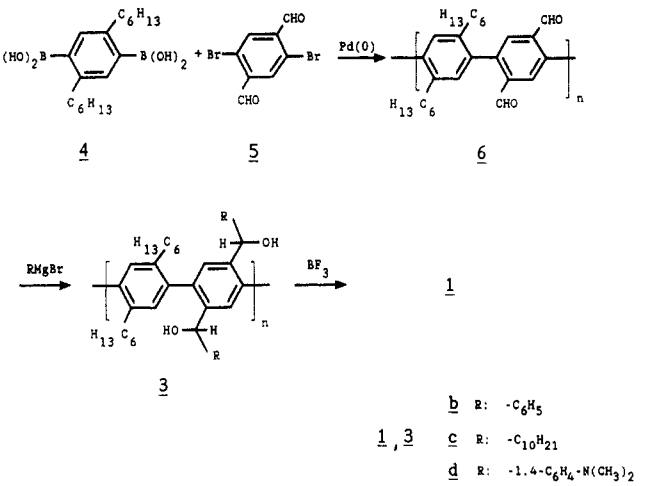
Therefore we have tested the coupling of 2,5-dihexyl-1,4-phenylenediboronic acid (**4**) with 2,5-dibromoterephthalic dialdehyde (**5**)[6] instead of the diketo monomer (Scheme II). Surprisingly enough, the polycondensation reaction proceeds successfully, and the polymeric coupling products **6** are fully soluble. When optimal reaction parameters are chosen, no side reactions of the Cannizzaro type take place under the alkaline conditions of the Pd(0)-catalyzed coupling.

The poly(2,5-diformyl-1,4-phenylene-2′,5′-dihexyl-1′,4′-phenylene) formed possesses a number-average molecular weight in the range of 5000, corresponding to a chain length of about 25 aromatic rings, in agreement with published[1,5] degrees of polymerization when using the coupling reaction according to Suzuki. In further experiments we have found that the primary coupling (polycondensation) step is also possible using 2,5-dibromoterephthalic dialdehyde bis(diethyl acetal) (**7**) instead of the aromatic dialdehyde (Scheme III). Coupling with the alkyl-substituted phenylenediboronic acid **4** leads to poly(2,5-bis(diethoxymethyl)-1,4-phenylene-2′,5′-dihexyl-1′,4′-phenylene) (**8**) with number-average molecular weights in the range of about 4000. Hydrolysis of **8** with dilute hydrochloric acid gives the polyaldehyde **6**, which is identical with the polymers generated via direct coupling of the components **4** and **5** (NMR spectroscopy).

Scheme I



Scheme II



† Part 10: Scherf, U., *Synth. Met.*, in press.

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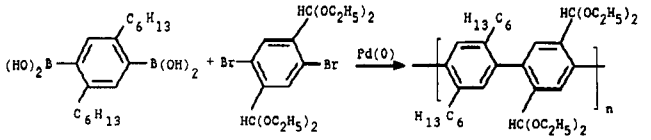
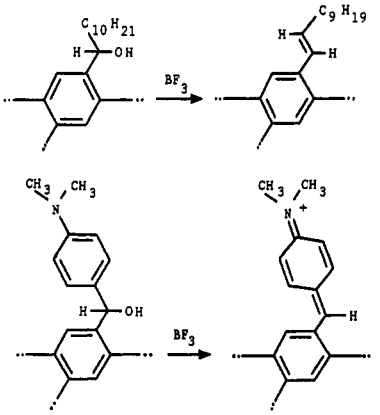
Scheme III



4 7 8

Scheme IV



The reaction of the formyl-substituted poly(*p*-phenylene) formed with metalloorganic species (especially Grignard reagents) leads to the generation of aromatic polyalcohols similar to the species **3** synthesized via reduction of the polyketones **2** in the route described earlier.[1] The advantage of the modified route is the possibility of avoiding the long alkyl chains pendant to the ladder-type macromolecules. Thus, a reaction of **6** with phenylmagnesium bromide leads to a product of structure **3** (R = C_6H_5). The subsequent ring-closure step to **1** takes place quantitatively within a few seconds with boron trifluoride etherate, as expected and described earlier.[1] In this case (R = C_6H_5) no structural defects are detectable according to NMR spectroscopy; there is no breakdown of polymeric chains during the polymer-analogous reaction steps.[1] If one reacts the polyaldehyde **6** with alkylmagnesium halides or with [4-(dimethylamino)phenyl]magnesium bromide, a different situation arises. In these cases, side reactions occur during the last polymer-analogous reaction step which compete with the electrophilic ring closure (Scheme IV). For the case where R is an alkyl side chain, 1,2-elimination occurs, and for the case where R is 1,4-$C_6H_4N(CH_3)_2$, delocalized cations are formed. These structural defects are detectable by means of ^1H NMR spectroscopic analysis (olefinic absorptions (R = alkyl) in the region 6.0–6.5 ppm or splitting of the $N(CH_3)_2$ methyl signal: 3.42/2.95 ppm). The degree of incomplete ring closure was determined to be in the range of 10–15%.

A comparison of the absorption behavior of the ladder-type poly(*p*-phenylene)s **1** with different substituents outside (R = C_6H_5 and 1,4-$C_6H_4C_{10}H_{21}$) demonstrates the existence of identical chromophoric systems (Table I, Figure 1). However, the molar absorption coefficients are distinctly higher in the case of the lower alkyl substituted ladder polymer **1b** (R = C_6H_5).

The incomplete ring closure which takes place when carrying out this key step of the synthetic sequence with the alkyl or (dimethylamino)phenyl derivatives **3c** and **3d** is manifested by a dramatic decrease in the absorption coefficients of the two longest wavelength absorption maxima. In addition, hypsochromically shifted absorptions occur (the most intensive one near 350 nm), corresponding to subunits with reduced length of conjugative

Table I
Longest Wavelength UV–vis Absorption Maxima of Ladder Polymers 1a[a] and 1b

	1a R = 1,4-$C_6H_4C_{10}H_{21}$	1b R = C_6H_5
λ_{max}, nm (ϵ, M^{-1} cm^{-1})	438 (27000)	443 (43000)
	412 (33000)	416 (34000)
	397 s (27000)	395 s (19000)

[a] Reference 1.

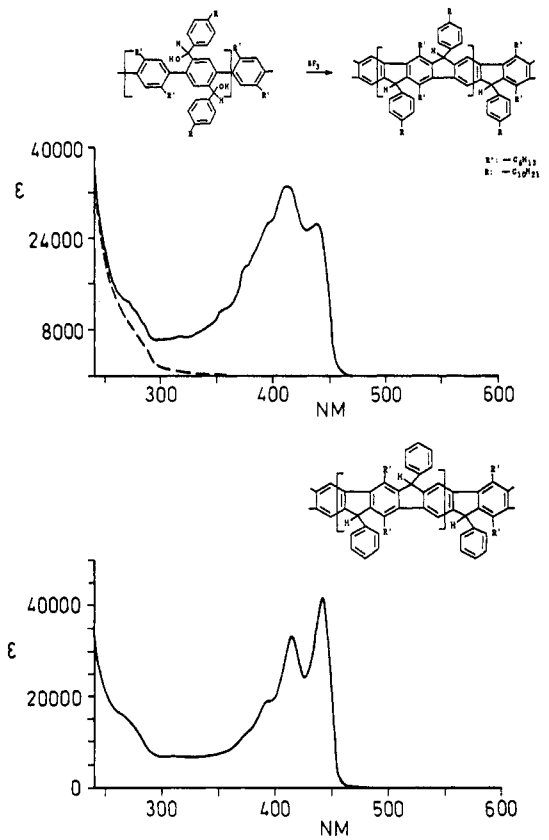


Figure 1. UV/vis absorption behavior of the ladder-type poly(*p*-phenylene)s **1a** (R = 1,4-$C_6H_4C_{10}H_{21}$) and **1b** (R = C_6H_5); the dashed line in the top part represents the spectrum of the open-chain precursor polymer **3a** (solvent: methylene chloride).

interaction (**1c** (R = $C_{10}H_{21}$), λ_{max} *354*, 374, 398, 412 s nm; **1d** (R = 1,4-$C_6H_4N(CH_3)_2$), λ_{max} *348*, 377, 396, 410 s nm).

The thermogravimetric analysis of **1a**[1] and **1b** shows a high thermal stability of the ladder polymers; up to 400 °C no detectable weight loss occurs. In a first elimination step (maximum ca. 470 °C) the alkyl side groups are removed quantitativly (57[1] and 33%, respectively).

Experimental Section

Reagents. The solvents (toluene, THF, methylene chloride) were used in commercial reagent grade quality. The preparation of polymers **6** and **8** was carried out under an argon atmosphere. The following compounds were synthesized according to the literature: 2,5-dihexyl-1,4-phenylenediboronic acid (**4**),[5] 2,5-dibromoterephthalic dialdehyde (**5**),[6] and 2,5-dibromoterephthalic dialdehyde bis(diethyl acetal) (**7**).[8] The Grignard reagents were prepared via well-known procedures.[7] All other chemicals are commercially available.

Poly(2,5-diformyl-1,4-phenylene-2′,5′-dihexyl-1′,4′-phenylene) (6). A solution of 2,5-dihexyl-1,4-phenylenediboronic acid (1.0 g, 3.0 mmol) and 2,5-dibromoterephthalic dialdehyde (0.88 g, 3.0 mmol) in 5 mL of toluene was added to 5 mL of an aqueous 1 M potassium carbonate solution. The mixture was refluxed, and 30 mg of tetrakis (triphenylphosphino)palladium(0) in 5 mL of toluene was added. After refluxing for 10 h, the mixture was poured into methanol (100 mL). The precipitate was recovered by filtration, washed with water, and redissolved

in methylene chloride. The resulting solution was dried, concentrated, and precipitated into acetone to yield a first fraction. Concentration of the filtrate and reprecipitation into methanol gave a second (lower molecular weight) fraction: fraction 1, yield 540 mg (48%), M_n(GPC) = 5100, M_w(GPC) = 7100; fraction 2, yield, 235 mg (21%), M_n(GPC) = 1500, M_w(GPC) = 3000. The M_n(GPC) values are in good agreement with data obtained from vapor pressure osmometry for the open-chain polymers as well as for the ladder-type polymers.[1]

Anal. Calcd for fraction 1 [$(C_{26}H_{32}O_2)_n$ (376.54)$_n$]: C, 82.94; H, 8.57. Found: C, 81.09; H, 8.39. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 10.00/10.03 (2 H), 8.14 (2 H), 7.28 (2 H), 2.52 (4 H), 1.47/1.19/0.88 (22 H); 10.20/7.93/7.21 (low intensity, chain-end features). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 191.6, 144.4, 139.3, 137.4, 137.0, 132.0, 130.5, 33.5/33.2, 31.8, 31.2, 29.5/29.4, 22.8, 14.3; 145.7/139.6/129.4/128.8 (low intensity, chain-end features).

Polymers 1b–d. Polymer **6** (100 mg, 0.266 mmol with respect to monomeric units) was dissolved in 20 mL of toluene and treated with a solution of the Grignard compound in THF (RMgBr, R = C_6H_5 (**1b**), R = $C_{10}H_{21}$ (**1c**), R = 1,4-$C_6H_4N(CH_3)_2$ (**1d**); 0.75 mmol/20 mL of THF). The mixture was stirred for 1 h at room temperature and then refluxed for 30 min. After cooling, 100 mL of 2 N hydrochloric acid was added, and the organic layer was isolated and carefully washed with water, 1 N $NaHCO_3$ solution, and water. The solution was dried ($MgSO_4$) and concentrated to dryness. The material was redissolved in 30 mL of methylene chloride and treated with boron trifluoride etherate (150 mg, 1.05 mmol). After 1 h of stirring at room temperature, 20 mL of ethanol was added to the mixture, followed by 50 mL of water. The organic layer was washed with water (6 × 100 mL), dried ($MgSO_4$), and concentrated. Precipitation into methanol gave polymers **1b–d** as yellowish powders. Yield: **1b**, 105 mg (79.5%); **1c** 98 mg (56.0%); **1d**, 82 mg (52.9%).

Anal. Calcd for **1b** [$(C_{38}H_{40})_n$ (496.73)$_n$]: C, 91.88; H, 8.12. Found: C, 89.63; H, 7.96; Br, ca. 1.0. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.52 (2 H), 7.18 (10 H), 5.09 (2 H), 2.80 (4 H), 1.25/1.13/0.95 (22 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.8, 149.6, 147.9, 143.9, 139.8, 139.2, 133.1, 129.1, 128.6, 126.8, 119.5, 54.3, 32.1, 31.1, 30.4, 28.8, 23.1, 14.6; 131.0/129.8/127.6/115.6 (C_{ar}Br) (low intensity, chain-end features).

1c: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.48/7.25 (2 H), 4.56/4.68 (2 H), 2.48 (4 H), 1.57/1.28/0.84 (68 H); 6.0–6.5 (low intensity, olefinic hydrogens according to side reactions, 1,2-elimination).

1d: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58 (2 H), 7.01/6.61 (8 H), 5.31/5.11 (2 H), 3.42/2.95 (12 H), 2.33 (4 H), 1.24/0.89 (22 H) (intensity ratio of both N(CH_3)$_2$ signals, 2.95/3.42 ppm (ca. 6:1)).

Measurements. ^{1}H and ^{13}C NMR spectral data were obtained on a Varian Gemini 200 and a Bruker AC 300 spectrometer. Gel permeation chromatography (GPC) analysis utilized PL gel columns (three columns, 10-μm gel, pore widths 500, 10^4, and 10^5 Å) connected with UV–vis and/or refractive index detection. All GPC analyses were performed on solutions of polymers in 1,2-dichlorobenzene at 70 °C (concentration of polymer: 2 g/L). Calibration was based on polystyrene standards with narrow molecular weight distributions.

The UV–vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer (room temperature, solutions in methylene chloride).

The thermal analysis was carried out using a Mettler 500 thermogravimetric analyzer between 20 and 800 °C (heating rate 10 K/min).

References and Notes

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Registry No. **4/5** (copolymer), 141397-78-6; **4/5** (SRU), 141397-82-2; **4/7** (copolymer), 141397-80-0; **4/7** (SRU), 141397-83-3.