Soluble poly(*para*-phenylene)s. 1. Extension of the Yamamoto synthesis to dibromobenzenes substituted with flexible side chains

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This paper describes the synthesis of poly(*para*-2,5-di-n-alkylphenylene)s (**2**) by an extension of the Yamamoto route to poly(*para*-phenylene) (PPP); that is, the Ni-catalysed coupling of dibromoaromatics. These products, in contrast to PPP, are soluble and have been characterized in detail by ^{1}H and ^{13}C-n.m.r. and high pressure liquid chromatography. The structures are highly regular with repeat units connected exclusively in a 1,4-fashion. The maximum average degree of polymerization (*DP*) obtained by this method is of the order of 13.

(Keywords: poly(*para*-2,5-di-n-alkylphenylene); poly(*para*-phenylene); Yamamoto synthesis)

INTRODUCTION

Poly(*para*-phenylene) has been an important target for synthesis in polymer science for many years[1,2]. This interest stems mainly from the expectation that such a material would display good thermal and oxidative stability as well as electrical conductivity in the oxidized or reduced states. Numerous attempts to synthesize PPP have been reported[3–14]. Direct routes from benzene have received most attention[3–10], but it turns out that all of them have serious limitations which are associated with the properties of PPP, an essentially insoluble and infusible material. Most direct routes led to low molecular weight materials of irregular structure. Due to the insolubility of these products an unambiguous elucidation of their structures was not possible. Indirect methods for the preparation of PPP have also gained some importance[11–14]. These syntheses proceed via appropriate precursor polymers which are converted to PPP in a final processing step and, in terms of achievable molecular weight, they proved to be far superior to the direct methods. Unfortunately, the PPPs synthesized from precursor polymers also have a considerable concentration of structural defects which have so far proved difficult to eliminate; 1,2-linkages and structural irregularities due to the aromatization processes have been observed. Hence, up to now, no method for the synthesis of structurally homogeneous and high molecular weight poly(*para*-phenylene) is available.

The solubility of oligomeric PPPs decreases dramatically with the number of benzene rings. For example, although *para*terphenyl will dissolve in toluene to the extent of 8.5 g l^{-1}, sexi*para*phenylene has a solubility of less than 10 mg l^{-1} (ref. 15). It is safe to assume that in the direct routes to PPP, precipitation of the growing species is at least partially responsible for the prevention of its further growth. This paper describes our initial results in a programme of work towards establishing a direct synthetic route capable of overcoming the tractability problem in PPPs.

STRATEGY

From the work of Kern, Heitz and others[15–17] it is known that attachment of methyl groups to oligomeric phenylenes increases their solubility. Kovacic has shown that insoluble PPP oligomers, obtained from benzene by oxidative coupling, can be made soluble by Friedel–Crafts alkylation[18]. Recently, the properties of some conformationally rigid polymers bearing flexible side chains have been investigated. Large decreases in melting points were observed together with considerable increases in the solubilities of these polymers[19,20]. Clearly, pendant groups may have a pronounced solubility effect on rigid polymers. Consequently, our strategy is based on monomers which already bear flexible chains.

Attachment of side chains to the aromatic nucleus limits the applicable polymerization reactions. Direct oxidative coupling of the kind used previously would be likely to induce scrambling of the chain positions, and/or chain isomerization, and/or degradation. No such undesired side reactions were observed in transition metal catalysed aryl/aryl coupling reactions[21], which are consequently our first choice routes. In the Yamamoto procedure 1,4-dibromobenzene is coupled to PPP in the presence of stoichiometric amounts of Mg under very mild Ni-catalysis[5]. Therefore, we decided to test the applicability of this method to 1,4-dibromobenzenes

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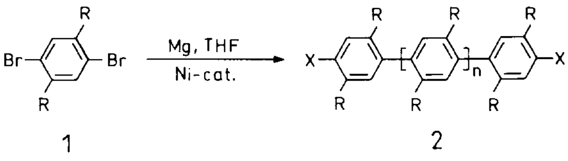
bearing flexible side chains in the 2- and 5-positions as the first stage of this programme.

Ni-catalysed aryl/aryl-coupling reactions are rendered more difficult by substituents in the *ortho* position[21,22]. Thus, in order to keep the steric and/or electronic influences of the side chains on the coupling process to a minimum, and to obtain n.m.r. spectra of the resultant polymers as simple as possible, monomers **1a** and **1b** were used (*Scheme 1*). These monomers have two unbranched alkyl chains in *para* positions, the lengths of the chains were chosen as 6 and 8 carbon atoms because, on the one hand, this was expected to be long enough to provide sufficient solubility and, on the other hand, it is short enough to suppress undesired side chain crystallization.

Scheme 1



a: R=n-hexyl; b: R=n-octyl; X=H or Br.

Besides the challenge inherent in the synthesis of such target polymers, there are additional features of interest in this work. Thus, for example, if the assumption that side chain substituted PPPs are soluble is valid then, for the first time, the molecular size and structure of such rigid systems can be investigated in detail. Especially, it ought to be possible to clarify whether or not the phenylene moieties are connected exclusively in the 1,4-(*para*) fashion. This, in turn, allows an examination of the regiospecificity of this polymerization reaction.

EXPERIMENTAL

General

All reagents were purchased from Fluka or Aldrich Chemical Co. and used without further purification. (dppp)Cl_2Ni and (bipy)Cl_2Ni were prepared according to the literature methods[23,24]. All solvents were dried under standard conditions. All reactions were carried out under N_2. Melting points were recorded on a Reichert Thermovar melting point microscope and are uncorrected. Mass spectra were obtained using a Varian MAT CH 7A spectrometer with EI ionization. I.r. spectra were obtained using a Nicolet *FT*i.r. 60 SX spectrometer. ^1H- and ^{13}C-n.m.r. spectra were obtained on a Bruker AC 300 spectrometer (300 and 75 MHz for ^1H and ^{13}C, respectively). The h.p.l.c. measurements were carried out using a Spectra Physics SP 8700 Solvent Delivery System (u.v. detection, 254 nm) with a RP-18 Lichrosorb column (5μ, 25 cm). Osmometric measurements were carried out using a Corona Wescan Model 232 A. Elemental analyses were obtained by Malissa & Reuter, Analytische Laboratorien, Gummersbach.

1-bromo-2,5-di-n-hexylbenzene (**3b**)

To a stirred and ice-cooled solution of 1,4-di-n-hexylbenzene (**3a**) (40.0 g, 0.162 mol) and iodine (0.2 g) in tetrachloromethane (30 ml), a solution of bromine (27.5 g, 0.172 mol) in tetrachloromethane (15 ml) was added slowly under rigorous exclusion of light. After stirring for 3 days at room temperature, potassium hydroxide solution (20%w/w, 30 ml) was added. The layers were separated, the aqueous one washed twice with chloroform (2 × 20 ml), and the combined colourless organic layer dried ($MgSO_4$). After removal of the solvent *in vacuo* the material was fractionally distilled under reduced pressure using a Boeshertz column (20 cm). Compound **3b** was obtained as colourless oil at 158–161°C/0.01 mm Hg (yield: 44.8 g, 85%). ^1H-n.m.r. ($CDCl_3$) δ 0.88 (t; 6H, CH_3), 1.29 (m; 12H, γ-ε-CH_2), 1.58 (m; 4H, β-CH_2), 2.50, 2.66 (2t; 4H, α-CH_2), 7.02 (AB; 2H, H-3, H-4), 7.33 (s; 1H, H-6); ^{13}C-n.m.r. ($CDCl_3$) δ 14.12 (q, CH_3), 22.65, 22.69, 29.01, 29.16, 30.07, 31.32, 31.76, 35.16, 35.83 (9t, CH_2), 124.30 (s, C–Br), 127.40, 129.94, 132.51 (3d, aromatic–C) 139.16, 142.31 (2s, aromatic–C); mass spectrum *m*/*e* (relative intensity) 326, 324 (M^+, isotope pattern one bromine atom, 15%), 255, 253 (M^+–C_5H_{11}, 30%). Analysis calculated for $C_{18}H_{29}Br$: C, 66.45; H, 8.99; Br, 24.56. Found: C, 66.28; H, 8.84; Br, 24.33.

(*2,5-di-n-hexylphenyl*)*boronic acid* (**3c**)

A solution of n-butyllithium (1.6 M, 44 ml) in hexane was added slowly to a cooled (−40°C) solution of 1-bromo-2,5-di-n-hexylbenzene (**3b**) (20.0 g, 61.6 mmol) in diethylether (150 ml). The mixture was allowed to warm to room temperature and was stirred for a further 2 h. This solution was transferred into a dropping funnel and added to a cooled (−60°C) solution of trimethylborate (19.2 g, 185 mmol) in ether (200 ml), and was then stirred for 8 h at room temperature. After hydrolysis with aqueous HCl (2 N, 300 ml), the layers were separated and the aqueous layer was extracted with ether (200 ml). The solvent was then removed from the combined organic layers and water (10 ml) and low boiling petroleum ether (200 ml) were added. A colourless crystalline mass precipitated which was recovered by filtration. The crystals were dried on a filter paper and were used without further treatment for the coupling reactions. Yield: 10.2 g (57%). The crystals contain water in a ratio of boronic acid:water = 2:1, as was shown by ^1H-n.m.r. integration. The n.m.r. spectra of **3c** indicate that partial self-condensation takes place. To establish the structure of **3c**, the material was converted into the corresponding cyclic ester through reaction of **3c** with ethylene glycol.

Cyclic ester from **3c** *and ethylene glycol*

Equimolar amounts of **3c** (1.00 g, 3.4 mmol) and ethylene glycol (0.21 g, 3.4 mmol) were dissolved in methylene chloride (100 ml) which was then distilled under normal pressure to remove the water azeotropically. The residue was heated for 5 min at 100°C/0.01 mm Hg to give the cyclic ester as a colourless oil. ^1H-n.m.r. ($CDCl_3$) δ 0.83 (t; 6H, CH_3), 1.27 (m; 12 H, γ-ε-CH_2), 1.55 (m; 4H, β-CH_2), 2.50, 2.79 (2t; 4H, α-CH_2), 4.28 (s; 4H, –O–CH_2), 7.08 (AB; 2H, H-3, H-4), 7.58 (s; 1H, H-6); ^{13}C-n.m.r. ($CDCl_3$) δ 14.04 (q; CH_3), 22.59, 29.07, 29.27, 31.55, 31.74, 32.97, 35.35, 35.51 (8t; CH_2), 65.68 (t; –O–CH_2–), 127.37 (broad s; C–B), 129.13, 131.17, 136.30 (3d; aromatic C), 139.14, 147.46 (2s; aromatic C); mass spectrum *m*/*e* (relative intensity) 316 (M^+, 41%), 145 (M^+ –C_5H_{11}, 100%); Analysis calculated for $C_{20}H_{33}BO_2$: C, 75.95; H, 10.52; B, 3.42. Found: C, 75.88; H, 10.65; B, 3.22.

2,2′,5,5′-tetra-n-hexylbiphenyl (**2a**, $n=0$, $X=H$)

A mixture of 1-bromo-2,5-di-n-hexylbenzene **3b** (5.00 g, 15.5 mmol), (2,5-di-n-hexylphenyl)boronic acid **3c** (4.45 g, 15.5 mmol) and $Pd(PPh_3)_4$ (0.55 g, 3 mol%) was refluxed in the heterogeneous system benzene (40 ml)/2M K_2CO_3 (25 ml) for 24 h with vigorous stirring. Then the mixture was allowed to cool to room temperature, the layers were separated and the aqueous one was extracted with low boiling petroleum ether (150 ml). The combined organic layers were dried over $MgSO_4$, filtered through silica gel and distilled, after removal of the solvent. **2a** ($n=0$) was obtained as a colourless oil, b.p. 160°C (0.01 mm Hg), yield (5.5 g, 72%). ^{1}H-n.m.r. ($CDCl_3$) δ 0.81, 0.87 (2t; 12H, CH_3), 1.04–1.70 (complex signals; 32H, β–ε–CH_2), 2.30 (m; 4H, α–CH_2 at sites *ortho* to ring junctions), 2.57 (t; 4H, α–CH_2 at sites *meta* to ring junctions), 6.92–7.20 (6H, aromatic-H); ^{13}C-n.m.r. ($CDCl_3$) δ 14.06 (q, CH_3), 22.52, 22.64, 29.04, 29.25, 30.99, 31.49, 31.66, 31.80, 32.85, 35.54 (10t, CH_2), 127.06, 128.54, 129.95 (3d, aromatic–C), 137.80, 139.46, 141.08 (3s, aromatic–C); mass spectrum, *m/e* (relative intensity) 490 (M^+, 21.5%) 419 (4%). Analysis calculated for $C_{36}H_{58}$: C, 88.09; H, 11.91. Found: C, 87.91; H, 12.06.

*2,2′,2″,5,5′,5″-hexa-n-hexyl-*p*-terphenyl* (**2a**, $n=1$, $X=H$)

The procedure was analogous to the one described for **2a** ($n=0$, $X=H$). The following reagents were used: (2,5-di-n-hexylphenyl)boronic acid **3c** (7.0 g, 24.1 mmol); 1,4-dibromo-2,5-di-n-hexylbenzene **1a** (4.0 g, 9.9 mmol); $Pd(PPh_3)_4$ (0.6 g, 3 mol%). Work-up gave **2a** ($n=1$) as a colourless oil, b.p. 250°C (0.01 mm Hg) which crystallized at room temperature. Recrystallization from ethanol yielded colourless needles (6.3 g, 87%, m.p. 47°C). ^{1}H-n.m.r. ($CDCl_3$) δ 0.80, 0.82, 0.88 (3t; 18H, CH_3), 1.05–1.70 (complex signals, 48H, β–ε–CH_2), 2.30 (m; 8H, α–CH_2 at sites *ortho* to ring junctions), 2.60 (t; 4H, α–CH_2 at sites *meta* to ring junctions), 6.98–7.20 (8H, aromatic–H); ^{13}C-n.m.r. ($CDCl_3$) δ 14.03, 14.08 (2q, CH_3), 22.54, 22.64, 29.05, 29.14, 29.27, 29.46, 30.78, 31.06, 31.18, 31.46, 31.66, 31.80, 32.77, 32.94, 33.11, 35.56, 35.62 (17t, CH_2), 127.06, 128.59, 128.68, 130.01, 130.17 (5d, aromatic–C), 137.10, 137.17, 138.06, 139.55, 139.84, 141.00, 141.17 (7s, aromatic–C); mass spectrum, *m/e* (relative intensity) 735 (M^+, 58). Analysis calculated for $C_{54}H_{86}$: C, 88.21; H, 11.79. Found: C, 88.42; H, 11.58.

Poly(para*(2,5-di-n-hexylphenylene)*) **2a**

Freshly distilled 1,4-dibromo-2,5-di-hexylbenzene[25] **1a** (15.0 g, 37 mmol) and magnesium (0.90 g, 37 mmol) were refluxed in tetrahydrofuran (80 ml) for about 1 h. The mixture was allowed to cool to room temperature and the Ni-complex A, B, C, or D (see *Table 1*) was added in one lot. The resulting, dark coloured solution was refluxed for 48 h. The whole mixture was then poured into acetone (500 ml), the solid material which precipitated was recovered by filtration through a Büchner funnel, washed with dilute HCl (100 ml) and dried under vacuum (0.01 mm Hg) for 2 h. To separate the last traces of inorganic salts, the polymer was extracted with toluene in a Soxhlet apparatus. The solution was then concentrated to about 20 ml and the product precipitated by adding acetone (500 ml). The polymer was recovered and freeze-dried in benzene, for yields see *Table 1*. The ^{1}H- and ^{13}C-n.m.r. data given below, do not contain signals related to end groups, which are discussed in the text. ^{1}H-n.m.r. ($CDCl_3$) δ (all signals are at least 30 Hz broad and almost unstructured) 0.85 (6H, CH_3), 1.00–1.65 (16H, CH_2), 2.45 (4H, α–CH_2), 7.08 (2H, aromatic–H); ^{13}C-n.m.r. ($CDCl_3$) δ 14.04, 14.10, (2q, CH_3), 22.61, 29.32, 29.46, 30.97, 31.19, 31.46, 31.76, 33.08 (8t, CH_2) 130.39 (d, aromatic–C), 137.44, 139.74 (2s, aromatic–C). For elemental analyses see *Table 1*.

Poly(para*(2,5-di-n-octylphenylene)*) (**2b**)

Procedure and yields were virtually identical with the ones described for **2a**. ^{1}H- and ^{13}C-n.m.r. shifts are also identical, the intensities change as expected.

Reduction of polymer **2a**

To a solution of polymer **2a** (1 g) in toluene (50 ml) a solution of n-butyllithium in hexane (1.6 M, 10 ml) was added dropwise at room temperature. This mixture was refluxed for 5 min and the resulting dark red solution was then quenched by adding it to methanol (10 ml) when the reduced polymer **2a** precipitated. The work-up was the same as described above. The n.m.r. spectra obtained were identical with those of unreduced material except for the end group effects discussed in the text. The elemental analysis for bromine indicated less than 0.05%.

RESULTS AND DISCUSSION

Monomer synthesis

Monomers **1a** and **1b** are easily accessible in two steps from 1,4-dichlorobenzene and were prepared on the 150 g scale, as described previously[25]. The purity of the monomers was checked by high field n.m.r. spectroscopy and h.p.l.c. The ^{1}H- and ^{13}C-n.m.r. spectra of **1a** and **1b** did not indicate any impurity. The h.p.l.c. trace of the

Table 1 Dependence of the $\overline{DP}$ of soluble PPP **2a** on the kind of Ni-complex added

Ni-complex	A	B	C	D
Monomer **1a** [g/mmol]	12.0/29.7	12.0/29.7	12.0/29.7	12.0/29.7
Ni-complex [mg/mol-%]	130/1.54	220/1.13	120/1.62	200/1.24
Polymer **2a**, isolated yields [g/%][a,b]	3.61/43	4.11/62	3.76/53	2.66/39
Soluble (g) **2a**[a]	4.74	2.48	3.29	4.17
Elemental Analysis in %C	81.54	81.92	78.75	76.79
%H	11.35	11.44	11.10	11.03
%Br	4.57	3.55	4.30	3.21
Average *DP* (h.p.l.c.)	8	12	8	6
Average *DP* (osmometry)	12	13	12	10

[a] In acetone

[b] Based on amount of monomer incorporated into the polymer and complete mass balance of organic material

representative monomer **1b** revealed a purity of at least 99.1%.

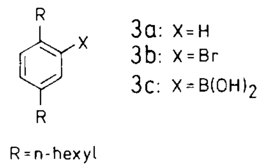
Ni-catalysed polycondensation

These reactions were carried out using monomers **1a** and **1b** in a slightly modified version of the procedure given by Yamamoto[5], for details see experimental section. In the initial experiments Ni(bipy)Cl$_2$ (0.5–1.5 mol%, bipy = 2,2′-bipyridyl) was used as precursor complex for the actual catalytically active species. (For a detailed mechanistic discussion see reference 26.) The reaction mixture was refluxed in THF for 48 h, giving a dark solution containing traces of suspended solid, presumably Mg salts. Polymeric material was obtained as a yellow to green precipitate when this mixture was poured into acetone. The colour arises from traces of catalyst residues. The sample reduced with n-butyllithium was completely colourless. The yields of precipitated material ranged from 40–60 wt%. As expected, polymer **2** turned out to be soluble in various organic solvents (chloroform, methylene chloride, toluene).

Synthesis of model compounds

Dimeric (n = 0, X = H) and trimeric (n = 1, X = H) species **2a** were prepared as model compounds. The synthesis of the dimer involved monobromination of **3a** to give **3b**, followed by conversion to the boronic acid **3c**, **3b** and **3c** were then coupled to **2a** (n = 0, X = H) under Pd catalysis[27,28] in a yield of 72%. The trimer **2a** (n = 1, X = H) was obtained analogously by coupling the dibromide **1a** with two equivalents of **3c** in a yield of 87% (*Scheme 2*). In our hands, this synthesis proved more effective than the coupling of monobromo Grignard with dibromobenzene derivatives, for which h.p.l.c. indicated an oligomeric mixture.

Scheme 2



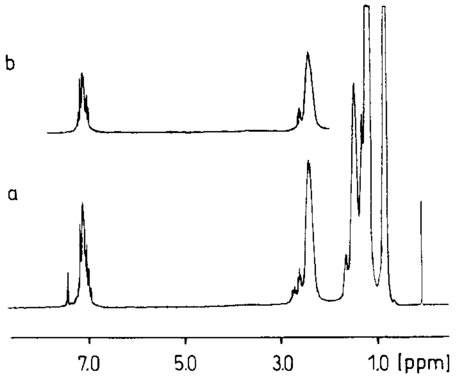


Figure 1 ^{1}H-n.m.r. spectra of polymer **2a**. (a) As polymerized; (b) after reduction of the bromine end groups

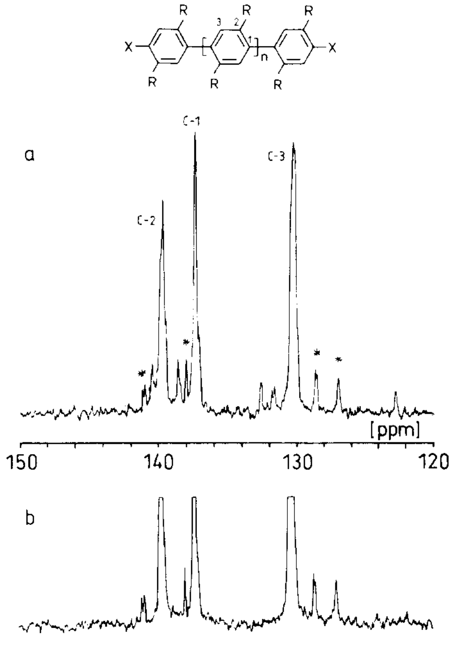


Figure 2 Aromatic region of the ^{13}C-n.m.r. spectrum of polymer **2b**. (a) As polymerized; (b) after reduction of the end groups

Structure elucidation of polymer 2

The molecular structures of polymers **2a** and **2b** were established by high resolution ^{1}H and ^{13}C-n.m.r. spectroscopy. The ^{1}H-n.m.r. spectra of polymers **2a** and **2b** showed four sets of lines in the correct intensity ratios, namely, a broad absorption for the aromatic protons at 7.08 ppm, a broad signal for the α-methylene groups at 2.45 ppm, and a huge signal for the rest of the methylenes of the alkyl chains, absorbing from 1.00–1.65 ppm, with a signal due to the methyl groups at 0.85 ppm. The spectrum revealed three additional, small peaks which arise from the termini, a sharp singlet at 7.45 ppm and two small triplets at 2.62 and 2.72 ppm, respectively. The signals at 7.45 and 2.72 ppm were assigned unambiguously to the termini bearing bromine (i.e. **2a** or **2b**, X = Br); the one at 2.62 ppm to the termini having hydrogen as end groups instead (i.e. **2a** or **2b**, X = H). This assignment was verified by a reduction of the bromine end groups. A representative part of polymer **2b** was treated with n-butyllithium followed by methanolic work-up, which resulted in the complete disappearance of the signals at 7.45 and 2.72 ppm and an equivalent increase in the intensity of the signal at 2.62 ppm (see *Figure 1*). All features of these n.m.r. spectra are therefore consistent with the proposed structure for polymer **2** but do not constitute an unambiguous proof of structure.

In principle, the average *DP* of polymer **2** could be calculated from the relative intensities of the three different α-methylene groups in the ^{1}H-n.m.r. spectrum. Unfortunately, the two end group triplets are not sufficiently well resolved from the main chain α-methylene signal to allow a precise intensity evaluation. However, the mere existence of end group signals indicates a relatively low *DP*, and photographic enlargement of the spectra shown in *Figure 1* followed by graphical integration of the peaks gives a $\overline{DP} \sim 6$ to 7.

Figure 2 shows an expansion of the aromatic region of the ^{13}C-n.m.r. spectrum of a sample of polymer **2b** before and after reduction by treatment with n-butyllithium and methanolic work up. In spectrum 2*a* three major and several minor signals are observed. An all *para*

(1,4) linked phenylene sequence is expected from the mode of synthesis and requires three major signals, as observed. The most intense signal at 130.39 ppm is readily assigned to the aromatic carbon in the repeat unit carrying a hydrogen, a conclusion confirmed in the DEPT spectrum (not shown). The signals at 137.44 and 139.74 ppm were also established as quaternary in the DEPT spectrum and are assigned to C-1 and C-2 although which is which cannot be defined unambiguously at present.

The important question, now that the main peaks are assigned to the expected *para*-substituted phenylene repeat unit, is whether the minor peaks arise from chain end features in these relatively low molecular weight materials, or from structural defects in the main chain. It turns out that these minor peaks can be entirely assigned by reference to the spectra of the model compounds, dimer (**2a**, n = 0, X = H) and trimer (**2a**, n = 1, X = H). It should be noted that for all practical purposes the a and b series can be treated as interchangeable in this spectroscopic analysis, since there is only a difference of two methylenes in the side chain alkyls and all the structural information is associated with the aromatic and α-methylene signals in both the ^{1}H- and ^{13}C-spectra.

When we compare the spectrum of the raw polymer, *Figure 2a,* which was shown to contain bromine by elemental analysis, with that of the reduced polymer, *Figure 2b,* which contains no bromine, it is clear that only the four peaks marked with an asterisk in spectrum a survive the reduction. It is difficult to make reliable intensity measurements on these relatively weak peaks, but when the spectra a and b were superimposed it was clear that the relative intensities of the surviving minor peaks in spectrum b had significantly increased. Clearly the signals which have been lost from spectrum a in going to spectrum b must have been associated with the brominated termini. The spectrum of the dimer (**2a**, n = 0, X = H), which is effectively pure unbrominated termini in the terms of this argument, shows three intense (at 127.06, 128.54 and 129.95 ppm) and three weaker (at 137.80, 139.46 and 141.08 ppm) signals in the aromatic region as expected from its structure. The minor peaks in the spectrum of the reduced polymer, *Figure 2b,* are at 127.10, 128.60, 138.06 and 141.04 completely consistent with their arising from the expected termini. The 'missing' peaks at 129.95 and 139.46 ppm are, of course obscured by the major signals. This convincing evidence that these polymers have (within the sensitivity limits of the analytical technique) a totally regular structure was reinforced by the spectrum of the trimer (**2a**, n = 1, X = H), see experimental section. This structural assignment is based entirely on data derived from the materials prepared in this study.

If we consider possible structural defects the only kind for which a plausible mechanism can be constructed would lead, via a nickel–aryne–hydrido intermediate, to a *meta*-arylene link. The work of Brown and Kovacic[29], and Professor Heitz of Marburg University on *meta* linked phenylenes established that such structures invariably display aromatic carbon resonances in the 125 ± 1 ppm region, no resonances are detectable in this region in our spectra. If there are any structural defects in these polymers they are not detectable by this technique. The Yamamoto method, in this modification, is clearly highly regiospecific.

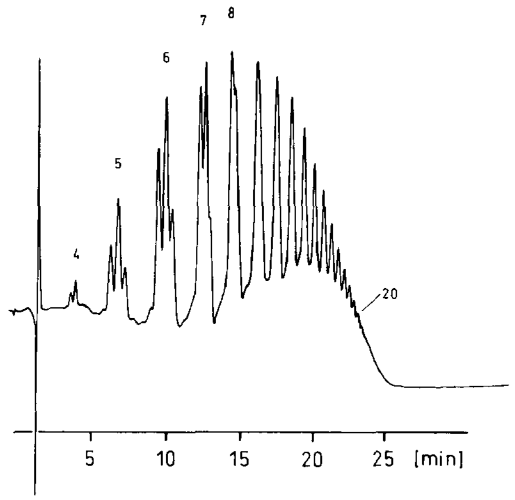


Figure 3 H.p.l.c. trace of polymer **2b** obtained with a methylene-chloride/acetonitrile gradient at room temperature

Product analysis by h.p.l.c.

In order to determine the *DP* of polymer **2**, it was analysed by h.p.l.c. chromatography. *Figure 3* displays a fully reproducible h.p.l.c. trace. Coinjection experiments with pure samples of the dimeric and trimeric model compounds showed that this series of peaks starts with the tetramer, the lower oligomers having been removed in the course of the work-up. This assignment reveals the somewhat disappointingly low molecular weight of polymer **2b**. Without a quantitative evaluation of the molecular weight distribution, but by simply counting the signal groups in the h.p.l.c. trace, an average *DP* of the order of 8 can be estimated, with largest species in this sample having a $\overline{DP}$ of *c.* 20.

The h.p.l.c. trace of polymer **2b** (*Figure 3*) has another interesting feature, the 'fine structure' of the low oligomeric peaks (4–8). The splitting reflects the resolution of the three possible end group combinations (H–H, H–Br, Br–Br) in these components. Comparison with the h.p.l.c. trace of reduced polymer **2b**, obtained under the same conditions, showed only one peak per oligomer. Since structural defects generally cause additional peaks in a h.p.l.c. diagram, the clean h.p.l.c. trace of reduced polymer **2b** nicely confirms the assignment of structure based on the n.m.r. spectra.

This Ni-catalysed coupling reaction is a polycondensation, but the h.p.l.c. diagram (*Figure 3*) does not reflect the molecular weight distribution expected for a well behaved reaction of this kind. As was briefly mentioned above, this is at least partially due to the work-up procedure during which the lowest oligomers are removed, which was confirmed by an h.p.l.c. trace recorded from a representative reaction mixture. A detailed mechanistic investigation would require a quantitative evaluation of the weight distribution which, in view of the inherent complications indicated above will be difficult to accomplish and is not available at present. Nevertheless, the combination of elemental analysis, mass balance, spectroscopy and h.p.l.c., allows a reasonable estimate of average *DP* of these samples to be made, and these estimates were confirmed by vapour pressure osmometry measurements (see *Table 1*).

Variation of Ni-complexes

The results described so far were quite satisfactory in regard to solubility and structural regularity of the novel n-alkyl substituted PPPs. Even though the achieved $\overline{DP}$ might be comparable with the ones obtained with the other direct methods, it did not match our initial objective. Hence, we tried to improve the procedure. All measures to guarantee the required precise stoichiometry were carefully taken (see experimental section), but did not lead to a significant improvement in any of many attempts. Some success was achieved by varying the structure of Ni-complexes added as catalysts, $Ni(bipy)Cl_2$ (A), $Ni(PPh_3)_2Cl_2$ (B), $Ni(acac)_2$ (C) and $Ni(dppp)Cl_2$ (D) (acac = acetylacetonate, dppp = 1,3-bisdiphenylphosphinopropane) were tested. The results are summarized in *Table 1*.

The average *DP*s given in *Table 1* were estimated from the h.p.l.c. data and by vapour pressure osmometry. As can be seen from these data, complex B was the most efficient catalyst for this process giving PPP with an average *DP* of 13. As expected, all n.m.r. spectra obtained from this material were also fully in agreement with the proposed structure. To the best of our knowledge, a PPP with an average *DP* of 13 represented the longest polymer of this kind known at the time of this work.

Unfortunately, we did not succeed in accomplishing any further improvement in this polycondensation. As evidenced in the n.m.r. and h.p.l.c. analysis, side reactions are responsible for destruction of the chain end functionality possibly via a partial hydrolysis of the Grignard species or a partial reduction of bromine end groups[30]. The required hydrogen atoms for such a reduction may be brought into the catalytic cycle via Ni-catalysed CH bond activation of the α–CH bond in THF[31]. Both effects would influence the stoichiometry of this polycondensation reaction in an undesirable way. Unfortunately, the requirement to dissolve the Grignard species limits the choice of solvents and we have been unable to find a solvent which allows a cleaner reaction than THF.

CONCLUSIONS

The regiospecificity of the Yamamoto coupling of 2,5-dibromo-1,4-di-n-alkylbenzenes **1a** and **1b** in the presence of stoichiometric amounts of magnesium and under catalysis from nickel complexes has been established. Regular 1,4-linked alkyl substituted poly(*para*-phenylenes) are obtained from this reaction. Side reactions resulting in loss of chain end functionality limit the molecular weights attainable, but it is clear that metal mediated coupling of alkyl substituted dibromoaromatics provides a feasible route to structurally regular, soluble and therefore processible, rigid rod polymers. The validity of the strategy is consequently established by this study.

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