Chem. Mater. **2004,** *16,* 3963−3971

Palladium-Catalyzed Cross-Coupling Reactions in the Synthesis of Novel Aromatic Polymers

Stephen Lightowler and Michael Hird*

Department of Chemistry, University of Hull, Hull, HU6 7RX, U.K.

Received April 19, 2004. Revised Manuscript Received July 12, 2004

Several novel aromatic polymers have been prepared through palladium-catalyzed cross-coupling reactions involving two single phenyl ring units, one containing two bromo substituents and the other containing either two boronic ester moieties or two tributyltin moieties. These sets of reactions were carried out under different conditions (catalyst, solvent, and base) in order to optimize the yield, the degree of polymerization, and the polydispersity. Following optimization of the reaction conditions, a series of novel, substituted polymers were prepared to show the scope of the methodology. The synthesis of the polymerizable aromatic intermediates proved interesting and challenging, particularly those with many substituents. The novel polymers generated are discussed in terms of their synthetic methods, degree of polymerizations, and polydispersities.

Introduction

Coupling reactions that generate an aryl−aryl bond have been available for many years, but until relatively recently all the methodologies suffered severe limitations, including poor yields, lack of tolerance toward the presence of various functional groups, only applicable to symmetrical couplings due to significant homocoupling, steric problems, toxicity, and difficulty in purification.[1−4] Palladium-catalyzed cross-coupling reactions in the synthesis of multi-aryl compounds have been developed to overcome such disadvantages. These relatively recent coupling reactions involve the joining of an aryl unit that contains a leaving group such as iodo, bromo, chloro, or triflate to an aryl unit that contains an organometallic moiety. Examples include the Negishi coupling (zinc organometallic),[5] Stille coupling (tin organometallic),[6] and the Suzuki coupling (boron organometallic).[7] The methodology of choice can depend on the particular synthesis under consideration; however, it is generally recognized that coupling reactions involving arylboronic acids and their analogous esters are the most effective in terms of high yields, easy purification, low homocoupling, high tolerance toward a wide range of functional groups, efficient for sterically hindered systems, operationally simple, and low toxicity of the boron units.[3,8,9] The latter point is perhaps the main reason for the massive popularity of the Suzuki methodologies over and above the Stille method which involves toxic tin derivatives. Cross-coupling reactions have now been developed to highly effective levels, and they have been elegantly applied in a wide variety of chemistry areas, such as liquid crystals,[2,8,10−12] pharmaceuticals,[13,14] natural products,[15] polymers,[16−22] and molecular electronics,[18,23−26] to prepare compounds that would not otherwise be possible.

Aryl−aryl bond-forming coupling reactions have been targeted toward the synthesis of conjugated, multiaryl polymers because of the vast potential of such materials in the various applications of semiconductors, for example, light-emitting materials for displays, organic transistors, information storage, optical signal processing, batteries, and solar energy converters. In order for a synthetic methodology to be successful in the preparation of polymers, a high conversion rate is essential, a

---

* To whom correspondence should be addressed. E-mail: m.hird@hull.ac.uk.

(1) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.
(2) Hird, M.; Gray, G. W.; Toyne, K. J. *Mol. Cryst. Liq. Cryst.* **1991**, *206*, 187.
(3) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
(4) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(5) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821.
(6) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.
(7) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.
(8) Gray, G. W.; Hird, M.; Lacey, D.; Toyne, K. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2041.
(9) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.
(10) Hird, M.; Goodby, J. W.; Gough, N.; Toyne, K. J. *J. Mater. Chem.* **2001**, *11*, 2732.
(11) Sharma, S.; Lacey, D.; Wilson, P. *Mol. Cryst. Liq. Cryst.* **2003**, *401*, 225.
(12) Schultz, A.; Laschat, S.; Saipa, A.; Giesselmann, F.; Nimtz, M.; Schulte, J. L.; Baro, A.; Miehlich, B. *Adv. Funct. Mater.* **2004**, *14*, 163.
(13) Potter, G. A.; McCague, R. J. *J. Org. Chem.* **1990**, *55*, 6184.
(14) Hadfield, J. A.; McGowan, A. T. *Synth. Commun.* **1998**, *28*, 1421.
(15) Nicolaou, K. C.; Fylaktakidou, K. C.; Monenschein, H.; Li, Y. W.; Weyershausen, B.; Mitchell, H. J.; Wei, H. X.; Hepworth, D.; Sugita, K. *J. Am. Chem. Soc.* **2003**, *125*, 15433.
(16) Scherf, U.; Mullen, K. *Synthesis* **1992**, 23.
(17) Schluter, A.-D.; Wegner, G. *Acta Polym.* **1993**, *44*, 59.
(18) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.
(19) Bochmann, M.; Kelly, K.; Lu, J. *J. Polym. Sci., Part A: Polym. Chem*, **1992**, *30*, 2511.
(20) Rehahn, M.; Schluter, A.-D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060.
(21) Rehahn, M.; Schluter, A.-D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991.
(22) Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Meijer, E. W. *Polymer* **1996**, *37*, 5017.
(23) Harriman, A.; Hissler, M.; Khatyr, A.; Ziessel, R. *Eur. J. Inorg. Chem.* **2003**, 955.
(24) Katz, H. E.; Laquindanum, J. G.; Lovinger, A. J. *Chem. Mater.* **1998**, *10*, 633.
(25) Raymond, F.; Di Cesare, N.; Belletete, M.; Durocher, G.; Leclerc, M. *Adv. Mater.* **1998**, *10*, 599.
(26) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365.

10.1021/cm0493694 CCC: $27.50

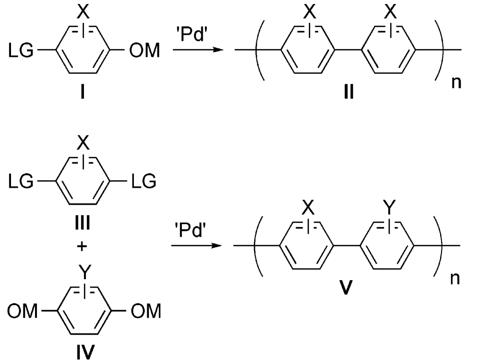


Figure 1. Two approaches to the generation of polymers through palladium-catalyzed cross-coupling reactions.

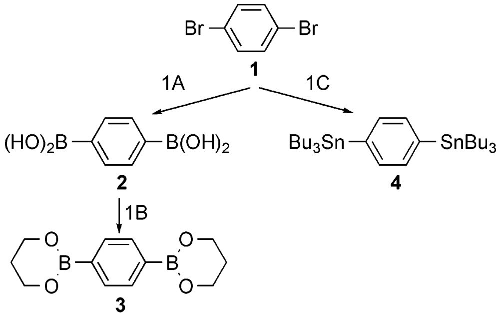
criterion which palladium-catalyzed cross-coupling reactions just about meet. There are two approaches (Figure 1) that have been taken in the use of palladium-catalyzed cross-coupling reaction in the synthesis of polymers; the first involves a single aryl unit (**I**) with a leaving group (LG) and an organometallic moiety (OM) to give a homopolymer (**II**) and the second involves an aryl unit with two leaving groups (**III**) and an aryl unit with two organometallic moieties (**IV**) to give a copolymer (**V**), or a homopolymer. In 1989 Rehahn et al.[20] reported a Suzuki coupling, of the former type shown in Figure 1, in the preparation of a homopolymer. Following this first example of a polymerization using a palladium-catalyzed coupling reaction, an enormous range of related research has been reported, including the preparation of a phenylene–thiophene copolymer in a Stille coupling of 2,5-di(tributylstannyl)thiophene and 1,4-didodecyloxy-2,5-diiodobenzene,[27] which is an example of the latter type shown in Figure 1.

Aims and Objectives

A glance at Figure 1 immediately reveals the enormous number of combinations that are possible in terms of type of aryl unit, leaving group, and organometallic unit. Then there are also numerous different types of palladium catalyst and different solvents that can be employed, and in the case of Suzuki couplings a base is essential and many different types are possible. Clearly, it is not possible to consider all combinations; hence, the initial aim was to find a reaction system that works well by using Suzuki and Stille coupling types and trying the most common combinations of catalyst, solvent, and base. After relatively straightforward optimization, a series of polymerizations were conducted to show the scope of the methodology in terms of attached functional groups, and to measure the degree of polymerization and the polydispersity. Subsequently, the size of the polymerizable precursors was extended to see if the degree of polymerization would remain, yet provide a polymer of high molecular weight. The materials prepared were not specifically designed for any particular application, but the various substituents were chosen to demonstrate synthetic applicability.

Discussion

Scheme 1



1A ... (i) Mg, THF; (ii) (MeO)$_3$B; (iii) 10% HCl or
(i) t-BuLi, THF; (ii) (MeO)$_3$B; (iii) 10% HCl
1B ... propane-1,3-diol, toluene
1C ... (i) Mg, THF; (ii) Bu$_3$SnCl; (iii) 10% HCl or
(i) t-BuLi, THF; (ii) Bu$_3$SnCl; (iii) 10% HCl

To investigate the synthesis of a range of substituted aromatic polymers, a wide variety of suitable monomer units were required to be prepared. Scheme 1 shows the synthesis of the most simple polymerizable monomer units. Compound **1** can be doubly metalated using either magnesium metal in a direct metalation or butyllithium in a metal–halogen exchange. The use of magnesium metal proved satisfactory, but time-consuming and low-yielding. The use of a large excess of tertiary butyllithium in hexane at reflux proved to be operationally more simple and less time-consuming and generated higher yields than the Grignard route. The double boronic acid generated (compound **2**) was isolated by hot filtration to remove the monoboronic acid and then used crude to form the double cyclic ester (compound **3**) of the diboronic acid which was thoroughly purified and characterized.

When arylboronic acids are used in palladium-catalyzed cross-coupling reactions, the main problem encountered is that the boronic acid is a mixture of boronic acid and the anhydride; additionally boronic acids tend to coordinate to THF strongly,[8] so hence it is difficult to determine the stoichiometry for coupling reactions. This unfortunate situation is not a problem for the synthesis of monomeric multi-aryls, but for polymer synthesis stoichiometric amounts of reagents are essential for efficient polymerization. The appropriate cyclic boronic esters are easily prepared and purified, and importantly they can be used as a direct replacement for the boronic acid in coupling reactions.

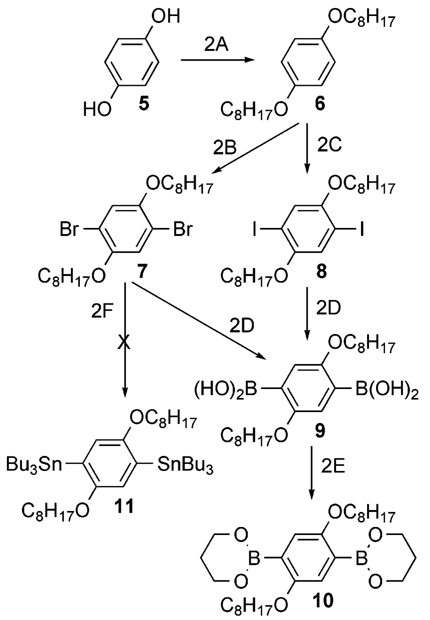
Tributylstannyl derivatives are also reported to be successful and widely applicable in palladium-catalyzed cross-coupling reactions.[6] The double tributylstannyl compound (**4**) was prepared in a manner similar to that used for the double boronic acid (compound **2**) except that the resulting double lithium derivative was quenched with tributyltin chloride.

Polymers based on unsubstituted aromatic units are often very insoluble and intractable, so long alkyl or alkoxy chains are often employed to circumvent such problems.[20] Octyloxy chains were chosen here, largely to avoid the reactive benzylic sites found in alkyl chains. The dioctyloxy-substituted diboronic acid **9** (or more importantly the dicyclic ester derivative **10**) and the analogous ditin compound **11** were important monomer units for polymerizations. Diboronic acid **9** was synthesized using a double metal–halogen exchange reaction optimized for the synthesis of compound **2** which involved the use of excess tertiary butyllithium in

---

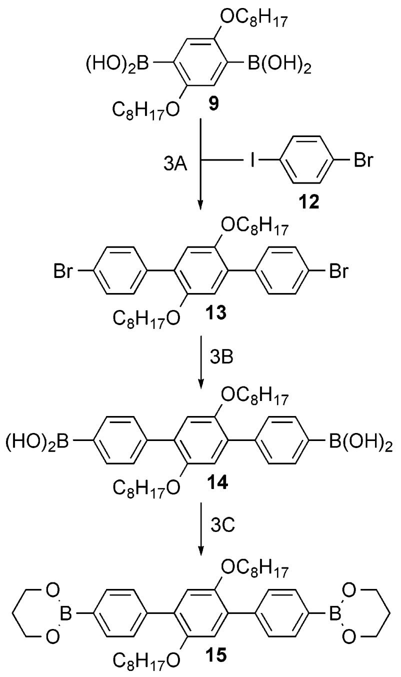
(27) Bao, Z.; Chan, W.; Yu, L. *Chem. Mater.* **1993**, *5*, 2.

Scheme 2



2A ... $C_8H_{17}Br$, K_2CO_3, butanone
2B ... Br_2, chloroform
2C ... KIO_3, I_2, H_2SO_4, H_2O, HOAc
2D ... (i) t-BuLi, hexane; (ii) $(MeO)_3B$, hexane; (iii) 10% HCl
2E ... propane-1,3-diol, toluene
2F ... (i) t-BuLi, hexane; (ii) Bu_3SnCl, hexane; (iii) 10% HCl

Scheme 3



3A ... $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O
3B ... (i) Mg, THF; (ii) $(MeO)_3B$; (iii) 10% HCl
3C ... propane-1,3-diol, toluene

hexane under reflux. From the dibromo compound **7** a yield of 47% of the desired diboronic acid **9** was generated; however, when the analogous diiodo compound **8** was used, a much higher yield (67%) resulted. The diboronic acid **9** was easily converted into the cyclic ester derivative **10** which was rigorously purified (Scheme 2).

The same optimized lithiation procedure was applied in the synthesis of the ditin compound **11**, but the desired product was not generated. Purification of the crude product gave a high yield of debrominated starting material **6**, showing that the double lithiation procedure was successful, but the subsequent reaction with tributyltin chloride failed. It would appear that steric factors are responsible for the failure to generate compound **11** which would certainly be rather crowded with two bulky alkoxy chains and two tributyltin groups in one phenyl ring.

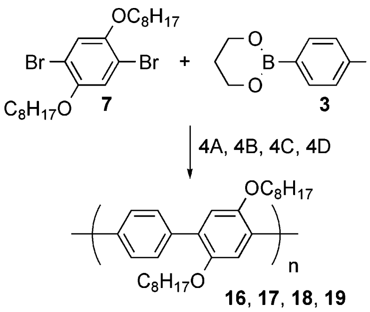
In addition to unsubstituted (compounds **1**, **3**, and **4**) and substituted (compounds **7**, **8**, and **10**) single ring polymerizable units, it was decided to synthesize three-ring analogues (compound **13** and **15**) in order to determine if higher molecular weight polymers could be generated. A standard Suzuki coupling of double boronic acid **9** with bromo-iodobenzene **12** generated a good isolated yield of the desired dibromoterphenyl **13**. The yield of 69% is remarkably high for this selective coupling reaction because there are several possible side reactions and polymerizations. However, a large excess of compound **12** was used and compound **9** was added dropwise; such conditions would likely favor the generation of compound **13**. The excess of compound **12** and byproducts were easily removed by column chromatography to generate a pure sample of compound **13** (Scheme 3).

The formation of the double boronic acid of the terphenyl material (compound **14**) by the preferred optimized route described above for compound **2** was expected to be problematic because of poor solubility in hexane even at reflux. Accordingly, the Grignard route was used with THF as the solvent, and surprisingly, in this case, the double Grignard formation was consistently 3 times faster than the formation of the double Grignard of the single ring system, and a high yield of the double boronic acid was generated. Formation of cyclic diester derivative **15** once again proved to be low yielding because of the purification process.

The first investigations into polymerizations involved optimizing the procedures in terms of choice of organometallic unit (boron or tin), choice of palladium catalyst, and various combinations of reaction conditions, for example, solvent, base (Suzuki) and actual boronic species (acid or ester). Such initial investigations revealed a very low degree of polymerization for homopolymers generated from the reaction of 1,4-dibromobenzene (**1**) with diboronic ester **3**, probably as a result of poor solubility of the product, and from the reaction of dibromo-dioctyloxybenzene **7** with dioctyloxy-diboronic ester **10**, probably as a result of steric hindrance at the site of the coupling. Initial investigations also revealed a significant advantage in terms of a high degree of polymerization and a low polydispersity of using catalyst that was freshly prepared immediately before use in the coupling reaction.

Accordingly, the polymerizations reported here begin with the preparation of polymer **16** (Scheme 4). Here conditions were employed that are frequently used with wide success in Suzuki coupling reactions of low molar mass systems. Polymer **16** was isolated in 66% yield with a reasonably high degree of polymerization (24) and a low polydispersity of 1.2. Suzuki couplings sometimes suffer from hydrodeboronation of the boronic acid, particularly where there is an electron-withdraw-

Scheme 4



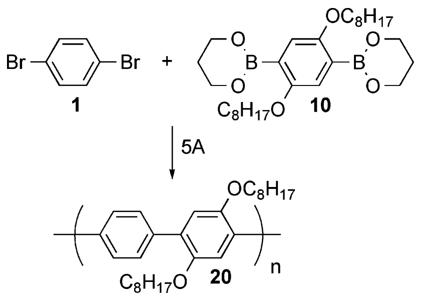
4A ... $Pd(PPh_3)_4$, Na_2CO_3, DME, H_2O
4B ... $Pd(PPh_3)_4$, K_3PO_4, DMF
4C ... $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O
4D ... $Pd(dppf)Cl_2$, Na_2CO_3, toluene, H_2O

ing substituent next to the boronic unit.[8,28] Such a problem can be circumvented by the use of anhydrous conditions,[28] and these were employed in the synthesis of polymer **17** using potassium phosphate as base and dry DMF as solvent. The yield of **17** was lower than that for polymer **16**; the degree of polymerization of **17** was also lower.

Clearly, a higher temperature for the coupling might be favorable in generating a polymer of higher molecular weight because of the higher rate of reaction and the greater solubility of the higher molecular weight product. Accordingly, the conditions used for the synthesis of polymer **18** were modified to use toluene as solvent in place of DME (used for the synthesis of polymer **16**). Polymer **18** was isolated in 68% yield (similar to polymer **16**), but the degree of polymerization was significantly higher at 31 with a slightly lower polydispersity (1.13). The standard tetrakis(triphenylphosphine)palladium(0) catalyst used for Suzuki coupling reactions is often out-performed by the dichloroferrocenepalladium(II) system;[29,30] hence, this catalyst was assessed under the conditions that provided the best results so far. However, the yield was lower (55%), the degree of polymerization was much lower (24), and polydispersity was higher (1.26), so overall there was a poor result for this polymerization system.

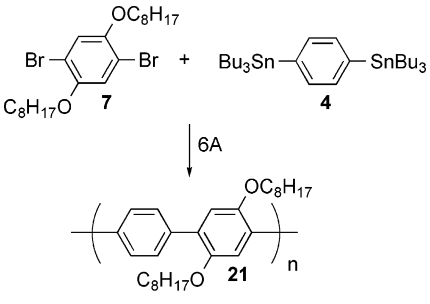
The best conditions so far for obtaining a high yield and a high degree of polymerization involved tetrakis(triphenylphosphine)palladium(0) catalyst and sodium carbonate base in a toluene−water solvent system, as used for the synthesis of polymer **18**. Hence, the same conditions were employed in the synthesis of polymer **20** (Scheme 5), which would result from having the component with the two octyloxy chains as the diboronic ester species (compound **10**) and the unsubstituted dibromo compound **1**, i.e., the reverse of the combination seen in Scheme 4. The result of this reversed combination of reagents was a similar yield (61%) of polymer **20** and a much lower polydispersity (1.04); however, the degree of polymerization was half that obtained for polymer **18**. Sterically hindered boronic acids (like those with electron-withdrawing units) are often prone to hydrodeboronation under aqueous base conditions, so perhaps such hydrodeboronation prevented larger molecular weight, but was not actually so prevalent so as to affect the overall yield. The low polydispersity could also be a result of the lower degree of polymerization being consistently controlled by a hydrodeboronation process. Overall, however, to maximize the degree of polymerization, it seems better to have the diboronic species as the more simple, unsubstituted coupling unit.

Scheme 5



5A ... $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O

Scheme 6



6A ... $Pd(PPh_3)_2Cl_2$, DMF

The polymerization was now evaluated using a Stille coupling under standard conditions for this type of coupling, which involves the tributyltin compound (**4**) and the dibromo-dioctyloxy unit (compound **7**) heated to 100 °C in DMF in the presence of a (dichlorodiphenylphosphine)palladium(II) catalyst. Stille couplings do not suffer from loss of the organometallic unit as some boronic acids do in the presence of base, and hence they survive for a longer period of time in the reaction conditions and hence a higher degree of polymerization than those obtained for the Suzuki couplings might be expected.

However, polymer **21** (Scheme 6) was isolated with a degree of polymerization of just 24, although the overall yield was good (55%) and the polydispersity was very low (1.06). Coupling reactions involving boron species are now widely used in preference to those involving tin species because of the toxicity associated with the tin salts produced. This important consideration, combined with a lower degree of polymerization, and the fact that polymer **21** from the "tin" coupling was dark brown in comparison to the colorless products (**16**−**20**) obtained through the "boron" polymerizations, prompted all subsequent polymerizations to use boron organometallic units and involve the conditions used for the synthesis of polymer **18**.

Schemes 7 and 8 show the synthesis of novel, functionalized polymers (**24** and **27**), which enables evaluation of the polymerization procedure for a range of functional groups. The results for both polymers (**24** and

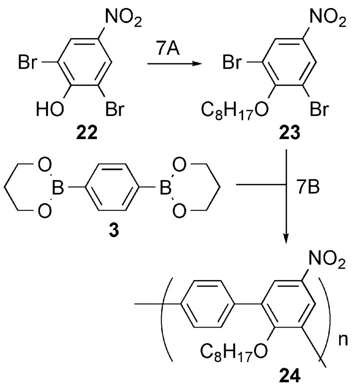
---

(28) Watanabe, T.; Miyaura, N.; Suzuki, A. *Synlett* **1992**, 207.

(29) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

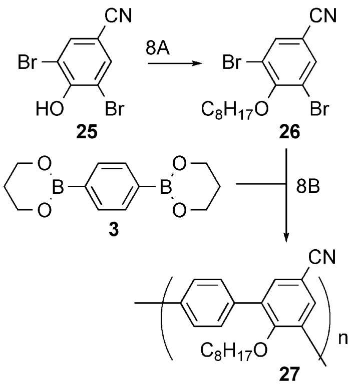
(30) Boyes, A. L.; Butler, I. R.; Quayle, S. C. *Tetrahedron Lett.* **1998**, *39*, 7763.

Scheme 7



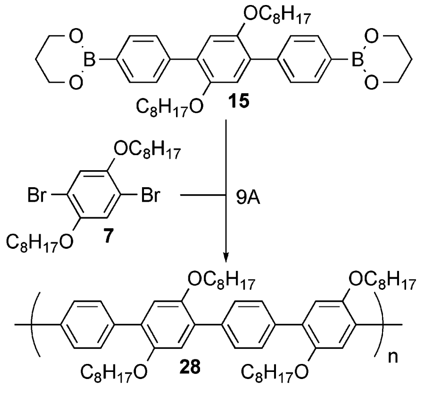
7A ... $C_8H_{17}Br$, K_2CO_3, butanone
7B ... $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O

Scheme 8



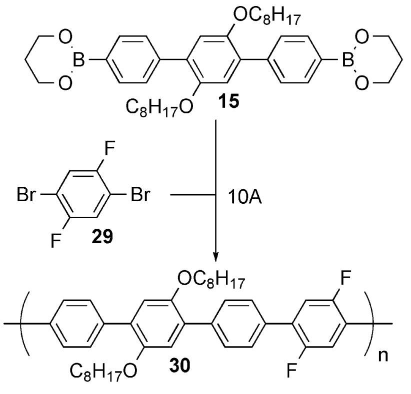
8A ... $C_8H_{17}Br$, K_2CO_3, butanone
8B ... $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O

Scheme 9



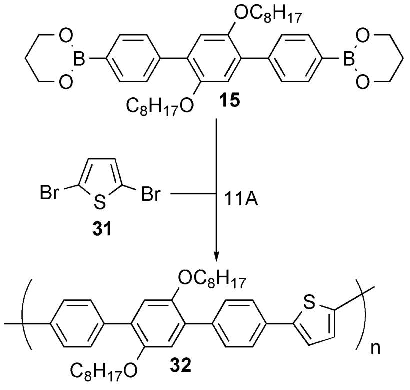
9A ... $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O

Scheme 10



10A ... $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O

Scheme 11



11A ... $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O

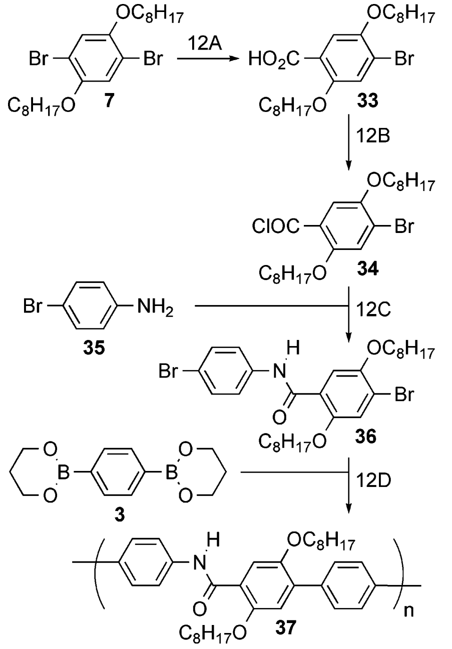
27) are remarkably similar, identical yields of 63% and identical degrees of polymerization of 27, and polydispersities of 1.25 and 1.17, respectively, which shows the consistency of the optimized polymerization conditions.

Scheme 9 shows the use of a three-ring boronic ester (**15**) in a polymerization with the single ring dibromodioctyloxybenzene unit (**7**) in an attempt to maintain the consistent degree of polymerization and hence generate a polymer with twice as many aromatic rings as for polymer **18**. In the event, polymer **28** was generated with a degree of polymerization of 22, but despite being much lower than that for polymer **18**, the overall molecular weight average of polymer **28** was nearly 1.5 times larger than that for polymer **18**, making a polymer of around 90 phenyl rings. Given the issues of solubility, it is not surprising that the degree of polymerization for polymer **28** would be lower, but clearly the larger monomer unit can result in a much larger polymer. This result is consistent with the reported research of Rehahn, who used a larger monomer system, but obtained a lower degree of polymerization. It would seem that solubility limits are being reached for these kind of polyaryl systems at around 100 phenyl rings.

Scheme 10 shows the polymerization of the three-ring boronic ester **15** with a dibromo-difluorobenzene unit (compound **29**) to give polymer **30**. Here the degree of polymerization of 24 gives a polymer with around 100 aromatic rings, only slightly higher than that for polymer **28**. Given the reduced steric hindrance of bromide **29** in comparison with the bromide **7**, a higher degree of polymerization might have been expected, perhaps further evidence for believing that the solubility limits of polymer size are being approached. Scheme 11 shows a similar polymerization to that shown in Scheme 10, except that the dibromoaryl unit is a thiophene (**31**). The resulting polymer (**32**) is almost identical in terms of degree of polymerization and polydispersity to polymer **30** (Scheme 10), again showing the consistency of results for the optimized reaction conditions of the coupling reaction, even for rather different aryl units.

Scheme 12 shows the deviation from a wholly directly linked polyaromatic system with the inclusion of an amide linkage within the polymer. The necessary aromatic dibromide (**36**) was the unit chosen to include the

Scheme 12



12A ... (i) n-BuLi, THF; (ii) CO_2 (solid); (iii) 10% HCl
12B ... oxalyl chloride, DMF, benzene
12C ... DME
12D ... $Pd(PPh_3)_4$, Na_2CO_3, toluene, H_2O

amide linkage, and the diboronic ester unit was the simple unsubstituted phenyl system **3**. The same optimized conditions for the coupling reaction were used as described for previous polymerizations to generate polymer **37**. Polymer **37** has a lower degree of polymerization and a higher polydispersity than for the standard directly linked polyaryl units synthesized by the same optimized method; this is no doubt the result of reduced solubility caused by the amide groups. However, once again the scope of the methodology has been extended without too much difference in the overall size of the polymer. The dibromide **36** is not symmetrical, and hence there will be a random distribution of the direction of the linking group in the resulting polymer.

Purification and Analysis of the Polymer Products

Polymers consist of a distribution of various molecules of identical structure, but of different size, and hence are by definition impure. However, polymers must be "purified" at least to remove unreacted monomer, low molecular weight units, and any inorganic material. Conventional techniques of purification used so successfully for low molecular weight materials cannot generally be applied to polymers because of very low volatility and very poor solubility. To isolate the organic material from inorganic salts and palladium residues, continuous Soxhlet extraction into toluene was used. The solution was then concentrated and the product was precipitated by the addition of acetone. Analysis of the filtrate from the precipitation process shows it to be a very effective method of removing low molecular weight organics, including unreacted monomers and lower molecular weight oligomeric and polymeric material.

The isolated polymeric products were analyzed by GPC as discussed above for individual polymers. It is known that GPC based on polystyrene standards tends to overestimate the size of conjugated polyaromatics of the type reported here because the rigid polymer chains have a disproportionately large hydrodynamic volume compared to the flexible coils of the polystyrene standards.[31] As part of current research a number of large, defined oligomeric multiphenylenes with a structure comparable to polymer **16**, for example, with up to 21 phenyl rings have been synthesized by sequential coupling reactions. Analysis of these defined oligomers by GPC gave molecular weight values of around 30–50% higher than was obtained by mass spectrometry, which is similar to previous results.[31] Accordingly, the overestimated values generated by GPC need to be taken into account in the above discussion. However, the results for the polymers reported here are consistent and comparable with each other and hence are useful and valid for the purpose.

Summary

Polymerizations involving palladium-catalyzed cross-coupling reactions have generated a range of novel aromatic polymers. A reaction system was optimized using consistent structural units, and it was found that a system involving a single ring dibromide with a single ring diboronic ester in the presence of a freshly prepared tetrakis(triphenylphosphine)palladium(0) catalyst and sodium carbonate base in a toluene–water solvent system (a Suzuki type coupling) gave the best results in terms of degree of polymerization, polydispersity, and ease of purification of the product, with the polymers consisting of around 63 aromatic rings. However, a value of 40 or 50 aromatic rings is more likely, given the average overestimation from the use of GPC. The couplings involving a di-tributyltin unit in a Stille coupling did give good results in terms of degree of polymerization and polydispersity, but the product was of poor visual quality.

The optimized synthetic method was then employed on a wider range of substrate types to show the scope for the incorporation of different functional groups into the polymer products. The results were remarkably consistent in terms of the quality of the polymer product, the degree of polymerization, and the polydispersity.

The polymerizations involving the larger, three-ring diboronic esters do not maintain the degree of polymerization obtained for the single ring units; however, it is still reasonably high and the polymers obtained were 1.5 times larger. These results suggest that such polymers consisting of around 100 aromatic rings are approaching the size limitation of such polymers due to solubility problems. Again, taking account of the average overestimated size as measured by GPC, these larger polymers are likely to consist of around 70 to 80 aromatic rings.

Experimental Section

Structural information of materials was obtained, where appropriate, by ^{1}H NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin-Elmer 882 spectrometer), and mass spectrometry (Finnigan-MAT 1020 spectrometer). The progress of some reactions, and the purity of

---

(31) Liess, P.; Hensel, V.; Schluter, A.-D. *Liebigs Ann.* **1996**, 1037.

certain materials, was determined by gas liquid chromatography (GLC) using a Chrompack CP-9001 gas chromatograph with a 10 m, 0.25 mm internal diameter, 0.12 mm fused silica capillary column. Melting points were determined using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP52 heating stage and FP5 temperature controller. Gel permeation chromatography (GPC) was used to assess the average molecular mass and polydispersity of polymers. The columns were PL Gel 5 mm mixed-D (2 × 30 cm) in conjunction with an ERC 7510 ERMA refractive index detector, calibrated with polystyrene standards. All GPC samples were analyzed in solution in THF.

The crude boronic acids were not analyzed for structure because they are frequently mixtures of the boronic acid and the anhydride, and they often contain coordinated THF; accordingly, full analysis was only carried out on the purified boronic ester derivatives.

Tetrakis(triphenylphosphine)palladium(0),[32] dichlorobis-(triphenylphosphine)palladium(II),[33] and dichloro[1,1′-bis-(diphenylphosphino)ferrocene]palladium(II)[29] were prepared according to literature procedures. Compounds **1**, **5**, **12**, **22**, **25**, **29**, **31**, and **35** are all commercially available.

1,4-Phenyldiboronic Acid (2). *Method 1.* Compound **1** (20.00 g, 0.08 mol) was dissolved in dry THF (200 mL), and 50 mL of the solution was added to a mixture of freshly ground magnesium turnings (15.15 g, 0.62 mol) and 1,2-dibromoethane (5 drops), under an atmosphere of dry nitrogen. The mixture was heated vigorously to initiate the reaction, and the remainder of the solution of compound **1** was added dropwise, with stirring, to the refluxing reaction mixture. The mixture was heated under reflux for 5 h (GLC analysis indicated a complete reaction) and then cooled to −78 °C. Trimethyl borate (21.35 g, 0.21 mol) was added dropwise at −78 °C and the mixture was allowed to attain room temperature overnight, and 10% aqueous hydrochloric acid (400 mL) was added. The product was extracted into ether (twice) and the combined ether layers were washed with water and dried (MgSO$_4$). The solvent was removed in vacuo and the crude product was crystallized from ethanol−water (1:1) to yield an off-white powder.

Yield: 4.61 g (33%).

Method 2. A solution of *tert*-butyllithium (100 mL, 1.7 M in pentane, 0.170 mol) was added dropwise to a stirred, cooled (−78 °C) solution of compound **1** (10.00 g, 0.042 mol) in dry THF (400 mL) under an atmosphere of dry nitrogen, and the mixture was stirred at −78 °C for 4 h. Trimethyl borate (21.35 g, 0.21 mol) was added dropwise at −78 °C and the mixture was allowed to attain room temperature overnight, and 10% aqueous hydrochloric acid (200 mL) was added. The product was extracted into ether (twice) and the combined ether layers were washed with water and dried (MgSO$_4$). The solvent was removed in vacuo and the crude product was crystallized from ethanol−water (1:1) to yield a colorless powder.

Yield: 2.86 g (41%).

1,4-Di[1,3,2]dioxaborin-2-ylbenzene (3). A stirred mixture of compound **2** (20.30 g, 0.12 mol), propane-1,3-diol (37.52 g, 0.49 mol), and toluene (500 mL) was heated to reflux overnight with azeotropic removal of water. The reaction mixture was cooled, the toluene was removed in vacuo, and the residue was poured into water. The product was extracted into ether (twice) and the combined ethereal extracts were dried (MgSO$_4$). The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel/hexane−dichloromethane, 1:1) to give a colorless solid which was crystallized from ethanol to yield a white crystalline solid.

Yield: 14.25 g (46%). mp: 120−122 °C. ^{1}H NMR (CDCl$_3$): δ 2.05 (4H, quint), 4.15 (8H, t), 7.75 (4H, s). IR $\nu_{\max}$ (cm^{-1}): 2950, 2920, 2880, 1475, 1410, 1390, 1145, 1115, 825, 710, 650. MS (*m*/*z*): 246 (M$^+$), 188, 175, 146, 130, 103, 85, 77, 65, 57.

1,4-Di(tributylstannyl)benzene (4). A solution of *tert*-butyllithium (60 mL, 1.7 M in pentane, 0.10 mol) was added dropwise to a stirred, cooled (−78 °C) solution of compound **1** (10.00 g, 0.042 mol) in dry THF (200 mL) under an atmosphere of dry nitrogen, and the mixture was stirred at −78 °C for 4 h. Freshly distilled tributyltin chloride (27.6 mL, 0.10 mol) was added dropwise, and the mixture was allowed to attain room temperature overnight. The mixture was poured into aqueous ammonium chloride and the product was extracted into ether (twice), and the combined extracts were washed with brine and dried (MgSO$_4$). The solvent was removed in vacuo and the crude product was purified by distillation to yield a colorless oil.

Yield: 13.73 g (82%). bp: 240−242 °C at 1 mmHg. ^{1}H NMR (CDCl$_3$): δ 0.90 (18H, t), 1.05 (12H, t), 1.35 (12H, sext), 1.51 (12H, quint), 7.40 (4H, s). IR $\nu_{\max}$ (cm^{-1}): 3040, 2960, 2920, 2880, 1465, 1375, 1075, 790, 690. MS (*m*/*z*): 656 (M$^+$), 595, 550, 486, 426, 369, 311, 197.

1,4-Dioctyloxybenzene (6). A stirred mixture of compound **5** (24.05 g, 0.22 mol), 1-bromooctane (127.10 g, 0.66 mol), and potassium carbonate (121.00 g, 0.88 mol) in butanone (500 mL) was heated under reflux for 48 h (GLC analysis indicated a complete reaction). The mixture was cooled and filtered and the solvent was removed in vacuo. The product was crystallized from ethanol to yield colorless crystals.

Yield: 61.29 g (84%). mp: 56−57 °C. ^{1}H NMR (CDCl$_3$): δ 0.90 (6H, t), 1.20−1.55 (20H, m), 1.75 (4H, quint), 3.90 (4H, t), 6.80 (4H, s). IR $\nu_{\max}$ (cm^{-1}): 3420, 2950, 2925, 2915, 2850, 1510, 1470, 1390, 1240, 1215, 1030, 825. MS (*m*/*z*): 334 (M$^+$), 222, 110, 69.

1,4-Dibromo-2,5-dioctyloxybenzene (7). Bromine (73.20 g, 0.46 mol) was added dropwise to a stirred, refluxing solution of compound **6** (61.30 g, 0.18 mol) in chloroform (400 mL), under an atmosphere of dry nitrogen. The mixture was heated under reflux overnight, cooled, and then washed with water, saturated aqueous sodium metabisulfite, and water, and the chloroform layer was dried (MgSO$_4$) and the solvent was removed in vacuo. The crude product was crystallized from ethanol to yield colorless crystals.

Yield: 72.25 g (80%). mp: 84−86 °C. ^{1}H NMR (CDCl$_3$): δ 0.90 (6H, t), 1.20−1.45 (16H, m), 1.50 (4H, quint), 1.80 (4H, quint), 3.95 (4H, t), 7.10 (2H, s). IR $\nu_{\max}$ (cm^{-1}): 2950, 2920, 2845, 1490, 1455, 1390, 1355, 1270, 1210, 1065, 1030, 1000, 850, 805. MS (*m*/*z*): 494 (M$^+$), 492 (M$^+$), 490 (M$^+$), 380, 268, 113, 69, 57.

1,4-Diiodo-2,5-dioctyloxybenzene (8). A mixture of compound **6** (65.84 g, 0.20 mol), iodine (55.20 g, 0.22 mol), potassium iodate (16.85 g, 0.08 mol), glacial acetic acid (600 mL), water (60 mL), and concentrated sulfuric acid (6 mL) was heated under reflux for 6 h. The mixture was cooled, and 20% aqueous sodium sulfate was added until the brown iodine color was no longer visible. The reaction mixture was filtered and the precipitate was washed with cold ethanol (500 mL). The crude product was recrystallized from ethanol/chloroform (1:1) to yield a light gray/brown crystalline solid.

Yield: 93.24 g (81%). mp: 52−53 °C. ^{1}H NMR (CDCl$_3$): δ 0.90 (6H, t), 1.20−1.40 (16H, m), 1.50 (4H, quint), 1.80 (4H, quint), 3.95 (4H, t), 7.15 (2H, s). IR $\nu_{\max}$ (cm^{-1}): 2925, 2860, 1490, 1485, 1390, 1355, 1265, 1220, 1070, 1020, 960, 845, 785, 720. MS (*m*/*z*): 586 (M$^+$), 361, 277, 235, 112, 55.

2,5-Dioctyloxyphenyl-1,4-diboronic Acid (9). *Method 1.* A solution of *tert*-butyllithium (287 mL, 1.7 M in pentane, 0.49 mol) was added dropwise to a stirred, refluxing mixture of compound **7** (80.00 g, 0.163 mol) in dry hexane (500 mL) under dry nitrogen, and the mixture was heated under reflux overnight. The mixture was cooled to −78 °C, trimethyl borate (152.50 g, 1.47 mol) was added dropwise at −78 °C, the mixture was allowed to attain room temperature overnight, and 10% aqueous hydrochloric acid (400 mL) was added. The product was extracted into ether (twice) and the combined ether layers were washed with water and dried (MgSO$_4$). The solvent was removed in vacuo and the crude product was crystallized from ethanol−water (1:1) to yield a colorless powder.

Yield: 32.05 g (47%).

---

(32) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(33) Tayim, H. A.; Bouldoukian, A.; Awad, F. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3799.

Method 2. Quantities: compound **8** (50.00 g, 0.09 mol), *tert*-butyllithium (251 mL, 1.7 M in pentane, 0.43 mol), and trimethyl borate (80.00 g, 0.77 mol).

The experimental procedure was as described for Method 1, except that compound **8** was used in place of compound **7**, to yield a colorless powder.

Yield: 24.00 g (67%).

1,4-Dioctyloxy-2,5-di[1,3,2]dioxaborin-2-ylbenzene (10). Quantities: compound **9** (20.00 g, 0.047 mol), propane-1,3-diol (14.50 g, 0.191 mol), and toluene (500 mL).

The experimental procedure was as described for the preparation of compound **3**. The crude product was purified by column chromatography (silica gel/hexane−dichloromethane, 1:1) to give a colorless solid which was crystallized from ethanol to yield a white crystalline solid.

Yield: 9.20 g (39%). mp: 115−116 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (6H, t), 1.20−1.45 (16H, m), 1.50 (4H, quint), 1.80 (4H, quint), 2.05 (4H, quint), 3.90 (4H, t), 4.15 (8H, t), 7.20 (2H, s). IR ν_{max} (cm^{-1}): 2940, 2900, 2820, 1480, 1415, 1385, 1275, 1150, 1125, 915, 720, 585. MS (*m*/*z*): 502 (M$^+$), 390, 278.

Attempted Preparation of 1,4-Dioctyloxy-2,5-di(tributylstannyl)benzene (11). A solution of *tert*-butyllithium (118 mL, 1.7 M in pentane, 0.20 mol) was added dropwise to a stirred, refluxing mixture of compound **7** (24.00 g, 0.050 mol) in dry hexane (200 mL) under dry nitrogen, and the mixture was heated under reflux overnight. The mixture was cooled to −78 °C and freshly distilled tributyltin chloride (66.63, 0.20 mol) was added dropwise; the mixture was allowed to attain room temperature overnight. The mixture was poured into aqueous ammonium chloride and the product was extracted into ether (twice); the combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by column chromatography (silica gel/hexane) to yield a colorless solid, which was shown to be compound **6** (12.5 g, 75%).

4,4″-Dibromo-2′,5′-dioctyloxy-[1,1′:4′,1″]-terphenyl (13). Tetrakis(triphenylphosphine)palladium(0) (1.30 g, 1.12 mmol) was added in one portion to a stirred, degassed mixture of compound **12** (5.40 g, 0.02 mol), sodium carbonate (6.00 g), 1,2-dimethoxyethane (20 mL), and water (60 mL) under dry nitrogen at room temperature. The mixture was heated under reflux and a solution of compound **9** (2.00 g, 4.74 mmol) in 1,2-dimethoxyethane (40 mL) was added dropwise. The mixture was heated under reflux overnight and allowed to cool; water was added and the product was extracted into ether (twice). The combined ethereal extracts were washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by column chromatography (silica gel/hexane with the gradual introduction of dichloromethane) to give a colorless solid, which was crystallized from ethanol to yield colorless crystals.

Yield: 2.10 g (69%). mp: 90−92 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (6H, t), 1.20−1.40 (20H, m), 1.65 (4H, quint), 3.90 (4H, t), 6.90 (2H, s), 7.50 (8H, m). IR ν_{max} (cm^{-1}): 2960, 2920, 2860, 1515, 1485, 1460, 1385, 1225, 1050, 1010, 915. MS (*m*/*z*): 646 (M$^+$), 644 (M$^+$), 642 (M$^+$), 421, 338, 260, 71, 57.

2′,5′-Dioctyloxy-[1,1′:4′,1″]-terphenyl-4,4″-diboronic Acid (14). Compound **13** (5.04 g, 7.82 mmol) was dissolved in dry THF (150 mL) and 20 mL of the solution was added to a mixture of freshly ground magnesium turnings (0.80 g, 0.03 mol) and 1,2-dibromoethane (5 drops), under dry nitrogen. The mixture was heated vigorously to initiate the reaction, and the remainder of the solution of compound **13** was added dropwise, with stirring, to the refluxing reaction mixture. The mixture was heated under reflux for 2 h (GLC analysis indicated a complete reaction) and then cooled to −78 °C. A solution of trimethyl borate (6.55 g, 0.06 mol) in dry THF (100 mL) was added dropwise to the cooled mixture, which was then allowed to attain room temperature overnight, and 10% hydrochloric acid (100 mL) was added. The product was extracted into ether (twice), the combined ether extracts were washed with water, dried ($MgSO_4$), and filtered, and the solvent was removed in vacuo. The residue was loaded onto a short chromatographic column (silica gel/dichloromethane) and eluted to remove all possible materials from the column. The silica gel was then added to THF (500 mL), and the mixture was heated to reflux and filtered while hot. The procedure was repeated 3 times in order to extract all of the product. The THF filtrates were combined and the solvent was removed in vacuo, to yield a gray, fluorescent crystalline solid.

Yield: 3.76 g (84%).

2′,5′-Dioctyloxy-4,4″-di[1,3,2]dioxaborin-2-yl-[1,1′:4′,1″]-terphenyl (15). Quantities: compound **14** (3.65 g, 0.01 mol), propane-1,3-diol (3.05 g, 0.040 mol), and toluene (200 mL).

The experimental procedure was as described for the preparation of compound **3**. The crude product was purified by column chromatography (silica gel/hexane−dichloromethane, 1:1) to give a colorless solid which was crystallized from ethyl acetate to yield a white crystalline solid.

Yield: 0.9 g (22%). mp: 120−122 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (6H, t), 1.20−1.40 (20H, m), 1.65 (4H, quint), 2.10 (4H, quint), 3.90 (4H, t), 4.20 (8H, t), 7.00 (2H, s), 7.60 (4H, d), 7.80, (4H, d). IR ν_{max} (cm^{-1}): 2930, 2860, 1620, 1490, 1390, 1350, 1320, 1280, 1210, 1160, 1130, 1050, 850, 650. MS (*m*/*z*): 654 (M$^+$), 571, 429, 346, 216, 102, 71, 57.

Poly(2,5-dioctyloxy-4,4′-biphenyl) (16). Tetrakis(triphenylphosphine)palladium(0) (0.0169 g, 0.015 mmol) was added in one portion to a stirred, degassed mixture of compound **7** (1.4379 g, 2.92 mmol), sodium carbonate (2.00 g), 1,2-dimethoxyethane (20 mL), and water (20 mL) under dry nitrogen at room temperature. The mixture was heated under reflux and a solution of compound **3** (0.7181 g, 2.92 mmol) in 1,2-dimethoxyethane (20 mL) was added dropwise. The mixture was heated under reflux overnight and allowed to cool. Water (100 mL) and acetone (100 mL) were added, and the crude product was filtered off, washed with 10% hydrochloric acid, water, and acetone, and dried in vacuo. The product was continuously extracted into toluene over 24 h using a Soxhlet apparatus. The solution was concentrated (20 mL) in vacuo and poured into acetone (100 mL). The resulting precipitate was filtered off, washed with acetone, and dried in vacuo to yield an off-white solid.

Yield: 0.78 g (66%). GPC: $M_n = 8343$ g mol^{-1} (DP 20.42), $M_w = 10\,020$ g mol^{-1} (DP 24.52). Polydispersity: 1.20.

Poly(2,5-dioctyloxy-4,4′-biphenyl) (17). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0169 g, 0.015 mmol), compound **7** (1.4375 g, 2.92 mmol), anhydrous tripotassium phosphate (2.00 g, 8.75 mmol), and compound **3** (0.7181 g, 2.92 mmol).

The experimental procedure was as described for the preparation of polymer **16**, except that dry *N*,*N*-dimethyl formamide was used as the solvent (no water) and that the mixture was heated to 110 °C to yield an off-white solid.

Yield: 0.61 g (51%). GPC: $M_n = 5998$ g mol^{-1} (DP 14.68), $M_w = 7120$ g mol^{-1} (DP 17.42). Polydispersity: 1.19.

Poly(2,5-dioctyloxy-4,4′-biphenyl) (18). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0171 g, 0.015 mmol), compound **7** (1.4380 g, 2.92 mmol), sodium carbonate (2.00 g), and compound **3** (0.7179 g, 2.92 mmol).

The experimental procedure was as described for the preparation of polymer **16**, except that toluene and water were used as the solvent system, to yield an off-white solid.

Yield: 0.81 g (68%). GPC: $M_n = 11\,432$ g mol^{-1} (DP 27.98), $M_w = 12\,879$ g mol^{-1} (DP 31.52). Polydispersity: 1.13.

Poly(2,5-dioctyloxy-4,4′-biphenyl) (19). Quantities were as follows: dichloro[1,1′-bis(diphenylphosphino)ferrocene]-palladium(II) (0.0113 g, 0.015 mmol), compound **7** (1.4377 g, 2.92 mmol), sodium carbonate (2.00 g), and compound **3** (0.7177 g, 2.92 mmol).

The experimental procedure was as described for the preparation of polymer **16**, except for the different catalyst and that toluene and water were used as the solvent system, to yield an off-white solid.

Yield: 0.65 g (55%). GPC: $M_n = 7874$ g mol^{-1} (DP 19.27), $M_w = 9930$ g mol^{-1} (DP 24.30). Polydispersity: 1.26.

Poly(2,5-dioctyloxy-4,4′-biphenyl) (20). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0175 g, 0.015 mmol), compound **1** (0.6890 g, 2.92 mmol), sodium carbonate (2.00 g), and compound **10** (1.4661 g, 2.92 mmol).

The experimental procedure was as described for the preparation of polymer **18** to yield an off-white solid.

Yield: 0.73 g (61%). GPC: $M_n = 5990$ g mol^{-1} (DP 14.66), $M_w = 6244$ g mol^{-1} (DP 15.28). Polydispersity: 1.04.

Poly(2,5-dioctyloxy-4,4′-biphenyl) (21). Quantities were as follows: dichlorobis(triphenylphosphine)palladium(II) (0.0108 g, 0.015 mmol), compound **7** (1.4410 g, 2.91 mmol), and compound **4** (1.9132 g, 2.91 mmol).

The experimental procedure was as described for the preparation of polymer **17**, except for the different catalyst and that no base was used, to yield a brown solid.

Yield: 0.65 g (55%). GPC: $M_n = 9430$ g mol^{-1} (DP 23.08), $M_w = 10\,002$ g mol^{-1} (DP 24.48). Polydispersity: 1.06.

1,3-Dibromo-5-nitro-2-octyloxybenzene (23). Quantities were as follows: compound **22** (25.05 g, 0.08 mol), 1-bromooctane (49.10 g, 0.25 mol), potassium carbonate (47.16 g, 0.34 mol), and butanone (500 mL).

The experimental procedure was as described for the preparation of compound **6**. The excess of 1-bromooctane was removed by distillation (bp 79−81 °C at 11 mmHg), and the residue was purified by column chromatography (silica gel/hexane with the gradual introduction of dichloromethane) to yield a yellow oil.

Yield: 21.43 g (62%). ^{1}H NMR (CDCl$_3$): δ 0.90 (3H, t), 1.20−1.45 (10H, m), 1.90 (2H, quint), 4.10 (2H, t), 8.40 (2H, s). IR $\nu_{\max}$ (cm^{-1}): 3100, 2940, 2840, 1530, 1440, 1385, 1345, 1260, 1135, 1075, 960, 900, 740. MS (*m/z*): 411 (M$^+$), 409 (M$^+$), 407 (M$^+$), 267, 185.

Poly(5-nitro-2-octyloxy-3,4′-biphenyl) (24). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0175 g, 0.015 mmol), compound **23** (1.1917 g, 2.91 mmol), sodium carbonate (2.00 g), and compound **3** (0.7154 g, 2.91 mmol).

The experimental procedure was as described for the preparation of polymer **18** to yield a yellow solid.

Yield: 0.60 g (63%). GPC: $M_n = 7160$ g mol^{-1} (DP 22.00), $M_w = 8921$ g mol^{-1} (DP 27.41). Polydispersity: 1.25.

3,5-Dibromo-4-octyloxybenzonitrile (26). Quantities were as follows: compound **25** (10.00 g, 0.04 mol), 1-bromooctane (21.25 g, 0.11 mol), potassium carbonate (20.62 g, 0.15 mol), and butanone (250 mL).

The experimental procedure was as described for the preparation of compound **23** to yield a colorless oil.

Yield: 13.41 g (95%). ^{1}H NMR (CDCl$_3$): δ 0.90 (3H, t), 1.20−1.45 (8H, m), 1.50 (2H, quint), 1.90 (2H, quint) 4.10 (2H, t), 7.80 (2H, s). IR $\nu_{\max}$ (cm^{-1}): 2940, 2860, 2240, 1540, 1450, 1390, 1270, 970, 885, 755, 615. MS (*m/z*): 391 (M$^+$), 389 (M$^+$), 387 (M$^+$), 267, 223, 171.

Poly(5-cyano-2-octyloxy-3,4′-biphenyl) (27). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0164 g, 0.014 mmol), compound **26** (1.1329 g, 2.91 mmol), sodium carbonate (2.00 g), and compound **3** (0.7163 g, 2.91 mmol).

The experimental procedure was as described for the preparation of polymer **18** to yield a gray solid.

Yield: 0.56 g (63%). GPC: $M_n = 7203$ g mol^{-1} (DP 23.58). $M_w = 8430$ g mol^{-1} (DP 27.60). Polydispersity: 1.17.

Poly(2,5,2″,5″-tetraoctyloxy-4,4‴-[1,1′:4′,1″:4″,1‴]-quaterphenyl) (28). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0036 g, 0.003 mmol), compound **7** (0.1395 g, 0.28 mmol), sodium carbonate (0.50 g), and compound **15** (0.1863 g, 0.28 mmol).

The experimental procedure was as described for the preparation of polymer **18** to yield an off-white solid.

Yield: 0.14 g (61%). GPC: $M_n = 16\,646$ g mol^{-1} (DP 20.37), $M_w = 18\,737$ g mol^{-1} (DP 22.93). Polydispersity: 1.13.

Poly(2,5-difluoro-2″,5″-dioctyloxy-4,4‴-[1,1′:4′,1″:4″,1‴]-quaterphenyl) (30). Quantities were as follows: tetrakis-(triphenylphosphine)palladium(0) (0.0031 g, 0.003 mmol), compound **29** (0.0653 g, 0.24 mmol), sodium carbonate (0.50 g), and compound **15** (0.1570 g, 0.24 mmol).

The experimental procedure was as described for the preparation of compound **18** to yield an off-white solid.

Yield: 0.09 g (63%). GPC: $M_n = 13\,063$ g mol^{-1} (DP 21.89), $M_w = 14\,757$ g mol^{-1} (DP 24.73). Polydispersity: 1.13.

Poly(2′,5′-dioctyloxy-4-(5-thiophen-2-yl)-4″-[1,1′:4′,1″]-terphenyl) (32). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0042 g, 0.004 mmol), compound **31** (0.0655 g, 0.27 mmol), sodium carbonate (0.50 g), and compound **15** (0.1772 g, 0.27 mmol).

The experimental procedure was as described for the preparation of polymer **18** to yield a pale yellow solid.

Yield: 0.07 g (46%). GPC: $M_n = 11\,592$ g mol^{-1} (DP 20.45), $M_w = 13\,620$ g mol^{-1} (DP 24.03). Polydispersity: 1.17.

4-Bromo-2,5-dioctyloxybenzoic Acid (33). A solution of *n*-butyllithium (5.9 mL, 2.5 M in hexane, 0.02 mol) was added dropwise to a stirred, cooled (−78 °C) solution of compound **7** (6.00 g, 0.01 mol) in dry THF (200 mL) under dry nitrogen. The reaction mixture was stirred at −78 °C for 1 h, and the reaction mixture was poured onto a large excess of solid carbon dioxide. The reaction mixture was allowed to warm to room temperature overnight and was acidified with ice-cold 36% hydrochloric acid. The product was extracted into ether (twice); the combined ether extracts were washed with water and dried (MgSO$_4$). The solvent was removed in vacuo, and the crude product was purified by column chromatography [silica gel/hexane−dichloromethane, 1:1, with the gradual change to dichloromethane] to yield a colorless solid.

Yield: 4.11 g (74%). mp: 88−90 °C. ^{1}H NMR (CDCl$_3$): δ 0.90 (6H, t), 1.20−1.55 (20H, m), 1.80 (4H, m), 4.05 (2H, t), 4.20 (2H, t), 7.30 (1H, s), 7.65 (1H, s), 11.0 (1H, s). IR $\nu_{\max}$ (cm^{-1}): 2960, 2940, 2860, 1680, 1500, 1450, 1380, 1270, 1220, 1040, 1010, 770. MS (*m/z*): 458 (M$^+$), 456 (M$^+$), 346, 248, 234, 216, 154, 136, 71.

***N*-(4-Bromophenyl) 4-bromo-2,5-dioctyloxybenzamide (36).** A solution of oxalyl chloride (1.94 g, 0.02 mol) in dry benzene (20 mL) was added dropwise to a stirred solution of compound **33** (3.50 g, 0.01 mol) and DMF (5 drops) in dry benzene (100 mL), and the mixture was stirred at room temperature overnight. The excess of oxalyl chloride and the solvent were removed in vacuo, and the residual crude 4-bromo-2,5-dioctyloxybenzoyl chloride (compound **34**) was dissolved in dry DME (30 mL) and added dropwise to a stirred solution of compound **35** (2.87 g, 0.02 mol) in dry DME (70 mL) at room temperature. The mixture was stirred at −76 °C for 30 min. 10% Hydrochloric acid was added, and the crude product was filtered, washed with water, and recrystallized from ethanol to yield colorless crystals.

Yield: 2.69 g (57%). mp: 83−85 °C. ^{1}H NMR (CDCl$_3$): δ 0.90 (6H, m), 1.20−1.55 (20H, m), 1.83 (2H, quint), 1.96 (2H, quint), 4.08 (2H, t), 4.15 (2H, t), 7.23 (1H, s), 7.50 (4H, 2xd), 7.81 (1H, s), 10.27 (1H, s). IR $\nu_{\max}$ (cm^{-1}): 3330, 2920, 2840, 1650, 1590, 1530, 1490, 1460, 1390, 1210, 1040, 780. MS (*m/z*): 613 (M$^+$), 611 (M$^+$), 609 (M$^+$), 439, 387, 329, 305, 215, 171, 136, 91.

Poly(*N*-(4-phenyl) 4′-(2,5-dioctyloxy)-4-biphenylcarboxamide) (37). Quantities were as follows: tetrakis(triphenylphosphine)palladium(0) (0.0168 g, 0.014 mmol), compound **36** (1.7788 g, 2.91 mmol), sodium carbonate (2.00 g), and compound **3** (0.7155 g, 2.91 mmol).

The experimental procedure was as described for the preparation of polymer **18** to yield a pale yellow solid.

Yield: 1.18 g (77%). GPC: $M_n = 9662$ g mol^{-1} (DP 18.31), $M_w = 12\,022$ g mol^{-1} (DP 22.78). Polydispersity: 1.24.

Acknowledgment. We thank the Department of Chemistry, University of Hull for providing research facilities, and the EPSRC for financial support.

CM0493694