

Soluble, rigid-rod polyimides having phenyl substituted pyromellitic diimide units via Pd-catalysed polycondensation

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The synthesis of a readily soluble, rigid-rod polyimide via Pd-catalysed polycondensation of 2,5-didodecylbenzene-1,4-diboronic acid and 3,6-diphenyl-*N,N'*-bis(4-bromo-2,5-didodecylphenylene) pyromellitic diimide is described. The polymer has been characterized by n.m.r., g.p.c. and osmometry showing that the Pd-catalysed polycondensation process proceeds practically without side reactions and is well suited for the synthesis of high molecular weight polyimides with defined structures.

(Keywords: polyimides; rigid-rod polymers; Pd-catalysed polycondensation; diphenylpyromellitic dianhydride)

Introduction

In a recent paper, a new, Pd-catalysed polymerization method has been reported which allows an efficient synthesis of rigid-rod polyimides¹. In contrast to the conventional polyimide syntheses²⁻⁸ the imide structure is already present in one of the monomers. By the attachment of flexible side chains to the rigid imide backbone, these polymers exhibit sufficient solubility to be characterized in solution whereas stiff-chain polymers are normally found to be insoluble in common organic solvents⁹⁻¹¹. The solubility of these polyimides, however, is still rather low because of strong charge-transfer interactions of the main chains¹². This makes a more extended analysis of these polymers very difficult. The introduction of additional bulky substituents in the pyromellitic diimide units should screen the interaction between the main chains and lead to a further increase of the solubility^{13,14}. On the other hand, the low reactivity of substituted pyromellitic dianhydrides during the process of imidization very often prevents the formation of high-molecular weight materials^{14,15}. In this paper the latter problem is circumvented by building up the imide ring already during the synthesis of the monomer. Thus the synthesis of the polyimide **3** obtained by Pd-catalysed polycondensation of monomer **1** with the substituted bisboronic acid **2** is reported. By virtue of the dodecyl side chains in the terphenylene units and two additional lateral phenyl substituents at each pyromellitic diimide unit this polyimide has a good solubility and can therefore be studied in solution by a variety of methods (Scheme 1).

Experimental

General. All chemicals and solvents were purchased from Aldrich or Fluka Chemical Co. and used without further purification. 2,5-Didodecylbenzene-1,4-diboronic acid **2** was synthesized as described before¹⁶. PdCl₂(1,1'-bis(diphenylphosphino)ferrocene) (Pd(dppf)Cl₂) and Pd(PPh₃)₄ were prepared according to known procedures from literature^{17,18}. Other materials, methods

and techniques were as previously described¹. For compounds **1**, **3**, **6** and **7**, the assignment of the absorptions in the ¹H and ¹³C n.m.r. spectra is made according to the numerals given in Scheme 2 and Figure 1, respectively.

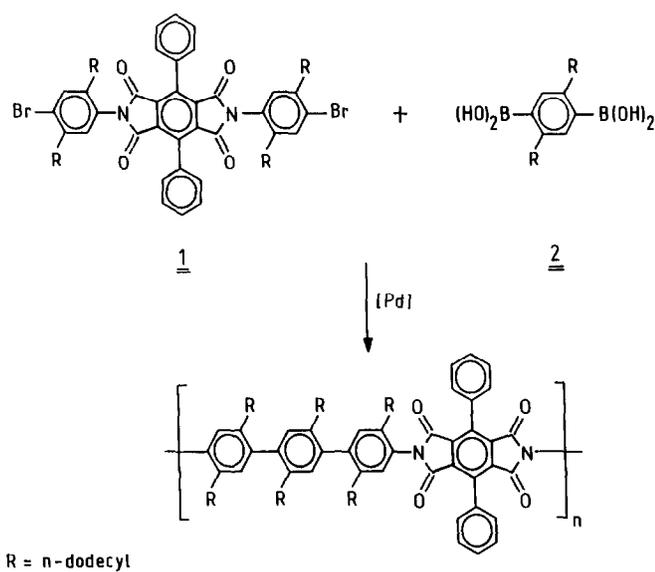
3,6-Dibromotetramethylbenzene (5). To a stirred solution of 1,2,4,5-tetramethylbenzene **4** (25.0 g, 186.6 mmol) and iodine (1.0 g, 7.8 mmol) in dichloromethane (150 ml) a solution of bromine (24 ml, 74.6 g, 467.0 mmol) in dichloromethane (100 ml) was added dropwise at room temperature under rigorous exclusion of light. The reaction mixture was refluxed for 1 h. Aqueous NaOH (5 M, 50 ml) was added subsequently to destroy the excess bromine. The aqueous layer was separated, the organic layer was washed with water and dried (MgSO₄). In an ice-bath, the product crystallized and was collected by filtration. The yield was 51.7 g (95%); m.p. 198°C (Literature¹⁹: 200°C).

¹H n.m.r. (CDCl₃) δ 2.46 (s; 12H, CH₃); ¹³C n.m.r. (CDCl₃) δ 22.26 (q; CH₃), 128.10 (s; aromatic-C³, C⁶), 134.98 (s; aromatic-C¹, C², C⁴, C⁵).

3,6-Diphenyltetramethylbenzene (6). Method a. 3,6-Dibromotetramethylbenzene (**5**) (21.0 g, 72.0 mmol), benzenboronic acid (35.0 g, 287.9 mmol), Pd(PPh₃)₄ (0.833 g, 0.72 mmol), aqueous Na₂CO₃ (1 M, 350 ml) and toluene (350 ml) were refluxed with stirring under N₂ for 5 days. The organic layer was separated, washed with water and dried (MgSO₄). The solvent was removed and the residue was dissolved in ethyl acetate (250 ml). Pure product **6** crystallized upon cooling from this solution and was collected by filtration. The yield was 17.5 g (85%).

Method b. Under N₂ a solution of benzenemagnesium bromide (65.2 g, 360.0 mmol) in dry diethyl ether (125 ml) was added dropwise to a stirred and heated (50°C) suspension of 3,6-dibromotetramethylbenzene (**5**) (50.0 g, 171.0 mmol), NiCl₂(1,3-bis(diphenylphosphino)-propane, dppp) (0.4 g, 0.74 mmol) and dry toluene (200 ml). The green-black mixture was refluxed for 5 days. After cooling (0°C) aqueous HCl (2 N, 100 ml) was added carefully to dissolve the magnesium salt. The organic layer was

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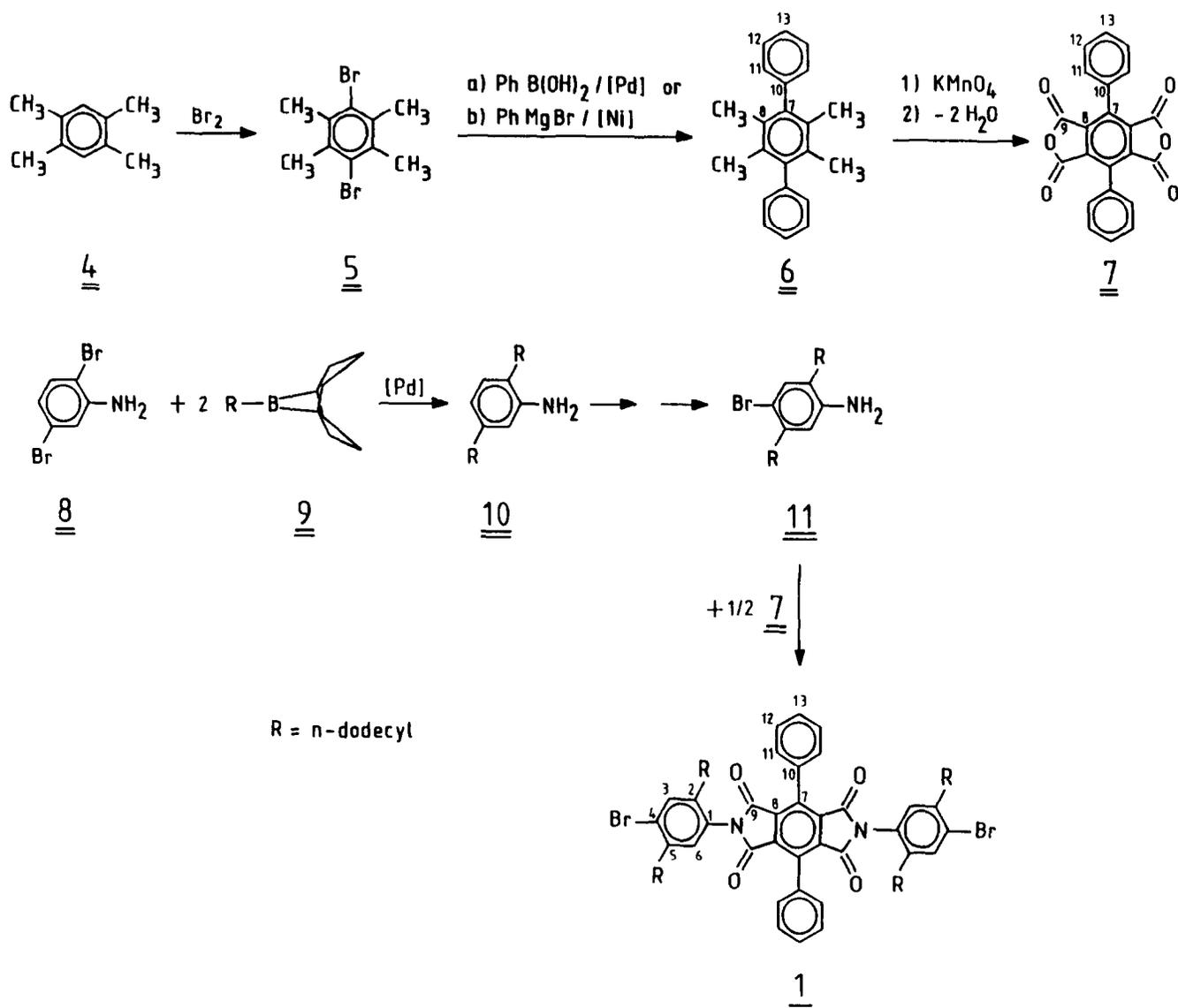


Scheme 1

separated and the product was isolated as described (cf. method a) yielding **6** in 30% (14.7 g); m.p. 211°C.

^1H n.m.r. (CDCl_3) δ 1.95 (s; 12H, CH_3), 7.19 (m; 4H, H^{11}), 7.32 (m; 2H, H^{13}), 7.42 (m; 4H, H^{12}); ^{13}C n.m.r. (CDCl_3) δ 18.09 (q; CH_3), 126.33 (d; C^{13}), 128.28, 129.47 (2d; C^{11} , C^{12}), 131.81 (s; C^8), 141.18, 142.75 (2s; C^7 , C^{10}).

3,6-Diphenylpyromellitic dianhydride (7). 3,6-Diphenyl-tetramethylbenzene (**6**) (7.0 g, 24.4 mmol), pyridine (300 ml) and water (40 ml) were heated (100°C) with stirring. Solid KMnO_4 (19.4 g, 122.0 mmol) was added in small portions and the mixture refluxed for 2 h. The warm solution was separated from the MnO_2 by filtration and the solvent was distilled under reduced pressure. Water (400 ml) and NaOH (16 g) were added to the residue. The mixture was heated (100°C) and KMnO_4 (19.4 g, 122.0 mmol) was added. After refluxing for 0.5 h, the excess KMnO_4 was destroyed by cautious addition of ethanol (20 ml). The hot solution was separated from the solid MnO_2 by filtration and acidified with aqueous HCl (5 M). The precipitate was collected by filtration, washed with water and dried (10 Pa, P_4O_{10}). The 3,6-diphenylpyromellitic acid was transformed into the



Scheme 2

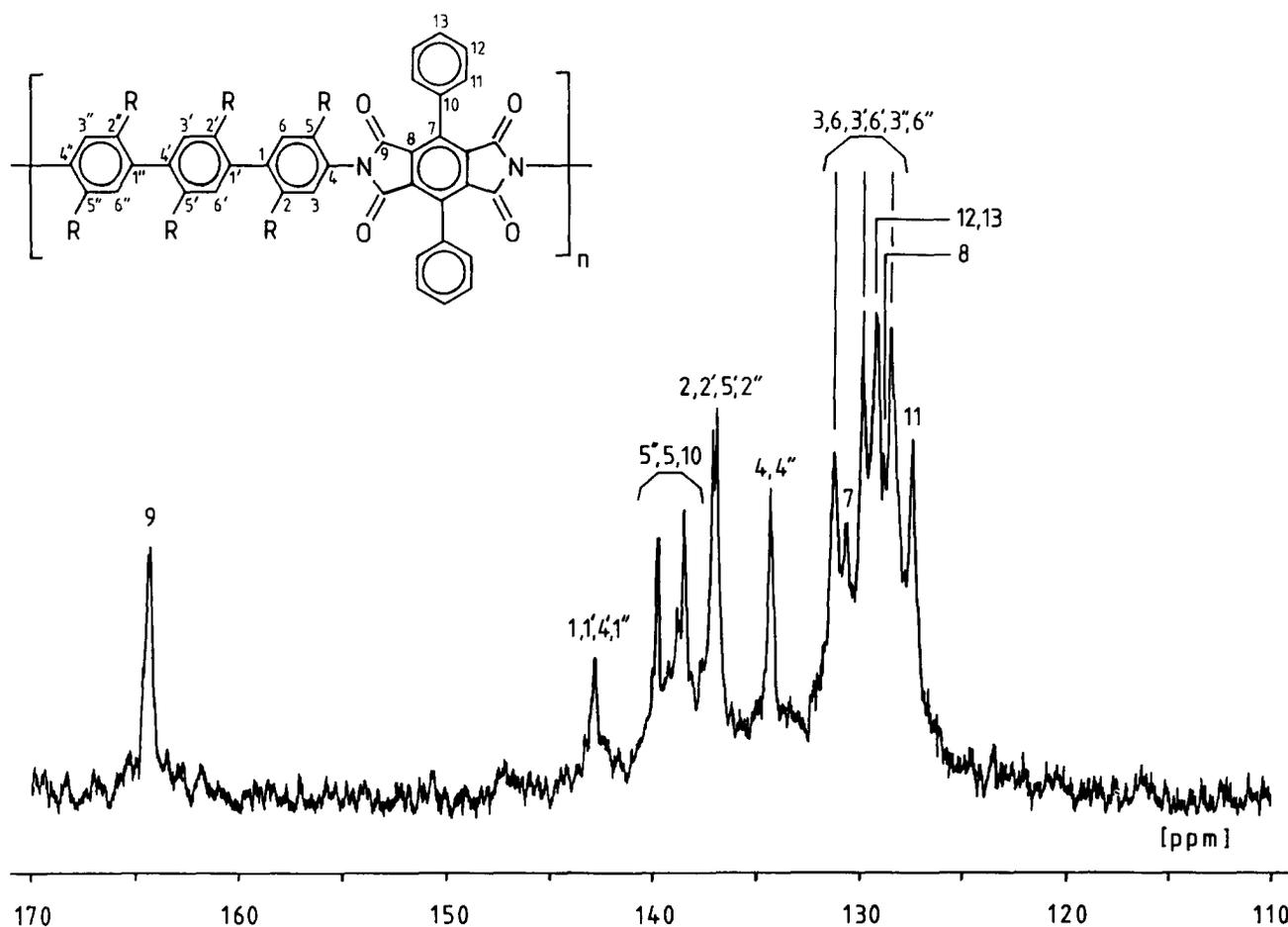


Figure 1 Aromatic region of the ^{13}C n.m.r. spectrum of polymer 3 measured in $\text{C}_2\text{D}_2\text{Cl}_4$ at 50°C

dianhydride 7 by heating (220°C) *in vacuo* (10 Pa) for 12 h yielding 5.2 g (58%) of a yellow solid.

^1H n.m.r. (DMSO-d_6) δ 7.54 (m; 6H, H^{11} , H^{13}), 7.59 (m; 4H, H^{12}); ^{13}C n.m.r. (DMSO-d_6) δ 127.66 (d; C^{11}), 129.54 (d; C^{13}), 129.63 (s; C^7), 129.73 (d; C^{12}), 134.94 (s; C^8), 138.23 (s; C^{10}), 160.10 (s; C^9).

2,5-Didodecylaniline (10). According to ref. 20, dodecene-1 (1.61 g, 9.6 mmol) and 9-borabicyclononane (0.5 M in tetrahydrofuran, 17.6 ml, 8.8 mmol) were stirred at room temperature for 1 h under N_2 . 2,5-Dibromoaniline (8) (1.0 g, 4.0 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (87.7 mg, 0.12 mmol) and aqueous NaOH (3 M, 7 ml, 21.0 mmol) were added and the mixture was stirred and refluxed for 7 days. After cooling, the organic layer was separated and dried (MgSO_4). The solvent was removed. The residue was dissolved in toluene, filtered over silica gel and recrystallized from ethanol. Yield: 0.51 g (30%); m.p.: 38°C (Literature¹: 38°C). The characterization and bromination of 10 yielding compound 11 were carried out as described previously¹.

3,6-Diphenyl-N,N'-bis(4-bromo-2,5-didodecylphenylene)-pyromellitic diimide (I). According to ref. 1, compound 1 was synthesized by reacting dianhydride 7 (2.5 g, 6.8 mmol) and 2,5-didodecyl-4-bromoaniline 11 (6.8 g, 13.5 mmol) in *m*-cresol (40 ml) and isoquinoline (3 ml). The yield was 5.7 g (63%); m.p.: $151\text{--}152^\circ\text{C}$.

^1H n.m.r. (CDCl_3) δ 0.87 (t; 12H, CH_3), 1.25 (m; 72H, CH_2), 1.51 (m; 8H, $\beta\text{-CH}_2$), 2.34, 2.62 (2m; 8H, $\alpha\text{-CH}_2$), 6.88, 6.94 (2s; 2H, H^6), 7.45, 7.49 (m; 12H, H^3 , H^{11} ,

H^{12} , H^{13}); ^{13}C n.m.r. (CDCl_3) δ 14.12 (q; CH_3), 22.69, 29.36, 29.46, 29.52, 29.64, 30.82, 31.02, 31.92, 35.69 (9t; CH_2), 125.72 (s; C^4), 127.74 (d; C^{11}), 128.65 (s; C^8), 129.44, 129.46 (2d; C^{12} , C^{13}), 129.97 (d; C^3), 130.22 (s; C^7), 133.58, 133.72 (2d; C^6), 134.33 (s; C^1), 138.80, 138.86 (2s; C^2), 139.92 (s; C^{10}), 140.86 (s; C^5), 164.25 (s; C^9).

Analysis calculated for $\text{C}_{82}\text{H}_{114}\text{N}_2\text{O}_4\text{Br}_2$: C, 72.87; H, 8.50; N, 2.07. Found: C, 72.76; H, 8.44; N, 2.04.

Synthesis of polyimide 3. Diimide 1 (2.7 g, 2.0 mmol) and 2,5-didodecyl-1,4-benzenediboric acid 2 (1.0 g, 2.0 mmol) were refluxed and vigorously stirred in the heterogeneous mixture of toluene (60 ml) and aqueous Na_2CO_3 (1 M, 30 ml) in the presence of $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 5×10^{-5} mol) for 5 days. The whole mixture was poured into acetone (300 ml). The solid material which precipitated was recovered by filtration, washed with diluted HCl (100 ml), water (100 ml) and acetone (100 ml) and dried *in vacuo* (10 Pa) for 24 h. The polymer was extracted with chloroform in a Soxhlet apparatus. The resulting solution was concentrated to about 50 ml and the product was precipitated by adding acetone (500 ml). The polymer was obtained in virtually 100% yield (3.2 g).

^1H n.m.r. ($\text{C}_2\text{D}_2\text{Cl}_4$, 50°C) δ 0.87 (t; 18H, CH_3), 1.24 (m; 108H, CH_2), 1.41 (m; 12H, $\beta\text{-CH}_2$), 2.38 (broad m; 12H, $\alpha\text{-CH}_2$), 7.01, 7.14 (2m; 6H, H^3 , H^6 , $\text{H}^{3'}$, $\text{H}^{6'}$, $\text{H}^{3''}$, $\text{H}^{6''}$), 7.54 (m; 10H, H^{11} , H^{12} , H^{13}); ^{13}C n.m.r. ($\text{C}_2\text{D}_2\text{Cl}_4$, 50°C) δ 13.64 (q; CH_3), 22.28, 28.96, 29.30, 31.56 (4t; CH_2), 127.43 (d; C^{11}), 128.65 (s; C^8), 128.81 (d; C^{12} , C^{13}), 128.44, 129.84, 131.20 (3d; C^3 , C^6 , C^3' , C^6' , C^3'' , C^6''), 130.68 (s; C^7), 134.31 (s; C^4 , $\text{C}^{4''}$), 136.89,

137.09 (2s; C², C^{2'}, C^{5'}, C^{2''}), 138.44, 139.79 (2s; C⁵, C^{5''}, C¹⁰), 142.81 (s; C¹, C^{1'}, C^{4'}, C^{1''}), 164.33 (s; C⁹).

Analysis calculated for (C₁₁₂H₁₆₆N₂O₄)_n: C, 83.84; H, 10.43; N, 1.75. Found: C, 82.24; H, 9.99; N, 1.69.

Results and discussion

Monomer synthesis. 3,6-Diphenylpyromellitic dianhydride **7** was a suitable starting material for the preparation of the diimide monomer **1**. It was prepared according to the route shown in *Scheme 2*.

1,2,4,5-Tetramethylbenzene **4** was reacted with two equivalents of bromine to give compound **5**, which was coupled with benzenboronic acid under Pd-catalysis (method a) or with benzenmagnesium bromide under Ni-catalysis (method b) yielding compound **6** in 85% and 30% yield, respectively. The dianhydride **7** was obtained by oxidation of **6** followed by dehydration of the tetracarboxylic acid intermediate.

4-Bromo-2,5-didodecylaniline **11** was synthesized by Pd-catalysed condensation²⁰ of 2,5-dibromoaniline **8** with two equivalents of the borane **9** followed by the bromination of **10** (*Scheme 2*). Finally, the dibromopyromellitic diimide derivative **1** was synthesized in 63% yield by reacting the dianhydride **7** with two equivalents of 4-bromo-2,5-didodecylaniline **11** in *m*-cresol. The purity of compound **1** was checked by ¹H n.m.r. spectroscopy by comparing the intensities of the ¹³C satellites of the aryl-H signals with those of potential impurities. The purity was estimated to be better than 98%.

Polycondensation and proof of structure. Equimolar amounts of diimide **1** and 2,5-didodecyl-1,4-benzenediboronic acid **2** were reacted in the presence of catalytical amounts of Pd(PPh₃)₄ in the heterogeneous system water (Na₂CO₃)/toluene (*Scheme 1*). Polymer **3** was recovered as a slightly yellow, fibrous material in virtually 100% yield. The structure proof of polymer **3** is chiefly based on its high resolution ¹H and ¹³C n.m.r. spectra. *Figure 1* shows the aromatic region of a representative sample of the material recorded in tetrachloroethane at 50°C.

The assignment of the absorptions of the aromatic carbons given in *Figure 1* is based on the spectra of the polyimides presented in the previous paper¹, the spectra of the monomers and on tabulated increments²¹. Two features are important. First, the spectrum exhibits the same signals as the ones which have already been assigned to a structurally homogeneous polyimide having unsubstituted pyromellitic diimide units¹. In addition, all absorptions corresponding to the lateral phenyl substituents were found. Second, there are no end group signals detected. From these observations it is evident that the Pd-catalysed coupling reaction of monomers **1** and **2** proceeds with very high regioselectivity and with a high conversion. The ¹H n.m.r. spectrum of polymer **3** also confirms the disappearance of signals related to end groups.

Molecular weight determination. Viscosity measurements in *o*-dichlorobenzene at 50°C yielded an intrinsic viscosity [η] of 2.7 dl g⁻¹. Because of the excellent solubility of polymer **3**, its molecular weight was determined by membrane osmometry. Measurements in *o*-dichlorobenzene at 50°C gave a \bar{M}_n of 72 300 g mol⁻¹

corresponding to a degree of polycondensation (\overline{DP}) \approx 45. A similar DP has been reached in the direct coupling of the phenyl groups for the synthesis of substituted poly(*p*-phenylene)s¹⁶. The \overline{DP} achieved here furthermore represents a tripling of the value achieved in the case of polyimides having unsubstituted diimide units¹. Comparison of the g.p.c. traces for polymer **3** (not shown) with those of the polyimides presented previously¹ also supports the significant increase of the \overline{DP} . Obviously, the substitution of the pyromellitic diimide units did not affect the reactivity of the imide **1**. On the contrary, the higher solubility of the growing polymers in the reaction mixture seems to be responsible for the significant increase of molecular weight.

Conclusions

The Pd-catalysed coupling reaction is established as an effective route to soluble, rigid-rod polyimides of regular structure and high DP having substituted pyromellitic diimide units. This synthesis provides access to an interesting new class of rigid-rod polymers. Their physical and mechanical properties as well as the behaviour in bulk and solution will be the subject of subsequent publications.

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