

Stereo- and Oligo-controlled Synthesis of Oligo[*p*-phenylene-(*E*)-vinylene]-*p*-benzoic Acid Derivatives: Basic Building Blocks for Oligo[*p*-phenylene-(*E*)-vinylene]

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Oligo[*p*-phenylene-(*E*)-vinylene]benzoic acids of up to four aromatic units are synthesized in complete oligo- and excellent (*E*)-stereo-control via an iterative modified Ramberg–Bäcklund reaction; these extended π -systems can be used to construct oligo [*p*-phenylene(*E*)-vinylene]s in good yields.

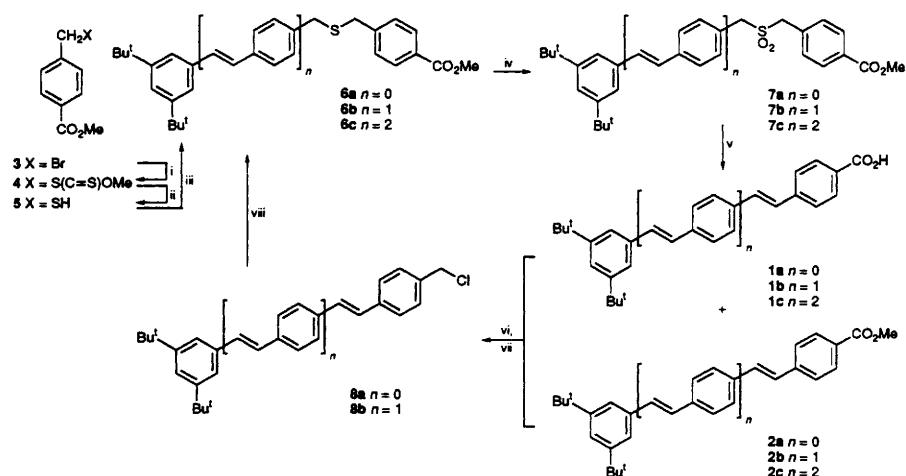
The search for novel electrically conducting materials is of fundamental and practical interest to the electronic industry.¹ The past decade has witnessed a rapid development in synthetic methodologies for organic polymers with conjugated polyaromatic or polyene chains for evaluation as electrical conductors and non-linear optical materials.² One particular class of conjugated polymer is poly(phenylene-vinylene) (PPV) which is based on the stilbenoid structure.³ However, the high polydispersity and low solubility of PPVs in organic solvents, along with the occurrence of geometrical isomerism, have hampered detailed studies of their physical properties and limited their applications. As a result, geometrically-defined oligomeric model systems of PPV that possess sufficient solubility in organic solvents have been synthesized⁴ and submitted for tests of their electrochemical properties.^{1c}

There are only a limited number of synthetic routes to oligo(phenylenevinylene)s (OPVs).³ In this communication we report a new synthetic approach which allows the iterative assemblage of OPVs in complete oligo- and excellent (*E*)-stereo-control. The basic building blocks for the synthesis of OPVs are the lower oligo[*p*-phenylene-(*E*)-vinylene]-*p*-benzoic acid derivatives **1** and **2**. These carboxylic acid derivatives can be synthesized in good yields and high (*E*)-stereoselectivities (Scheme 1) using a modified Ramberg–Bäcklund procedure.⁵ Starting from methyl 4-bromomethylbenzoate **3**, the corresponding methyl xanthate **4**† could be obtained in quantitative yield.⁶ Treatment of **4** with sodium methoxide in methanol led to the thiol **5**, which was coupled *in situ* to 3,5-di-*tert*-butylbenzyl bromide to give the thioether **6a**‡ in 70% overall yield. The thioether **6a** was then oxidized with oxone⁷ in refluxing methanol to yield the sulfone **7a**‡ as a crystalline solid in 81% yield. The sulfone methyl ester **7a** was then subjected to a modified Ramberg–Bäcklund procedure employing alumina-supported potassium hydroxide–dibromodifluoromethane-*tert*-butyl alcohol⁵ at 5–10 °C, in the course of which hydrolysis of the ester linkage occurred to afford the stilbene carboxylic acid **1a**‡ in 80% yield. The presence of only an (*E*)-carbon–carbon double bond ($J = 16.4$ Hz) was

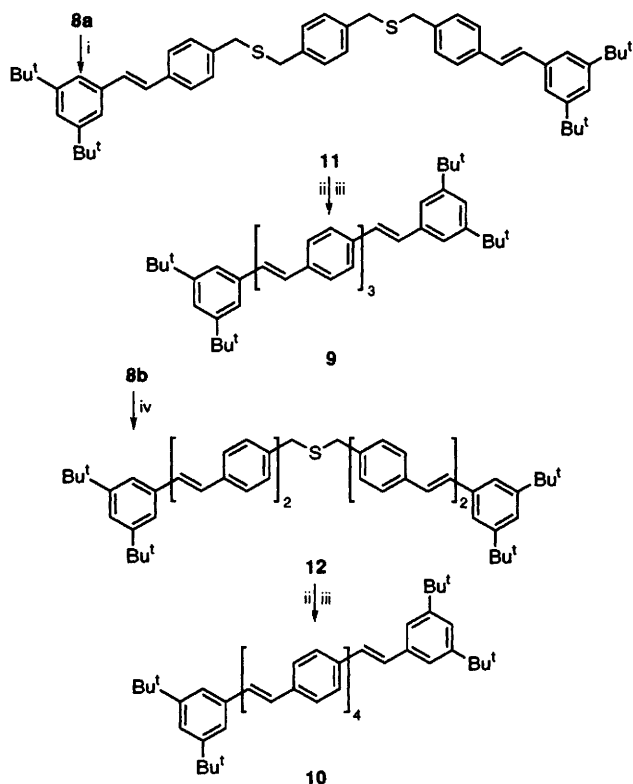
revealed in the ¹H NMR spectrum of this acid and the signals for the three aromatic protons of the 3,5-di-*tert*-butylphenyl ring coincided as a sharp singlet (δ 7.40). A small amount (<2%) of the corresponding methyl ester **2a** could also be detected, indicating that the hydrolysis was just short of completion under the reaction conditions. The mixture of carboxylic acid **1a** and methyl ester **2a** was then converted to the corresponding benzyl chloride **8a**‡ in 81% yield via a reduction (lithium aluminum hydride)–chlorination (thionyl chloride) sequence. The chloride **8a** served as the starting material for the next higher homologue of **1a** and the first iterative reaction cycle was completed.

The next iterative cycle began with the coupling of **8a** with **4** to give the thioether **6b**‡ in 81% yield. The sulfone **7b**,‡ synthesized from the thioether **6b** in 90% yield, was subjected to the one-flask Ramberg–Bäcklund procedure⁵ to give a 2 : 3 mixture of the (styryl)stilbene carboxylic acid **1b**‡ and the corresponding methyl ester **2b**‡ in 90% total yield. The (*E*)-configurations of both double bonds in either the acid **1b** ($J = 16.2$ and 15.7 Hz) or the methyl ester **2b** ($J = 16.3$ and 16.0 Hz) were confirmed by ¹H NMR and again no (*Z*)-isomer could be detected. The presence of an extra styryl substituent probably increases the hydrophobicity of the sulfone **7b** and hence retards the rate of heterogeneous ester hydrolysis and a mixture of acid and ester was formed. Reduction of this mixture with lithium aluminum hydride followed by chlorination of the resulting alcohol gave the homologous benzyl chloride **8b**‡ in 58% overall yield.

Repeating the same iterative synthetic sequence, the chloride **8b** was converted to the sulfone **7c**‡ via the thioether **6c**‡ in overall 45% yield. Application of the Ramberg–Bäcklund reaction methodology on the sulfone **7c** gave a 10 : 1 mixture of the methyl ester **2c**‡ and the carboxylic acid **1c**. In compound **2c**, while the merged ¹H NMR signals (*s*, δ 7.14) for the central double bond precluded stereochemical assignment, nevertheless the (*E*)-configurations of the newly formed and the terminal double bonds were ascertained by the two large coupling constants ($J = 16.4$ and 14.3 Hz) in the ¹H



Scheme 1 Reagents: i, CS₂, KOH, MeOH, THF; ii, NaOMe, MeOH; iii, NaOMe, 3,5-di-*tert*-butylbenzyl bromide, MeOH; iv, oxone, MeOH; v, KOH–Al₂O₃, CBr₂F₂, Bu^tOH; vi, LiAlH₄, THF; vii, SOCl₂, CCl₄; viii, **4**, NaOMe, MeOH



Scheme 2 Reagents: *i*, 1,4-bis(mercaptomethyl)benzene, KOH, EtOH, CH₂Cl₂; *ii*, oxone, MeOH; *iii*, KOH–Al₂O₃, CBr₂F₂, Bu^tOH; *iv*, Na₂S, CH₂Cl₂, EtOH

NMR spectrum. Since no other olefinic protons could be detected, we concluded an all (*E*)-stereochemistry for the trienic ester **2c**.

To demonstrate that these carboxylic acid derivatives such as **1** or **2** are useful building blocks for the synthesis of OPVs, the conjugated pentamer **9** and hexamer **10** were prepared (Scheme 2). The pentamer **9** was assembled by a [2 + 2 + 1] coupling method. Thus, 2 equivalents of the benzyl chloride **8a** were coupled to 1 equivalent of the linker 1,4-bis(mercaptomethyl)benzene to give the bis-sulfide **11** in 87% yield. Oxidation of the bis-sulfide **11** with oxone followed by the Ramberg–Bäcklund reaction gave the pentamer **9**†^{4a} in 81% overall yield. The hexamer **10**, on the other hand, was constructed using a [3 + 3] coupling protocol. The benzyl chloride **8b** was self-coupled with sodium sulfide to give the symmetrical thioether **12**,‡ which was converted to the conjugated hexamer **10**†^{4a} via the corresponding sulfone, employing the Ramberg–Bäcklund conditions in 70% overall yield. For the pentamer **9**, the ¹H NMR of the newly formed olefinic protons appeared coincidentally as a singlet (δ 7.13); while for the hexamer **10**, the olefinic protons of the newly formed central double bond are chemically equivalent. As a result, the (*E*)-stereochemical configurations of these newly formed double bonds are difficult to confirm. Nonetheless, both the pentamer **9** and hexamer **10** were isolated as a single compound from the reaction mixture. Since no (*Z*)-stilbenes have ever been isolated from the modified Ramberg–Bäcklund reactions of primary dibenzylic sulfones,⁵ we believe that all the double bonds in compounds **9** and **10** exist solely in (*E*)-configurations.

In conclusion, we have demonstrated that our modified Ramberg–Bäcklund reaction conditions can be used to synthesize oligo[*p*-phenylene-(*E*)-vinylene]benzoic acid derivatives and oligo[*p*-phenylene-(*E*)-vinylene]s in good yields and in excellent (*E*)-stereoselectivities. No (*Z*)-(E) isomerisation is

necessary as compared to the Wittig olefination employed by Müllen.^{4a} By choosing the appropriate benzyl chloride **8**, OPVs of different chain lengths can be synthesized. This method therefore offers a high degree of flexibility and versatility. These oligo[phenylene-(*E*)-vinylene]benzoic acid derivatives can also be linked to a polymeric backbone to generate polymers which may have interesting optical, photochemical and photophysical properties.⁸

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Footnotes

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‡ All new compounds were characterized on the basis of their ¹H and ¹³C NMR spectra, mass spectral data and elemental analyses, for which satisfactory results were obtained. Physical and selected spectral data for: **1a**: mp 230–232 °C; δ_H (CDCl₃, 250 MHz) 1.37 (18 H, s, 2 Bu^t), 7.13 (1 H, d, *J* 16.4, CH=C), 7.30 (1 H, d, *J* 16.4, C=CH), 7.40 (3 H, s, ArH), 7.62 (2 H, d, *J* 8.4, ArH) and 8.11 (2 H, d, *J* 8.4, ArH); δ_C (CDCl₃, 62.5 MHz) 31.5, 34.9, 121.2, 122.9, 126.3, 126.9, 127.8, 130.7, 133.1, 136.1, 143.2, 151.3 and 171.0. **1b**: mp 290–292 °C. **2b**: mp 189–190 °C. **2c**: mp 266–267 °C. **4**: mp 32–34 °C. **6a**: mp 44–46 °C. **6b**: mp 52–54 °C. **6c**: mp 144–147 °C. **7a**: mp 203–204 °C. **7b**: mp 183–185 °C. **7c**: mp 253–255 °C. **8a**: mp 110–111 °C. **8b**: mp 163–164 °C. **9**: mp 281–285 °C (lit.^{4a} mp 294 °C); δ_H (CDCl₃, 270 MHz) 1.37 (36 H, s, 4 Bu^t), 7.09 (2 H, d, *J* 16.2, 2 C=CH), 7.13 (4 H, s, 2 CH=CH), 7.19 (2 H, d, *J* 16.5, 2 HC=C), 7.35–7.38 (6 H, m, terminal ArH) and 7.53 (12 H, s, internal ArH). **10**: mp > 290 °C (lit.^{4a} mp 307 °C); δ_H (2[H]₈THF, 250 MHz) 1.36 (36 H, s, 4 Bu^t), 7.15 (2 H, d, *J* 16.5, 2 C=CH), 7.22 (6 H, s, 3 CH=CH), 7.26 (2 H, d, *J* 16.5, 2 HC=C), 7.36 (2 H, d, *J* 2, terminal ArH), 7.42 (4 H, d, *J* 2, terminal ArH) and 7.56 (16 H, s, internal ArH). **12**: mp 191–194 °C.

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