Templated Ceramic Microstructures by Using the Breath-Figure Method

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Abstract: We describe the synthesis of two cyclobutadiene(cyclopentadienyl)-cobalt-containing poly(p-phenylene ethynylene)s (PPEs) and their use as precursors for stable ceramic surface coatings. Organometallic PPEs were shaped into hexagonally ordered assemblies by using the breath-figure method. Such breath figures can be washed away with an appropriate solvent. Upon pyrolysis at 500°C under either nitrogen or air, the bubble arrays persist as ceramics and are insoluble in organic solvents or water. The formed pyrolyzed bubble arrays were analyzed by optical and scanning electron microscopy, as well as energy dispersive X-ray microanalysis (EDX). The composition of the ceramic materials is discussed based on EDX and IR data.

Keywords: breath figures · bubble arrays · ceramics · organometallic polymers · self-assembly

Introduction

We report on hexagonally microstructured Si−C−Co and Si−Co−O ceramics produced from precursor polymers that form self-assembled bubble arrays using the breath-figure method.

Non-oxide Si−C ceramics are inorganic materials that are hard, resistant to high temperatures, oxidizing and reducing agents, and insoluble in organic solvents. Ceramic materials can be shaped by using a precursor polymer that is cast into a mould, cross-linked, and thermolyzed.[1–3] Polysilanes and polycarbosilanes are utilized towards this end. High unsaturation and good processability of the precursor polymers are prerequisites. Microstructured ceramics have potential use in photonic crystals, as support for vertebrate cell growth, and as dirt-repellent coatings showing the "lotus leaf" effect,[4] while backfilling ceramic arrays with organic semiconductors would provide access to novel device architectures.

It would be tedious to scratch microstructures into thin ceramic films. There have been widespread efforts to utilize templating methods instead. A common approach is to infiltrate a colloidal crystal, made from polystyrene spheres, with a soluble inorganic precursor. The precursor is processed into a highly cross-linked preceramic from which the polystyrene particles are burned off at temperatures above 480°C. Alternatively, arrays of silica nanospheres can be backfilled and the spheres removed later by hydrofluoric acid. Impressive three-dimensional structures have been obtained by both methods, but the dimensions of the skeletal structures are fixed and dependent upon the size of the templates, that is, the polystyrene or silica mesospheres.[5, 6]

Condensing water vapor forms small droplets on cold surfaces. An example of this process is the fogging of glass or metal, first investigated by Lord Rayleigh.[7] Water droplets form patterns, "breath figures" on solid *and* liquid surfaces.[8] If moist air is blown over a dilute solution of polystyrene in a volatile solvent, breath figures can be "fossilized" as hexagonally ordered polymeric bubble arrays.[9] This effect was harnessed to imprint micron-sized bubble arrays onto polymers of widely different structure.[10–13] Srinivasarao et al.[14] investigated the mechanism of bubble-array formation and fabricated polymeric arrays in which the size of the monodisperse bubbles varied in the range of 0.2–20 microns. The generation of bubble arrays is simple yet dynamic with respect to the size of the bubbles, and can be dependent on polymer structure. We report bubble arrays of silicon-containing organometallic polymers[15] that change into microstructured ceramic materials at temperatures above 500°C. The originally interconnected bubble arrays turn into a mesh of

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self-assembled ceramic "picoliter beakers"[10a] after pyrolysis.

Results and Discussion

Reaction of the cobalt–cyclobutadiene complex **1**[16] with diiodide **2** and a Pd/Cu catalyst[17,18] furnished polymer **3**[15] (Scheme 1) in a yield of 88%, a molecular weight (M_n) of
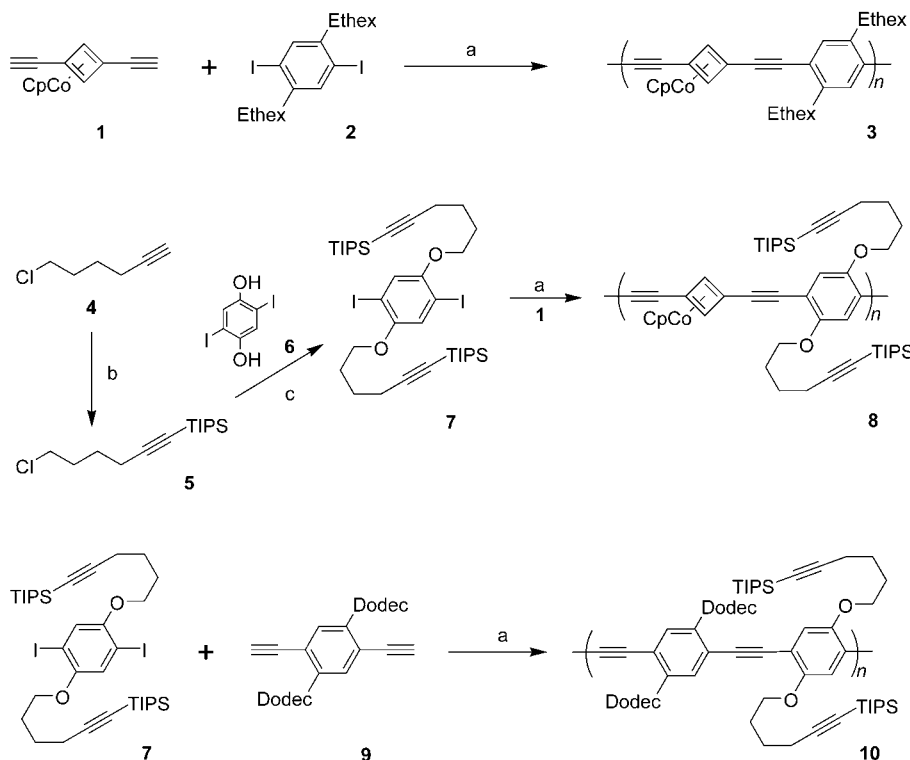
Scheme 1. Syntheses of polymers **3**, **8**, and **10**. a) [PdCl$_2$(Ph$_3$P)$_2$], CuI/THF, piperidine; b) Lithium diisopropyl-amide (LDA), triisopropylsilylchloride (TIPSCl), THF; c) DMF, K$_2$CO$_3$. Abbreviations: Ethex = (2-ethyl)hex-yl, Cp = cyclopentadienyl, Dodec = dodecyl.

2.7×10^4, and a polydispersity index (PDI) of 9.1 (bimodal). Compound **3** is deep yellow, of fibrous appearance, and soluble in chloroform, THF, and dichloromethane. The silylated monomer **7** was prepared by reacting 6-chlorohexyne **4** with lithiumdiisopropylamide (LDA) and quenching the resulting anion with chlorotriisopropylsilane (TIPSCl) to give **5**. A base-catalyzed reaction of **5** with the hydroquinone derivative **6** provided monomer **7**. Coupling of the cyclobutadiene complex **1** with **7** under standard Pd catalysis conditions furnished polymer **8** in an 84% yield as a flaky, deep yellow, and nonfluorescent material after aqueous workup and precipitation into methanol; **8** was isolated with a M_n of 1.3×10^4 and a PDI of 1.6. To access a cobalt-free polymer, the diiodide **7** was coupled to 1,4-diethynyl-2,5-bis-dodecylbenzene **9**. The resulting PPE **10** was obtained in an 89% yield as a highly fluorescent, yellow solid, soluble in common organic solvents. According to gel permeation chromatography, the molecular weight of **10** is 30.4×10^3

with a PDI of 4.54. Polymers **3**, **8**, and **10** were characterized by their NMR and IR spectra.

We attempted to cast bubbles from **3** but only badly mis-shapen arrays formed. Upon co-dissolution of **3** with a 3.2-fold excess of carboxy-terminated polystyrene, well-developed bubble arrays were obtained from a carbon disulfide/pentane mixture (2:1 v/v, Figure 1). The bubbles change size from domain to domain. Single domains, however, show perfectly monodisperse patches of hexagonally arranged bubble arrays. Upon heating to 530 °C, most of the polymeric substance has been removed by pyrolysis and only a small amount of material is left (Figure 1, right). The hexagonal ordering, nevertheless, is still visible in the remaining ridges (Figure 1, right).

Small changes in the polymer structure can lead to better bubble arrays when using the breath-figure method. Some silyl-substituted PPEs formed bubble arrays easily.[19] However, polymer **10** did not give any useful bubble arrays and its oligomer ($P_n = 5$; P_n = degree of polymerization) showed defective arrays. When polymer **8** was subjected to the conditions of breath-figure formation, bubble arrays of excellent quality resulted in the first experiments when using CS$_2$ and forced airflow. It is not clear what determines the successful formation of bubble arrays from specific polymers but we think that it is the compounded effects of molecular structure, molecular weight, and polydispersity. At the moment we are investigating the molecu-
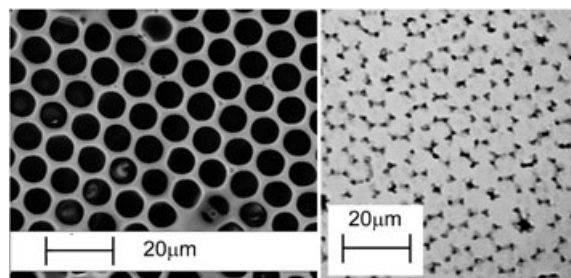

Figure 1. Left: SEM image of a bubble array formed from a mixture of polystyrene (65%) and polymer **3** at ambient temperature (EHT = 20.00 kV, WD = 21 mm). Right: Same material, pyrolyzed at 530 °C, viewed under a conventional light microscope. All polystyrene has burned off as seen in this optical micrograph.

lar-weight dependency upon the propensity of bubble formation.

Figure 2 displays an optical micrograph of the bubble arrays formed from **8** ($P_n = 15$). The bubbles are uniform and approximately 5 µm in diameter. The inset shows the
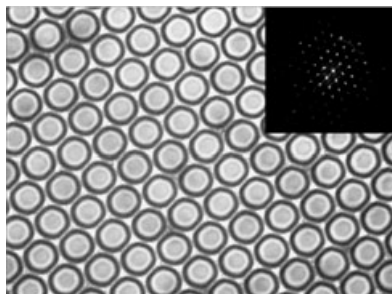

Figure 2. Optical micrograph (conventional light microscope) of the bubble arrays of **8** at ambient temperature. The black rings are due to the lack of depth of focus in light microscopy. The bubbles are approximately 5 microns in diameter. The inset is a diffraction pattern of the bubble array taken with a Bertrand lens. The width of the picture is 65 microns.

diffraction pattern of this bubble array taken through a Bertrand lens, confirming the hexagonal ordering. Bubble arrays of **8** remained intact upon heating to $>500\,°C$, consistent with earlier experiments performed upon organometallic PPEs. It was shown that polymers of the same type as **8** attained a nematic liquid crystalline phase but did not melt.[15] The bubble arrays were heated to $530\,°C$ under nitrogen and collapsed from open interconnected structures into more compact honeycomb-like arrays of picoliter-sized holes. Figure 3 displays a scanning electron micrograph (SEM) image of the arrays after pyrolysis. Most of the material survived the pyrolysis conditions, and the
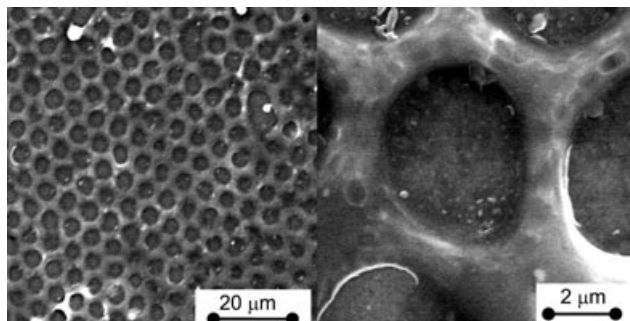

Figure 3. Left: SEM image of the bubble array of polymer **8** after a pyrolysis under nitrogen up to $530\,°C$ (1000-fold magnification). Right: Same material at higher magnification (8000-fold).

mass loss is small. That is not surprising as the degree of unsaturation in **8** is high. Polystyrene on the other hand depolymerizes above $480\,°C$ and that explains why mixed bubbles formed from **3** and polystyrene are greatly reduced upon pyrolysis.

To quantify the mass loss, thermogravimetric analyses (TGA) of **8** were performed under nitrogen and under air (Figure 4). Under nitrogen (Figure 4, right) there was a weight loss of 5.6% up to $264\,°C$ and a combined weight loss of 12.8% at $450\,°C$. The pyrolyzed material was amorphous according to powder X-ray diffraction analysis. The IR spectrum showed the total absence of any C−H stretching bands or organic functional-group bands, ascertaining that **8** was converted into an amorphous ceramic. To gain insight into which organic fragments might be lost upon pyrolysis, high-temperature mass spectrometry was performed on grains of **8**. Mass spectra run at 200 and $206\,°C$ did not show any common or specific degradation patterns. At $451\,°C$, signals at 189 and 207 amu were observed. These peaks cannot be attributed to specific fragments stemming from the original polymer structure. The combined results suggest that
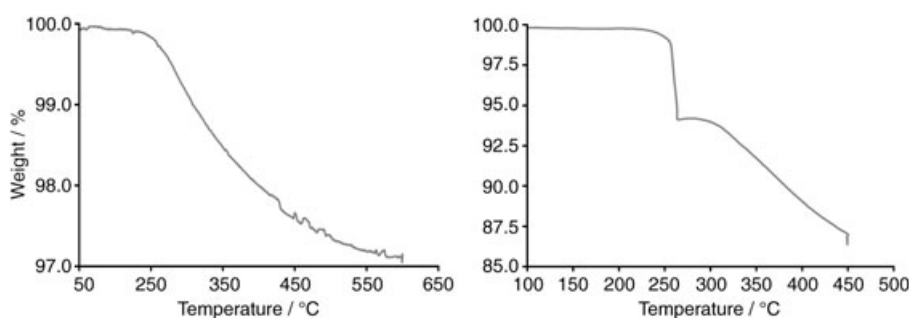

Figure 4. Right: TGA of **8** under nitrogen. Up to $265\,°C$, 5.6% of weight is lost. Up to $450\,°C$, 12.8% weight is lost. Left: TGA of **8** in air. Up to $600\,°C$, 2.8% weight is lost. The vertical axis is weight (%) for both graphs.

mostly hydrogen is lost and that cross-linking occurs, but without cleavage of any specific molecular fragments during pyrolysis. The loss of small molecules is not uncommon in the pyrolysis of carbon-rich organometallic materials as shown by Vollhardt et al. for the pyrolysis of dicobalt–octacarbonyl complexes of tolanes and similar systems.[20] Scanning electron microscopy allowed us to determine the elemental composition of the ceramic formed from **8** by using energy dispersive X-ray microanalysis (EDX).[21] The N_2-pyrolyzed ceramic formed from **8** contains 69.08% carbon, 12.49% oxygen, 8.30% silicon, and 10.13% cobalt according to EDX. Upon pyrolysis, only loss of hydrogen would be expected. Loss of methane was not evidenced by mass spectrometry, so all of the heavier elements should be conserved in the ceramic. Within the experimental error margins of EDX, the recorded data support a stoichiometry of approximately $C_{49}CoO_2Si_2$ (elemental analysis calcd (%): C 80.0, O 4.36, Si 7.63, Co 7.96). The deviation of the obtained values (up to 10%) from the calculated values is common in the

EDX measurement of lighter elements such as carbon and oxygen, while higher elements are determined with greater accuracy. The increased value for the oxygen content, however, could either be an artifact or might occur as a consequence of trace oxidation of **8** during pyrolysis. Due to the relatively large error margin in EDX measurements it is difficult to strictly exclude other, similar stoichiometries. We conclude that the pyrolysis of **8** under nitrogen leads to an amorphous ceramic containing C, Si, Co, and some oxygen. Within experimental error margins, these results are suggestive of a preservation of the starting stoichiometry for all elements except hydrogen.

The ceramic bubbles are conserved in air at elevated temperatures. Heating of the bubble array, which is shown in Figure 3, to 530 °C in air led to a slightly altered array with thinner but sharper walls (see Figure 5), suggesting that
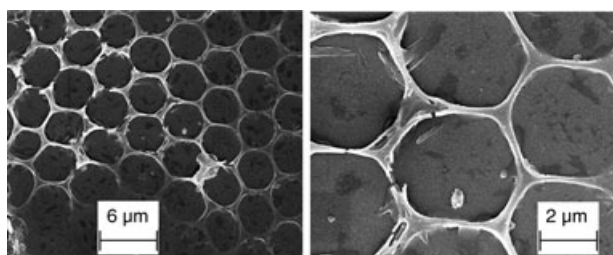

Figure 5. SEM image of the bubble array of polymer **8** after a second pyrolysis in air at two different magnifications.

some more material is burned off during this process. The ligaments that connect the inorganic picoliter holes are reduced from 1 micron to approximately 0.5 microns. However, the overall microscopic structure persists and is actually increased in sharpness.

The TGA trace of the pyrolysis of **8** in air is shown in Figure 4 (left). Upon heating to 600 °C, a weight loss of only 2.8 % was observed; this was curious. The concomitant EDX data showed that there is no carbon left in the ceramic, but the oxygen content is increased. A composite of the stoichiometry $Co_2Si_4O_{11}$ is formed (elemental analysis calcd (%): Co 29.02, Si 27.66, O 43.33; found: Co 23.71, Si 22.13, O 54.18; EDX). The oxygen values deviate by the greatest percentage, but, as mentioned earlier, determination of lighter elements is prone to some error in EDX measurements.[20] The oxide ceramic is amorphous and does not show any X-ray diffraction pattern. Under these conditions we have probably formed a cobalt silicate or a mixed SiO_2/Co_2O_3 ceramic. We speculate that the pyrolysis in air has burned out the carbon, but at the same time has oxidized the silicon and the cobalt, so that the oxidative removal of carbon is compensated for by the uptake of oxygen under formation of the ceramic oxide. This process explains the very low weight loss upon pyrolysis of **8** in air.

Conclusion

By using the breath-figure method it is easy to make microstructured oxide and non-oxide ceramics from conjugated precursor polymers. The organometallic cyclobutadiene(cyclopentadienyl)cobalt-containing polymer **8** is an excellent choice for the fabrication of self-assembled bubble arrays. Upon heating, under nitrogen or air, to temperatures above 500 °C, the microscopic ordering of the bubble arrays is preserved. Under nitrogen a Si–C–Co ceramic with low amounts of oxygen is obtained, while in air all of the carbonaceous matter is burned off and instead a Si–Co–O ceramic of the approximate composition $Co_2Si_4O_{11}$ is formed. In the future we plan to investigate these cobalt silicate ceramics for catalytic purposes[22] and expand this facile fabrication method to ferrocene-containing polymers. These should produce magnetite and ferrosilicate microstructures that could be utilized as magnetic and electronic materials.[3]

Experimental Section

General: The ^{1}H and ^{13}C NMR spectra were taken with a Varian Mercury 300 MHz or a Bruker AMX 400 MHz spectrometer using broadband probe heads. Proton chemical shifts are referenced to the residual peaks of $CDCl_3$ at $\delta = 7.24$ ppm (vs TMS). The ^{13}C{^{1}H} resonances are referenced to the central peak of $CDCl_3$ at $\delta = 77.0$ ppm (vs TMS) or [D$_4$]dichloroethane at $\delta = 74.0$ ppm. Compounds **1**, **2**, and **9** were prepared in accordance with published procedures. SEM images were taken and EDX was performed on a LEO 1530 thermally-assisted FEG SEM, equipped with an EDX unit by Oxford Instruments. Additional SEM images were taken on a Hitachi S800 thermally assisted FEG SEM.

The molecular weights of the obtained polymers were determined by gel permeation chromatography (GPC) on a Shimadzu SCL-SPD-LC-10 AT system with an integral UV/Vis detector. The samples were run on standard cross-linked polystyrene Waters GPC columns with polystyrene standards using chloroform as the solvent.

Bubble preparation: The bubbles were cast from a solution of 3 mg polymer per mL of carbon disulfide, and prepared at a temperature of 23 °C, a humidity of 84 %, and an airspeed varying between 150 and 300 m min^{-1}.[10,14] Bubbles of polymer **3** were cast from a solution of 1 mg polymer and 3.5 mg polystyrene ($M_r = 25 \times 10^3$) in a CS_2/pentane mixture (800/400 µL, v/v). Air speed and moisture were as stated above.

Bubble pyrolysis under nitrogen: The samples were pyrolyzed under nitrogen in a tube furnace with the following setup: The samples were placed in a quartz tube sealed at one side with nitrogen flowing through it. The probe container was placed into a tube furnace equipped with a second quartz tube of a wider diameter. The ends of the latter tube were capped with glass-fiber wool. Samples were heated to 100 °C and held for 1 h, then heated to 200 °C and held for another hour, and finally heated to 600 °C and held for 3 h. The samples remained under nitrogen during cooling to around 300 °C. At this point, the color had changed from orange to slate gray.

Bubble pyrolysis in air: Samples subjected to pyrolysis under nitrogen were cooled to room temperature; the sample was then heated overnight to 800 °C in air using the same setup as described above.

Synthesis of polymer 3: In a flame-dried Schlenk flask 1,3-diethynylcyclobutadiene(cyclopentadienyl)cobalt **1** (300 mg, 1.35 mmol) and 1,4-bis(2-ethyl)hexyl-2,5-diiodobenzene **2** (749 mg, 1.35 mmol) were dissolved in a mixture of piperidine (3.5 mL) and THF (1.5 mL). The solution was degassed by three pump–freeze cycles. Bis(triphenylphosphine)palladium(II) chloride (23.5 mg, 33.5 µmol, 2.5 mol %) and copper(I) iodide (6.4 mg, 34 µmol, 2.5 mol %) were added in a stream of nitrogen. The mixture was

heated up to 40 °C for 48 h. The highly viscous reaction mixture was allowed to cool to room temperature, taken up in chloroform, and washed with water (25 mL), 10 % aqueous ammonia solution (25 mL), and 25 % aqueous hydrochloric acid (25 mL). The chloroform solution was concentrated in vacuo to 25 mL, and then added to methanol (1 L). The sand-like yellow polymer that precipitated was filtered off, washed with methanol, and dried in vacuo using an oil pump (622 mg, 88 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 7.10$ (s, 2H), 5.02 (s, 5H), 4.62 (s, 2H), 2.58 (s, 4H), 1.60 (m, 2H), 1.28 (br s, 16H), 0.89 ppm (m, 12H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 40 °C): $\delta = 140.60$, 132.78, 122.79, 91.12, 89.63, 81.13, 68.13, 64.10, 50.63, 47.64, 32.57, 25.69, 23.04, 14.00, 9.80 ppm; IR (KBr): $\tilde{\nu} = 2954$, 2927, 2920, 2911, 2892, 2869, 2856, 2178, 1455, 1434, 1412, 1378, 1107, 1001, 811 cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} $(\varepsilon) = 369$ nm (0.507×10^6); GPC (polystyrene standard): $M_n = 26\,976$, PDI = 9.1 (bimodal).

Synthesis of 5: Under nitrogen, 6-chlorohexyne **4** (10.0 g, 85.8 mmol) was dissolved in dry THF (100 mL). The mixture was cooled to -78 °C. Lithium diisopropylamide (2 N solution in heptane, 42.9 mL, 85.8 mmol) was added dropwise. The mixture was stirred for 10 min and allowed to warm to -10 °C and stirred for a further 30 minutes. It was then cooled to -78 °C and triisopropylsilylchloride (16.5 g, 85.8 mmol) was added dropwise. The mixture was stirred for 24 h, then slowly poured into water and extracted with chloroform. The organic solution was washed with 0.5 N HCl. The organic layer was separated and dried over MgSO$_4$ and the solvent was removed. The remaining oil was distilled using an oil pump vacuum (80 °C) to yield **5** as a light-brown oil (21.6 g, 92 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 3.58$ (t, 2H), 2.32 (t, 2H), 1.92 (m, 2H), 1.70 (m, 2H), 1.07 ppm (s, 21H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 108.18$, 81.16, 44.76, 31.73, 26.24, 18.95, 11.64 ppm; IR (KBr): $\tilde{\nu} = 678$, 879, 968, 1015, 1251, 1297, 1446, 2131, 2167, 2243, 2522, 2562, 2622, 2684, 2716, 2721, 2804, 2834, 2853, 3024 cm^{-1}; MS: m/z calcd for [C$_{15}$H$_{29}$ClSi]: 272.93; found: fragmentation.

Synthesis of 7: 1,4-Hydroxy-2,5-diiodo benzene **6** (3.00 g, 8.29 mmol), potassium carbonate (11.5 g, 82.9 mmol), and **5** (9.05 g, 33.5 mmol) were dissolved in dimethylformamide (200 mL). The mixture was heated to reflux for 48 h, allowed to cool to room temperature, diluted with dichloromethane and washed with 1 N HCl (2×150 mL). The solvent was removed in vacuo and the crude solid was purified by chromatography on silica gel (1:1, dichloromethane/hexane) to yield **7** as a colorless, crystalline solid (2.99 g, 43 %). M.p. 48 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 7.17$ (s, 2H), 3.99 (t, 2H), 2.38 (t, 2H), 1.97 (m, 2H), 1.80 (m, 2H), 1.10 ppm (s, 42H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 152.89$, 122.90, 108.69, 86.56, 80.99, 69.94, 28.56, 25.85, 19.94, 19.08, 11.68 ppm; IR (KBr): $\tilde{\nu} = 658$, 961, 1046, 1210, 1250, 1346, 1385, 1463, 1682, 2166, 2359, 2722, 2866, 2944, 3086 cm^{-1}; MS: m/z calcd for [C$_{36}$H$_{60}$I$_2$O$_2$Si$_2$]: 834.84; found: 834.4.

Synthesis of polymer 8: Diiodo monomer **7** (0.738 g, 0.883 mmol) and diethynyl monomer **1** (0.196 g, 0.875 mmol) were dissolved in THF (2 mL) and piperidine (1.5 mL) in an oven-dried Schlenk flask. The flask was frozen, evacuated, and flushed with nitrogen four times after which [PdCl$_2$(Ph$_3$P)$_2$] (6.2 mg, 8.8 μmol) and CuI (1.7 mg, 8.8 μmol) were added. The mixture was allowed to stir at room temperature for 48 h. The solvent was removed and the mixture dissolved in dichloromethane, washed with 1 N HCl, 1 N NH$_4$OH, and water. The organic layer was dried over MgSO$_4$ and the solvent removed. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol three times to yield **8** as an orange solid (0.599 g, 84 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 6.81$ (m, 2H), 5.04 (m, 5H), 4.68 (m, 4H), 1.95 (m, 4H), 1.79 (m, 4H), 1.07 ppm (m, 42H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 153.90$, 116.73, 108.54, 69.04, 64.48, 56.11, 28.33, 25.49, 19.50, 18.63, 11.33 ppm; IR (KBr): $\tilde{\nu} = 677$, 791, 881, 1003, 1034, 1067, 1263, 1377, 1462, 1502, 1649, 2166, 2361, 2723, 2754, 2849, 2926, 2962, 3111, 3389 cm^{-1}; GPC (polystyrene standards): $M_n = 13.4 \times 10^3$, PDI = 1.59.

Synthesis of polymer 10: Diiodo monomer **7** (0.500 g, 0.599 mmol) and diethynyl monomer **9** (0.280 g, 0.605 mmol) were dissolved in THF (2 mL) and piperidine (1.5 mL) in an oven-dried Schlenk flask. The flask was frozen, evacuated, and flushed with nitrogen three times, after which [PdCl$_2$(Ph$_3$P)$_2$] (4.2 mg, 5.9 μmol) and CuI (1.1 mg, 6.0 μmol) were added. The mixture was allowed to stir at room temperature for 48 h. Dichloro-

methane was added, and the solution was washed with 1 N HCl, 1 N NH$_4$OH, and water. The organic layer was dried over MgSO$_4$ and the solvent concentrated. The resulting polymer was dissolved in dichloromethane and precipitated out of methanol three times to yield **10** as a yellow solid (0.556 g, 89 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 7.38$ (m, 2H), 6.92 (m, 2H), 4.11 (m, 4H), 2.87 (m, 4H), 2.38 (m, 4H), 2.03 (m, 4H), 1.82 (m, 4H), 1.16 (m, 46H), 1.07 (m, 36H), 0.88 ppm (m, 6H); ^{13}C{^{1}H} NMR (75 MHz, [D$_4$]dichloroethane, 25 °C): $\delta = 153.30$, 142.00, 132.24, 122.77, 116.68, 114.12, 108.52, 94.09, 90.56, 80.70, 69.43, 35.19, 31.92, 30.60, 29.72, 29.67, 29.50, 29.37, 28.34, 25.35, 22.69, 19.55, 18.61, 14.10, 11.55, 11.40, 11.26 ppm; IR (KBr): $\tilde{\nu} = 677$, 798, 816, 858, 1013, 1265, 2172, 2332, 2359, 2866, 2926, 2959 cm^{-1}; GPC (polystyrene standards): $M_n = 30.4 \times 10^3$, PDI = 4.54.

TGA measurements: These measurements were taken on a Shimadzu TGA-50 Thermogravimetric Analyzer. The samples were weighed into a 40 μL alumina crucible and the lid was punctured. Each sample was heated from 25–600 °C at a rate of 25 °C min^{-1} under nitrogen.

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