Soluble poly(*para*-phenylene)s. 2. Improved synthesis of poly(*para*-2,5-di-n-hexylphenylene) via Pd-catalysed coupling of 4-bromo-2,5-di-n-hexylbenzeneboronic acid

Matthias Rehahn, Arnulf-Dieter Schlüter* and Gerhard Wegner
Max Planck Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, FRG

and W. James Feast
University of Durham, Department of Chemistry, South Road, Durham DH1 3LE, UK
(Received 17 August 1988; accepted 16 November 1988)

The synthesis of poly(*para*-2,5-di-n-hexylphenylene) via the palladium catalysed coupling of 4-bromo-2,5-di-n-hexylbenzeneboronic acid is described. The reaction yields structurally homogeneous products with the highest degrees of polymerization for poly(*para*-phenylene) derivatives yet recorded, namely $\overline{DP}\sim 30$. The products are soluble and have been characterized by n.m.r., g.p.c. and osmometry.

(Keywords: poly(*para*-2,5-di-n-hexylphenylene); 4-bromo-2,5-di-n-hexylbenzeneboronic acid; degrees of polymerization)

INTRODUCTION

The preceding paper described a synthesis of soluble derivatives of poly(*para*-phenylene) (PPP), the poly(*para*-2,5-di-n-alkylphenylene)s[1]. Because these polymers were soluble in common organic solvents the molecular structure and degrees of polymerization were established in detail. They were structurally homogeneous, all *para* linked, but the average degrees of polymerization (*DP*) were only of the order of 13. These types of polymer have several features which make them potentially very interesting in respect of various aspects of material science. They have conformationally rigid backbones, constructed from planar π-systems, and flexible alkyl side chains which render them soluble and hence processable. They may be envisaged as 'hairy rods' with the rod being a potentially interesting feature from the electrooptical and mechanical properties point of view. Processability is imparted to these otherwise intractable structures via the side chains, which also give a potential method of separating individual rods from each other at a distance controlled by the length of the alkyl substituents. Potential applications for such polymers are related to the fields of liquid crystals, electrically conducting materials, molecular composites and non-linear optics. Such materials may be transformable, in favourable cases, to the unsubstituted PPP by thermal cleavage of the pendant chains.

It is reasonable to expect that a conformationally rigid polymer will display its ultimate polymer properties at a much lower *DP* than a flexible one. Even if this is true in case of soluble PPPs, the *DP* of 13 attained in our earlier work seems unlikely to be sufficiently high. In this paper we describe a method for obtaining such polymers with significantly greater *DP*.

EXPERIMENTAL

General

The g.p.c. measurements were carried out using a Waters 150-C ALC/GPC (u.v. detection, 300 nm). Other methods and techniques were as previously described[1].

4-bromo-2,5-di-n-hexylbenzeneboronic acid (**1**). A solution of n-butyllithium (1.6 M, 31 ml) in hexane was added slowly to a cooled (−40°C) solution of 1,4-dibromo-2,5-di-n-hexylbenzene (20.0 g, 49.5 mmol) in diethylether (200 ml). The mixture was allowed to warm to room temperature and was stirred for further 2 h. This solution was transferred into a dropping funnel and added to a cooled (−60°C) solution of trimethylborate (15.4 g, 148.6 mmol) in ether (400 ml). It was then stirred for 8 h at room temperature. After hydrolysis with aqueous HCl (2 M, 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. Further purification was achieved by column chromatography (Kieselgel S) with toluene as eluent to remove by-products and followed by methyl-*t*-butyl ether furnishing monomer **1** in a purity of >98% (n.m.r. spectroscopy). The yield was 11.1 g (61%). The crystals contained water in a ratio of boronic acid:water = 2:1, as was shown by ^{1}H-n.m.r. integration. The n.m.r. spectra of monomer **1** indicate that partial self-condensation takes place. To

---

* To whom correspondence should be addressed

0032-3861/89/061060-03$03.00

establish the structure of monomer **1**, the material was converted into the corresponding cyclic ester.

Cyclic ester from monomer **1** *and ethylene glycol.* Equimolar amounts of monomer **1** (1.26 g, 3.4 mmol) and ethylene glycol (210 mg, 3.4 mmol) were dissolved in methylene chloride (100 ml), the solvent was 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. ^{1}H n.m.r. ($CDCl_3$) δ 0.88 (t; 6H, CH_3), 1.30 (m; 12H, γ–ε-CH_2), 1.57 (m; 4H, β-CH_2), 2.67, 2.79 (2t; 4H, α-CH_2), 4.28 (s; 4H, -O-CH_2-), 7.35, 7.63 (2s; 2H, arom. H); ^{13}C n.m.r. ($CDCl_3$) δ 14.10 (q; CH_3), 22.67, 29.23, 30.19, 31.76, 32.76, 35.02, 35.71 (7t; CH_2), 65.80 (t; -O-CH_2-), 126.00 (broad s; C–B), 128.04 (s; C–Br), 133.30, 138.17 (2d; arom. c), 138.50, 149.54 (2s; arom. C):; mass spectrum *m*/*e* (relative intensity) 396, 394 (M^+, isotope pattern for one bromine, 30%), 325, 323 (M^+–C_5H_{11}, 40%). Analysis calculated for $C_{20}H_{32}BrBO_2$: C, 60.78; H, 8.16; B, 2.74; Br, 20.22. Found: C, 60.64; H, 8.15; B, 2.69; Br, 20.35.

Poly(para-*2,5-di-n-hexyl-phenylene*) (**2**). Carefully purified monomer **1** (2.88 g, 7.8 mmol), $Pd(PPh_3)_4$ (45 mg, 3.9×10^{-2} mmol, 0.5 mol%), benzene (40 ml) and aqueous Na_2CO_3 (2 M, 30 ml) were refluxed and vigorously stirred under N_2 for 48 h. The whole mixture was then poured into acetone (200 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 24 h. To separate the last traces of catalyst residues and inorganic salts, the polymer was extracted with toluene in a Soxhlet apparatus for *c*. 20 h. The resulting solution was then concentrated to about 20 ml and the product precipitated by adding acetone (200 ml). The polymer was recovered and freeze-dried with benzene. Yields: 1.83 g (96%). ^{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, 29.31, 29.45, 30.97, 31.20, 31.46, 31.76, 33.08 (8t; CH_2), 130.39 (d; aromatic C), 137.44, 139.74 (2s; aromatic C). Elemental analysis calculated for $(C_{18}H_{28})_n$: C, 88.43; H, 11.57. Found: C, 87.65; H, 11.66.

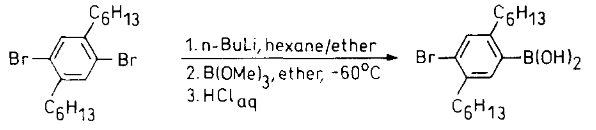
RESULTS AND DISCUSSION

In our initial approaches to the synthesis of polymer **2** via nickel catalysed Grignard coupling[1], only relatively low *DP* products were obtained. Chain growth terminating side reactions, such as reduction of the aryl halide, and difficulty in maintaining stoichiometric balance inhibited the very high reaction conversions necessary to give high *DP* materials. With this in mind, we looked for other transition metal catalysed coupling reactions which allow circumvention of these problems. Suzuki[2] and Miller[3] have described the Pd-catalysed coupling of various bromobenzene derivatives with benzene boronic acid which proceed with good to excellent yields. These authors also investigated the influence of substituents attached at the *ortho* position on this reaction, which was found to be virtually negligible. Hence, we decided to adapt this coupling reaction for our polymer synthesis.

Monomer synthesis

1,4-dibromo-2,5-di-n-hexylbenzene[4] was a suitable starting material for the preparation of the required AB-type monomer **1** via the route shown in Scheme 1.

Scheme 1



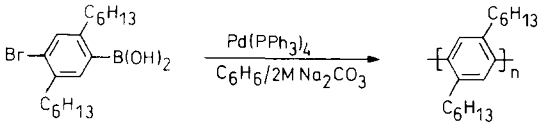
1

1,4-dibromo-2,5-di-n-hexylbenzene was reacted with one equivalent of n-butyllithium at low temperature to give the monolithiated species, which was then converted to compound **1** by adding it to excess trimethylborate, followed by acid hydrolysis of the intermediate. Monomer **1** was obtained in an overall yield of 61%. The monomer prepared in this way was obtained as a hydrate, for the purposes of polymerization the exact degree of hydration was unimportant but for the purposes of elemental analysis, n.m.r. and mass spectroscopic characterization it was necessary to prepare the cyclic borate ester with ethylene glycol (see experimental section). The purity of the cyclic ester derivative of **1** was checked by high field ^{1}H-n.m.r. spectroscopy by comparing the intensities of the ^{13}C-satellites of the aryl C–H signal with those of impurities. The purity was estimated to be better than 98%.

Polymerization and structure proof

Monomer **1** was treated with 0.5 to 1.5 equivalents of $Pd(PPh_3)_4$ in the heterogeneous system water (Na_2CO_3)/benzene under reflux for 2 days (see *Scheme 2*). Polymer **2** was precipitated by pouring the whole mixture into a large excess of acetone. When 0.5% Pd catalyst was used, colourless material was recovered from this process in yields of virtually 100%. The amount of acetone soluble oligomeric material was negligible. When greater concentrations of catalyst were used similar yields of pale yellowish product were obtained.

Scheme 2 Synthesis of poly(*para*-2,5-di-n-hexylphenylene)



1 2

The molecular structure of polymer **2** was established on the basis of its ^{13}C-n.m.r. spectrum. *Figure 1* shows the aromatic region of a representative sample of the material recorded in chloroform at room temperature. Two features are important. First, the spectrum exhibits the same signals as the ones which have already been assigned to *para*-linked polymer **2** (ref. 1). Secondly, there are no end group signals detected. From these observations it is evident that the Pd-catalysed coupling reaction of monomer **1** yielding polymer **2**, proceeds with very high regiospecificity and with a much higher conversion than the corresponding Ni-catalysed synthesis. The ^{1}H-n.m.r. spectrum of polymer **2** also confirmed the disappearance

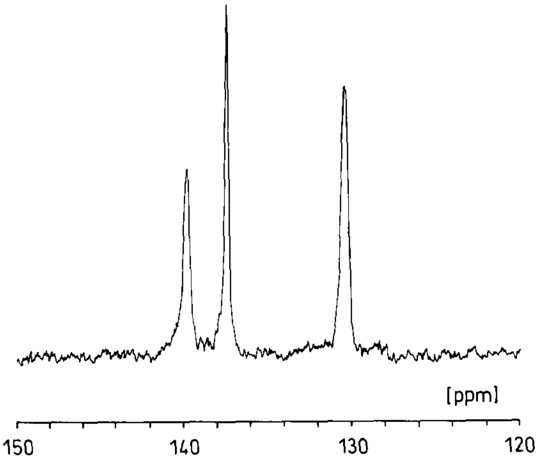


Figure 1 Aromatic region of the ^{13}C-n.m.r. spectrum of polymer **2**

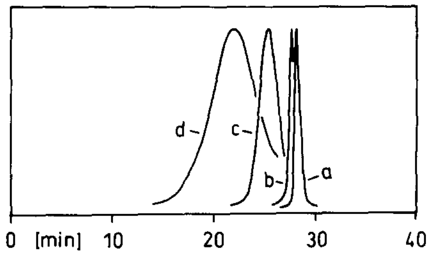


Figure 2 G.p.c. for samples of polymer **2** in 1,2-dichlorobenzene, using a 500, 10^4, 10^5 column set. (a) Dimer; (b) trimer; (c) $\overline{DP}\sim 12$; (d) $\overline{DP}\sim 28$

of signals related to end groups, indicating a significant improvement in the achieved *DP* compared to our earlier work.

Molecular weight

The absence of end group signals from the ^{1}H- and ^{13}C-n.m.r. spectra of the samples of poly(*para*-2,5-di-n-hexylphenylene) produced in this work indicates that a polymer has been formed rather than the telomers of earlier studies. We have previously shown that h.p.l.c. is capable of resolving telomers of polymer **2** (ref. 1). Attempts to analyse the product of this synthesis by h.p.l.c. were unsuccessful, in as much as an essentially unresolved long retained broad peak was observed. Our previous work[1] provided samples of the dimer and trimer, and a sample of polymer **2** of $\overline{DP}\sim 12$ (osmometry). A sample produced in this work was shown to have a $\overline{DP}$ of 28 by vapour pressure osmometry in toluene solution (Corona Wescan, Model 232A, calibrated with benzil). The g.p.c. traces for polymer **2** with n = 2, 3, *c*. 12 and this sample are reproduced in *Figure 2*. This data clearly establishes that a polymer with a $\overline{DP}\geqq 28$ has been produced because the osmotic pressure measurement gives a pessimistic estimate of molecular weight as a consequence of its susceptibility to trace impurities and the interpretation of g.p.c. data for soluble rigid rod polymers is as yet uncertain.

CONCLUSIONS

The palladium catalysed coupling of *para*-bromobenzene-boronic acid derivatives is established as an effective route to substituted PPPs of regular structure and high *DP*. This synthesis provides access to an interesting new class of processable rigid rod polymers, the physical and mechanical properties of which will form the subject of subsequent publications.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the excellent technical assistance given by Beate Müller (h.p.l.c.) and Regina Dorn (osmometry, g.p.c.). This work was supported by the Bundesministerium für Forschung und Technologie.

REFERENCES

1 Rehahn, M., Schlüter, A.-D., Wegner, G. and Feast, W. J. *Polymer* 1989, **30**, 1054
2 Miyaura, N., Yanagi, T. and Suzuki, A. *Synth. Commun.* 1981, **11**, 513
3 Miller, R. B. and Dugar, S. *Organometallics* 1984, **3**, 1261
4 Rehahn, M., Schlüter, A.-D. and Feast, W. J. *Synthesis* 1988, 386