polymer communications

Polyarylenes and poly(arylenevinylene)s: 8. The first soluble ladder polymer with 1,4-benzoquinone-bismethide subunits*

Ullrich Scherf and Klaus Müllen
Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-6500 Mainz, Germany

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The incorporation of alternating 1,3- and 1,4-phenylene subunits into a planar, rigid ladder-type polymer leads to polyphenylene macromolecules of high structural regularity. The polymer is formed in a two-step process involving the preparation of a suitably substituted polyphenylene backbone, followed by ring closure via polymer-analogous Friedel-Crafts cyclization. The ladder-type polyphenylene is an appropriate precursor for generating polymers with 1,4-benzoquinone-bismethide substructures.

(Keywords: ladder polymers; polymer-analogous reactions; 1,4-benzoquinone-bismethides; low band-gap polymers)

Introduction

Recently, we reported the synthesis of poly(*p*-phenylene)-type ladder polymers with fluorene repeating units (**1**)[1]. This represents the first example of a structurally defined, soluble ladder polymer prepared via a two-step process. The synthetic sequence involves the generation of a suitably functionalized polymeric backbone, followed by a polymer-analogous ring-closure reaction. An optimal design of the precursor structure used is of primary importance to guarantee a quantitative and uniform building reaction towards the final ladder polymer.

Besides the synthetic challenge in preparing such double-stranded structures, these macromolecules are of interest: (1) as the first planar, structurally defined poly(*p*-phenylene)s with outstanding electronic properties[2]; and (2) as potential starting materials for low band-gap poly(phenylenemethide)s (**2**) generated via dehydrogenation of **1**.

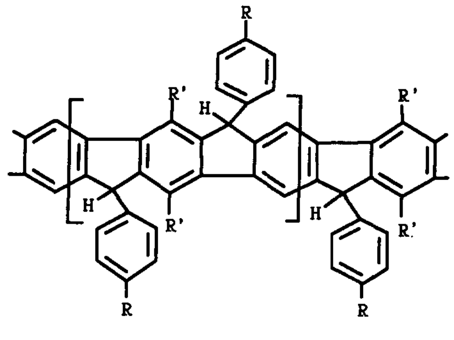
In this communication, we describe the conversion of bridged polyphenylene ladder polymers into fully unsaturated ribbon-type molecules with 1,4-benzoquinone-bismethide structural units.

Unfortunately, the synthesis of quinoid ladder-type polymers (**2**) possessing a degenerate ground state involves problems concerning the high chemical instability of such species[3,4]. To avoid these problems, we chose a structural variant of **1**, the non-conjugated phenylene-type ladder polymer **7** with alternating 1,4- and 1,3-phenylene structural units in the double-stranded chain, and subjected it to dehydrogenation experiments.

Experimental

Reagents. The solvents used were of commercial p.a. grade. The following compounds were synthesized according to the literature: 2,5-dihexyl-1,4-phenylenediboronic acid (**3**)[5], 2,5-dibromoisophthalic acid[6], 1,4-bis(4-tert-butylbenzoyl)-2,5-dibromobenzene[1], and 1,3-bis(4-decylbenzoyl)-4,6-dibromobenzene (**4**) was prepared in a similar manner as described for 1,4-bis(4-decylbenzoyl)-2,5-dibromobenzene in reference 1 (decylbenzene and 4,6-dibromoisophthaloyl chloride as starting materials). All other chemicals used are commercially available. The preparation of polymers **5**–**8** was carried out under an argon atmosphere.

Poly[4, 6-bis(4-decylbenzoyl)-1, 3-phenylene-2′, 5′-dihexyl-1′,4′-phenylene] (**5**). A solution of **3** (0.334 g, 1 mmol) and **4** (0.725 g, 1 mmol) in 5 ml of toluene was added to 5 ml of an aqueous potassium carbonate solution (2 N). The mixture was refluxed, and 30 mg of tetra kis(triphenylphosphino)palladium(0) in 5 ml of toluene were added. After refluxing for 1 day the mixture



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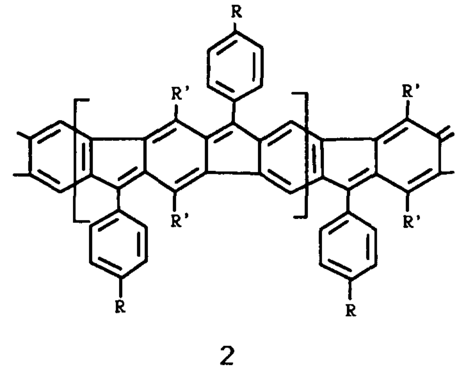

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* For part 7 see reference 1

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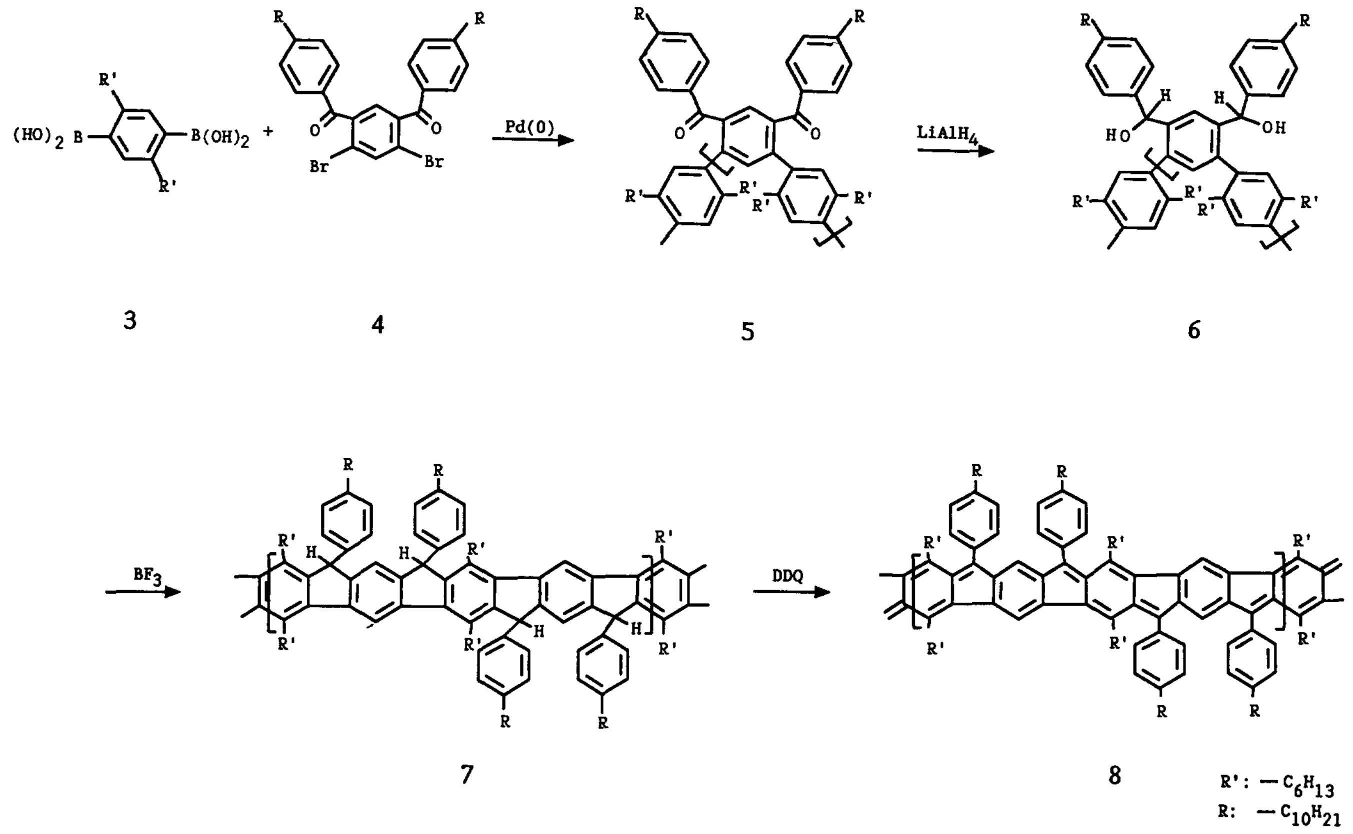


was poured into methanol (100 ml). The precipitate was recovered, washed with dilute HCl (100 ml) and redissolved in toluene. The resulting solution was dried over $MgSO_4$, concentrated, and the polymer precipitated by adding methanol. Yield: 620 mg (77%) of **5**.

^{1}H n.m.r. (200 MHz, $CDCl_3$): $\delta = 7.52$, 7.18, 7.02, 6.76, 2.48 (4H), 2.27 (4H), 1.23 (48H), 0.85 (12H).

^{13}C n.m.r. (50 MHz, $CDCl_3$): $\delta = 196.6$, 148.6, 142.0, 137.5, 136.8, 135.1, 133.4, 130.1, 130.6, 128.6, 128.2, 36.1, 32.8, 31.9, 29.5, 29.6, 29.5, 29.4, 22.7, 14.1.

Poly[4, 6-bis(4-decyl-α-hydroxybenzyl)-1, 3-phenylene-2',5'-dihexyl-1',4'-phenylene] (**6**). A solution of **5** (600 mg, 0.741 mmol) in 50 ml of toluene was added to a suspension of lithium aluminium hydride (LAH) (280 mg, 7.36 mmol) in 50 ml of tetrahydrofuran (THF). The mixture was stirred for 30 min at room temperature and carefully quenched with ethanol, water and dilute HCl. The organic layer was washed (water), dried and concentrated to dryness. The polymer was redissolved in THF and precipitated into water. Yield: 530 mg (88%) of **6**.

^{1}H n.m.r. (200 MHz, $CDCl_3$): $\delta = 8.11$, 7.35, 7.03, 6.61, 5.92/5.64 (2H), 2.55 (8H), 1.98/1.62/1.35 (48H), 0.95 (12H).

^{13}C n.m.r. (75 MHz, $CDCl_3$): $\delta = 142.0$, 141.2, 140.3, 140.0, 138.6, 137.3, 130.8, 128.3, 127.0, 73.3, 35.7, 33.0, 31.9, 29.7, 29.4, 22.7, 14.1.

Polymer 7. A solution of **6** (500 mg, 0.614 mmol) in 50 ml of dichloromethane was treated with boron trifluoride etherate (1.8 g, 12.7 mmol). After stirring for 5 min at room temperature, 20 ml of ethanol was added to the mixture, followed by 50 ml of water. The organic layer was carefully washed with water, dried and concentrated. Precipitation into acetone gave **7** as a light orange powder. Yield: 430 mg (90%).

^{1}H n.m.r. (200 MHz, $CDCl_3$): $\delta = 8.39/8.24$, 7.04/7.02, 6.90, 5.03 (2H), 3.01 (4H), 2.58 (4H), 1.35 (48H), 0.85 (12H).

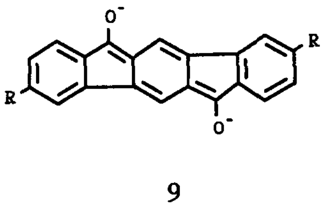
^{13}C n.m.r. (75 MHz, $CDCl_3$): $\delta = 149.1$, 148.1, 141.1, 140.7, 139.2, 133.1, 128.8, 128.5, 122.1, 117.4, 53.8, 36.1, 32.4, 31.9, 30.1, 23.2, 14.5.

Polymer 8. A solution of **7** (100 mg, 0.132 mmol) in 30 ml of benzene was treated with 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) (35 mg, 0.153 mmol) and heated to 55°C for 6 h. The deep blue solution formed was concentrated to dryness *in vacuo*. The residue was redissolved in dichloromethane and the suspension centrifuged to remove the solid by-products. Then the solvent was distilled off and the residue carefully washed with dry acetone. Yield: 83 mg (83%).

^{1}H n.m.r. (200 MHz, $CDCl_3$): $\delta = 7.15$, 6.92, 4.95 (w), 2.83 (4H), 2.49 (4H), 2.0–1.0 (52H), 0.8 (12H).

^{13}C n.m.r. (50 MHz, $CDCl_3$): $\delta = 149.3$, 148.2, 146.9, 145.2, 142.8, 141.4, 138.9, 135.7, 134.3, 133.3, 128.8, 123.0, 118.7, 53.7, 36.1, 32.2, 31.9, 29.9, 23.1, 14.6.

*3,9-Di-tert-butyl-6, 12-dioxy-indeno(1, 2-*b*)fluorene dianion (**9b**, R = -tert-butyl).* The dianion **9b** was prepared according to Ebel and Deuschel[7]. The blue coloured solution was generated in a mixture of ethanol and water (1:1).



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Measurements. ^{1}H and ^{13}C n.m.r. spectral data were obtained on a Bruker WH 90, a Varian Gemini 200 and a Bruker AC 300 spectrometer. Gel permeation chromatography (g.p.c.) analysis utilized PL-gel columns (particle size 10 μm, pore width 500, 10^4 and 10^5 Å) connected to u.v./vis, and/or refractive index detectors. All g.p.c. analyses were performed on solutions of polymers in 1,2-dichlorobenzene at 70°C (polymer concentration: 2 g l^{-1}). Calibration was based on narrow polystyrene standards. The u.v./vis. spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer (solutions in dichloromethane), while the emission spectra were obtained with a Spex fluorescence spectrometer.

Results and discussion

The synthesis of **7** was carried out using the alkyl-substituted 1,3-dibenzoyl-4,6-dibromobenzene derivative **4** as the coupling component instead of the corresponding 1,4-dibenzoyl-2,5-dibromobenzene derivative, following the general synthetic route published[1]. The Pd(0)-catalysed coupling reaction with **3** (Suzuki method[8]) leads to soluble open-chain polyphenylene precursors (**5**) with a number average molecular weight (M_n) in the range of 6000–8000. Reduction of the polyketone (**5**) with LAH to the polyalcohol (**6**) and subsequent ring-closure with boron trifluoride etherate provides the ladder-type polyphenylene (**7**).

It is important that there is no cleavage of polymeric chains during the polymer-analogous reaction sequence **5** → **6** → **7** (*Table 1*) and that no structural defects are detectable by ^{1}H and ^{13}C n.m.r. spectroscopy.

The ^{13}C n.m.r. spectrum of **7** exhibits 10 absorptions for the 11 non-equivalent carbons in the aromatic region as well as the signal of the -CHR- bridge (53.7 ppm).

The electron absorption spectra of **6** and **7** (*Table 2*, *Figure 1*) in the u.v./vis. region show a pronounced bathochromic shift for the longest wavelength absorption (λ_{max} = 381 nm for **7**) during the conversion of the non-planar open-chain structure **6** into the planar ladder polymer **7**. The longest wavelength absorption of **7** is found between that of the corresponding poly(p-phenylene) ladder polymer **1**[1] (λ_{max} = 438 nm) and that of a bridged p-terphenyl [6,12-dihydro-indeno(1,2-b)-fluorene; λ_{max} = 334 nm][9], representing formally the longest subunit with conjugative interaction in the ladder polymer **7**. In open-chain polyphenylenes, the incorporation of 1,3-phenylene subunits is known to significantly inhibit the π-conjugation along the chain[10]. It is not clear whether in the case of **7** the effective conjugation is due to a different electronic behaviour of the 1,3-phenylene unit or to the flattening of **6** into the ribbon-type structure **7**.

Table 1 Molecular weights of polymers **5–8**

Compound	$\bar{M}_n$^{a}	$\bar{M}_w$^{a}	$\bar{M}_n/\bar{M}_w$
5	5200	7100	1.38
6	7900	18 500	2.33
7	7500	10 200	1.37
8	6200	10 200	1.63

^{a}Determined by g.p.c. (1,2-dichlorobenzene, 70°C, polystyrene standard calibration, u.v./vis. detection: **5**, **6** and **7**, 300 nm; **8**, 600 nm)

Table 2 Absorption behaviour of polymers **5–8**

Compound	U.v./vis. absorption^a wavelength (nm) (absorption coefficient)	Colour
5	265 (62 000)	Colourless
6	282sh (3700)	Colourless
7	381 (26 000) 361 (15 000)	Light orange
8	605 (~6000) 571sh, 643sh	Blue

^{a}Solutions of the polymers in dichloromethane

A plot of the fluorescence emission of **7** against the fluorescence excitation (maximum of shortest wavelength fluorescence emission = 383 nm; maximum of longest wavelength fluorescence excitation = 381 nm) shows a very small Stokes loss and reflects the rigid geometry of the ladder polymer.

The conversion of **7** into a polymer with 1,4-benzoquinone-bismethide subunits (**8**) takes place in a simple fashion via dehydrogenation with DDQ.

According to ^{1}H n.m.r. spectroscopy ~90% conversion takes place. The spectra of the products show a decrease in intensity of the signal centred at δ = 5.03 ppm (-CHR- bridge) to ~10% of the original value. In the ^{13}C n.m.r. spectrum of **8** two new absorptions (142.8 and 135.8 ppm) are detectable, which are readily assigned to the quinoid substructures generated. The poly(quinone-bismethide) **8** is e.s.r.-inactive, reflecting the absence of unpaired electrons. The electronic absorption spectrum of **8** (*Figure 2*, *Table 2*) shows a new broad absorption

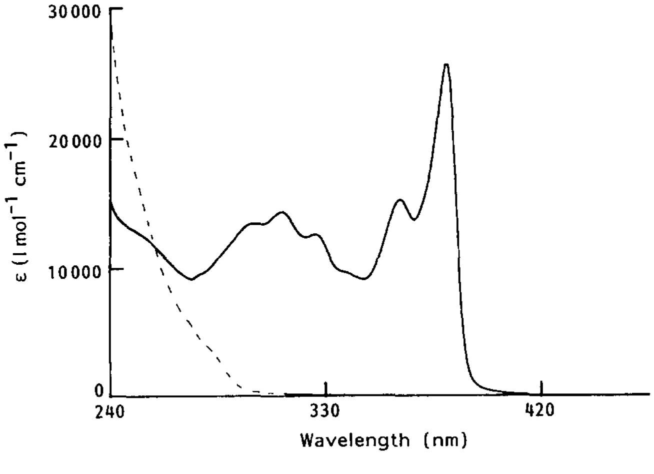

Figure 1 U.v./vis. absorption spectra of **6** (– – –) and **7** (——)

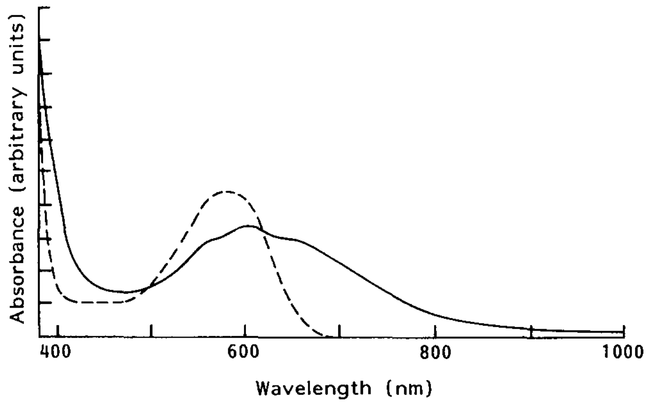

Figure 2 Vis. absorption spectra of **8** (——) and **9b** (– – –)

in the vis.-region ($\lambda_{max} = 605$ nm) due to the 1,4-benzoquinone-bismethide units generated. In the n.i.r. region no absorption is detectable. *Figure 2* also shows the vis. absorption characteristics of the only known quinone-bismethide compound **9** (**a**, R = -H[7]; **b**, R = -t-butyl). The maximum of the longest wavelength absorption of this model compound ($\lambda_{max} = 581$ nm) lies in the same range as that of **8**; the absorption of polymer **8**, however, is broader as a consequence of the conjugative interaction between the subunits in the ladder-type poly(quinone-bismethide).

Polymer **8** is stable in solution or in the solid state (film) with the exclusion of oxygen, but decomposes slowly over a period of several weeks in the presence of oxygen (air).

The ^{13}C n.m.r. spectra of oxidized samples of **8** show a new signal (83.5 ppm) in the aliphatic region, which can be attributed to triarylmethanol subunits. The final oxidation products are colourless polymers with u.v./vis. absorption behaviour similar to **7**.

Acknowledgements

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