A General Strategy for the Synthesis of Conjugated Polymers Based upon the Palladium-Catalysed Cross-Coupling of Grignard Reagents with Unsaturated Halides

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Palladium-catalysed cross-coupling between aromatic bis-organomagnesium reagents and aromatic dihalides has been experimentally evaluated as a general methodology for the synthesis of soluble conjugated polymers such as poly(*p*-phenylene)s **6** and **7**, poly(*p*-terphenylenevinylene) **8**, poly(phenylenethiophene) **9** and poly(phenylenepyridine) **10**. Appropriate experimental conditions were first found in model reactions and then applied to the synthesis of polymers. Molecular mass values were determined both by GPC and by MALDI-TOF spectrometry. The latter technique also permitted accurate determination of the terminal groups of the polymeric chains.

Introduction

Conjugated organic polymers have been demonstrated to be important materials for applications in electronic and photonic devices.[1] Owing to their special electronic properties, they should be able to perform all the functions of traditional inorganic semiconductors, with the primary advantage of their ease of processing.[2] As a result, these organic materials have been employed for the manufacture of organic light-emitting diodes,[3] polymer-based photovoltaic cells[4] and organic field effect transistors.[5] Furthermore, they also show great promise as components of plastic lasers[6] and "molecular electronic devices".[7]

From a chemical point of view, conjugated polymers are available in a wide variety of molecular structures. Poly(arylenevinylene)s, polyphenylenes, polythiophenes and poly(aryleneethynilene)s are some of the most interesting classes of such new organic materials.

Different synthetic approaches for each type of conjugated polymer have frequently been proposed, but the development of general methodologies is much more difficult and consequently less common. Useful strategies currently under extensive investigation are based upon transition metal- and, especially, palladium-mediated coupling reactions, which are among the most effective processes for the formation of carbon-carbon bonds. The Heck reaction has been widely employed for the synthesis of poly(phenylenevinylene) (PPV) and its derivatives,[8] and the Cassar−Heck−Sonogashira reaction is currently the method of choice for the synthesis of poly(aryleneethynylene)s.[9] The Suzuki−Miyaura cross-coupling reaction has been demonstrated to be a valuable methodology for the synthesis both of PPVs and of poly(*p*-phenylene)s (PPPs).[10] As also shown by our work, the Stille coupling is a suitable means of access to a number of conjugated polymers.[11]

Surprisingly, transition metal-catalysed cross-coupling between Grignard reagents and unsaturated electrophiles has so far only rarely been exploited as a route to conjugated polymers, despite its widespread use as a crucial step in the preparation of a great variety of organic compounds. An important but isolated exception is represented by the Yamamoto procedure, which affords poly(phenylene)s and oligophenylenes[12] and consists of the self-coupling of dihalobenzenes in the presence of stoichiometric amounts of Mg, with mild Ni catalysis. Polythiophenes,[13] poly(3-alkylthiophene)s[14] and random copoly(thiophenephenylene)s[15] have been synthesised by a similar procedure. The synthesis of regioregular head-to-tail-coupled poly(3-alkylthiophene)s, based on Ni-catalysed polymerization of organomagnesium reagents derived from bromo or dibromo alkylthiophenes, has also been reported.[16] More recently, an application of cross-coupling between aromatic Grignard reagents and aromatic halides to the synthesis of PPPs has appeared.[17] However, no information concerning the reaction conditions was given, and even the degree of polymerization of the resulting materials was unspecified.

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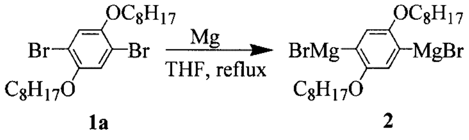
In connection with our continued interest in the development of methodologies for the synthesis of polyconjugated materials,[11c−11e,18] and in order to enlarge the range of opportunities offered by transition metal-mediated cross-coupling processes of organometallic reagents, we decided to conduct a systematic investigation of Pd-catalysed cross-coupling between organomagnesium compounds and unsaturated halides as a general route to various conjugated polymeric structures.

Results and Discussion

Synthesis of the Organometallic Monomer

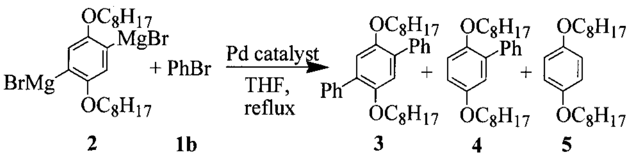
To explore the feasibility of this approach experimentally, we decided to synthesise, as a key reagent, the aryl bis-organomagnesium compound **2**, starting from the readily available 1,4-dibromo-2,5-bis(octyloxy)benzene (**1a**), bearing the two long alkoxy chains necessary to obtain polymeric soluble materials (Scheme 1). The aromatic dihalide **1a** was therefore added to a suspension of an excess of magnesium powder in boiling THF, and the complete formation of the bis-Grignard reagent **2** was ascertained by GC-MS and ^{1}H NMR after quenching of the reaction mixture with deuterium oxide.



Scheme 1

Model Reaction

Coupling between **2** and bromobenzene **1b** in the presence of a Pd catalyst appeared to be a model reaction suitable for the search for appropriate experimental conditions for the polymerization process (Scheme 2).



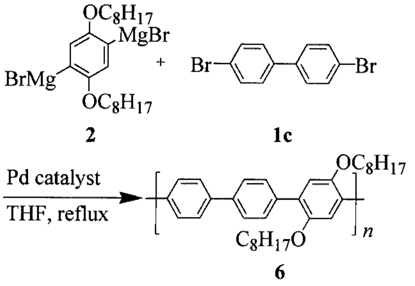
Scheme 2

Various Pd complexes were tested as catalysts, and the outcome is shown in Table 1.

Use of the catalytic systems tris(dibenzylideneacetone)-dipalladium(0) [$Pd_2(dba)_3$]/triphenylarsane (entry 1) or dichloro[1,1′-bis(diphenylphosphanyl)ferrocene]palladium-(II) [$PdCl_2$(dppf)] (entry 5) resulted in the lowest amounts of by-products **4** and **5** and the best overall yields. Lower yields were obtained either when the amount of the catalytic system $Pd_2(dba)_3/AsPh_3$ was raised from 1.5% to 3% (entry 2), or when tetrakis(triphenylphosphanyl)palladium-(0) [$Pd(PPh_3)_4$] was used as catalyst (entry 3). In contrast, only by-products **4** and **5** were recovered when the chelating phosphane 1,4-bis(diphenylphosphanyl)butane (dppb) was used as ligand (entry 4).

Model Polymerization Process

In view of the best results obtained in the model reactions, the first polymerization process − the reaction between **2** and 4,4′-dibromobiphenyl **1c** (Scheme 3) − was studied with the use both of $Pd_2(dba)_3$ in the presence of $AsPh_3$ (Table 1, entry 1) and of $PdCl_2$(dppf) as catalysts (Table 1, entry 5).



Scheme 3

According to the generally accepted mechanism for these reactions,[19] when a Pd^{II} compound is used in the cross-coupling process, initial reduction to the effective catalytic Pd^0 species by the Grignard reagent occurs. As a result, a small proportion of the organometallic monomer is consumed, resulting in an imbalance in the monomer stoichiometry, which might cause a decrease in the degree of polymerization. Therefore, when $PdCl_2$(dppf) was the catalyst, it was necessary to use a small excess of **2** to offset the amount consumed by the reduction of the Pd^{II} complex to the effective Pd^0 catalytic species.

Table 1. Cross-coupling between Grignard reagent **2** and bromobenzene **1b**

Entry	Catalyst	Added Ligand (L)	L/Pd	Cat. (%)[a]	Overall Yield (%)[b]	**3** (%)[c]	**4** (%)[c]	**5** (%)[c]
1	$Pd_2(dba)_3$	$AsPh_3$	4	1.5	96	83	14	3
2	$Pd_2(dba)_3$	$AsPh_3$	4	3	83	81	17	2
3	$Pd(PPh_3)_4$	−	−	1.5	88	81	16	3
4	$Pd_2(dba)_3$	dppb	2	1.5	66	0	73	27
5	$PdCl_2$(dppf)	−	−	1.5	94	81	16	3

[a] The catalyst percentage is related to the number of mol. of the organometallic reagent. [b] Yields refer to isolated mixtures of compounds **3**, **4** and **5**. [c] Percent ratios (**3**:**4**:**5**) were determined by GC analyses.

Table 2. Preparation of polymer **6**

Entry	Catalyst	Time (d)	Yield (%)	M_n [a][b] (Da)	M_w [a][c] (Da)	M_w/M_n	DP[d]
1	$PdCl_2(dppf)$	6	60	8180	11760	1.44	17
2	$Pd_2(dba)_3/Ph_3As$	6	56	6290	8840	1.41	13

[a] Determined by Gel Permeation Chromatography (GPC) with uniform polystyrene standards and THF as solvent. [b] Number average molecular mass. [c] Weight average molecular mass. [d] Number average degree of polymerization.

The data shown in Table 2 indicate that the use of $PdCl_2(dppf)$ as the catalyst produced the best outcomes both in terms of yield and of molecular mass values as measured by Gel Permeation Chromatography (GPC).

In order to obtain more detailed information about the characteristics of the polymerization process, we performed a MALDI-TOF mass spectrometry analysis of material **6** obtained by use of the two different catalysts. Although Time-of-Flight (TOF) mass spectrometry combined with Matrix-Assisted Laser Desorption Ionization (MALDI) has been widely employed for the analysis of conventional polymers,[20] only a few reports deal with the application of this technique to conjugated polymers.[21]

The MALDI-TOF mass spectra of polymer **6**, prepared with both catalysts as discussed above, are shown in Figure 1 and Figure 2.

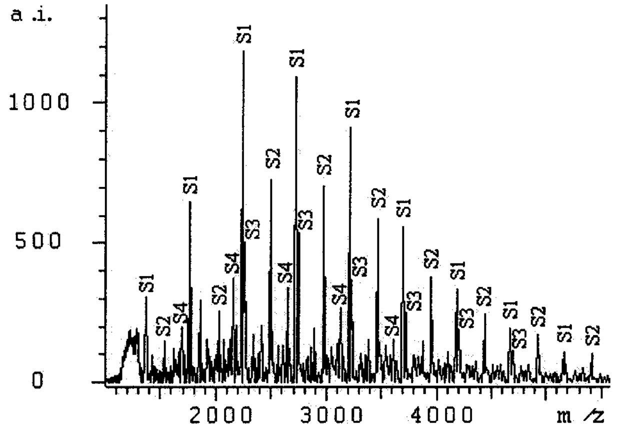


Figure 1. MALDI-TOF mass spectrum of polymer **6** obtained with $PdCl_2(dppf)$ as catalyst

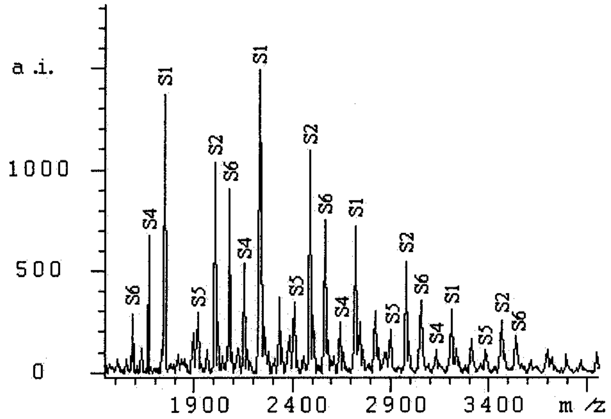


Figure 2. MALDI-TOF mass spectrum of polymer **6** obtained with $Pd_2(dba)_3/AsPh_3$ as catalyst

These spectra show a discrete distribution of molecular mass values, with $M_n = 3430$ and $M_w = 3900$ (as derived from the spectrum in Figure 1) or $M_n = 2940$ and $M_w = 3250$ (as derived from the spectrum in Figure 2). These molecular mass values are markedly lower than those determined by the GPC analysis. Actually, the gel permeation chromatography technique is generally expected to overestimate the molecular mass values of rigid, rod-like materials, owing to the difference of their hydrodynamic behaviour from that of the randomly coiled polystyrene polymers used as standards.[22] On the other hand, mass-discrimination phenomena are reported to occur, in particular at the higher molecular mass end, in the MALDI-TOF spectra of polydisperse polymers (polydispersity > 1.1), and this drawback may result in substantially underestimated molecular mass values calculated on the basis of these mass spectra for such polymers.[20]

However, useful structural information can be obtained from the MALDI-TOF spectra of polymer **6**. The structures of polymeric chains with all their possible terminations are shown in Figure 3, and attributions to the corresponding peaks are marked in the spectra of Figure 1 and Figure 2.

Analysis of the two spectra indicates some differences in the nature of the terminal groups for polymer **6** obtained with the different catalysts.

In the spectrum of Figure 1 ($PdCl_2(dppf)$ used as catalyst), chains terminating in two brominated biphenyl units (S_1 series), in two dialkoxy phenyl units (deriving from protonation of the organometallic functionalities: S_3 series), and in both these end groups (S_2 series) largely predominate over mono-dehalogenated chains (S_4 series), while only trace amounts of S_5 and S_6 series are present. On the contrary, for polymerization performed with $Pd_2(dba)_3/AsPh_3$ as catalyst (Figure 2), dehalogenated chains (S_5 and S_6 series) make a more relevant contribution to the composition of the resulting polymer. The minor occurrence of the reductive dehalogenation process observed with $PdCl_2(dppf)$ as catalyst suggests, at least in this case, the possibility of an increase in the molecular mass of the polymer **6** by further reaction of polymeric chains still bearing one or two reactive halogen atoms with the dibromomagne-

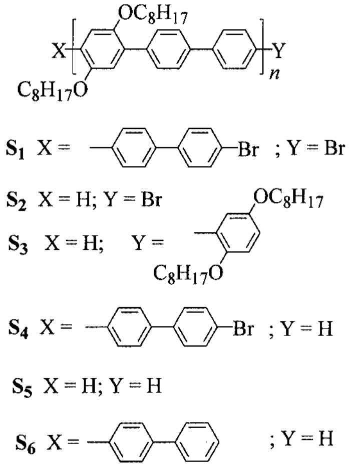
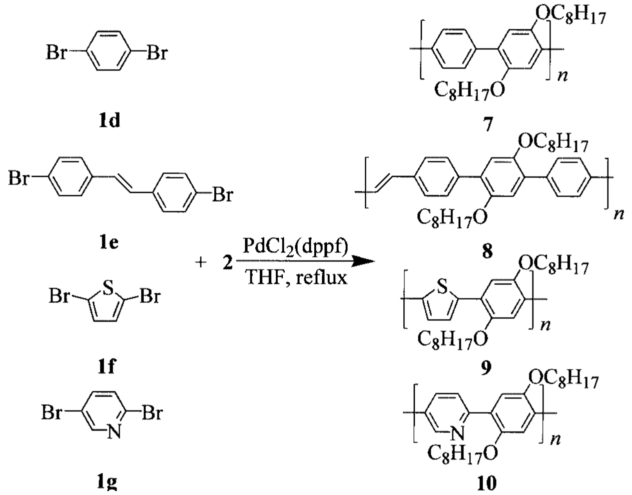


Figure 3. Structures of chains with all their possible terminations for polymer **6**



Scheme 4

sium compound **2**. In order to evaluate this possibility, we tested a post-polymerization procedure by two different experimental approaches:

1) A 1:1 ratio between **2** and **1c** was initially used. After 6 days of reaction time, a further 50% of Grignard reagent was added, together with the amount of catalyst necessary to keep the catalyst/organometallic reagent ratio unchanged.

2) The experiment was performed as above, but no further amount of catalyst was added.

By comparison of the MALDI-TOF mass spectra obtained under the two different sets of conditions, it was found that there was no substantial increase in the average molecular mass values in comparison with those of the polymer obtained by the original methodology, although significant differences in the relative proportions of chains bearing different end groups were observed.

All the above observations concerning polymer **6** suggested the reasonable conclusion that the precipitation of the growing chains should be the main factor responsible for the prevention of their further growth. Secondary pathways involving either the organometallic reagent or the catalyst should play minor roles.

Synthesis of Polymers with Different Structures

With the aim of expanding the scope of the cross-coupling reaction of Grignard reagents to the synthesis of conjugated polymers other than polyphenylenes **6** and **7** (Scheme 4), we examined the treatment of the dibromoaromatic monomers **1e−g** with the organometallic reagent **2**. Polymers **8**, **9** and **10** were obtained, and the outcome of the reactions is reported in Table 3.

Fair to good yields were obtained with all the monomers, and the molecular mass values determined by GPC with polystyrene as standard were similar to those obtained with other organometallic polymerization methodologies, such as the Stille[11] or Suzuki[23] procedures.

MALDI-TOF analyses were performed on each of the materials obtained (Figure 4) and the molecular mass values calculated from their spectra are reported in Table 4, together with the corresponding values obtained by GPC-HPLC.

Table 3. Polymerization reactions between **2** and dihalides **1d−g**

Polymer	Yields (%)[a]	M_n [b] [c] (Da)	M_w [b] [d] (Da)	M_w/M_n	DP[e]
7	51	3980	6690	1.68	10
8	58	4150	5910	1.43	8
9	40	4260	7080	1.67	10
10	73	4400	6350	1.45	11

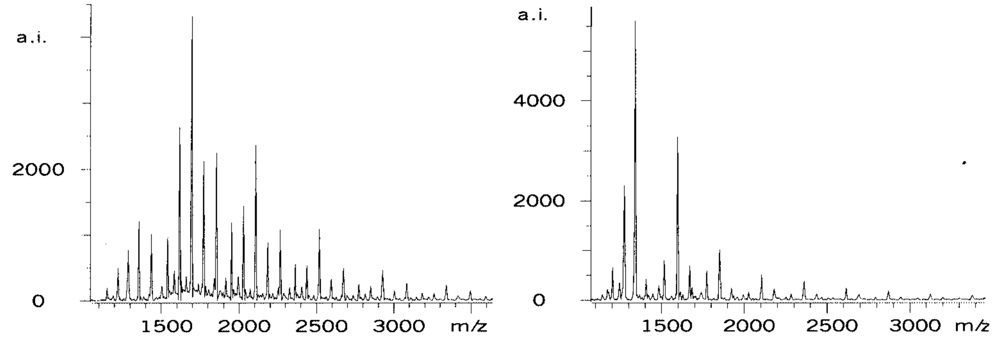
[a] Reaction time 6 days. [b] Determined by Gel Permeation Chromatography (GPC) with uniform polystyrene standards and THF as a solvent. [c] Number average molecular mass. [d] Weight average molecular mass. [e] Number average degree of polymerization.

As expected, the MALDI-TOF molecular mass determination gave values lower than those obtained by the GPC method. The high-mass discrimination phenomena mentioned above may be considered the origin of this discrepancy.

Analysis of the mass spectra of polymers **7**, **8** and **10** reveals that, as in the case of polymer **6**, chains bearing one or two bromine atoms as terminal groups are prevalent with respect to those ending with dehalogenated aryl groups deriving from the dihalide monomer. In contrast, polymer **9** shows a uniform distribution of chains with all the possible terminations.

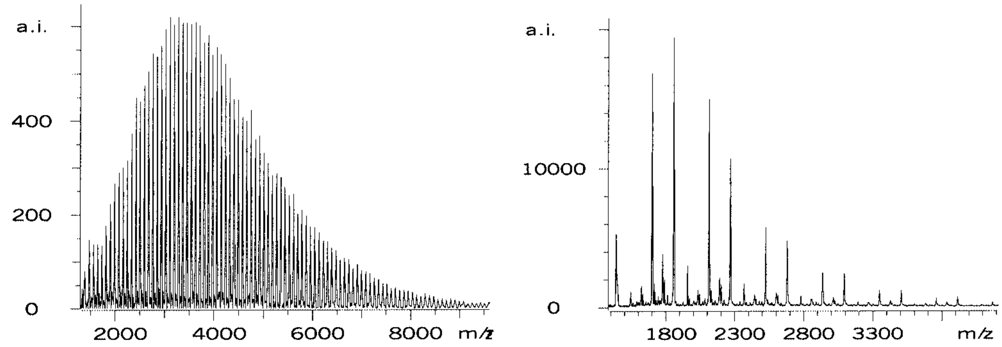
Conclusion

Our work has shown that cross-coupling between Grignard reagents and aromatic dihalides represents a general route to polyconjugated polymers. The procedure is experimentally straightforward and allows the preparation of a variety of structures by simple variation of the components used in the process. Complete characterization of the materials produced was performed by MALDI-TOF mass spec-



Polymer **7**

Polymer **8**



Polymer **9**

Polymer **10**

Figure 4. MALDI-TOF spectra of polymers **7**−**10**

Table 4. Comparison of molecular mass values and degrees of polymerization determined by GPC-HPLC and MALDI-TOF MS.

	GPC				MALDI-TOF			
Polymer	M_n (Da)	M_w (Da)	M_w/M_n	DP	M_n (Da)	M_w (Da)	M_w/M_n	DP
7	3980	6690	1.68	10	2520	2930	1.16	6
8	4150	5910	1.43	8	2030	2240	1.10	4
9	4260	7080	1.66	10	4040	5310	1.32	10
10	4400	6350	1.45	11	2550	2820	1.11	6

trometry, and the molecular mass values determined were also compared with those resulting from the more traditional GPC technique. On the whole, this procedure compares well with other methodologies, such as the Stille and Suzuki cross-coupling polymerizations. Indeed, polymers synthesised by our methodology in many cases displayed molecular mass values similar to those of the same materials obtained either by Stille[11b] or Suzuki[23] cross-coupling techniques. However, our approach presents the distinctive advantage of a direct preparation of the organometallic monomer, whereas aromatic organotin[11b] and organoboron[24] compounds are prepared from the corresponding lithium or Grignard reagents or, in the case of arylboronates, also by a more expensive and less straightforward Pd-catalysed borylation of aryl halides with dialkoxyborane.[25]

Experimental Section

General Remarks: GC analyses were performed on a gas chromatograph equipped with a SE-30 (methyl silicone, 30 m × 0.25 mm id) capillary column. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 MHz and at 125 MHz, respectively, using the residual $CHCl_3$ as the standard at $\delta = 7.24$ ppm for ^1H spectra and the $CDCl_3$ signal at $\delta = 77$ ppm for ^{13}C spectra. MALDI-TOF analyses were performed on a Bruker Omniflex MALDI-TOF instrument operating in linear mode with an accelerating voltage of 19 kV. Samples were prepared in dithranol with a total loading of polymer around 100 pmol and a matrix/analyte ratio of about 500:1. The positive ions were generated with the 337 nm laser beam from a nitrogen laser. Mass calibrations were performed externally with equine cytochrome C and angiotensin II, which span the mass range of interest. The spectra reported are the sum of 80 shots. Molecular mass values were determined with a Hewlett−Packard

HP 1050 liquid chromatograph instrument, with THF as a solvent and a Plgel 5μ Mixed-D 300 × 7.5 mm column. Tetrahydrofuran was distilled from benzophenone ketyl immediately prior to use. $PdCl_2$(dppf)[26] and 1,4-dioctyloxybenzene[8d] were prepared as reported in the literature. $Pd(PPh_3)_4$, $Pd_2(dba)_3$, $AsPh_3$ and dppb were commercial products.

1,4-Dibromo-2,5-dioctyloxybenzene (1a): This compound was prepared by a procedure adopted in similar cases.[27] Br_2 (2.4 mL, 46.84 mmol) dissolved in 5 mL of acetic acid was added to a solution of 1,4-dioctyloxybenzene (3.500 g, 10.46 mmol) and sodium acetate (0.197 g, 2.40 mmol) in acetic acid (16 mL). After 8 h, a white solid had precipitated from the reaction mixture. The solid was filtered through sintered glass and washed with CH_3OH. The crude product was crystallised twice from methanol and thoroughly dried by heating in vacuo (10^{-3} mbar) at 70 °C for three hours, after which 4.025 g (78% yield) of white crystals (m.p. 67−68 °C) were obtained. IR (KBr): $\tilde{\nu}$ = 1496, 1460, 1362, 1212, 1067, 1029, 999, 808 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 6 H), 1.22−1.40 (m, 16 H), 1.43−1.52 (m, 4 H), 1.80 (quintet, J = 7.0 Hz, 4 H), 3.94 (t, J = 6.5 Hz, 4 H), 7.08 (s, 2 H) ppm.

Preparation of Grignard Reagent 2: A suspension of magnesium powder (1.383 g, 56.91 mmol) in dry THF (10 mL) was activated with a drop of 1,2-dibromoethane and heated to reflux. A solution of 1,4-dibromo-2,5-dioctyloxybenzene **1a** (9.340 g, 18.97 mmol) in 37 mL of anhydrous THF was added dropwise. After 4 hours, GC-MS analysis of an aliquot of the reaction mixture quenched with deuterium oxide showed completion of reaction. The concentration of the solution (0.398 M) was determined by standard volumetric methods.

Model Cross-Coupling Reaction: A THF solution of Grignard reagent **2** (0.398 M, 1.6 mL, 0.64 mmol) was added dropwise to a mixture of bromobenzene **1b** (0.207 g, 1.32 mmol), $Pd_2(dba)_3$ (0.009 g, 0.010 mmol) and $AsPh_3$ (0.024 g, 0.08 mmol) in 5 mL of dry THF. The mixture was heated under reflux for 24 h, and the reaction was quenched with a saturated solution of NH_4Cl. The aqueous phase was extracted with ethyl acetate. The solution was then dried over anhydrous Na_2SO_4, and the solvent was evaporated at reduced pressure. The residue was dissolved in petroleum ether and purified by elution on silica gel. A mixture of **3**, **4** and **5** was recovered, and its composition was determined by gas chromatography and MS-GC.

Typical Polymerization Reaction. Synthesis of Poly(2,5-dioctyloxy-4,4′,4′′-terphenylene) (6): A solution of Grignard reagent **2** (0.398 M, 8 mL, 3.18 mmol) was added dropwise, under nitrogen atmosphere at room temperature, to a mixture of 4,4′-dibromobiphenyl **1c** (0.981 g, 3.14 mmol) and $PdCl_2$(dppf) (0.034 g, 0.05 mmol) in anhydrous THF (12 mL). The mixture was heated under reflux for 6 days, quenched with a saturated solution of NH_4Cl, diluted with water, and extracted three times with CH_2Cl_2. The solvent was evaporated at reduced pressure, and the crude product was extracted in a Soxhlet apparatus with methanol for 24 h in order to remove inorganic salts, and then with hexane for 24 h to eliminate low molecular mass fractions. Finally, a Soxhlet extraction with $CHCl_3$ afforded a greenish solid (0.915 g, 60% yield). IR (KBr): $\tilde{\nu}$ = 1487, 1468, 1387, 1210, 1057, 1004, 821 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.75−1.00 (m, 6 H), 1.10−1.90 (m, 24 H), 3.80−4.10 (m, 4 H), 7.06−7.12 (m, 2 H), 7.50−7.82 (m, 8 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.09, 22.66, 26.12, 29.26, 29.36, 31.79, 69.68, 116.20, 126.57, 128.62, 129.93, 130.045, 130.41, 131.865, 137.365, 139.445 ppm.

Polymers 7−10 were prepared by the same procedure.

Poly(2,5-dioctyloxy-4,4′-bisphenylene) (7): Yield: 51%. IR (KBr): $\tilde{\nu}$ = 1488, 1471, 1384, 1261, 1208, 1094, 1029, 802 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$ at 45 °C): δ = 0.70−1.00 (m, 6 H), 1.10−1.85 (m, 24 H), 3.80−4.10 (m, 4 H), 7.00−7.80 (m, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$ a 45 °C): δ = 14.02, 22.64, 26.15, 29.26, 29.49, 29.69, 31.63, 69.69, 116.63, 129.09, 130.80, 131.06, 131.22, 137.12, 150.66 ppm.

Poly(2′,5′-dioctyloxy−4,4′,4′′-terphenylenevinylene) (8): Yield: 58%. IR (KBr): $\tilde{\nu}$ = 1487, 1468, 1387, 1209, 1057, 1004, 821 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.82−0.96 (m, 6 H), 1.16−1.58 (m, 20 H), 1.64−1.84 (m, 4 H), 3.84−4.03 (m, 4 H), 6.96−7.75 (m, 12 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.06, 22.66, 26.15, 29.25, 29.47, 31.81, 69.93, 116.44, 126.14, 128.47, 129.86, 130.73, 136.24, 137.86, 150.64.

Poly[1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene] (9): Yield: 40%. IR (KBr): $\tilde{\nu}$ = 1488, 1467, 1408, 1380, 1269, 1213, 1033, 790 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.70−1.05 (m, 6 H), 1.10−1.90 (m, 24 H), 3.75−4.25 (m, 4 H), 6.80−7.65 (m, 4 H) ppm.

Poly[1,4-(2,5-dioctyloxyphenylene)-2,5-pyridine] (10): Yield: 73%. IR (KBr): $\tilde{\nu}$ = 1591, 1506, 1464, 1423, 1357, 1232, 1204, 1032, 844 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.70−1.05 (m, 6 H), 1.10−1.60 (m, 20 H), 1.65−1.95 (m, 4 H), 3.80−4.25 (m, 4 H), 7.00−9.05 (m, 5 H) ppm.

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