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Functionalized Poly- and Oligo-phenylenes: Variations on the Suzuki Cross-Coupling of Functionalized Aryl Dibromides with the 1,3-Propanediol Diester of 2,5-Dialkyl-1,4-phenylenediboronic Acid[1]

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The synthesis of substituted poly(phenylene)s, in particular poly(1,4-phenylene)s, by palladium-catalyzed Suzuki coupling of the 1,3-propanediol diester of 2,5-dialkyl-1,4-phenylenediboronic acid with various aryl dibromides is described. Optimized reaction conditions for the polymerization of nitro group containing monomers were developed in this study. For example, poly(4,6-dinitro-2',5'-dihexyl-3,4'-biphenylylene) was obtained at 37 °C with the catalyst dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) [$PdCl_2$(dppf)] in THF and aqueous $NaHCO_3$ in quantitative yield with a number average degree of polymerization of $P_n = 27$. These reaction conditions are among the mildest reported in the literature. Monomers, not only with the nitro group, but also with the following substituents were polymerized: fluoro, nitrile, *N,N*-dimethylamino, and trifluoromethyl. 2,5-Dibromopyridine was also used as monomer. The polymers gave M_n values of typically 3 - 7 kg / mol except for the nitrile-substituted polymer poly[(2,5-didodecyl-1,4-phenylene)-*alt*-(2-cyano-1,4-phenylene;3-cyano-1,4-phenylene)] which had a $M_n = 87$ kg/mol and $P_n = 130$. © 1997 Elsevier Science Ltd.

1 Introduction

We are employing transition metal-catalyzed aryl coupling reactions[2,3] in order to synthesize functionalized poly(phenylene)s.[4-10] The Suzuki cross-coupling links arylboronic acids or their esters (as organometallic equivalents) and aryl halogenides under catalysis of palladium compounds. Arylboronic acids and esters are stable, crystalline, and easy-to-purify compounds at ambient conditions; and a great many of substituents have been shown to be compatible with the conditions of Suzuki coupling.[11-13] Furthermore, Suzuki coupling also allows the high-yield coupling of aryl compounds bearing substituents in an ortho-position.[14] It is, therefore, an interesting method for the production of substituted poly(phenylene)s.

Variations on the original conditons as reported by Suzuki were tailored for specific cases. Some of these conditions or "protocols" are listed in Table 1. The work refered to in protocols 1 through 7 of Table 1 deals with the synthesis of biaryls. Protocols 1, 4 and 5 describe the conditions used for the coupling of nitro-substituted aryl bromides; protocols 2 and 3 have been used for couplings where the positions ortho to the coupling site were occupied with methyl groups. Protocol 6 describes the only use of dichloro[1,1'-bis(diphenylphosphino)-ferrocene]palladium(II) [$PdCl_2$(dppf)] so far to produce biaryl compounds. Protocol 7 depicts the use of a recently developed catalyst showing the highest activity of any catalyst employed until now for Suzuki couplings of phenylboronic acid with certain bromobenzenes. Protocols 1[15,16] and 8 have been used for the synthesis of substituted poly(1,4-phenylene)s.

Here we report optimized conditions for the polymerization through Suzuki coupling of nitro-substituted dibromobenzenes (section 2) and other aryl dibromides (section 3) with the ester of alkyl-substituted phenylenediboronic acid. Protocols 9 through 11 describe these developments. This study also contains a description of the synthesis and characterization of ten novel poly(phenylene)s with the following substituents: nitro, fluoro, nitrile, N,N-dimethylamino, trifluoromethyl.

2 Polymerization of Dibromobenzenes 2 and 4a to 4c Substituted with Nitro Groups

We are investigating the polymerization of dibromobenzenes bearing nitro groups because the nitro group on the polymer can be reduced to a polymeric amine.[25,26,27] The resulting materials are likely to have interesting electronic and chemical properties. Few reports concerning polymers with nitro substituents appended to a fully conjugated backbone appeared in the literature: The syntheses of poly(1,4-phenylene)-vinylenes with no more than one nitro group on each benzene ring were reported using a variety of preparative strategies.[28-31] Also Ullmann coupling of 4,4'-diiodo-3,3'-dinitro-biphenyl produced a completely insoluble nitro-substituted poly(1,4-phenylene).[32]

Suzuki coupling between nitrobromobenzenes and arylboronic acids to give biaryls have appeared in the literature: Bromonitrobenzene and phenylboronic acids with methyl substituents were coupled (protocol 1, Table 1) to give yields greater than 95 % for a variety of substitution patterns. Only for 2-nitrobromobenzene and 2,4,6-(trimethylphenyl)boronic acid, where steric congestion interfered with the coupling, did the yield drop to 88 %.[33] In another study phenylboronic acid was coupled with 3-, 4-, or 5-nitro-2-methyl-bromobenzene and also (2-methylphenyl)boronic acid with 2-nitro-bromobenzene in a yield greater than 95 % (protocol 4, Table 1).[34] Furthermore phenylboronic acid was coupled with 4-bromonitrobenzene in a yield greater than 95 % (protocol 5, Table 1).[35] In a number of studies the coupling of nitro-substiuted phenylboronic acids with aryl bromides were undertaken, which resulted in varying yields.[33,36,17,18]

This study revealed that none of the above mentioned Suzuki coupling conditions led to polymers when applied to dibromobenzenes containing a nitro group despite the satisfactory yields reported for the model biphenyls. We used the Suzuki coupling as described by protocols 9 through 11, which were developed in this study, to polymerize the nitrodibromobenzenes 2 (section 2.1; Scheme 1) and 4a-c (section 2.2; Scheme 3) with the 1,3-propanediol diester of 2,5-dihexyl-1,4-phenylenediboronic acid (1a). The results of selected, representative trials for the polymerization of monomer 2 are listed in Table 2. The molar masses of the polymers derived from 4a - 4c are reported in Table 3 and their compositional data in Table 5.

Table 1: Reaction conditions of Suzuki couplings known from the literature (No. 1 - 8) and developed in this study (No. 9 - 11)

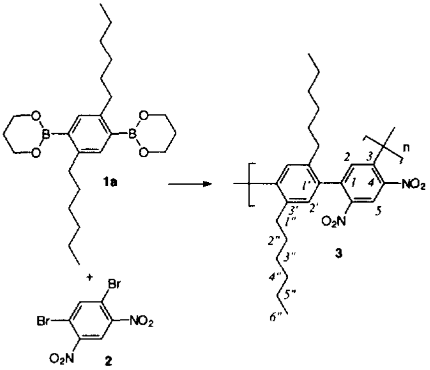
No.	protocol	equiv.[a]	conc. / mol×l^{-1}	aqu. base	organic phase	equiv.[a] ×100	catalyst	T / °C	t / h
1	Suzuki I [11]	2	2	Na_2CO_3	benzene[b]	3	$Pd(PPh_3)_4$	reflux	
2	Suzuki II [17,18]	1.5		Tl_2CO_3	benzene[c,d]	3	$Pd(PPh_3)_4$	80	6
3	Suzuki III [19]	1.5	1.5	$Ba(OH)_2$	1,2-dimethoxyethane	2	$Pd(PPh_3)_4$	80	20
4	Gronowitz [12]	2	2	Na_2CO_3	1,2-dimethoxyethane	3	$Pd(PPh_3)_4$	reflux	
5	Beletskaya [20]	2.5		K_2CO_3	acetone[e]	2	$Pd(OAc)_2$	65	2.5
6	Thompson [21]	1.4		$N(Et)_3$	DMF[c]	3	$PdCl_2(dppf)$	90	12
7	Herrmann, Beller [22,23]	2		K_2CO_3	ortho-xylene[c]	0.05	palladacycle[f]	130	16
8	Rulkens, Wegner [24]	6	1.5	Na_2CO_3	THF, toluene[g]	1[h]	$Pd(PPh_3)_4$	75[h]	72[h]
9	funct. poly-*p*-phenylenes **6c-i** [i]	10	2	$NaHCO_3$	THF[g]	1	$Pd(PPh_3)_4$	75	72
10	nitro-trimer **5**, -polymer **6a,b** [i]	2	2	Na_2CO_3	THF, toluene[g]	1	$Pd(PPh_3)_4$	45	36
11	nitro-polymer **3** [i]	2	2	$NaHCO_3$	THF[g]	1.5	$PdCl_2(dppf)$	37	36

[a]: equiv. per coupling unit - [b]: dissolution of the boronic acid in a minute amount of ethanol - [c]: no water is used - [d]: the dibutyl ester of the boronic acid is used - [e]: acetone : water = 1 : 1 by volume, the original Beletskaya procedure uses DMF instead of acetone - [f]: 1.5 equiv. of phenylboronic acid used; *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) as palladacycle used - [g]: the 1,3-propanediol ester of the boronic acid is used - [h]: original reference: 0.003 equiv. catalyst and 11 days at a bath temperature of 100 °C - [i]: this work.

2.1 Improving Suzuki Coupling: Polymerization of 2 with 1a

The accepted mechanism[12,37,38] of the Suzuki coupling involves oxidative addition of the aryl halogenide to a palladium (0) species to form an aryl palladium (II) halide. By inductive effect and by resonance, this step should be favored with an aryl bromide substituted with an electron withdrawing group in the ortho or para position. Therefore we started out with a monomer having nitro groups both in ortho and para positions for each bromine atom, 1,5-dibromo-2,4-dinitrobenzene (2). Compound 2 was polymerized with 2,5-dihexyl-1,4-phenylenediboronic acid (1a), to give the nitro-substituted polymer 3. Scheme 1 sketches this reaction; the molar mass data and the experimental conditions for the most successful trial producing 3 are given in entry 1 of Table 2.

A typical protocol used for polymerizations involving Suzuki coupling of aromatic rings is given in entry 1 of Table 1 [15,16] and employs palladium(0)tetrakis(triphenylphosphine) [$Pd(PPh_3)_4$] as catalyst at temperatures of at least 80 °C; however, we found that switching to $PdCl_2(dppf)$ and lowering the temperature to 37 °C gave higher molar mass polymers that were compositionally more pure as will be outlined below.



Scheme 1

Polymer 3 was well characterized by elemental analysis (Table 2, entry 1) and was nearly colorless with a slightly yellowish tint. The polymer was soluble in common organic solvents like toluene, THF, or CH_2Cl_2. It was insoluble in methanol or acetone. The ^1H NMR spectrum (Figure 1) shows three peaks in the aromatic region for the three heterotopic protons of the repeat unit and four peaks for the hexyl chain. The ^{13}C NMR spectrum (Figure 2) shows seven peaks in the aromatic region for the seven heterotopic carbon atoms of the repeat unit and six peaks for the hexyl chains. Peaks suggesting end groups or compositional inhomogenities are absent. Molar masses, molar mass distributions and elemental compositions depend on the polymerization conditions as shown in Table 3.2.

Figure 1: ^{1}H-NMR spectrum of 3 in tetrachloroethane-d2 at 100 °C

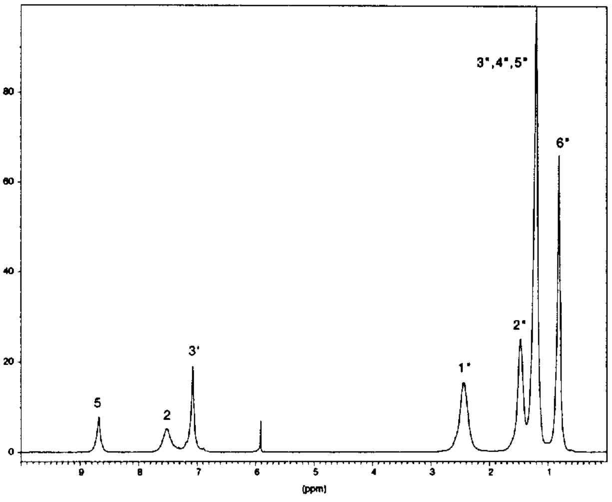
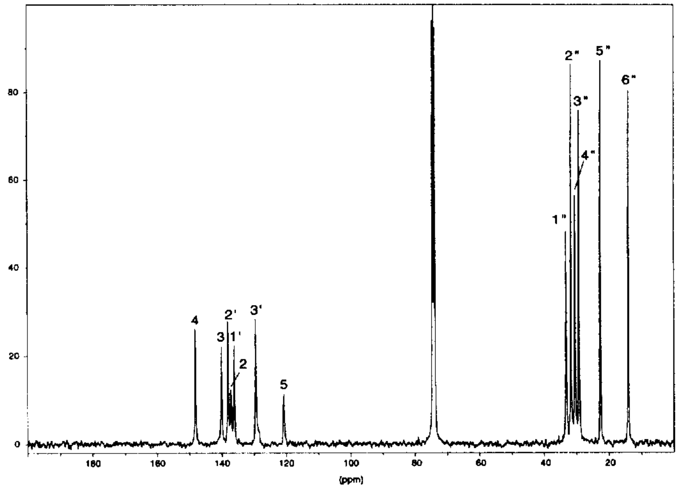


Figure 2: ^{13}C-NMR spectrum of 3 in tetrachloroethane-d2 at 100 °C



2.1.1 Polymerizations at 80 °C

As mentioned above, typical Suzuki couplings are carried out at temperatures well above 70 °C. Using this as a basis, we examined the effect of varying the catalyst on the polymerization to find that in the presence of Tl_2CO_3, the strongest base used in these experiments, and with THF as the solvent, $PdCl_2$(dppf) gave the highest yields and molar masses. Based on these two criteria, the catalysts were ranked as follows: $PdCl_2(PPh_3)_2$ (entry 11, Table 2) << $Pd(PPh_3)_4$ (entry 12) < $Pd(OAc)_2(PPh_3)_2$ (entry 13) < $PdCl_2$(dppf). Further

Table 2: Selective, representative trials for the polymerization of 1a with 2 to form polymer 3

No.	GPC[a] THF				found[b]			yield	equiv.[c]	aqueous	organic	equiv.[c]	catalyst	T[e]
	M_n	M_{peak}	M_w	D	C	H	N	/ %		base[d]	phase	x100		/ °C
1	20	35	100	5.0	[g]69.85	7.39	6.33	>95	2	$NaHCO_3$	THF	1.5	$PdCl_2(dppf)$	37
2	3.6	7.0	8.0	2.2	62.39	5.63	5.46	89	2	Na_2CO_3	THF	1.5	$PdCl_2(dppf)$	37[f]
3	4.1	7.5	13.5	3.3	67.66	6.82	5.90	>95	1	Tl_2CO_3	THF	1.5	$PdCl_2(dppf)$	37
4	7.2	9.9	12	1.7	[h]69.34	7.19	6.14	>95	1	Tl_2CO_3	THF	1.5	$PdCl_2(dppf)$	20
5	5.4	10	11	2.0	68.43	7.25	5.79	>95	2	$NaHCO_3$	THF	1.5	$Pd(PPh_3)_4$	37
6	5.2	11	12	2.2	66.82	6.82	5.90	>95	2	Na_2CO_3	THF	1.5	$Pd(PPh_3)_4$	37
7	3.4	5.5	6.6	1.9	67.47	5.69	5.44	>95	1	Tl_2CO_3	THF	1.5	$Pd(PPh_3)_4$	37
8	3.0	6.0	7.0	2.3	67.85	6.39	5.80	92	1	Tl_2CO_3	THF	1.5	$Pd(PPh_3)_4$	20
9	6.9	7.5	44	6.4	69.66	7.26	6.65	>95	2	Na_2CO_3	THF, toluene	1	$Pd(PPh_3)_4$	45
10	2.2	2.4	2.8	1.2				84	2.5	K_2CO_3	THF	2	$Pd(OAc)_2$	20
11	1.1	1.6	2.1	2.0	59.67	6.60	5.14	54	1	Tl_2CO_3	THF	1	$PdCl_2(PPh_3)_2$	80
12	1.7	5.3	6.6	3.8	66.69	7.45	5.42	51	1	Tl_2CO_3	THF	1	$Pd(PPh_3)_4$	80
13	5.3	19	20	3.8	67.58	7.47	5.96	58	1	Tl_2CO_3	THF	1	$Pd(OAc)_2(PPh_3)_2$	80
14	8.4	16	65	7.7	69.79	6.34	5.95	>95	1	Tl_2CO_3	THF, toluene	1	$Pd(PPh_3)_4$	80
15	7.7	17	54	6.8	70.06	7.13	5.88	77	2	Na_2CO_3	THF, toluene	1	$Pd(PPh_3)_4$	80
16	24	54	300	12	69.86	7.08	5.60	65	2	$NaHCO_3$	THF	1.5	$PdCl_2(dppf)$	80

[a]: polystyrene calibration, kg/mol - [b]: calculated C 70.22, H 7.37, N 6.82 - [c]: equivalents per coupling unit - [d]: base concentration 2 mol × l^{-1} - [e]: all reactions were carried out for 36 h - [f]: trial was run at 6 °C for 12 h, then at 37 °C for 36 h - [g]: Br: 0.61 % - [h]: Br: 0.77 %.

experiments revealed that Tl_2CO_3 was the best base for $Pd(PPh_3)_4$ in THF / toluene (entry 14, Table 2); Na_2CO_3 was the next best (entry 15), and $NaHCO_3$ gave only oligomers.

At high temperatures, every combination of base and catalyst yielded polymers which formed hard, brittle, brown to black films. Furthermore the yields were typically less than 100 %, the molar mass distribution was broad, and the ^{1}H-NMR spectra showed extraneous peaks. These results indicated that side reactions were occurring. Our next move was to retain the optimal catalyst, $PdCl_2$(dppf), but to temper the polymerization conditions by using the weakest base, $NaHCO_3$, in an effort to preserve the nitro compounds from decomposition.

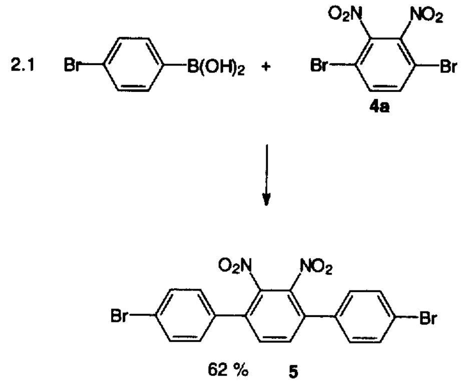
$PdCl_2$(dppf) with $NaHCO_3$ at 80 °C (entry 16, Table 2) gave the highest molar mass polymer measured in the entire study. But side reactions had not been quenched and these conditions resulted again in a low yield, broad molar mass distribution and a brown product with extraneous peaks in its ^{1}H-NMR spectrum.

In fact, subsequent ^{1}H-NMR studies revealed that the monomer 2 was unstable in a mixture devoid of catalyst, containing only aqueous base, THF and toluene at 75 °C. 2,5-Dibromonitrobenzene (4b) and 1,4-dibromo-2,5-dinitrobenzene (4c) were tested as well and, similar to 2, after 24 h at 75 °C, extraneous peaks were found in the ^{1}H NMR spectra of the nonvolatile part of the reaction mixtures. Could a temperature be reached at which the nitro compounds would not decompose but at which the monomers would still polymerize?

Transmetallation of the palladium (II) complex with the arylboronic acid is assumed to be the rate-determining step for the coupling[38,39]. Keeping this in mind, we were nevertheless encouraged to discover, that at least the first step, oxidative addition, occured instantaneously at 30 °C. The ^{1}H-NMR spectrum of an equimolar mixture of 2 and $Pd(PPh_3)_4$ in THF-d8 contained no signals characteristic of 2 immediately after mixing.

2.1.2 Polymerizations at 37 °C

Next, at a reduced temperature, we tried the coupling reaction depicted in Scheme 2. Note that a molecule of 4-bromophenylboronic acid could couple with either 1,4-dibromo-2,3-dinitrobenzene (4a) or another molecule of the boronic acid. However, when 2.1 equivalents of the boronic acid and 1 equivalent of 4a were allowed to react at 45 °C (protocol 10, Table 1), the nitro-substituted trimer 4 was isolated after 3 recrystallizations in 62 % yield.



Scheme 2

The formation of the trimer 5 demonstrates for the first time selectivity between two aryl bromides for Suzuki cross-coupling. The selectivity can be attributed to the strong activating influence of the nitro groups. So far this kind of selectivity was not deemed possible[13] because of the reaction temperature required, which is higher than that needed for other coupling methods.[40-43] Up until now it has been acknowledged only that the greater reactivity of iodides in comparison to bromides allowed selective cross-coupling.[44]

With these findings, we returned to the polymerization of 2 and retested the conditions of the last trial described (the $PdCl_2$(dppf) catalyst and aqueous $NaHCO_3$ in THF), but now at 37 °C (protocol 11, Table 1). These conditions resulted in the most successful polymerization for a nitro monomer thus far; the data for this trial are given in entry 1 of Table 2 and the polymer itself was described in more detail above.

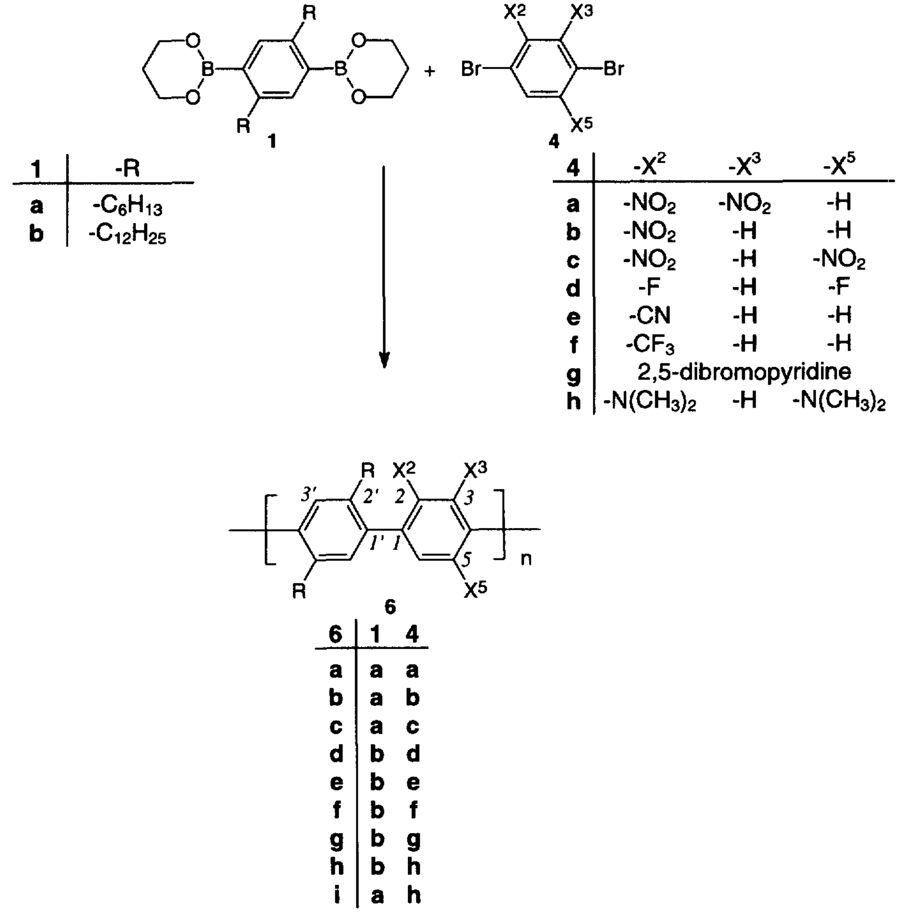
Decreasing the temperature further, we found that trials at 6 °C using the $PdCl_2$(dppf) with Na_2CO_3 gave only oligomers. Raising the temperature to 20 °C and using an even stronger base such as Tl_2CO_3 (entry 4, Table 2) also failed to improve on the results obtained with $NaHCO_3$ at 37 °C. Even at 37 °C, bases such as Na_2CO_3 (entry 2) and Tl_2CO_3 (entry 3) did not give higher degrees of polymerization; and neither did switching from $PdCl_2$(dppf) to $Pd(PPh_3)_4$ (entries 5 to 9).

It is important to note that addition of even only a few drops of toluene to a reaction mixture where $NaHCO_3$ is the base prevents coupling, regardless of the catalyst. This is because the presence of toluene in a water / THF mixture lowers the water content of the organic phase drastically and this lowers the concentration of hydroxide anions in the organic phase and concomittantly the polarity of the organic phase. In the case of aqueous $NaHCO_3$, the hydroxide ion concentration is lowered to a level which does not allow efficient displacement of the bromide anion from the organopalladium bromide by the hydroxide anion to give an organopalladium hydroxide, nor formation of the boronate anion.[38]

The result that $Pd(PPh_3)_4$ has a higher catalytic acitvity - as measured by degree of polymerization - in THF and toluene as compared to THF alone is unexplained; compare the low temperature trials (without toluene: entry 6, Table 2; with toluene: entry 9). In the presence of toluene, $Pd(PPh_3)_4$, with Na_2CO_3 produced a polymer with the second highest M_w of the study. Ligand-free palladium sources such as $Pd(OAc)_2$ gave only oligomers (entry 10). This is in contrast to published results of couplings using these catalysts in aqueous single phase systems (protocol 5, Table 1), where yields of greater than 95 % were reported.

2.2 Nitro-substituted Poly(1,4-phenylene)s 6a - 6c from 4a - 4c with 1a

Scheme 3 and Table 3 depict the polymerization of para-dibromo substituted nitrobenzenes 4a-c to give the poly(1,4-phenylene)s 6a-c, compositional data are given in Table 5.



1	-R
a	$-C_6H_{13}$
b	$-C_{12}H_{25}$

4	$-X^2$	$-X^3$	$-X^5$
a	$-NO_2$	$-NO_2$	-H
b	$-NO_2$	-H	-H
c	$-NO_2$	-H	$-NO_2$
d	-F	-H	-F
e	-CN	-H	-H
f	$-CF_3$	-H	-H
g	2,5-dibromopyridine		
h	$-N(CH_3)_2$	-H	$-N(CH_3)_2$

6	1	4
a	a	a
b	a	b
c	a	c
d	b	d
e	b	e
f	b	f
g	b	g
h	b	h
i	a	h

Scheme 3

Table 3: Molar mass data for polymerizations of functionalized aryl dibromides 4 to form functionalized poly(1,4-phenylene)s 6

	GPC[a]						
6	M_n	M_{peak}	M_w	D	P_n[b]	P_n	P_w
a	7.2	7.8	12	1.7[c]	12	18	29
b	21	65	77	3.6[c]	56	57	210
c	not soluble				14		
d	7.2	4.7/19	18	2.5[d,e]	16	14	34
e	87	820	1400	16[d]		169	2700
f	5.3	7.1	11	2.0[c]	4	10	20
g	5.9	4.6	9.6	1.6[c]	15	12	20
h	3.3	3.9	5.3	1.6[c]	5	6	9
i	4.0	4.8	5.8	1.2[c]		10	14

[a]: polystyrene calibration, kg/mol - [b]: determined from bromine contents - [c]: THF - [d]: 1,2-dichlorobenzene - [e]: sample onyl partially filtered through 1 µm membrane, bimodal distribution with a spike for the low molar mass fraction, measured at 60 °C.

The polymerizations of 4a and 4b with 1a was brought about under the conditions of protocol 10 of Table 1 at the low temperature of 45 °C which was used for the formation of the trimer 5 with 4a. Both polymers 6a and 6b were pale yellow powders. The NMR spectra of 6a showed one peak for each heterotopic nucleus (^{1}H-NMR spectrum: Figures 3; ^{13}C-NMR spectrum: Figure 4). The entries for these polymers in Table 3 list further data.

Figure 3: ^{1}H-NMR spectrum of 6a in tetrachloroethane-d2 at 80 °C

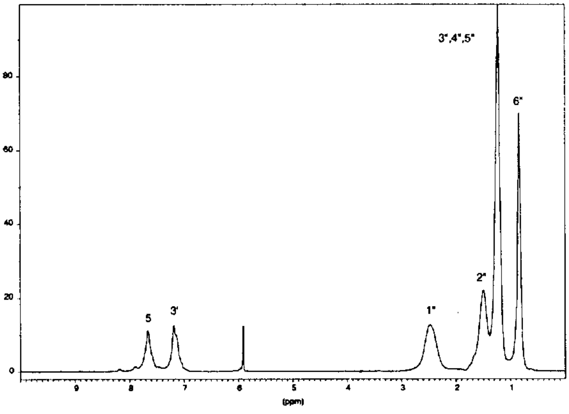
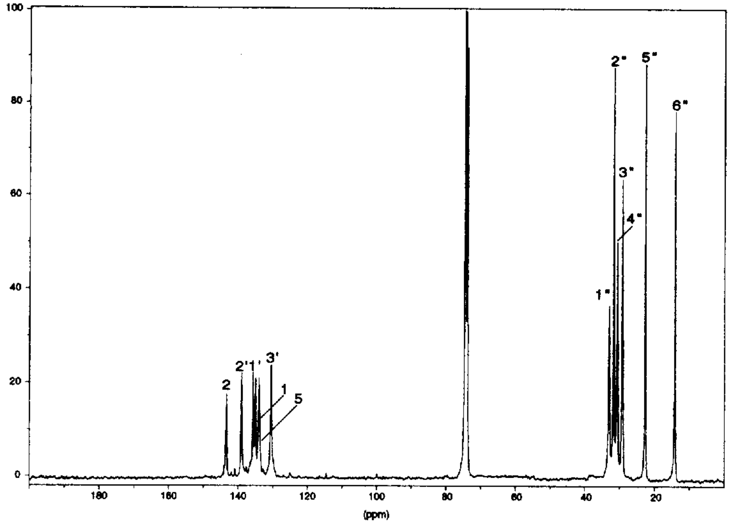


Figure 4: ^{13}C-NMR spectrum of 6a in tetrachloroethane-d2 at 80 °C



The polymerization of 4c and 1a was carried out under conditions described in protocol 9 of Table 1 (THF, $Pd(PPh_3)_4$, $NaHCO_3$, 75 °C). An insoluble, yellow material precipitated out of the reaction after only two hours, which, 72 hours later, upon isolation only swelled in nitrobenzene, 1,2-dichlorobenzene, and N-methylpyrrolidinone. Elemental composition (6c, Table 3) suggested the formation of poly(2,5-dinitro-2',5'-dihexyl-4,4'-biphenylylene) (6c) with $P_n = 14$ as estimated by the bromine contents. Since 4c eventually decomposed under the polymerization conditions (see section 2.1.1) and since the polymer nevertheless was produced, coupling had to be much faster than the side reactions in this case. Attempting the reaction with protocol 8 of Table 1 (THF / toluene, Na_2CO_3) resulted in a dark, brown precipitate in lower yield. In that case coupling appears to be slower than side reactions.

2.3 Conclusions Concerning Suzuki Coupling

The following conclusions can be drawn concerning the reaction conditions: The typical conditions for Suzuki couplings are too harsh for aromatic compounds with nitro groups. High molar mass, compositionally and constitutionally pure polymers 3 are obtained at 37 °C, instead of 80 °C, and with $NaHCO_3$ and $PdCl_2(dppf)$. Although the accelerating influence of a strong base, like TlOH, was already pointed out in the literature [45], the implications of the two-phase nature of the reaction mixture was so far not mentioned. Choosing a water-rich organic phase like THF allows the use of $NaHCO_3$, whereas a toluene / THF mixture requires Na_2CO_3.

With 1,2-dimethoxyethane as solvent for the organic phase instead of THF it was already shown in the literature that 3 equivalents $NaHCO_3$ is a strong enough base for efficient coupling.[46] In a recent investigation the usual Suzuki conditions were varied to accomodate sterically hindered boronic acids by using strong base (protocols 2 and 3, Table 1), but in our case the use of a stronger base does not pose advantages (entries 2 and 3, Table 2). In fact the conditions of protocol 11 in Table 1 we developed for the polymerization of 2 with 1a uses the exact stoichiometric amount of base required for polymerization. To our knowledge this is the first example of a successful polymerization not using excess base and one more indication of the high reactivity of the investigated system.

The higher catalytic activity of the $PdCl_2(dppf)$ catalyst in comparison to $Pd(PPh_3)_4$ in THF with nitrobromobenzenes is noteworthy. However, $PdCl_2(dppf)$ was rarely used for the cross-coupling of boronic acids: Electron-deficient substituted 6-halo-2-aminopyrazinoate esters have been cross-coupled with a variety of areneboronic acids using protocol 6 of Table 1. Alkylboronic esters have been coupled with iodobenzene using 0.03 equivalents $PdCl_2(dppf)$ at 50 °C for 16 h with either 3 equivalents TlOH in THF / H_2O or 1.5 equivalents Tl_2CO_3 in THF.[17,47,48]

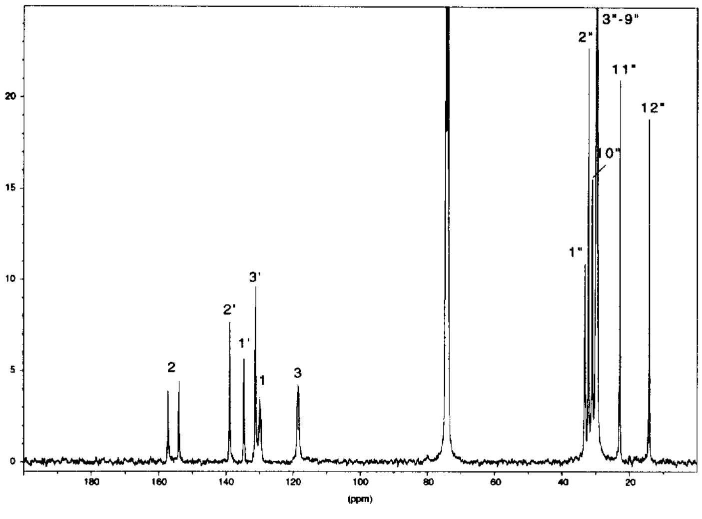
The use of the boronic esters versus the boronic acids does not seem to have any effect on the efficiency of coupling, as we have experienced in our laboratory. The esters crystallize nicely and therefore are easier to purify and to use stochiometrically.

3 Polymerization of Functionalized Aryl Dibromides 4d to 4h

Besides the dibromobenzenes substituted with nitro groups, 1,4-dibromobenzenes substituted with -F, -CN, and $-N(CH_3)_2$, $-CF_3$, as well as 2,5-dibromopyridine (4h), were exposed to 1 under coupling conditions (Scheme 3 and Table 3, 5). These monomers did not show signs of decomposition at temperatures of 75 °C in the presence of base, as did the aromatic nitro compounds. Therefore we used protocols 9 and 10 of Table 1 namely 75 °C with excess base - to compensate for the lower reactivity.

Reaction of 1,4-dibromo-2,5-difluorobenzene (4d) with the 1,3-propanediol diester of 2,5-didodecyl-1,4-phenylenediboronic acid (1b) under the conditions of protocol 9, Table 1 resulted in a sparingly soluble, white powder, which precipitated from the reaction mixture. The ^{13}C-NMR spectrum clearly proves the formation of poly(2,5-difluoro-2',5'-didodecyl-4,4'-biphenylylene) 6d (Figure 5). Each heterotopic carbon is represented by one peak, except for the carbon connected to the fluorine at 155.61 , which shows the expected coupling of ^{13}C-^{19}F, giving a doublet with $J = 243$ Hz.

Figure 5: ^{13}C-NMR spectrum of 6d in tetrachloroethane-d2 at 100 °C



Reaction of 2,5-dibromobenzonitrile (4e) with 1b resulted in a polymer of high molar mass (entry of polymer 6e in Table 4): M_n = 66.8 kg/mol, as determined by membrane osmometry using a hollow fiber membrane in toluene-solution.[49] This polymer 6e has 260 linked phenylene units based on the number average of the molar mass. The polydispersity index is very broad (D = 16), as determined by GPC in 1,2-dichlorobenzene with polystyrene calibration. NMR spectra for this polymer are given in Figures 6 and 7. The solubility of the polymer in THF should allow the reduction of the benzonitrile group to the benzylamine group with $LiAlH_4$. The nitrile group is less reducible to amines than nitro group. However, the nitrile group might offer advantages if a benzylamine rather than an anilin structure is desired.

Other functionalized aryl dibromides 4f - 4i gave oligomers upon reaction with 1b. Oligomer 6h derived from N,N,N',N'-tetramethyl-1,4-diamino-2,5-dibromobenzene 4h has a P_n = 17, as determined by end group analysis of the N-methyl groups at 2.76 in the ^{1}H-NMR spectrum. The 1,1,2,2-tetrachloroethane solution of this polymer is blue at room temperature. This color reversibly disappears at 80 °C. The blue color might stem from the charge transfer band of donor-acceptor complexes composed of the electron-rich N,N,N',N'-tetramethylphenylenediamine units with the 1,1,2,2-tetrachloroethane solvent molecule.

Oligomers were formed with both 2,5-dibromotrifluoromethylbenzene 4f or 2,5-dibromopyridine 4g as monomers. Poly(1,4-phenylene)s containing pyridine units from 4g were synthesized using nickel-catalyzed coupling methods[50] with higher degrees of polymerization than achieved here.[51-53]

Figure 6: ^{1}H-NMR spectrum of 6e in tetrachloroethane-d2 at 100 °C

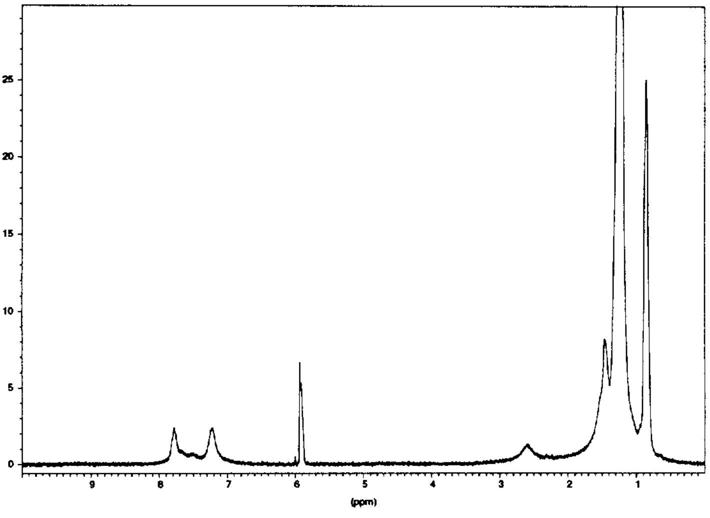
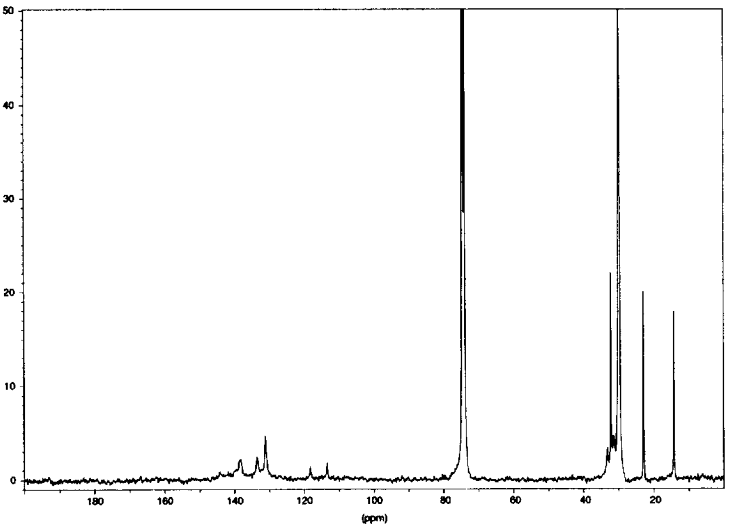


Figure 7: ^{13}C-NMR spectrum of 6e in tetrachloroethane-d2 at 100°C



4 Characterization of Polymers

Table 4 displays GPC data revealing the solvent-dependency of the molar mass with polystyrene standards for two examples of 3 and also for 6e. Polymer 3 is made up of phenylene units alternatingly linked at the 1,4- and 1,3-positions. Attempts to determine number average and mass average molar masses (M_n, M_w) and the polydispersity index (D) by GPC gave surprising results. Varying the solvent resulted in different values for the molar masses, as indicated in Table 4. In all cases, calibration with polystyrene in the respective solvent was used. The apparent M_n was found to be double the value in THF as compared to 1,2-dichlorobenzene or toluene as the solvent. We have no sound explanation of this unexpected behavior but we suspect that this polymer may adopt a very different conformation in each solvent.

Table 4: Solvent-dependency of GPC data of polymers 3 and 6e

GPC[a]	polymer **3**[c]				polymer **3**[d]				polymer **6e**			
	M_n[e]	M_{peak}	M_w	D	M_n[f]	M_{peak}	M_w	D	M_n[g]	M_{peak}	M_w	D
THF	20	35	100	5	7.2	9.9	12	1.7	77	1060	542	7.0[h]
o-DCB[b]	8.7	20	22	2.6	4.2	6.0	7.7	1.8	87.4	819	1370	16
toluene	11	23	25	2.1	5.5	6.6	8.5	1.6				

[a]: polystyrene calibration, kg/mol - [b]: 1,2-dichlorobenzene - [c]: obtained under polymerization conditions of entry 1, Table 2 - [d]: obtained under polymerization conditions of entry 4, Table 2 - [e]: M_n determined from bromine contents as 13 kg/mol - [f]: M_n determined from bromine contents as 10 kg/mol - [g]: M_n determined by membrane osmometry in toluene using a hollow fiber membrane as 66.8 kg/mol - [h]: exclusion limit surpassed.

The other polymers described in this study are functionalized poly(1,4-phenylene)s, with a conformation of a worm-like chain. The polymers derived from monomers 2 and 4a dissolved in the same solvents, e.g. THF, toluene, CH_2Cl_2. The polymer made from 4c, with dihexyl chains as solubilizing groups ($R = C_6H_{13}$), was completely insoluble, whereas the polymer made from 4d, with didodecyl chains as solubilizing groups ($R = C_{12}H_{25}$), was soluble in hot tetrachloroethane. Each functionalized poly(phenylene) has its minimum alkyl chain length for solubilization, depending on the functional group and its arrangement. The high molar mass polymer 6e as well as all the other polymers derived from unsymmetrical aryl dibromides were soluble in many common organic solvents. The head-to-head and head-to-tail isomerism seems to enhance solubility.

The conclusion of this investigation is that the Suzuki coupling is a highly useful tool to synthesize polyphenylenes with functional groups attached to the aromatic repeat units. For the first time polyphenylenes carrying the following substituents have been prepared: nitro, fluoro, nitril, trifluormethyl and dimethylamino. The Suzuki coupling succeeded in every case when suitable modifications were made for each substituent or substituent pattern. For nitro group containing monomers particularly mild conditions were found to work best and polymers of acceptable degrees of polymerization around 30 were obtained. Polymers of very high molecular weight were obtained from the nitril substituted monomer.

5 Experimental

Solvents (all of p.a. grade) and starting materials not explicitly mentioned below were bought from either Aldrich, Fluka, Merck, Riedel-de Haën or Lancaster. THF and toluene were dried over sodium with benzophenone and distilled under argon prior to use. Reaction temperatures quoted refer to the external bath. - Thermogravimetric analysis under N_2: thermo balance Mettler TG 50; thermal properties under N_2: Mettler DSC 30 differential heat flow calorimeter with TC 10

A and TC 11 processors - heating and cooling rate 10 K/min; the onset of the melting endotherm corresponds to the given melting points. - Elemental analysis: Analytisches Laboratorium des Organischen Instituts der Johannes Gutenberg-Universität Mainz; bromine threshold value 0.3 %. - MS : Trio 2000 mass spectrometer of Fisions-instruments (EI electron impact, 70 eV); FAB (fast atom bombardment) spectra: ZAB2-SE-FPD-spectrometer of VG-Biotech, glycerine / DMF mixture as matrix. - NMR: Bruker AC 300 FT-NMR spectrometer, solvent peaks were used as internal standard (solvent / ^1H / ^{13}C: 1,1,2,2-tetrachloroethane / 5.92 / 74.2; THF / 3.57, 1.72 / 67.4, 25.3). For a number of samples DEPT spectra with a pulse angle of 135 ° of the ^{13}C nuclei have been aquired and the peak listing includes in parenthesis the number of protons attached to the carbon. NMR spectra were recorded for a number of samples of different molar mass of several given polymers. Peaks were assigned to end groups, if their intensity decreased with increasing molar mass in comparison to the total intensity. - UV-Vis: Lambda 2 spectrophotometer from Perkin-Elmer, quartz cuvettes with a thickness of 1 cm were employed. - IR: Perkin-Elmer FT-IR spectrometer Paragon 1000; solids were measured as KBr pellets, liquids as neat film between two NaCl plates. - Gel permeation chromatography was performed in THF, toluene and 1,2-dichlorobenzene, calibrated with polystyrene standards.

1,3-Propanediol Diester of 2,5-Dialkyl-1,4-phenylenediboronic acid (1): 2,5-Dialkyl-1,4-phenylenediboronic acid was prepared according to a literature procedure.[54] For purification, 1 was dissolved in THF and precipitated with hexane. This procedure was then repeated. The diboronic acid was esterified with 2.05 equivalents of 1,3-propanediol in CH_2Cl_2 in a Dean-Stark water trap. The ester 1 was recrystallized from ethylacetate / hexane and then THF.

1,5-Dibromo-2,4-dinitrobenzene (2): Prepared according to a literature procedure.[55]
1,4-Dibromo-2,5-dinitrobenzene (4c) and 1,4-Dibromo-2,3-dinitrobenzene (4a): Prepared and separated according to the literature.[56,57]
2,5-Dibromobenzonitrile (4e): Prepared according to a literature procedure[58] and recrystallized three times from ethanol.
N,N,N',N'-Tetramethyl-1,4-diamino-2,5-dibromobenzene (4f): Prepared according to a literature procedure.[59]

$Pd(PPh_3)_4$: Prepared according to a literature procedure.[60]

^1H-NMR Spectrum of Base- and Heat-treated 2, 2,5-Dibromonitrobenzene (4b), and 4c: Each of the mentioned nitro-substituted dibromobenzenes was heated according to the conditions of protocols 6 and 7 of Table 1, though without boronic acid and without catalyst, for only 24 h. After 24 h multiplets between 1.5 - 2.0 and between 7.0 - 7.2 were found in the nonvolatile part of the tested mixtures for all three nitro compounds. These signal groups were also found in the high temperature couplings between 1a and 2 as described in section 2.1.1 next to other unwanted peaks especially in the aromatic region. We did not further analyze the products but immediately proceeded to find out the necessary temperature for coupling to occur efficiently.

^{1}H-NMR spectrum of Pd(PPh$_3$)$_4$ and 2 at 30 °C in THF-d8: Pd(PPh$_3$)$_4$ had multiplets at 7.20 and 7.06 in an intensity ratio of 3 : 2. Furthermore multiplets occured at 7.69 and 7.43 in a ratio of 2 : 3. The latter two have a combined intensity 32 times lower than the former two. An equimolar amount of 2 was added to the catalyst solution. Immediately after addition of 2, the proton signals corresponding to this molecule (two singlets at 8.45 and 8.23) had disappeared. After 90 minutes two multiplets centered at 7.66 and 7.30 were recorded in an intensity ratio of 1 : 4 and in an intensity equal to the initial catalyst. The intermediate time was characterized by the disappearance of several multiplets and the exclusive formation of the two mentioned multiplets. Signals corresponding in intensity to the nitrated benzene ring were two doublets of doublets at 8.09 (J = 3.5 Hz, J' = 0.8 Hz) and 7.96 (J = 7.4 Hz, J = 2.0 Hz). These signals also disappeared within 90 minutes.

4,4''-Dibromo-2',3'-dinitro-1',4'-terphenyl (5): 2.0 g (16 mmol) Phenylboronic acid were reacted with 2.5 g (7.7 mmol) 1,4-dibromo-2,3-dinitrobenzene (4a) in a procedure analogous to that described below for polymerizations using the conditons of protocol 10 of Table 1. After the reaction was completed, the aqueous phase was extracted using an equal volume of toluene. The combined organic phases were washed with water, dried with MgSO$_4$; and the solvent was evaporated. Three recrystallizations from toluene. Yield: 2.3 g (62 %) after recrystallization. $C_{18}H_{10}Br_2N_2O_4$ (478.10 g/mol): calcd. C 45.22, H 2.11, Br 33.43, N 5.86, found C 45.07, H 2.72, Br 33.36 N 4.99. MS (FD); m/z (%): 476.0 (98), 477.9 (100), 479.8 (77). mp 250 °C, ΔH_{mp} = 33.1 kJxmol^{-1}. ^{1}H NMR (THF-d8, room temperature) : δ = 7.82 (s; 2 H), 7.66 (d; 4 H, J = 8 Hz), 7.35 (d; 4 H, J = 8 Hz). ^{13}C NMR (THF-d8, room temperature): δ = 143.45, 135.57, 134.83, 134.69 (CH), 133.16 (CH), 130.60 (CH), 124.64. IR (KBr) ν / cm^{-1} = 1591m, 1549s, 1503m, 1466s, 1412m, 1394m, 1359s, 1076s, 1009s, 892m, 822s, 790s, 739m, 720m, 529s.

General Procedure for Polymerization: A nitrogen-purged flask connected to a reflux condenser was charged with catalyst, base and equimolar amounts of 1 and aryl dibromide. Air in the flask was replaced by N$_2$ through successively applying vacuum and restoring atmospheric pressure with N$_2$ for five times. Water was freed of air by refluxing it and bubbling N$_2$ through it at the same time for 90 minutes. Water, THF and toluene were added to the flask. The concentration in the organic phase was kept between 50 g to 100 g polymer / l solvent. The two-phase mixture was vigorously stirred with a magnetic stirring bar and kept at the stated temperature for the stated amount of time. After the reaction was finished, the poly(1,4-phenylene)s 6 were precipitated out of the organic phase into methanol, the poly(3,4'-biphenylylene) 3 into hexane. The polymer was redissolved in THF, filtered and reprecipitated into methanol for all cases.

With nitro-substituted aryl dibromides, the absence of side-reactions can be monitored by the color of the aqueous phase: Only if Suzuki coupling occurs exclusively does the aqueous phase remain clear and colorless throughout the reaction. For the other functionalized aryl dibromides, the aqueous phase remained clear and colorless under the quoted conditions as well.

Poly(4,6-dinitro-2',5'-dihexyl-3,4'-biphenylylene) (3): For reaction conditions, see protocol 11, Table 1. - All polymers produced by the low-temperature methods are pale yellow powders, characteristic of the nitrated benzene chromophore. Repeat unit $C_{24}H_{30}N_2O_4$ (410.51 g/mol). ^1H NMR (tetrachloroethane-d2, 100 °C): δ = 8.68 (s; 1 H), 7.52, (s; 1 H), 7.08 (s; 2 H), 2.44 (s; 4 H), 1.46 (s; 4 H), 1.19 (s; 12 H), 0.81 (s; 4 H). ^{13}C NMR (tetrachloroethane-d2, 100 °C): δ = 148.17, 140.08, 138.06, 137.15 (CH), 136.08, 129.42 (CH), 120.72 (CH), 33.15 (CH_2), 31.67 (CH_2), 30.39 (CH_2), 29.16 (CH_2), 22.54 (CH_2), 14.99 (CH_3). IR (KBr) ν / cm^{-1} = 2928s, 2856s, 1605m, 1588s, 1534s, 1466m, 1343s, 918w, 901w, 832m, 724w.

Poly(2,3-dinitro-2',5'-dihexyl-4,4'-biphenylylene) (6a): For reaction conditions, see protocol 10, Table 1. - Pale yellow powder. - ^1H NMR (tetrachloroethane-d2, 80 °C): δ = 7.66 (s; 2 H), 7.19 (s; 2 H), 2.47 (s; 4 H), 1.49 (s; 4 H), 1.22 (s, 12 H), 0.84 (s; 6 H). ^{13}C NMR (tetrachloroethane-d2, 80 °C): δ = 143.30, 138.96, 135.65, 134.96, 133.93 (CH), 130.41 (CH), 33.01 (CH_2), 31.68 (CH_2), 30.65 (CH_2), 29.18 (CH_2), 22.62 (CH_2), 14.16 (CH_3). IR (KBr) ν / cm^{-1} = $3421m_{br}$, 2927s, 2855s, 1558s, 1458m, 1354s, 1073w, 900w, 847w, 710w.

Poly[(2,5-dihexyl-1,4-phenylene)-*alt*-(2-nitro-1,4-phenylene;3-nitro-1,4-phenylene)] (6b): For reaction conditions, see protocol 10, Table 1. - Pale yellow powder. - ^1H NMR (tetrachloroethane-d2, 100 °C): δ = 8.02 (s; 1 H), 7.63 (s), 7.48 (s), 7.41 (s) (7.80 - 7.30: 2 H), 7.22 (s), 7.12 (s) (7.30-6.90: 2 H), 2.61 (s), 2.47 (s) (3.20 - 1.90: 4 H), 1.51 (s; 4 H), 1.22 (s; 12 H), 0.84 (s; 6 H). ^{13}C NMR (tetrachloroethane-d2, 100 °C): δ = 149.38, 142.69, 139.36, 138.38, 137.93, 137.31, 134.90, 133.24, 132.38, 132.01, 130.65, 129.79, 128.58, 124.85, 33.09, 31.68, 30.63, 29.22, 22.62, 14.08. IR (KBr) ν / cm^{-1} = 2924s, 2854s, 1530s, 1464s, 1346s, 1249m, 1188w, 1047w, 1029m, 898m, 846m, 763m, 722m.

Poly(2,5-dinitro-2',5'-dihexyl-4,4'-biphenylylene) (6c): For reaction conditions, see protocol 9, Table 1. - The yellow, powdery precipitate was filtered and washed with saturated Na_2CO_3 solution and then thoroughly washed with water. IR (KBr) ν / cm^{-1} = 2955m, 2928s, 2856m, 1545s, 1466m, 1343s, 1263w, 909w, 845m.

Poly(2,5-difluoro-2',5'-didodecyl-4,4'-biphenylylene) (6d): For reaction conditions, see protocol 9, Table 1. - The colorless, powdery precipitate was filtered and washed with saturated Na_2CO_3 solution and then thoroughly with water. ^1H NMR (tetrachloroethane-d2, 100 °C): δ = 7.36, 7.20 (7.52 - 7.15: 2 H), 7.09 (s; 2 H), 2.57 (s; 4 H), 1.52 (s; 4 H), 1.24 (s; 36 H), 0.85 (s; 6 H). ^{13}C NMR (tetrachloroethane-d2, 100 °C): δ = 155.61 (d; J = 243 Hz), 138.91, 134.59, 131.16 (CH), 129.88, 118.31 (CH), 33.18 (CH_2), 32.06 (CH_2), 30.98 (CH_2), 29.78 (CH_2), 22.77 (CH_2), 14.13 (CH_3). IR (KBr) ν / cm^{-1} =2920s, 2851s, 1518m, 1483s, 1467m, 1404m, 1377m, 1271m, 1169m, 1057w, 880m, 779m, 721m.

Poly[(2,5-didodecyl-1,4-phenylene)-*alt*-(2-cyano-1,4-phenylene;3-cyano-1,4-phenylene)] (6e): For reaction conditions, see protocol 9, Table 1. - Colorless, fibrous material. - ^1H NMR (tetrachloroethane-d2, 100 °C): δ = 7.77 (s), 7.23 (s) (8.20 - 6.80: 5 H), 2.60 (s; 4 H), 1.46 (s; 4 H) (s; 36 H), 0.85 (s; 6 H). ^{13}C NMR (tetrachloroethane-d2, 100 °C): δ = 138.53, 133.60 (CH), 131.14 (CH), 118.22, 113.41, 33.10 (CH_2), 32.70 (CH_2), 31.49, 31.22, 29.79 (CH_2), 22.78 (CH_2), 14.16 (CH_3). IR (KBr) ν / cm^{-1} = $3425m_{br}$, 2924s, 2853s, 2228w, 1700w, 1636w, 1466m, 1377w, 1064w, 900w, 848w, 721w, 668w. UV-Vis (CH_2Cl_2) λ_{max}/ nm (ε / m^2xmol^{-1}) = 230 (4300), 270 (2100), 300_{sh} (1300). Fluorescence band between 590 nm and 640 nm with peak maximum at 609 nm (excitation at 515 nm and 647 nm).

Poly[(2,5-didodecyl-1,4-phenylene)-alt-(2-trifluoromethyl-1,4-phenylene;3-trifluoromethyl-1,4-phenylene)] (6f): For reaction conditions, see protocol 9, Table 1. - Colorless powder. - ^{1}H NMR (tetrachloroethane-d2, 80 °C): δ = 7.82 (m; 1 H), 7.60 (s; 1 H), 7.42 (s; 1 H), 7.23 (m; 2 H), 2.53 (m_{br}; 4 H), 1.52 (s; 4 H), 1.25 (s; 36 H), 0.87 (s; 6 H). ^{13}C NMR (tetrachloroethane-d2, 80 °C): δ = 141.60, 140.07, 138.26, 137.34, 136.98, 134.96 (CH), 134.02 (CH), 132.06 (CH), 131.29 (CH), 130.23 (CH), 129.09 (CH), 127.26 (CH), 126.36 (CH), 125.17, 122.71, 121.54, 118.47, 33.10 (CH_2), 32.12 (CH_2), 31.61 (CH_2), 30.87 (CH_2), 29.84 (CH_2), 22.86 (CH_2), 14.22 (CH_3). IR (KBr) ν / cm^{-1} =2923s, 2852s, 1468m, 1322m, 1288w, 1249w, 1169s, 1129s, 900w, 848w, 721w.

Poly[(2,5-didodecyl-1,4-phenylene)-*alt*-(2,5-pyridinediyl;3,6-pyridinediyl) (6g): For reaction conditions, see protocol 9, Table 1. - Powder with a slightly yellowish tint. - ^{1}H NMR (tetrachloroethane-d2, 100 °C): δ = 8.73 (s; 1 H), 7.77 (s; 1 H), 7.50 (s; 1 H), 7.39 (s; 1 H), 7.24 (s; 1 H), 4.16 (s; 0.18), 2.82 (s; 2 H), 2.68 (s; 2 H), 2.05 (s; 0.11 H), 1.57 (s; 4 H), 1.26 (s; 36 H), 0.87 (s; 6 H). ^{13}C NMR (tetrachloroethane-d2, 100 °C): δ = 159.00, 149.43 (CH), 140.35, 138.77 (CH), 136.74 (CH), 135.54, 131.53 (CH), 123.40 (CH), 33.16 (CH_2), 32.06 (CH_2), 31.56 (CH_2), 29.79 (CH_2), 22.78 (CH_2), 14.14 (CH_3); end groups: 150.37, 125.46. 26.2 IR (KBr) ν / cm^{-1} = 2920s, 2850s, 1592m, 1465s, 1362m, 1092w, 1071m, 1020m, 1004w, 900m, 844m, 723m.

Poly(N,N,N',N'-tetramethyl-2,5-diamino-2',5'-didodecyl-4,4'-biphenylylene) (6h): For reaction conditions, see protocol 9, Table 1. - Powder with a slightly yellowish tint. - ^{1}H NMR (tetrachloroethane-d2, 80 °C): δ = 7.25 (s), 7.15 (m), 6.87 (m) (7.60 - 6.40: 4 H), 2.51 (s; 16 H), 1.49 (s; 4 H), 1.24 (s; 36 H), 0.86 (s; 6 H), endgroup: 2.76 (s; 0.70 H). ^{13}C NMR (tetrachloroethane-d2, 80 °C): δ = 145.71, 140.02, 137.82, 134.60, 131.22 (CH), 121.96 (CH), 44.01 (CH_3), 33.33 (CH_2), 32.13 (CH_2), 31.04 (CH_2), 29.90 (CH_2), 22.86 (CH_2), 14.26 (CH_3), end groups: 148.23, 141.63, 128.87 (CH), 124.63 (CH), 123.07 (CH), 44.91 (CH_3). IR (KBr) ν / cm^{-1} = 2923s, 2852s, 2823m, 2778m, 2362w, 2344w, 1508m, 1489m, 1466m, 1456m, 1397w, 1376w, 1288w, 1175w, 1144m, 1096w, 1058m, 953m, 902w, 886m, 721m.

Poly(2,5-N,N,N',N'-tetramethylamino-2',5'-dihexyl-4,4'-biphenylylene) (6i): For reaction conditions, see protocol 8, Table 1. - Powder with a slightly yellowish tint. - ^{1}H NMR (tetrachloroethane-d2, room temperature): δ = 7.16 (m; 4H), 2.64 (m; 12 H), 1.45 (s; 4 H), 1.18 (s; 12 H), 0.79 (s; 6 H). ^{1}H NMR (tetrachloroethane-d2, 80 °C): δ = 7.22 (s), 7.13 (s), 6.91 (s) (8.00 - 6.30: 4 H), 2.54 (m; 12 H), 1.50 (s; 4 H), 1.21 (s; 16 H), 0.83 (s; 6 H). ^{13}C NMR (tetrachloroethane-d2, 80 °C): δ = 145.82, 140.10, 137.85, 134.62, 131.20 (CH), 122.04 (CH), 43.99 (CH_3), 33.28 (CH_2), 32.00 (CH_2), 30.93 (CH_2), 29.55 (CH_2), 22.80 (CH_2), 14.23 (CH_3); end groups: 148.22, 129.31 (CH), 128.49 (CH), 125.59, 124.61 (CH), 123.05 (CH), 118.44, 62.16 (CH_2), 44.89 (CH_3), 35.74

(CH$_2$), 21.62. IR (KBr) ν / cm^{-1} = 2925s, 2855s, 2823m, 2778m, 1508m, 1488m, 1455m, 1397m, 1376m, 1291m, 1179m, 1143m, 1096w, 1058m, 955m, 902w, 885m, 720w.

Table 5: Compositional data and yields for functionalized poly(1,4-phenylene)s **6**

		mass percent				
6	repeat unit mol. mass / g×mol^{-1}	C	H	N	X	yield / %
		calculated found				
a	410.51	24	30	2	O: 4	>95
		70.22	7.37	6.82		
		66.07	7.23	6.06	Br: 1.63	
b	365.51	24	31	1	O: 2	86
		78.87	8.55	3.83		
		77.54	8.52	3.33	Br: 0.39	
c	410.51	24	30	2	O: 4	88
		70.22	7.37	6.82		
		67.82	8.02	6.39	Br: 1.36	
d	524.82	36	54		F: 2	>95
		82.39	10.37			
		81.01	10.39		Br: 0.96	
e	513.85	37	55	1		>95
		86.49	10.79	2.73		
		85.84	10.62	2.63	Br: 0	
f	556.84	37	55		F: 3	74
		79.81	9.96			
		76.05	9.73		Br: 3.27	
g	489.83	35	55	1		79
		85.82	11.32	2.86		
		82.83	11.29	2.63	Br: 1.08	
h	574.98	40	66	2		86
		83.56	11.57	4.87		
		80.55	11.32	4.00	Br: 2.95	
i	406.65	28	42	2		72
		82.70	10.41	6.89		
		80.68	10.30	5.70		

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