

Conjugated Organometallic Polymers Containing Vollhardt's Cyclobutadiene Complex: Aggregation and Morphologies

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Dedicated to Professor Richard D. Adams

Abstract: Organometallic polymers were prepared by acyclic diyne metathesis (ADIMET) or by Pd-catalyzed coupling of 1,3-diethynylcyclobutadiene(cyclopentadienyl)cobalt with a suitably substituted diiodobenzene. The polymers obtained by Heck coupling show a degree of polymerization (P_n) of 20–60. The monomers for ADIMET were made by the Pd-catalyzed coupling of [1,3-bis(trimethylsilylethynyl)-2,4-bis(trimethylsilyl)cyclobutadiene](cyclopentadienyl)cobalt to 1-bromo-2,5-

dialkyl-4-propynylbenzenes in the presence of KOH in yields of 40–48%. The monomers carry hexyl, ethylhexyl, and (*S*)-3,7-dimethyloctyl side chains. Polymerization of the propynylated monomers furnishes organometallic polymers with a P_n of up to 230 arylene-ethynyl-

ene units. The polymers were fully characterized by polarizing microscopy, transmission electron microscopy, circular dichroism, differential scanning calorimetry, and X-ray diffraction (XRD). They show nematic, lyotropic liquid crystalline phases as well as chiroptical properties from which aggregation in poor solvents and in the solid state can be concluded. Lamellar or irregular honeycomb-shaped morphologies in these organometallic polymers can be detected by electron microscopy.

Keywords: aggregation • conjugation • liquid crystals • organometallic compounds • polymers • supramolecular chemistry

Introduction

Aggregation and supramolecular ordering is an increasingly important topic of macromolecular science.^[1] Aggregates of conjugated polymers such as poly(*paraphenylene-vinylene*)s,^[2] poly(*paraphenylene-ethynylene*)s (PPE),^[3] or polythiophenes^[4] have significantly different physical, optical, and electronic properties from those of single molecules of these polymers. Aggregation of conjugated polymers is (potentially) relevant to device technology^[5a, b] and molecular electronics,^[5b] but is likewise of fundamental interest. Organometallic materials have been a focus of considerable attention during the last decade.^[6, 7] The field has flourished since Manners' elegant synthetic access to high-molecular-weight polyferrocenylsilanes by ring-opening polymerization (ROP).^[8] Organometallic polymers can combine exotic structures with attractive properties. Redox activity, electric conductivity, or

magnetic responses are easily achieved.^[6] While a significant amount of literature deals with the synthesis of organometallic polymers,^[6–9] their properties have been less well explored. Only a handful of reports describe their liquid crystalline and phase behavior.^[9] Even less is known about the aggregation of organometallic polymers^[9a] and how far they resemble structurally related organic systems. In this contribution, we describe novel, conjugated, organometallic polymers **9a–c** (including a chiral example, **9c**) prepared by acyclic diyne metathesis (ADIMET)^[10, 11] and give a full account^[9b] of the synthesis of the liquid crystalline, organometallic PPE derivatives **3a–f**. The aggregation, phase (i.e. liquid crystalline) behavior and morphology of **3** and **9a–c** are examined.

Results and Discussion

Simple organometallic PPEs 3: In 1,3-diethynyl-substituted cyclobutadiene complexes, the two alkyne groups are arranged in a linear fashion, which is suitable for the synthesis of rigid organometallic polymers. Vollhardt's diethynyl (**1**) is available on a multigram scale and can be used for this purpose.^[12] The Pd-catalyzed coupling of diynes to aromatic

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diiodides is a powerful method for the synthesis of poly(arylene-ethynylene)s.^[13] We have demonstrated previously,^[9b] that careful optimization of the reaction conditions results in the coupling of **1a** and **1b** to aromatic iodides **2a–e** under Heck–Cassar–Sonogashira–Hagihara conditions.^[13–15] The choice of amine base was critical and only piperidine led to polymers **3** with acceptable molecular weights and polydispersities (PDI).^[13a, c] Table 1 gives yield, molecular weight and

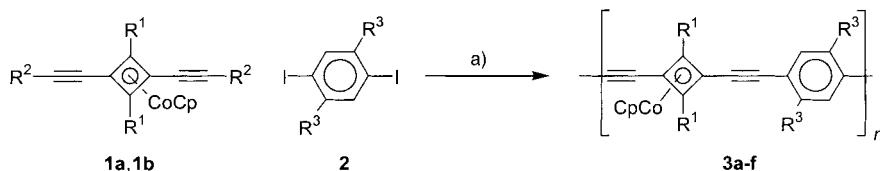
Table 1. Substituent pattern, yield, molecular weight, and polydispersities of polymers **3a–f**.

3	R ¹	R ³	Yield [%]	M _n [$\times 10^3$]	P _n ^[a]	M _w /M _n
a	H	hexyl	75	4.7	18	3.5
b	SiMe ₃	H	86	4.3	18	1.7
c	H	dodecyl	79	24	58	2.8
d	SiMe ₃	hexyl	74	5.1	18	2.6
e	SiMe ₃	dodecyl	79	4.9	12	4.1
f	SiMe ₃	(S)-3,7-dimethyloctyl	80	21	29	3.0

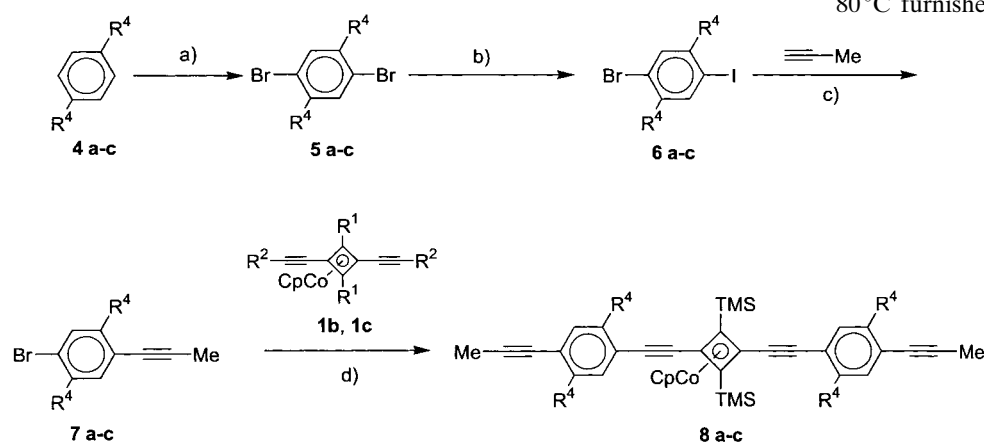
[a] GPC data according to polystyrene standard in chloroform.

PDI of **3a–f**. The molecular weights of **3a–f** are within the expected range owing to the use of a Pd²⁺-catalyst precursor that consumes a fraction of the diyne **1b** to form the catalytically active [(PPh₃)₂Pd⁰]. The created stoichiometric imbalance prevents the formation of high-molecular-weight polymers **3**.

The polymers **3** were purified either by double precipitation into methanol and pentane or by preparative gel-permeation chromatography (**3d**). They are yellow or red to tan-colored, form strong, free-standing, transparent films when cast from chloroform solution, and are stable under ambient conditions for extended (years) periods of time (Scheme 1).

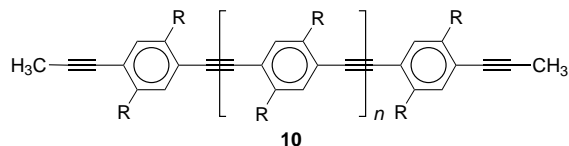


Scheme 1. Synthesis of the organometallic polymers **3** by Pd-catalyzed coupling. **1a**: R¹ = R² = H, **1b**: R¹ = TMS, R² = H; R³ = H, hexyl, (S)-2,7-dimethyloctyl, dodecyl. a) (PPh₃)₂PdCl₂, CuI, piperidine.



Scheme 2. Synthesis of the monomers **8**. **1b**: R¹ = TMS, R² = H, **1c**: R¹ = R² = TMS; R⁴ = hexyl, 2-ethylhexyl, (S)-2,7-dimethyloctyl. a) Br₂, RT, 12 h. b) *n*-BuLi, -78 °C, I₂. c) (PPh₃)₂PdCl₂/CuI/piperidine, RT, 12 h. d) (PPh₃)₂PdCl₂/CuI/PPh₃ 20% KOH in EtOH HN(*i*Pr)₂, 83 °C, 12 h.

Organometallic polymers by alkyne metathesis: Recently, we reported a simple protocol for alkyne metathesis that utilizes a mixture of [Mo(CO)₆] and 4-chlorophenol or 4-trifluoromethylphenol in situ.^[10b, c, 11] This "instant" catalyst forms in off-the-shelf reagents at elevated temperatures. It metathesizes dipropynylated benzenes to high-molecular-weight poly(phenylene-ethynylene)s (**10**) with extrusion of 2-butyne.^[10]



10a: R = hexyl, **10b**: R = 2-ethylhexyl, **10c**: R = 3,7-dimethyloctyl

These catalysts are effective for hydrocarbon monomers, but the high temperatures required and the aggressive phenols may be incompatible with organometallic monomers. We envisioned **8a–c** (see Scheme 2 below) as substrates for ADIMET (see Scheme 3) which would form the organometallic polymers **9**. ADIMET is suited to access high-molecular-weight conjugated organometallic polymers and allows the synthesis of organometallic polyarylene-ethynylenes in which the organometallic units are separated by two phenylene-ethynylene groups (**9**) rather than by one, such as in **3**.

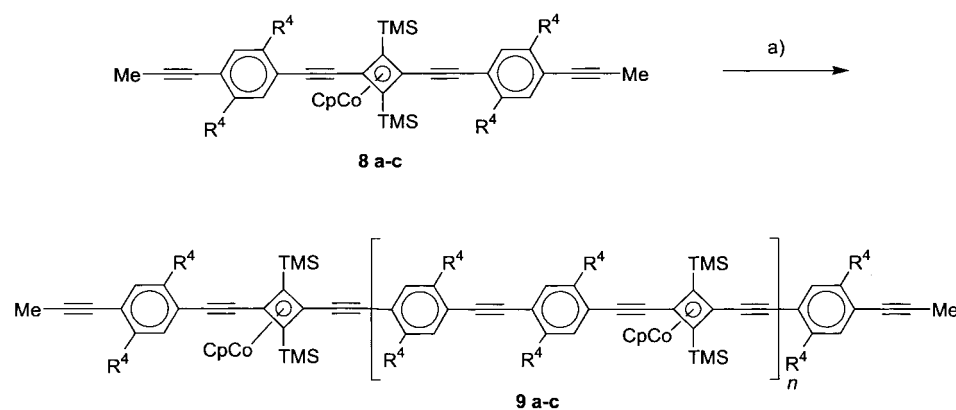
Monomer synthesis: The monomers **8a–c** should be accessible from **1b**^[12] and the hitherto unknown 4-bromo-2,5-dialkylpropynylbenzenes (**7a–c**) by Pd-catalysis (Scheme 2). The dibromides **5**,^[10d, 13] prepared from **4**, were treated with *n*-BuLi (-78 °C, THF). Treatment of the intermediate mono-

lithiated benzene with elemental iodine furnished **6a–c** in high yields in a streamlined version of Godt's protocol.^[16]

In Heck type couplings, aryl iodides are more active than aryl bromides, and the reaction of **6a–c** with an equimolar amount of propyne selectively leads to **7a–c** in 65–75% yield. Attempts to couple **7a–c** to **1b** by utilizing NEt₃ at 80 °C furnished **8** in only 13–

15% yield. Heitz has reported an in situ deprotection/coupling scheme,^[17] in which TMS-substituted alkynes were directly connected to aromatic halides. A slight variation of this protocol couples **1c** to **7** in diisopropylamine as solvent/base, with [(PPh₃)₂PdCl₂]/CuI as catalyst, and with ethanolic KOH as deprotecting agent to selectively remove the TMS groups at the alkyne units. The ADIMET monomers **8a–c** are isolated in a respectable 40–48% yield (Scheme 2).^[15–17]

Polymerization reaction: The use of 20 mol% [Mo(CO)₆] in combination with 100 mol% 4-trifluorocresol is necessary for the successful ADIMET of **8a–c**.^[18] The reaction was conducted for 16 h at 150 °C in 1,2-dichlorobenzene. Similar conditions have previously been optimized for the synthesis of PPEs **10**^[14a] and furnished the yellow or yellow-brown polymers **9a–c** after a standard workup (Scheme 3). ¹H NMR and



Scheme 3. Alkyne metathesis to the polymers **9**. R⁴ = hexyl, 2-ethylhexyl, (*S*)-2,7-dimethyloctyl, dodecyl. a) Mo(CO)₆, *p*HOC₆H₄CF₃, 1,2-dichlorobenzene, 145 °C, 48 h, H₃C≡C–CH₃ ↑.

¹³C NMR spectra demonstrated that **9** had formed without appreciable defects and reinforced our notion that instant catalysts effectively metathesize dipropynylated monomers as long as no basic hetero atoms (i.e. with free electron pairs) are present. The difference in solubility of the polymers **9a–c**, which is dependent on their side chains, is remarkable. Polymer **9a** (R = hexyl) is almost insoluble. Only 40% of the precipitate, mostly low-molecular-weight material, could be redissolved by sonication in chloroform. The introduction of branching into the side chains, such as in **9b** (R = 2-ethylhexyl), leads to improved solubility. The (*S*)-3,7-dimethyloctyl substituent gives polymers **9c**, which are very soluble, even in hexanes, yet the chiral **9c** forms almost quantitatively and has a high degree of polymerization (Scheme 3).

Table 2 displays the molecular weights of **9a–c**, with **9c** consisting of chains with a number average of 2.3×10^2 arylene-ethynylene units (determined by gel permeation chromatography; GPC). Since the monomer contains three arylene-ethynylene units, a P_n of 77 results in a molecular weight (M_n) of 85 kDa. In the ¹H NMR spectra of polymers **9a–c** the propyne end groups at $\delta = 2.06$ were hardly detectable, if at all, which is additional evidence for their substantial molecular weights. Alkyne metathesis is thus

Table 2. Substituent pattern, yield, molecular weight, and polydispersities of polymers **9a–c**.

9	R ¹	R ⁴	Yield [%]	M_n GPC (10 ³)	P_n ^[a] GPC	P_n NMR ^[b]	M_w/M_n
a	SiMe ₃	hexyl	40 %	37	43	34	3.4
b	SiMe ₃	2-ethylhexyl	83 %	60	61	–	2.9
c	SiMe ₃	(<i>S</i>)-3,7-dimethyloctyl	93 %	85	77	97	3.7

[a] GPC data according to polystyrene standard in chloroform. [b] P_n was determined by NMR spectroscopy by integrating over the residual propyne protons at $\delta = 2.01$ and comparing the integrals with that of the Cp ring.

effective for making **9**. ADIMET is competitive to Pd-catalyzed couplings and actually superior to the Pd-catalyzed couplings in terms of yield, molecular weight, and purity of the obtained polymers.

Optical and chiroptical properties of **3f** and **9a–c**:

UV/Vis spectra of PPEs **10** in poor solvents or in the solid state have a strong aggregation-induced band at 439 nm.^[3a] The likely reason for the occurrence of this aggregate-induced band is the planarization of the PPE backbone.^[19b] We compared UV/Vis spectra of the organometallic polymers **9a–c** and **3a–f** taken in pure chloroform, chloroform/methanol mixtures, and in the solid state. Sample spectra of **9c**, which is representative for polymers **3** and **9**, are shown in

Figure 1 (top). The differences between solution and the solid-state spectra both in **3** as well as in **9** are small. The availability of the chiral polymers **9c** and **3f** allowed their aggregation to be examined by circular dichroism (CD) spectroscopy.^[3, 19] The bottom half of Figure 1 shows the CD spectra of **9c** in the presence of an increasing amount of methanol as nonsolvent.

For up to 50% methanol, no CD signal is visible for **9c**. At higher methanol concentrations, a derivative, “bisignate” (with both positive and negative sign) CD signal centered at 374 nm develops. The intensity of this signal increases until the methanol content reaches 70%. More methanol leads to a weaker CD signal, owing to precipitation of **9c**. The g value of **9c** reaches 0.0026—a factor of three smaller than that of the corresponding PPE **10c**,^[3b] but more than double the value determined by Scherf for a dialkoxy-substituted PPE.^[18a] The distinctly bisignate and symmetric shape of the signal indicates aggregation of the polymer chains owing to the interaction of the chromophores through exciton coupling.^[1–3] In contrast, the structurally similar PPEs **10c** have a CD spectrum in which the aggregate band is almost “monosignate” and could arise from a largely intramolecular contribution. The aggregation in dialkyl PPEs **10** is preceded by planarization,^[18b] while the bisignate band in **9c** suggests the

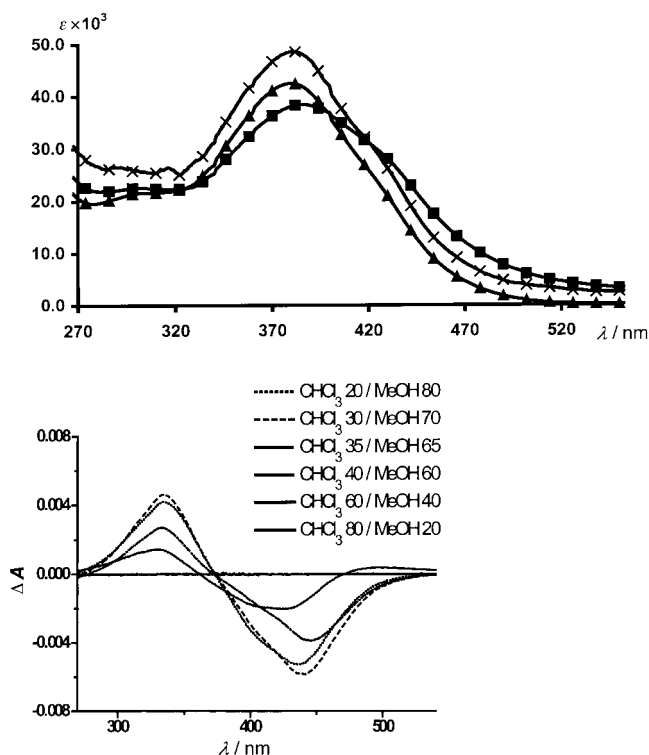


Figure 1. Top: UV/Vis spectrum of **9c** in chloroform (\blacktriangle), in methanol/chloroform 70:30 (\blacksquare), and in the solid state (\times). Bottom: CD spectrum of **9c** in chloroform with increasing content of methanol.

presence of only *intermolecular* processes upon aggregate formation. Polymer **9c** cannot planarize owing to its structural constraints (vide infra). Its aggregates are *not* detectable by UV/Vis spectroscopy. Contrary to this, in most conjugated organic polymers, aggregate formation is accompanied by changes in the UV/Vis spectra. In the chirally substituted polymer **3f**, benzene and cyclobutadiene-CpCo units alternate. Addition of methanol to a solution of **3f** in chloroform does *not* lead to the appearance of a CD spectrum, even at high concentrations, neither does **3f** show any chiroptical activity in the solid state, unlike **9c**. The bulky organometallic fragments in **3f** must disrupt the interaction of the chiral side chains, by acting as a stereochemical “insulator”. To understand this behavior it was necessary to obtain information on the solid-state structures of **3** and **9**.

Solid-state structure and liquid crystalline phase behavior of **3** and **9**:

The polymers **3** and **9** are isolated as yellow to tan-colored powders when precipitated from methanol and pentane. Films obtained by either solution casting or spin-coating are yellow and transparent. These films appear isotropic (black) under an optical microscope (crossed polarizers). The “as obtained” polymers **3** and **9** are amorphous and give a weak halo of scattered intensity as their powder X-ray-diffraction pattern. When polymer **3d** was recrystallized from pentane, by slow evaporation, distinct diffraction peaks in its XRD pattern were observed ($d = 11.2$ (100), 7.1, 6.4, 5.1, 4.8, 4.3, 3.7 Å). The bulky cobalt complex prevents the formation of parallel stacks; therefore, regardless of their orientation, the polymer chains of **3** or **9** will not be capable of assuming flat, boardlike structures. Instead, a cylindrical morphology

may be expected.^[19] A molecular model of a single chain of **3d** (PC Spartan Pro, MM2 force field) is shown in Figure 2. The “wing-span” of the bistrimethylsilyl-substituted cyclobutadiene complexes is 10.5 Å. This value corresponds fairly well



Figure 2. Representation of a polymer chain of **3e**. The calculation was performed with the MM2 force-field by utilizing Spartan Pro. Note the irregular conformational and rotational positions of the bulky side chains and the likewise bulky CpCo units in this polymer.

to the d spacing of 11.2 Å observed in the diffraction pattern of **3d**, and suggests 11.2 Å as the distance between two polymer chains. The hexyl groups could be folded into the remaining space and would not contribute significantly to intermolecular order in these polymers. In **3f** a d spacing of 11.5 Å is obtained, close to the value of the (100) spacing of **3d**. These diffraction data are substantially different from the ones obtained for the dihexyl-substituted PPEs **10a**.^[10c] PPEs form doubly lamellar, smectic or “smectic” phases, in which the wing-span of the solubilizing groups attached to the benzene nucleus is directly correlated to the prominent low-angle (100) diffraction peak.^[10c, d]

The diffraction peak recorded at 6.4 Å for **3d** could represent half of the repeating unit along the long axis of the macromolecule; this indicates that it is the (020) diffraction, with the (010), (030) and so forth systematically absent due to an interdigitated packing of the main chains. How to further interpret the diffraction data is not clear though. For both polymers **3** and **9** it would be difficult to assume the same structure in the solid state as for **10**. The polymers **9** show only diffuse scattering in their XRD patterns^[20] and do not develop a diffraction pattern after crystallization. Either **9** is truly disordered, or any crystalline/liquid crystalline (i.e., ordered) domains are very small.

The bulky organometallic groups will most likely force **3d** and **3f** into a cylindrical phase. We expect their liquid crystalline behavior to be different from that of dialkyl PPEs **10**, for which highly ordered, flat, doubly lamellar “smectic” phases have been reported. Heating an amorphous film of **3d** to temperatures above 155 °C leads to a Schlieren texture, which is indicative of a nematic phase.^[20] Variable temperature XRD shows that all crystalline order has disappeared at this temperature; this corroborates the inference that it is a nematic phase. The isotropic state has not been reached by 220 °C, at which temperature **3d** begins to decompose, changing from yellow to dark brown. This enantiotropic behavior is supported by differential scanning calorimetry (DSC), in which **3d** shows an endothermic phase transition at 130 °C (0.42 kcal mol⁻¹ per repeating unit, side-chain melting) and a structural change at 155 °C. These transitions are only

observed in the first heating curve but occur reproducibly in different samples. No transitions are recorded upon cooling or reheating; this suggests that the polymer's solid-state structure is "arrested" after the first heating cycle. The phase behavior of copolymers **9** is different. Amorphous films of rubbery or plastic **9b** and **9c** do not develop any texture (polarizing microscope) when heated. This is surprising, as the rigid organometallic chains of **9** should impart sufficient order to give a thermotropic-nematic phase.

It is possible to obtain *lyotropic*-nematic phases of **9** by slow evaporation of solutions of **9b** and **9c** in an atmosphere of chloroform over a period of several days (see Figure 3). In these preparations, well-developed Schlieren type textures occur. Heating the specimen to 110 °C under a polarizing microscope gives rise to an isotropic, "black" melt. Recooling to ambient temperature keeps **9** in the amorphous state, without optical birefringence, and suggests that re-entry into the liquid crystalline phase is kinetically hindered. Attempts to monitor the disappearance of the liquid crystalline phase of **9b** and **9c** by DSC were not successful. This suggests that the enthalpy for this phase transition (and its degree of order) is very small indeed. This behavior is similar to that of **3e** (vide supra). The absence of XRD patterns in **9** in the presence of a Schlieren texture suggests a nematic liquid crystalline phase.^[19] The incorporation of a second phenylene-ethynylene unit into the main chain (i.e., polymer **9**) severely disrupts the solid-state ordering of the rigid organometallic rods and leads to their weak angular correlation (parallel alignment). Efficient packing in **9** seems to be frustrated, so that even by slow evaporation of a solution of **9b** and **9c** in 1,2-dichlorobenzene or chloroform, respectively only a lyotropic nematic liquid crystalline phase is observed.

Transmission electron microscopy (TEM) of **3d**, **3f**, and **9c**:

To obtain more information about the solid state structure of the novel organometallic polymers, TEM was performed upon **3d**, **3f** and **9c**. Suitable films were obtained by layering a dilute solution of the polymer in dichloromethane carefully onto a water surface. Carbon shading of the polymer films at an angle of 5° was used to maximize the contrast. Polymer **9c** forms irregular honeycombed nanostructures which are composed of fibrils 25–42 nm wide (Figure 4, top). The fibrils enclose open spaces of 100–250 nm. This morphology resembles the open nano-networks observed by Müllen and Rabe in the self-assembly of PPEs on surfaces.^[5, 21] In contrast to **9c**, both **3d** and **3f** exhibit clear lamellar morphologies (Figure 4, middle and bottom). Polymer **3d** shows brush-type lamellae, similar to the ones reported for another polymer that contains **1** as its structural element.^[9c] Single lamellae in these brushes are approximately 18 nm wide: the width of one lamella thus corresponds to the length of one polymer strand (**3d**, $P_n = 18$, length of repeating unit in **3** = 1.1 nm, chain length of **3d** ≈ 20 nm). These data support the idea of a perpendicular orientation of the long axis of the polymer chains (**3d**) in these fibrils, similar to that which was observed in ref. [9c]. The chiral polymer **3f** has a slightly higher molecular weight ($P_n = 21$, $d = 24$ nm) and the observed width of the lamellae is increased to 28 nm. In addition, Figure 4 (bottom) shows that only 3–5 lamellae are grouped together.

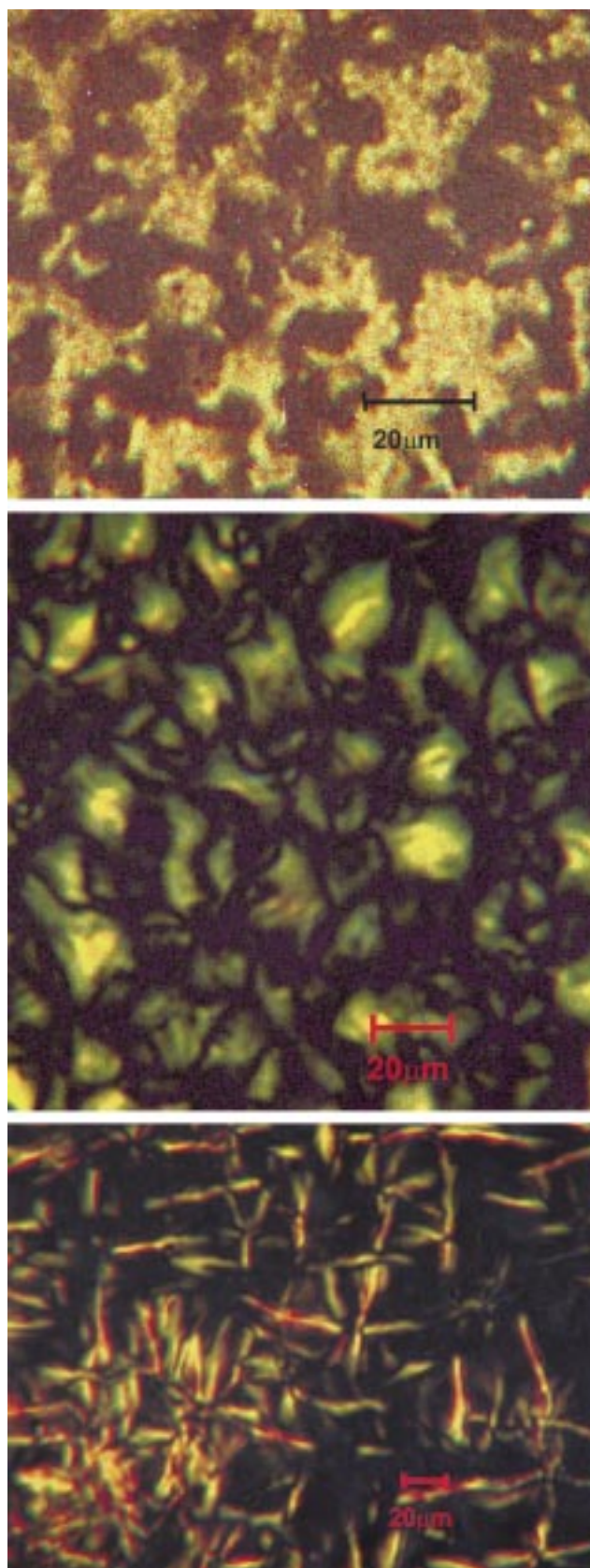


Figure 3. Schlieren texture of the frozen lyotropic phase under crossed polarizers of a polarizing microscope. Top: Polymer **9c** ($R = 2$ -ethylhexyl). Middle: Polymer **9b** ($R = (S)$ -3,7-dimethyloctyl). Bottom: Polymer **3f**. That this polymer forms batons, and not schlieren, suggests a higher, lamellar order in the arrangement of the main chains.

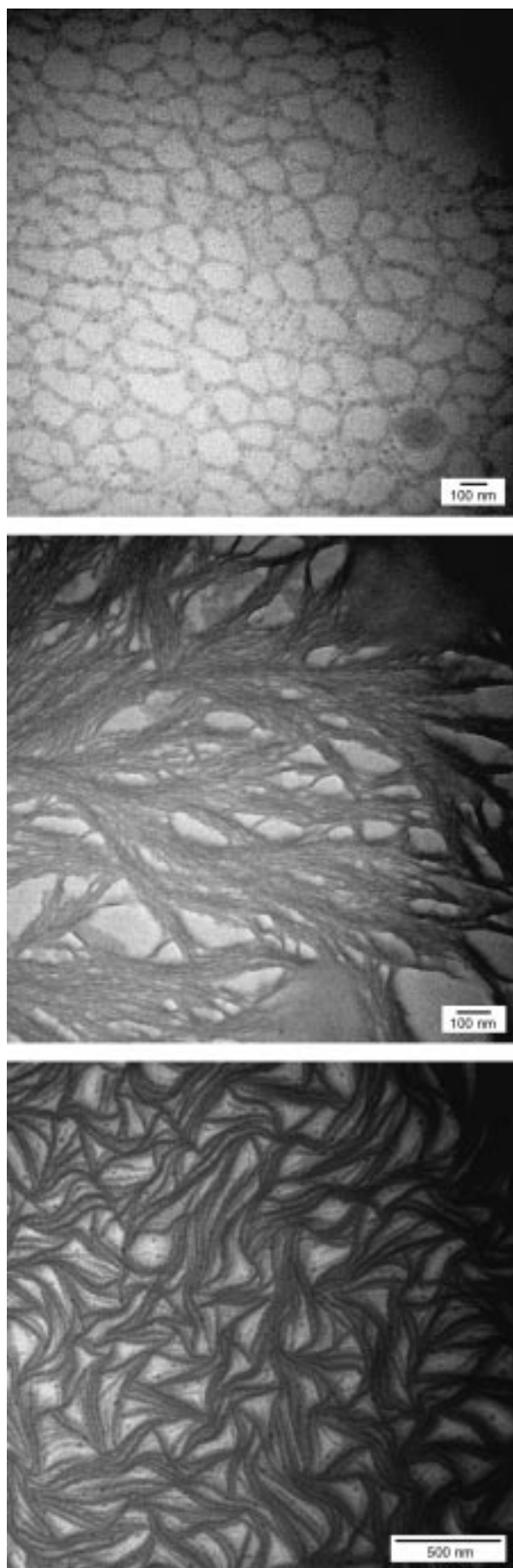


Figure 4. Top: TEM picture of a thin film of polymer **9c**. The irregular honeycombs are separated by fibrils which are 25–42 nm thick. Middle: Lamellar brushes of polymer **3d**. The lamellae are 20 nm wide and several μm long. Bottom: Short lamellae formed by **3f**. The lamellae are 28 nm wide and 0.2–0.3 μm long. All pictures were obtained after carbon shading of films deposited onto a copper grid. Bars indicate size of features.

The lamellae are quite short, 0.2–0.3 μm , but considerably beyond the length of a single polymer chain of **3f**. The morphologies of **3** resemble those of the high-molecular-weight bisethylhexyl PPE **10b**, in which lamellar structures (width = 36 nm) are observed. In the case of **10b**, the length axes of the polymer chains and the fiber are aligned in parallel, owing to the very high aspect ratio of **10b**,^[10c, d] so that, despite their resemblance, the super-structures of **3** and **10** originate from distinctly different *molecular* arrangements.

Comparison of polymers 3, 9, and 10: PPEs **10** are the polymers in this series that show the highest degree of order (for an in-depth discussion of solid-state structures of PPEs **10** see refs. [10c, d, 13a]). PPEs show a) strong XRD patterns, b) strong UV/Vis responses when comparing solution to solid-state spectra,^[3a] c) strong chiroptical responses,^[3b] d) well-developed thermotropic liquid crystalline phases,^[10d] and e) well-resolved lamellar morphologies in which the axes of polymer chains and fibrils are aligned when examined by TEM.^[10c]

Polymers **9** a) are XRD amorphous, b) have identical solution and solid-state UV/Vis spectra, c) have a substantial “bisignate” chiroptical display response, but d) only develop lyotropic nematic phases, and e) irregular honeycomb morphologies with fairly well defined features on the 100 nm scale.

Polymers **3** have a) significant XRD patterns, but these are only weakly influenced by the nature of the solubilizing alkyl chains, b) identical solution and solid-state UV/Vis spectra, c) *no* chiroptical signal, but d) enantiotropic thermotropic liquid crystalline behavior. The polymers **3d** and **3f** form e) spectacularly developed lamellar phases in which the long axes of the fibrils are *perpendicularly* oriented to the axes of the polymer chains.

Polymers **9** are only weakly ordered and form irregular-honeycomb nanostructures, but noticeably show aggregation according to their CD spectra. Polymers **3** display a much higher solid-state order, but of a distinctly different type from that in PPEs **10**. While **10** are lamellar, boardlike structures,^[10c, d] the bulky polymers **3** probably assume a lamellar-cylindrical phase, in which the TMS groups and not the alkyl chains are the primary structure-defining elements. A lamellar cylindrical phase would explain the absence of a chiroptical response and yet the development of highly ordered supramolecular structures.

Conclusion

This contribution describes the synthesis of the novel conjugated polymers **9**, which contain cyclobutadiene complexes in the main chain. The polymers were made by ADIMET of **8** with $[\text{Mo}(\text{CO})_6]/4$ -hydroxybenzotrifluoride mixtures. The investigation of the materials properties of **3**

and **9** and their comparison to the PPEs **10** leads to a series in which the degree of order decreases from $10 > 3 \gg 9$. A satisfying model for the solid-state structure of **3** (a lamellar cylindrical ordering), fundamentally different from the structure reported for the related organic polymers **10**, is proposed on grounds of the collected optical, thermal, and TEM data. The aggregation behavior of these organometallic polymers was examined and is a consequence of effective side-chain interactions in the solid state; in some cases, this results in an induced backbone–backbone interaction (polymers **9**). The introduction of organometallic units into conjugated polymers thus opens up possibilities of structural order not accessible to organic reference polymers of similar topology. In the future we will examine the semiconductor properties of **3** and **9** in proof-of-concept solid-state devices.

Experimental Section

General instrumentation: NMR spectra were obtained on Varian Gemini 200 and Varian Mercury 400 Instruments, or on a Bruker AC 300 or Bruker AMX 500 spectrometer. The IR spectra were obtained on a Nicolet FTIR 320. The mass spectra were obtained on a Varian CH7a and a VG Instruments ZAB2. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 15 and a Jasco Series V 530 UV/Vis spectrophotometer. GPC was performed on a Shimadzu LC6AD with a SCL10A system controller by utilizing a Waters Styragel HMWGE 7.8 × 300 mm column with polystyrene standards and chloroform (flow rate 1 mL min⁻¹) as eluent. DSC was performed on a Mettler DSC 30. Polarizing microscopy was performed on a Zeiss Axiophot or a polarizing microscope from Polish Optical Works equipped with a homebuilt camera system. TEM was performed in the South Carolina Electron Microscopy Center, at the University of South Carolina on a Hitachi H 8000 or on a Jeol 100 CX II with an attached digital AMT CCD camera. Circular dichroism (CD) spectroscopy was performed on a Jasco Series J 715 spectropolarimeter at the MPI für Polymerforschung. Powder diffraction was performed on a Rigaku D/Max 2200 powder X-ray diffractometer at 298 K.

Preparation of films for transmission electron microscopy (TEM) and polarizing microscopy: Suitable films for TEM were obtained by dissolving the respective polymer (**3**, **9**) in chloroform or dichloromethane. A small drop of the highly diluted solution was then placed on a water surface very carefully, to avoid the drop sinking to the bottom of the container. Held by the surface tension of water, the solution spread out to give a very thin film that was lifted from the surface by a nitrocellulose-coated copper grid used for TEM. The grid was carefully dried and then placed in a carbon evaporator, where it was shaded at an angle of 5° to obtain maximum contrast. Suitable specimens for polarizing microscopy were either obtained by spin casting a dilute solution of the respective polymer (**3**, **9**) onto a glass slide or by casting a drop of a concentrated solution of the polymer onto a glass slide and evaporating the solvent in a saturated atmosphere of chloroform. After 48 h the lyotropic or frozen lyotropic textures had formed and were examined by polarizing microscopy.

General experimental conditions: The Pd-catalyzed couplings were performed under inert conditions with exclusion of air and water. House nitrogen (obtained from the evaporation of commercial liquid nitrogen) was utilized without further purification. ACS reagent grade 1,2-dichlorobenzene, chloroform, dichloromethane, and piperidine were used as obtained. THF was distilled over potassium benzophenone prior to use for the halogen–metal exchange experiments. The catalysts and catalyst precursors, including [(Ph₃P)₂PdCl₂], [Mo(CO)₆], and 4-(trifluoromethyl)phenol, were used as obtained. Analytical thin-layer chromatography was performed on Merck silica-gel plates (on aluminum foil), and preparative column chromatography was performed with Merck flash silica gel (230–400 mesh). Eluents are given in the specific experimental descriptions. Melting points are uncorrected. Elemental analyses were performed by Willi Dindorf at the Institut für Organische Chemie der Universität Mainz.

General procedure “A” for the synthesis of polymers **3a–f from the Pd-catalyzed coupling of **1** with **2**:** Under a blanket of dry N₂, an oven-dried Schlenk flask was charged with CuI (10 mol %), [(PPh₃)₂PdCl₂] (2–5 mol %), and an equimolar amount of **1** and **2**. Then piperidine (approx. 10 mL) was added. The mixture was stirred for 18–24 h at a temperature of 21–26 °C. During this time, precipitation of insoluble ammonium salts and a considerable darkening of the reaction mixture were observed. Removal of the ammonium salts by filtration and high-vacuum transfer of the piperidine was followed by precipitation of the crude polymer into methanol. The resulting yellow flakes were filtered, redissolved in chloroform, and precipitated into cold pentane. The suspension was held at –10 °C for 24 h and filtered cold. The precipitated polymer **3** was collected and dried at ambient temperature under high vacuum for 24 h.

Synthesis of **3a:** According to general procedure **A**, **1a** (151 mg, 0.669 mmol), 1,4-dihexyl-2,5-diiodobenzene (333 mg, 0.669 mmol), [(PPh₃)₂PdCl₂] (23.7 mg, 0.0033 mmol), and CuI (4.2 mg, 0.022 mmol) were dissolved in piperidine (10 mL) and allowed to react. Workup resulted in a yellow, film-forming material **3a**. Yield: 241 mg, 71 %; IR (KBr): $\tilde{\nu}$ = 3105, 2955, 2925, 2856, 2190 cm⁻¹; ¹H NMR (CDCl₃): δ = 7.18 (s, 2H), 5.06 (s, 5H), 4.66 (s, 2H), 2.46 (brs, 4H), 1.61 (brs, 4H), 1.36 (brs, 12H), 0.93 (brs, 6H), end groups are visible at δ = 7.56 (s); this is suggestive of a proton in the vicinity of a C–I group; ¹³C NMR (CDCl₃): δ = 142.21, 132.14, 128.32, 91.50 (alkyne-C), 89.33 (alkyne-C), 81.67 (Cp-C), 64.62, 55.85, 34.43, 32.11, 31.04, 29.63, 23.14, 19.02; elemental analysis calcd (%) for [C₃₁H₃₅Co]_n ([466.54]_n): C 75.95, H 7.36; found C 71.13, H 7.25 (incomplete combustion).

Synthesis of **3b:** According to general procedure **A**, **1b** (142 mg, 0.385 mmol), 1,4-diiodobenzene (127 mg, 0.385 mmol), [(PPh₃)₂PdCl₂] (14.2 mg, 0.020 mmol), and CuI (2.8 mg, 0.015 mmol) were dissolved in piperidine (10 mL) and allowed to react. Workup resulted in a red, film-forming material **3b**. Yield: 140 mg, 82 %; IR (KBr): $\tilde{\nu}$ = 3015, 2962, 2898, 2192, 2127 cm⁻¹; ¹H NMR (CDCl₃): δ = 7.27 (s, 4H), 4.97 (s, 5H), 0.37 (s, 18H), end groups give weak singlets at δ = 7.11, 7.64; ¹³C NMR (CDCl₃): δ = 130.94, 123.66, 91.08 (alkyne-C), 81.68 (Cp-C), 77.11, 76.08, 65.39, –0.31 (Si(CH₃)₃); elemental analysis calcd (%) for [C₂₅H₂₇CoSi₂]_n ([442.58]_n): C 67.85, H 6.15; found C 62.54, H 6.11 (incomplete combustion).

Synthesis of **3c:** According to general procedure **A**, **1a** (150 mg, 0.674 mmol), 1,4-didodecyl-2,5-diiodobenzene (450 mg, 0.674 mmol), [(PPh₃)₂PdCl₂] (24.7 mg, 0.035 mmol), and CuI (5.3 mg, 0.028 mmol) were dissolved in piperidine (10 mL) and allowed to react. Workup resulted in a yellow, film-forming material **3c**. Yield: 339 mg, 79 %; IR (KBr): $\tilde{\nu}$ = 3104, 2953, 2923, 2853, 2188 cm⁻¹; ¹H NMR (CDCl₃): δ = 7.17 (s, 2H), 5.06 (s, 5H), 4.67 (s, 2H), 2.65 (brs, 4H), 1.55 (brs, 4H), 1.29 (brs, 36H), 0.88 (brs, 6H); ¹³C NMR (CDCl₃): δ = 142.20, 132.95, 122.95, 91.45 (alkyne-C), 89.29 (alkyne-C), 81.58 (Cp-C), 64.61, 55.78, 35.82, 33.76, 32.48, 31.54, 31.50, 31.38, 31.19, 24.52, 15.71; elemental analysis calcd (%) for [C₄₃H₅₉Co]_n ([634.86]_n): C 81.31, H 9.37; found C 76.86, H 9.04 (incomplete combustion).

Synthesis of **3d:** According to general procedure **A**, **1b** (177 mg, 0.480 mmol), 1,4-dihexyl-2,5-diiodobenzene (239 mg, 0.480 mmol), [(PPh₃)₂PdCl₂] (17.0 mg, 0.024 mmol), and CuI (5.4 mg, 0.028 mmol) were dissolved in piperidine (10 mL) and allowed to react. Workup resulted in a red, film-forming material **3d**. Yield: 229 mg, 78 %; IR (KBr): $\tilde{\nu}$ = 3105, 2956, 2927, 2869, 2190, 2132 cm⁻¹; ¹H NMR (CDCl₃): δ = 7.14 (s, 2H), 5.00 (s, 5H), 2.67 (brs, 4H), 1.60 (brs, 4H), 1.35 (brs, 12H), 0.92 (brs, 6H), 0.39 (s, 18H); ¹³C NMR (CDCl₃): δ = 141.83, 132.53, 123.61, 93.93 (alkyne-C), 90.84 (alkyne-C), 81.96 (Cp-C), 76.28, 66.24, 34.66, 32.63, 31.29, 29.87, 23.47, 14.64, 0.04; UV/Vis (CHCl₃): λ_{max} (ϵ) = 361 nm (24600); (80 % MeOH): λ_{max} (ϵ) = 355 nm (24200); (film): λ_{max} = 361 nm; elemental analysis calcd (%) for [C₃₇H₅₁CoSi₂]_n ([610.90]_n): C 72.75, H 8.14; found C 66.65, H 8.14 (incomplete combustion).

Synthesis of **3e:** According to general procedure **A**, **1b** (161 mg, 0.438 mmol), 1,4-didodecyl-2,5-diiodobenzene (292 mg, 0.438 mmol), [(PPh₃)₂PdCl₂] (17.0 mg, 0.024 mmol), and CuI (4.0 mg, 0.021 mmol) were dissolved in piperidine (10 mL) and allowed to react. Workup resulted in a red, film-forming material **3e**. Yield: 280 mg, 82 %; IR (KBr): $\tilde{\nu}$ = 3105, 2955, 2925, 2845, 2190, 2128 cm⁻¹; ¹H NMR (CDCl₃): δ = 7.14 (s, 2H), 4.99 (s, 5H), 2.66 (brs, 4H), 1.61 (brs, 4H), 1.28 (brs, 36H), 0.89 (t, ³J(H,H) = 6.1 Hz, 6H), 0.38 (s, 18H); ¹³C NMR (CDCl₃): δ = 141.84, 132.53, 123.63, 93.92 (alkyne-C), 90.86 (alkyne-C), 81.96 (Cp-C), 76.26, 66.25, 34.69, 32.70, 31.53, 30.46, 30.26, 30.12, 23.54, 14.63, –0.05 (Si(Me₃)₃); elemental analysis

calcd (%) for $[C_{49}H_{75}CoSi_2]_n$ ([779.22]_n): C 73.19, H 9.50; found C 68.95, H 10.01 (incomplete combustion).

Synthesis of 3f: According to general procedure **A**, **1b** (101 mg, 0.275 mmol), 1,4-diiodo-2,5-bis[(S)-3,7-dimethyloctyl]benzene (163 mg, 0.267 mmol), $[(PPh_3)_2PdCl_2]$ (1.9 mg, 0.0028 mmol), and CuI (3.0 mg, 0.0016 mmol) were dissolved in piperidine (3 mL) and allowed to react. Workup resulted in a yellow-brown, soluble material **3f**. Yield: 140 mg, 71%; IR: $\tilde{\nu}$ = 2953, 2867, 2360, 2184 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.09 (s, 2H), 4.94 (s, 5H), 2.63 (brs, 4H), 1.60–1.13 (br m, 20H), 0.94 (m, 6H), 0.85 (m, 12H), 0.26 (s, 18H); ^{13}C NMR ($CDCl_3$): δ = 141.02, 131.62, 122.91, 93.21 (alkyne-C), 90.02 (alkyne-C), 81.26 (Cp-C), 75.47, 65.42, 39.35, 37.81, 37.53, 37.25, 37.03, 32.63, 32.51, 31.32, 31.18, 27.97, 24.68, 22.751, 22.64, 19.63, 1.00; UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 364 nm (24200); (80% MeOH): λ_{max} (ϵ) = 357 nm (23800); (film): λ_{max} = 366 nm.

General procedure "B" for the synthesis of compounds 6a–c: A solution of **5a–c** in THF was cooled to $-78^\circ C$ under an inert atmosphere. After addition of *n*-BuLi, the reaction mixture was stirred for 20 min. The monolithiated intermediate was treated with a solution of iodine in dry THF. Reduction of the excess iodine with a saturated solution of Na_2SO_3 , aqueous workup, extraction with hexanes, and removal of solvent in vacuo, followed by column chromatography (hexanes), furnished **6a–c**.

Synthesis of 6a: An oven-dried Schlenk flask was charged with **5a** (10.0 g, 24.7 mmol) and THF (200 mL). *n*-BuLi (18.5 mL, 29.6 mmol, 1.6 M in hexane), then iodine (7.53 g, 29.7 mmol) in THF (50 mL) were added according to general procedure **B**. Crystallization from ethanol yielded colorless crystals of **6a**. Yield: 8.50 g, 75%; 1H NMR ($CDCl_3$): δ = 7.60 (s, 1H), 7.31 (s, 1H), 2.62 (t, $^3J(H,H)$ = 7.8 Hz, 4H), 1.57–1.52 (m, 4H), 1.37–1.30 (m, 12H), 0.90–0.87 (m, 6H); ^{13}C NMR ($CDCl_3$): δ = 144.46, 141.33, 140.11, 132.62, 124.35 (ar-Br), 98.78 (ar-I), 40.17, 35.40, 31.70, 30.21, 29.91, 29.13, 29.09, 22.71, 14.22.

Synthesis of 6b: An oven-dried Schlenk flask was charged with **5b** (24.0 g, 52.1 mmol) and THF (150 mL). *n*-BuLi (44.0 mL, 61.6 mmol, 1.4 M in hexane), then iodine (15.9 g, 62.6 mmol) in THF (150 mL) were added according to general procedure **B** to give a colorless oil **6b**. Yield: 22.72 g, 86%; 1H NMR ($CDCl_3$): δ = 7.59 (s, 1H), 7.29 (s, 1H), 2.58–2.56 (m, 4H), 1.71–1.66 (m, 2H), 1.27–1.28 (m, 16H), 0.92–0.87 (m, 12H); ^{13}C NMR ($CDCl_3$): δ = 143.45, 141.31, 141.11, 140.40, 133.83, 124.57 (ar-Br), 99.16 (ar-I), 44.21, 39.67, 39.28, 32.33, 32.20, 28.72, 25.61, 25.45, 23.15, 14.24, 10.91.

Synthesis of 6c: An oven-dried Schlenk flask was charged with **5c** (6.07 g, 11.8 mmol) and THF (100 mL). *n*-BuLi (8.8 mL, 14.1 mmol, 1.6 M in hexane), then iodine (3.64 g, 14.3 mmol) in THF (50 mL) were added according to general procedure **B** to give a colorless oil **6c**. Yield: 5.76 g, 93%; 1H NMR ($CDCl_3$): δ = 7.61 (s, 1H), 7.32 (s, 1H), 2.67–2.53 (m, 4H), 1.60–1.40 (m, 4H), 1.39–1.23 (m, 12H), 1.20–1.12 (m, 4H), 0.97–0.94 (m, 6H), 0.89–0.87 (d, $^3J(H,H)$ = 6.6 Hz, 12H); ^{13}C NMR ($CDCl_3$): δ = 144.73, 141.60, 140.11, 132.64, 124.38 (ar-Br), 98.77 (ar-I), 39.41, 37.94, 37.60, 37.28, 37.15, 37.11, 33.15, 32.91, 28.11, 24.88, 24.85, 22.91, 22.83, 19.84, 19.79.

General procedure "C" for the synthesis of 7a–c: A Schlenk flask of known volume that contained the appropriate amount of a 4-bromo-2,5-di(alkyl)iodobenzene **6a–c**, $[(PPh_3)_2PdCl_2]$, and CuI was evacuated. After addition of piperidine, the reaction vessel was filled with 1 atm of propyne. A colorless precipitate formed after 30 min. The reaction mixture was stirred or shaken for a total period of 12 h. Aqueous workup and extraction with hexanes furnished **7a–c** after chromatography (silica gel/hexanes).

Synthesis of 7a: Compound **6a** (6.01 g, 13.3 mmol), $[(PPh_3)_2PdCl_2]$ (0.194 g, 0.277 mmol), CuI (0.030 g, 0.16 mmol) and piperidine (20 mL) were allowed to react in a 300 mL Schlenk flask according to general procedure **C** to furnish **7a** as colorless oil. Yield: 3.35 g, 75%; IR: $\tilde{\nu}$ = 2940, 2859, 2233 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.32 (s, 1H), 7.20 (s, 1H), 2.69–2.61 (m, 4H), 2.06 (s, 3H), 1.64–1.56 (m, 4H), 1.54–1.32 (m, 12H), 0.92–0.89 (m, 6H); ^{13}C NMR ($CDCl_3$): δ = 143.57, 138.78, 133.26, 132.27, 123.44 (ar-Br), 122.53, 89.07 (alkyne-C), 77.93 (alkyne-C), 35.63, 33.86, 31.79, 31.74, 30.44, 29.93, 29.18, 22.75, 22.71, 14.16, 14.14, 4.30; UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 253 (19600), 259 nm (20400); MS (70 eV, EI): m/z (%): 364 (100) $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{31}Br$ (363.37): C 69.41, H 8.60; found C 69.40 H 8.67.

Synthesis of 7b: Compound **6b** (7.89 g, 15.5 mmol), $[(PPh_3)_2PdCl_2]$ (0.108 g, 0.155 mmol), CuI (0.015 g, 0.079 mmol), and piperidine (20 mL) were allowed to react in a 350 mL Schlenk flask according to general procedure **C** to furnish **7b** as colorless oil. Yield: 3.80 g, 60%; IR: $\tilde{\nu}$ = 2928, 2871 cm^{-1} ;

1H NMR ($CDCl_3$): δ = 7.26 (s, 1H), 7.13 (s, 1H), 2.57–2.53 (m, 4H), 2.04 (s, 3H), 1.67–1.61 (m, 2H), 1.30–1.24 (m, 18H), 0.88–0.84 (m, 12H); ^{13}C NMR ($CDCl_3$): δ = 142.91, 138.03, 134.51, 133.58, 123.77 (ar-Br), 122.65, 89.43 (alkyne-C), 78.29 (alkyne-C), 40.25, 39.94, 39.32, 38.26, 32.65, 32.47, 29.00, 28.85, 25.78, 25.58, 23.16, 14.24, 14.21, 10.97, 10.86, 4.54; UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 253 (17750), 260 nm (18300); MS (70 eV, EI): m/z (%): 420 (100) $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{39}Br$ (419.48): C 71.58, H 9.37; found C 71.68, H 9.32.

Synthesis of 7c: Compound **6c** (5.76 g, 10.2 mmol), $[(PPh_3)_2PdCl_2]$ (0.104 g, 0.149 mmol), CuI (0.015 g, 0.078 mmol), and piperidine (20 mL) were allowed to react in a 225 mL Schlenk flask according to general procedure **C** to furnish **7c** as colorless oil. Yield: 3.30 g, 70%; IR: $\tilde{\nu}$ = 2925, 2868 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.32 (s, 1H), 7.20 (s, 1H), 2.75–2.56 (m, 4H), 2.06 (s, 3H), 1.64–1.41 (m, 4H), 1.41–1.23 (m, 12H), 1.19–1.15 (m, 4H), 0.96 (d, 6H, 3J = 6.4 Hz), 0.89 (d, 12H, 3J = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ = 144.02, 139.21, 133.31, 132.42, 123.48 (ar-Br), 122.54, 89.25 (alkyne-C), 77.94 (alkyne-C), 39.46, 39.44, 38.03, 37.33, 37.21, 37.17, 33.35, 32.92, 32.88, 31.66, 28.11, 24.92, 24.85, 22.87, 22.79, 19.82, 19.79, 4.51; UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 252 (18700), 259 nm (19400); MS (70 eV, EI): m/z (%): 476 (100) $[M]^+$; elemental analysis calcd (%) for $C_{29}H_{47}Br$ (475.59): C 73.24, H 9.96; found C 73.95, H 9.81.

General procedure "D" for the synthesis of 8a–c: Compounds **7a–c**, the organometallic complex **1c**, PPh_3 , $[(PPh_3)_2PdCl_2]$, CuI and a measured amount of 5% ethanolic KOH were dissolved in diisopropylamine under nitrogen. The solution was heated under reflux for 12 h. Addition of hexanes to the reaction mixture, aqueous workup, and removal of the solvent in vacuo, followed by column chromatography (silica gel/hexanes) gave **8a–c** as yellow oils.

Synthesis of 8a: Compound **7a** (0.492 g, 1.35 mmol), **1c** (0.330 g, 0.642 mmol), PPh_3 (0.018 g, 0.069 mmol), $[(PPh_3)_2PdCl_2]$ (0.024 g, 0.034 mmol), CuI (3.0 mg, 0.016 mmol), and ethanolic KOH (5%, 3 mL) were dissolved in diisopropylamine (5 mL) according to general procedure **C** to furnish **8a**. Yield: 0.230 g, 40%; IR: $\tilde{\nu}$ = 2926, 2856, 1493 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.17 (s, 2H), 7.11 (s, 2H), 4.96 (s, 5H), 2.08 (s, 6H), 1.64–1.58 (m, 8H), 1.35–1.32 (m, 24H), 0.97–0.89 (m, 12H), 0.37 (s, 18H); ^{13}C NMR ($CDCl_3$): δ = 141.77, 140.67, 132.14, 131.45, 122.65, 122.54, 92.67 (alkyne-C), 89.95 (alkyne-C), 89.80 (alkyne-C), 81.11 (Cp-C), 78.76 (alkyne-C), 75.38, 65.44, 34.10, 33.89, 31.98, 31.73, 30.61, 30.47, 29.80, 29.30, 29.15, 22.79, 22.72, 14.26, 4.67, –0.09; UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 313 (4960), 330 nm (5300); MS (70 eV, EI): m/z (%): 933 (100) $[M - 2CH_3]^+$; elemental analysis calcd (%) for $C_{61}H_{85}CoSi_2$ (964.61): C 78.49, H 9.18; found C 78.00, H 9.81.

Synthesis of 8b: Compound **7b** (1.83 g, 4.37 mmol), **1c** (1.03 g, 2.01 mmol), PPh_3 (0.052 g, 0.023 mmol), $[(PPh_3)_2PdCl_2]$ (0.071 g, 0.10 mmol), CuI (0.010 g, 0.053 mmol), and ethanolic KOH (5%, 3 mL) were dissolved in diisopropylamine (5 mL) according to general procedure **C** to furnish **8b**. Yield: 1.05 g, 48%; IR: $\tilde{\nu}$ = 2957, 2927, 2871, 1461 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.15 (s, 2H), 7.09 (s, 2H), 4.96 (s, 5H), 2.63–2.60 (m, 8H), 2.08 (s, 6H), 1.69–1.67 (m, 4H), 1.35–1.29 (m, 36H), 0.93–0.85 (m, 24H), 0.37 (s, 18H); ^{13}C NMR ($CDCl_3$): δ = 140.74, 139.68, 132.73, 132.64, 123.26, 122.86, 92.63 (alkyne-C), 90.35 (alkyne-C), 89.99 (alkyne-C), 81.12 (Cp-C), 79.17 (alkyne-C), 75.32, 65.56, 40.26, 40.09, 38.07, 32.60, 32.50, 31.69, 28.94, 25.82, 25.71, 23.19, 23.17, 22.77, 14.29, 14.23, 11.01, 4.70, –0.05; UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 314 (43350), 330 nm (45080); MS (70 eV, EI): m/z (%): 1045 (100) $[M - 2CH_3]^+$; elemental analysis calcd (%) for $C_{69}H_{101}CoSi_2$ (1045.64): C 79.26, H 9.74; found C 79.09, H 10.21.

Synthesis of 8c: Compound **7c** (2.04 g, 4.30 mmol), **1c** (1.02 g, 1.98 mmol), PPh_3 (0.042 g, 0.17 mmol), $[(PPh_3)_2PdCl_2]$ (0.061 g, 0.087 mmol), CuI (8.0 mg, 0.042 mmol) and ethanolic KOH (5%, 3 mL) were dissolved in diisopropylamine (5 mL) according to general procedure **C** to furnish **8c**. Yield: 0.943 g, 43%; IR: $\tilde{\nu}$ = 2953, 2925, 1493 cm^{-1} ; 1H NMR ($CDCl_3$): δ = 7.18 (s, 2H), 7.12 (s, 2H), 4.97 (s, 5H), 2.77–2.61 (m, 8H), 1.40–1.21 (m, 24H), 1.20–1.10 (m, 8H), 0.98–0.95 (m, 12H), 0.90–0.87 (m, 24H), 0.38 (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 142.09, 140.84, 131.88, 131.54, 122.77, 122.51, 92.75 (alkyne-C), 89.96 (alkyne-C), 89.75 (alkyne-C), 81.16 (Cp-C), 78.77 (alkyne-C), 75.42, 65.43, 39.46, 39.44, 38.04, 37.75, 37.42, 37.22, 32.91, 32.71, 31.69, 31.49, 28.09, 24.86, 24.83, 22.84, 22.76, 22.73, 19.79, 14.24, 4.69, –0.03; UV/Vis ($CHCl_3$): λ_{max} (ϵ) = 313 (63150), 329 nm (64730); MS (70 eV, EI): m/z (%): 1157 (100) $[M - 2TMS]^+$; elemental analysis calcd (%) for $C_{77}H_{117}CoSi_2$ (1157.86): C 79.87, H 10.19; found C 78.93, H 9.89.

General procedure "E" for the polymerization of 8a–c: Monomers 8a–c and the catalyst precursors $[\text{Mo}(\text{CO})_6]$ (20 mol %) and 4-hydroxybenzotri-fluoride (1 equiv with respect to the monomer 8a–c) were dissolved in 1,2-dichlorobenzene and stirred for 48 h at 150 °C, while butyne was removed by a slow stream of nitrogen. The solution was cooled and the precipitated polymers 9a–c were dissolved by the addition of CH_2Cl_2 . The organic layer was washed with 20 mL of each of H_2O , 10% NaOH, and 25% HCl. Addition of methanol precipitated the polymer 9, which was filtered and vacuum-dried.

Synthesis of 9a: Compound 8a (0.234 g, 0.251 mmol), 4-hydroxybenzotri-fluoride (0.041 g, 0.24 mmol), and $[\text{Mo}(\text{CO})_6]$ (0.013 g, 0.049 mmol) in 1,2-dichlorobenzene (10 mL) were allowed to react according to general procedure E. Workup after sonication of the precipitated polymer in CHCl_3 for 1 h resulted in the brittle yellow 9a. Yield: 0.090 g, 40%, soluble fraction; IR: $\tilde{\nu} = 2917, 2849, 1498, 1461 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 7.28$ (brs, 2H), 7.15 (brs, 2H), 4.97 (brs, 5H), 2.78–2.67 (brm, 8H), 1.65–1.53 (brm, 8H), 1.32 (brm, 24H), 0.88 (brm, 12H), 0.06 (brs, 18H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 141.68, 140.88, 132.22, 131.66, 123.41, 122.03, 93.43$ (alkyne-C), 89.85 (alkyne-C), 81.16 (Cp-C), 75.59, 65.41, 34.19, 31.91, 30.71, 29.78, 29.36, 22.81, 14.26, –0.05; UV/Vis (CHCl_3): λ_{max} (ϵ) = 382 nm (23 150); (70% MeOH): λ_{max} (ϵ) = 389 nm (21 050); (film): λ_{max} = 386 nm.

Synthesis of 9b: Compound 8b (0.461 g, 0.441 mmol), 4-hydroxybenzotri-fluoride (0.072 g, 0.44 mmol), and $[\text{Mo}(\text{CO})_6]$ (0.023 g, 0.083 mmol) in 1,2-dichlorobenzene (10 mL) were allowed to react according to general procedure E. Workup resulted in the brown plastic polymer 9b. Yield: 0.363 g, 83%; IR: $\tilde{\nu} = 2957, 2922, 2869, 2183, 1503 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 7.21$ (brs, 2H), 7.12 (brs, 2H), 4.96 (brs, 5H), 2.62 (brm, 8H), 1.70 (brm, 4H), 1.28 (brm, 36H), 0.89–0.84 (brm, 24H), 0.06 (brs, 18H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 140.63, 139.82, 132.72, 132.59, 124.00, 122.44, 93.32$ (alkyne-C), 90.38 (alkyne-C), 81.16 (Cp-C), 75.51, 65.51, 40.14, 38.42, 38.10, 32.48, 32.38, 28.94, 28.72, 25.75, 23.21, 14.25, 11.02, 10.98, –0.01; UV/Vis (CHCl_3): λ_{max} (ϵ) = 378 nm (39 580); (70% MeOH): λ_{max} (ϵ) = 375 nm (37 780); (film): λ_{max} = 378 nm; elemental analysis calcd (%) for $\text{C}_{65}\text{H}_{91}\text{CoSi}_2$ (986.59): C 78.95, H 10.08; found C 77.49, H 9.32.

Synthesis of 9c: Compound 8c (0.435 g, 0.376 mmol), 4-hydroxytrifluoro-benzene (0.062 g, 0.37 mmol), and $[\text{Mo}(\text{CO})_6]$ (0.018 g, 0.068 mmol) in 1,2-dichlorobenzene (10 mL) were allowed to react according to general procedure E to give the rubbery polymer 9c. Yield: 0.381 g, 93%; IR: $\tilde{\nu} = 2953, 2867, 2183, 1497 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 7.26$ (brs, 2H), 7.13 (brs, 2H), 4.94 (brs, 5H), 2.70 (brm, 8H), 1.64–1.46 (brm, 8H), 1.32–1.24 (brm, 24H), 1.12 (brm, 8H), 0.95 (brm, 8H), 0.84 (brm, 24H), 0.04 (brs, 18H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 141.98, 141.05, 131.90, 123.51, 122.00, 92.96$ (alkyne-C), 89.90 (alkyne-C), 81.18 (Cp-C), 75.58, 65.37, 39.43, 38.17, 37.77, 37.34, 32.97, 31.89, 31.58, 30.16, 29.75, 28.08, 24.87, 22.78, 19.82, –0.01; UV/Vis (CHCl_3): λ_{max} (ϵ) = 380 (42 500); (70% MeOH): λ_{max} (ϵ) = 386 nm (38 450); (film): λ_{max} = 382 nm; elemental analysis calcd (%) for $\text{C}_{73}\text{H}_{106}\text{CoSi}_2$ (1097.71): C 79.65, H 9.89; found C 74.77, H 9.80; incomplete combustion.

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