Poly(4′-vinylhexaphenylbenzene)s: New Carbon-Rich Polymers

Christian Kübel, Shu-Ling Chen, and Klaus Müllen*

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

Received November 18, 1997; Revised Manuscript Received June 11, 1998

ABSTRACT: Poly(4′-vinylhexaphenylbenzene) is a new, readily soluble polymer with hexaphenylbenzene side groups. The hexaphenylbenzene moieties can be cyclodehydrogenated oxidatively with $CuCl_2/AlCl_3$ yielding hexa-*peri*-hexabenzocoronene units and resulting in linked polycyclic aromatic hydrocarbons (PAHs). The synthesis of copolymers with methyl methacrylate (MMA) or styrene is also possible. Cyclodehydrogenation of the MMA copolymer leads to a partially soluble material, which can be characterized by UV/vis spectroscopy.

Introduction

Graphitic materials are among the most important industrial products due to their mechanical and electronic properties.[1] Usually high temperatures are necessary to obtain partially graphitized or carbonized materials upon pyrolysis of precursors such as small aromatic molecules, petroleum, or coal tar pitches.[2] In the carbo mesophase at temperatures between 400 and 700 °C, different aromatic structures with diameters of a maximum of approximately 1 nm are formed.[3] To obtain completely carbonized/graphitized materials, temperatures of 2000−3000 °C have to be employed.[2] We have demonstrated[4] that large graphite subunits can be selectively synthesized under mild reaction conditions by applying the oxidative cyclodehydrogenation conditions Kovacic used for the polymerization of benzene derivatives.[5] The reaction of suitable oligophenylene precursors with $CuCl_2/AlCl_3$ at room temperature yields large, well-defined polycyclic aromatic hydrocarbons[4] (PAHs) with diameters of up to 3 nm.

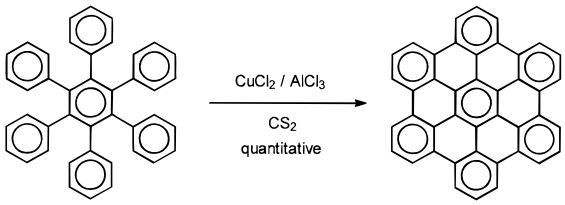
In this work we apply this method to polymers containing suitable oligophenylene side groups to obtain linked PAHs. Polymers **1a/b** with hexaphenylbenzene (HPB; Scheme 1) side groups can be regarded as precursors for this purpose. HPB itself can be cyclodehydrogenated quantitatively under Kovacic conditions to yield hexa-*peri*-hexabenzocoronene (HBC)[4] as an insoluble brown material. The reaction is completed at room temperature within 2 days, but remarkably even after 5 days of reaction time, no additional intermolecular bond formation is observed.

Analogous treatment of polymers **1a** and **1b** should yield HBC units linked by a polymer chain. One expects that the packing behavior of the PAH units would be disturbed strongly by the polymer chain, as can be seen in the case of many other side-chain polymers without a spacer.[6]

Results and Discussion

Monomer Synthesis. The monomers used to synthesize polymers **1a/b** were 4′-vinylhexaphenylbenzene (**5**; Scheme 2) and 4′-(4-vinylphenylene)hexaphenylbenzene (**8**; Scheme 3). These materials were readily accessible via Diels−Alder reaction of tolans **2** or **6** with 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (tetracyclone, **3**), leading to monosubstituted hexaphenylbenzenes **4** or **7**, which could then be subjected to a Stille coupling[7] to introduce the vinyl group.

Scheme 1. Cyclodehydrogenation of Hexaphenylbenzene



4-Bromotolan (**2**) was synthesized by Pd(0)-catalyzed Hagihara−Sonogashira coupling[8] of phenylacetylene with 4-bromoiodobenzene. At low temperatures the reaction led selectively to the formation of **2** in high yield (82%). The [4 + 2] cycloaddition of tolan **2** and tetracyclone **3** resulted in (4-bromophenyl)pentaphenylbenzene (**4**) in 85% yield. The vinyl group was introduced by a $Pd(PPh_3)_4$-catalyzed Stille coupling of **4** with tributylvinylstannane in 60% yield.

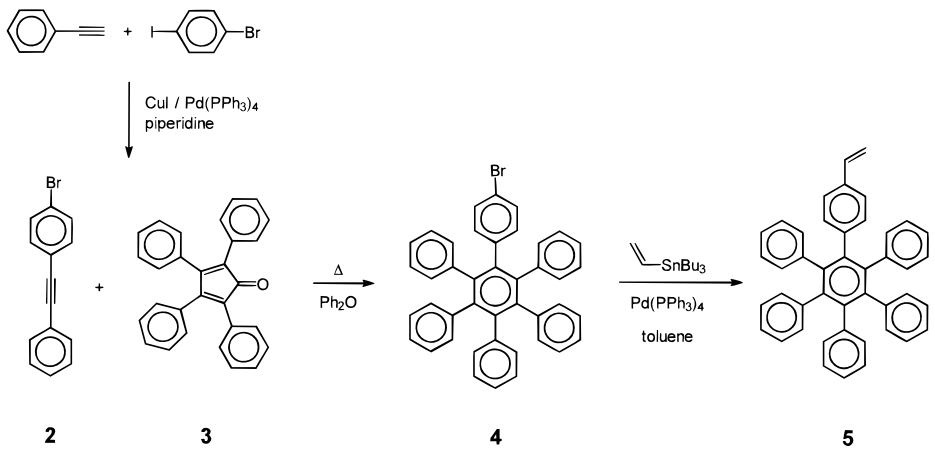
Hagihara−Sonogashira coupling[8] of phenylacetylene with an excess of 4,4′-dibromobiphenyl led to the formation of 4-(4′-bromophenyl)tolan (**6**), which could be reacted analogously with **2**, resulting in 4′-(4-vinylphenylene)hexaphenylbenzene (**8**) in 58% overall yield.

Polymer Synthesis. The styrene derivatives **5** and **8** (Scheme 4) were polymerized in toluene with azobis(isobutyronitrile) (AIBN) as the initiator to 76% (**1a**) and 78% (**1b**) yield, respectively. The resulting polymers are colorless solids and readily soluble in most common organic solvents such as tetrahydrofuran (THF), CH_2Cl_2, or toluene. Therefore, they could be characterized by nuclear magnetic resonance (NMR) spectroscopy as well as by gel permeation chromatographic (GPC) analysis.

GPC analysis of **1a** revealed a monomodal molecular weight distribution with a number average (M_n) of 11 100 and a weight average (M_w) of 26 800 (polydispersity index PDI = 2.4) corresponding to an average degree of polymerization of about 20. This molecular weight is remarkably high, compared to $M_n = 6050$ for poly(vinyl-*p*-terphenyl) published by Trial and Khanna,[9] if one takes into account the size of the hexaphenylbenzene side groups, which should sterically shield the propagating vinyl radical. On the other hand, various biphenyl derivatives with large substituents in the 4′-position have been synthesized with similar molecular weights.[10] Nevertheless, none of these substituents

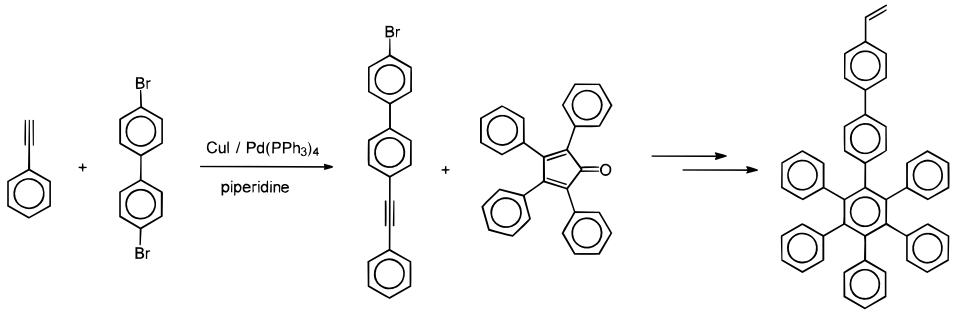
S0024-9297(97)01707-5 CCC: $15.00
Published on Web 08/21/1998

Scheme 2. Synthesis of 4′-Vinylhexaphenylbenzene (5)



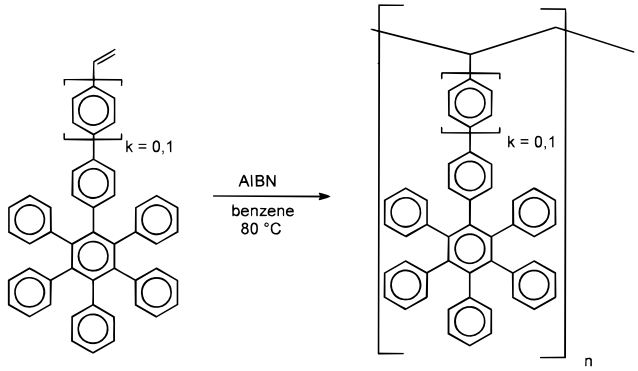
2 **3** **4** **5**

Scheme 3. Synthesis of 4′-(4-Vinylphenylene)hexaphenylbenzene (8)



6 **3** **8**

Scheme 4. Synthesis of Homopolymers with Hexaphenylbenzene Side Groups (1a/b)



5 / 8 **1a/b**

were sterically as demanding as the hexaphenylbenzene substituents. To evaluate the exact mass of the oligomers, matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS)[11] was applied to **1a**. The maximum intensity[12] was observed for molecules with 8 repeat units. All oligomers with up to 65 repeat units could be resolved (Figure 1), differing by the monomer mass of 560 g/mol. The observed molecular masses corresponded to n HPB units, two AIBN initiator fragments, and a potassium ion, thus indicating that the dominant termination mode was a recombination of two polymer chains as is known for styrene itself.[13]

The results for the analogously synthesized poly[4′-(4-vinylphenylene)hexaphenylbenzene] **1b** were quite similar. The molecular weight of **1b** was higher than that of **1a** (M_n = 14 800, M_w = 27 200, PDI = 1.8), as expected with the sterically less demanding side group.

Both polymers **1a** and **1b** were thermally stable with decomposition temperatures of 450−460 °C. Furthermore, it was possible to prepare spin-coated films on glass of both polymers from a toluene solution.

The synthesis of copolymers with pendent hexaphenylbenzene groups (**5** or **8**) was possible by conducting the polymerization in the presence of styrene or methyl methacrylate (MMA) (Scheme 5). We used GPC analysis in combination with ^{1}H NMR experiments to verify the synthesis of random copolymers. GPC analysis showed a monomodal molecular weight distribution for the copolymers **9a/b** and **10a/b** with M_n = 16 300−19 800 and PDI = 1.6−1.8 (for exact values for each polymer, see the Experimental Section). ^{1}H NMR analysis left no doubt that the polymer contains the hexaphenylbenzene units as well as the added comonomer.

The styrene copolymers **10a/b** were synthesized using a reaction mixture containing 95.3 mol % styrene and 4.7 mol % of **5** (21.0 wt %) or **8** (23.2 wt %). ^{1}H NMR analysis of the resulting copolymers revealed a HPB content of 2.6 mol % for **10a** and 4.7 mol % for **10b**. This clearly shows a reduced reactivity for 4′-vinylhexaphenylbenzene (**5**) compared to styrene. The reactivity of the propagating vinyl radical is reduced by the pentaphenylbenzene groups in **5**, whereas in the case of **8** the reactivity is comparable to styrene itself.

An explanation for the reduced reactivity of **5** is a steric shielding of the propagating vinyl radical by the *o*-phenyl rings in **5**, whereas electronic effects should have only a minor influence on the reactivity. Because of steric reasons, the phenyl rings of the HPB group are strongly tilted[14] with respect to each other, thus allowing only a small π-orbital overlap, which excludes strong

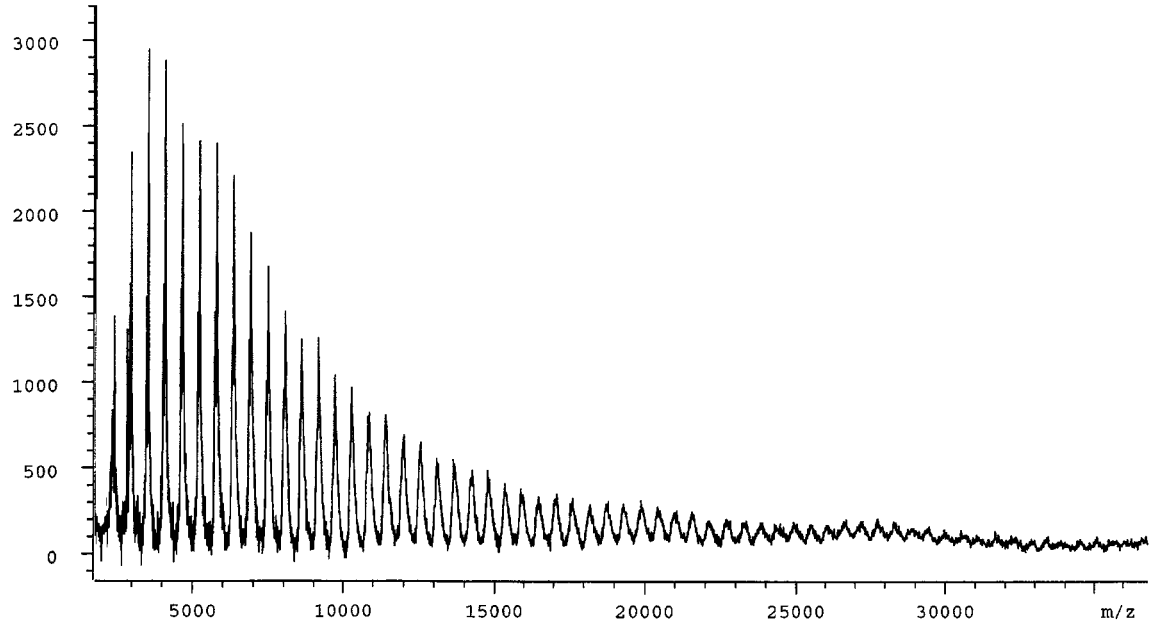
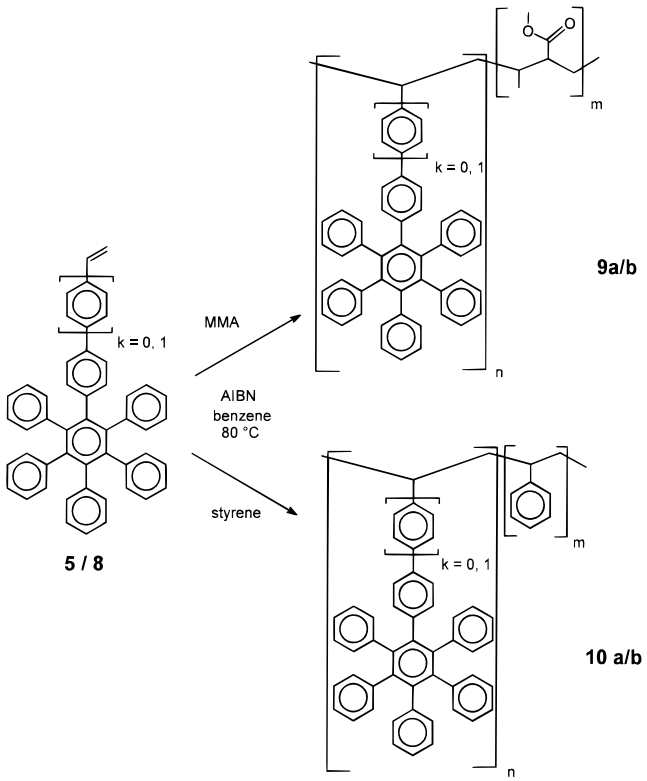


Figure 1. MALDI-TOF mass spectrometry of **1a** dissolved in THF, with dithranol/K^+ matrix. Polymers with 5−65 repeat units differing by the monomer mass are resolved.

Scheme 5. Synthesis of MMA or Styrene Copolymers with Hexaphenylbenzene Side Groups (9a/b or 10a/b)



electronic interactions between them. This prevents spin delocalization into the HPB unit and the formation of main-chain polymers with hexaphenylbenzene units.

The reaction mixture for the synthesis of the MMA copolymers **9a/b** contained 90.9 mol % MMA and 9.1 mol % of monomers **5** (35.8 wt %) or **8** (38.8 wt %). The composition of the copolymers could be analyzed in detail by ^{1}H NMR. In the case of **9b**, the polymer contained 9.8 mol % (41.8 wt %) hexaphenylbenzene units, which is a slightly higher content than that in the initial reaction mixture. Thus, the reactivity of the vinyl radical in monomer **8** is similar to that of MMA. This led to the formation of a random copolymer as can be seen by the signals of the O−CH_3 group in the ^{1}H NMR spectrum (Figure 2). The signal at 3.59 ppm corresponds to a MMA sequence,[15] whereas the signals at 2.7−3 ppm with an intensity of 5.5% correspond to a MMA group with a hexaphenylbenzene unit next to it. Thus, more than every second HPB unit is next to an MMA group, resulting in, on average, 3 or 4 HPB units next to each other. This indicates a slightly preferred reaction of a HPB endgroup with another HPB monomer, but the composition of the polymer is still more or less random. Polymer **9a** contained 7.5 mol % HPB units, and its ^{1}H NMR analysis led to results similar to those in the case of **9b**.

By addition of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO), it is possible to perform a controlled radical polymerization of styrene. It has been shown[16] that TEMPO-end-capped polymers are able to reinitiate a radical polymerization in the presence of further monomer to form block copolymers. We tried to synthesize block copolymers with a polystyrene and a poly(4′-vinylhexaphenylbenzene) block by this method, but TEMPO only acted as an inhibitor for the polymerization of **5** as well as **8**.

The hexaphenylbenzene units have only a minor influence on the thermal stability of the copolymers **9a/b** and **10a/b**, which is only slightly higher than that of the parent polymers. The effect of the hexaphenylbenzene units on the glass transition temperatures is much more profound. In the case of the styrene copolymers, the glass transition temperature is shifted by about 15−20 °C to higher temperatures, and in the case of the MMA copolymers, it is shifted by 40−50 °C to higher temperatures.

Cyclodehydrogenation. The homopolymers **1a/b** and the MMA copolymers **9a/b** were subjected to an oxidative cyclodehydrogenation reaction under conditions which we already used successfully for the intramolecular cyclodehydrogenation of suitable oligophenylenes.[4] In the case of these oligophenylenes, the reaction is nearly quantitative. In contrast, when Kovacic[5] originally applied the reaction to benzene derivatives, he obtained polymers with many structural

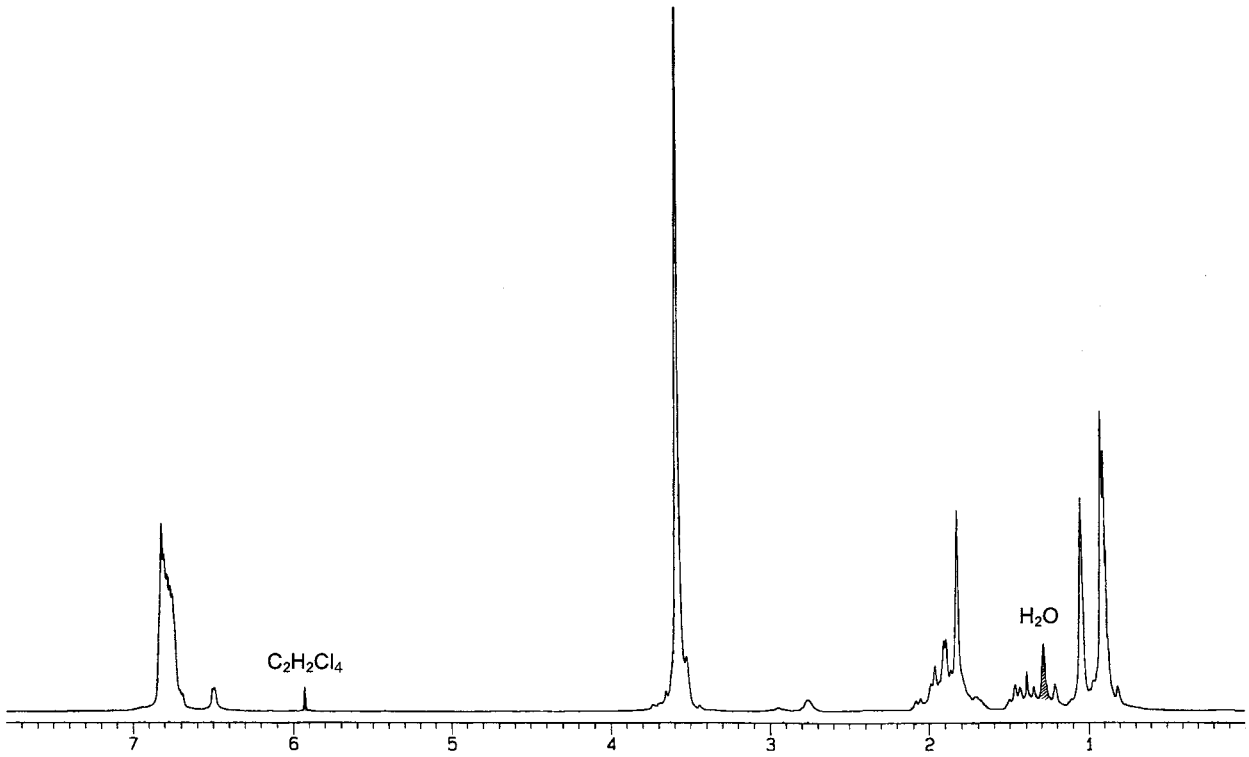


Figure 2. ^{1}H NMR spectrum of **9a** measured in $C_2D_2Cl_4$ at 403 K. The signal at 3.59 ppm corresponds to the O−CH_3 group in a MMA sequence, whereas the signal at 2.7−3 ppm corresponds to a MMA group next to a hexaphenylbenzene unit.

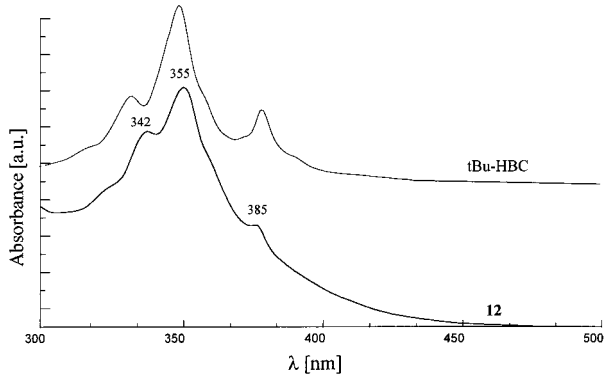


Figure 3. UV/vis absorption spectra of **12** and hexa-*tert*-butyl-HBC in $C_2H_2Cl_4$ recorded at room temperature.

defects. Under the same conditions polystyrene proved to undergo both cross-linking and chain scission, while the bulky hexaphenylbenzene groups in **1** seem to stabilize during cyclodehydrogenation.

The cyclodehydrogenation of **9a** with copper(II) chloride/aluminum(III) chloride in CS_2 at room temperature led to the precipitation after 6 h of a brown solid, **12**, which was stirred for an additional 4 days to achieve a more complete reaction.

Compound **12** was insoluble in most common organic solvents, such as hexa-*peri*-hexabenzocoronene, but by extraction with boiling 1,1,2,2-tetrachloroethane, it was possible to obtain a solution of a fraction of **12**. This solution was analyzed by UV/vis absorption spectroscopy, and its spectrum clearly resembled the characteristic UV/vis spectrum of hexa-*tert*-butylhexa-*peri*-hexabenzocoronene (Figure 3). By comparison of the extinction coefficients of **12** and *tert*-butyl-HBC, the degree of cyclodehydrogenation could be estimated to be about 2 HBC units per polymer chain, corresponding to about 18% yield. Thus, a (partial) polymer analogous cyclodehydrogenation yielding HBC units was achieved. However, it was not possible to evaluate the average degree of cyclodehydrogenation because the main product fraction with higher reaction yields was insoluble in all common organic solvents as expected by analogy to the low solubility of HBC.

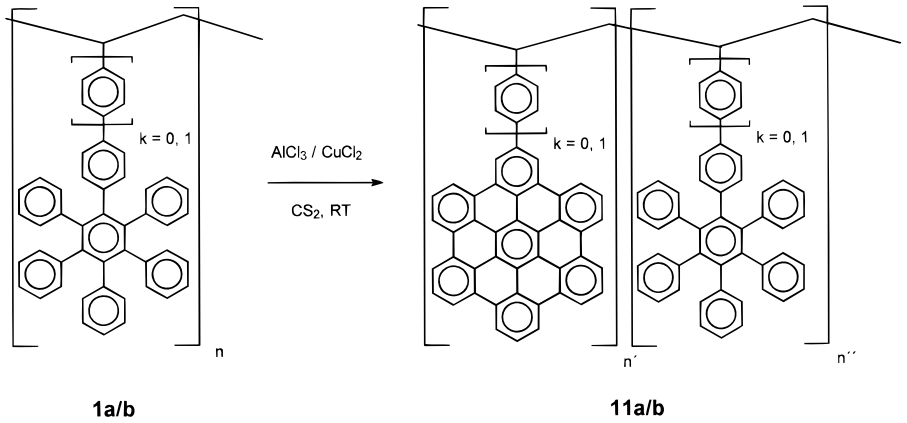
Cyclodehydrogenation of **1a** led to the formation of a completely insoluble brown solid, **11a** (Scheme 6). Elemental analysis[17] resulted in a hydrogen content of 5.60% (calc. 5.70%) for the hexaphenylbenzene polymer **1a**, whereas after cyclodehydrogenation a hydrogen content of 3.72% was measured for **11a**, which corresponds to a nearly quantitative reaction.[18]

Laser desorption (LD)-TOF MS, which is limited to molecular weights of about 3000 Da, was used to analyze the cyclodehydrogenated polymer **11a**. Fragments, generated during laser desorption, corresponding to HBC−$(CH)_n$ with $n = 0-3$ were clearly resolved, and peaks corresponding to HBC−$((CH)_3-HBC)_m$ with $m = 1-3$ could be observed with low intensities. The absence of any other species indicates that no unspecific decomposition took place during cyclodehydrogenation.

The X-ray powder diffraction patterns of **1a** and **11a** are shown in Figure 4. HPB polymer **1a** is amorphous, whereas after cyclodehydrogenation **11a** showed two broad peaks corresponding to about 13 and 3.6 Å. The broad peaks indicate a strongly distorted packing of the repeat units. The value 13 Å is close to the diameter of a HBC molecule (15 Å) and probably indicates a tilted arrangement of the HBC units, which is typical for PAHs. The value 3.4−3.7 Å is a common stacking distance in planar polycyclic aromatic hydrocarbons, whereas the distance between two HPB molecules is larger. Thus, the 3.6-Å spacing indicates the formation of planar subunits.

The cyclodehydrogenation of **1a/b** yielding hexa-*peri*-hexabenzocoronene units can also be seen by infrared

Scheme 6. Cyclodehydrogenation of Oligophenylene Polymers



1a/b **11a/b**

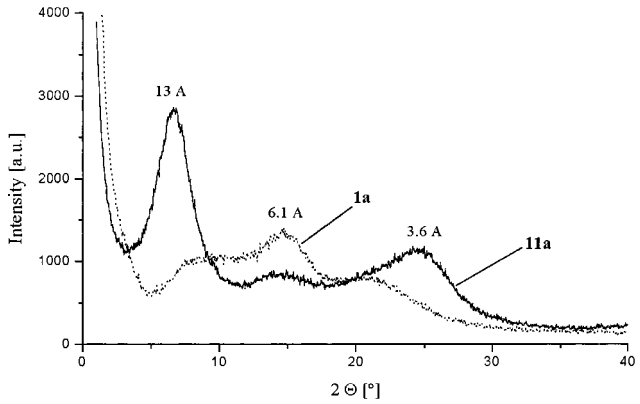


Figure 4. X-ray powder diffraction diagrams of **1a** and **11a**. After cyclodehydrogenation there are new reflections at 13 and 3.6 Å observable, which correspond to the diameter of HBC and its stacking distance.

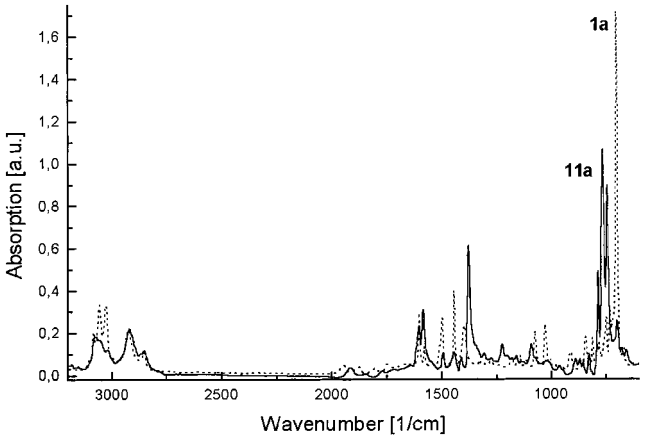


Figure 5. IR spectra of **1a** and **11a**. The intense peak at 698 cm^{-1} corresponding to monosubstituted phenyl rings in HPB has mostly vanished after cyclodehydrogenation, giving rise to new peaks at 738, 762, and 783 cm^{-1} attributed to trisubstituted phenyl rings in HBC.

(IR) spectroscopy when the typical IR bands of HBC and HPB are compared. An intense absorption corresponding to the C−H deformation vibration of trisubstituted benzenes was observed at 739 and 761 cm^{-1} for HBC, whereas HPB showed an intense absorption corresponding to the C−H deformation vibration of monosubstituted benzenes at 698 and 730 cm^{-1}. The precursor polymers **1a**/**b** exhibited an absorption at 698 cm^{-1} corresponding to HPB units. In contrast, the absorptions at 738, 762, and 783 cm^{-1} (**11a**) and 742, 764, and 784 cm^{-1} (**11b**) for the cyclodehydrogenated products indicate the formation of HBC units, whereas the peaks at 698 cm^{-1} are reduced. A quantitative analysis[19] of the IR spectra revealed the formation of 90% hexa-*peri*-hexabenzocoronene units (Figure 5).

Conclusion

We presented new soluble polymers and copolymers with hexaphenylbenzene side groups which are available via a straightforward approach. These carbon-rich polymers had been cyclodehydrogenated using Kovacic conditions,[5] which we already used successfully for quantitative intramolecular cyclodehydrogenation resulting in PAHs.[4]

All analytical methods employed so far indicate that the polymer-analogous cyclodehydrogenation results in polymers containing a large extent of large graphitic subunits under mild reaction conditions, thus giving a new and easy access to carbon-rich polymers at low temperatures.

Further work is in progress using electron microscopy to elaborate the morphology and the structure of the insoluble materials obtained.

Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. Silica gel (Kieselgel 60, Merck, Darmstadt) was used for column chromatography. The eluents are given in the experimental procedures. Argon was used for all preparations as an inert gas. Solvents and starting materials were purified according to standard procedures, when necessary. ^1H and ^{13}C NMR spectra were recorded using a Bruker AMX 300 and a Bruker DRX 500. Mass spectra were obtained using a Varian CH7A, a VG Instruments ZAB-2, and a Bruker Reflex-TOF.

Gel Permeation Chromatography. The GPC analysis was carried out using a Waters GPC with PL gel as the column material and THF as the solvent and a UV detector. The retention time was calibrated with polystyrene standards purchased from Polymer Standards Service.

Differential Scanning Calorimetry. The DSC measurements were carried out on a Mettler DSC 30. The sample was heated in an aluminum pan under a nitrogen atmosphere at a rate of 10 K/min.

X-ray Diffraction. The X-ray diffraction patterns were recorded using a Siemens D 500 Kristalloflex with graphite-monochromated Cu Kα radiation, emitted by a rotating Rigaku RV-300 anode.

General Procedure for Stille Coupling. A total of 1.0 mmol of bromo compound **2** or **4** and 1.2 mmol of tributylvinylstannane were dissolved with 0.02 mmol of $Pd(PPh_3)_4$ in

20 mL of toluene together with a few crystals of 2,6-di-*tert*-butyl-4-methylphenol to prevent polymerization. The solution was heated to reflux for 4−6 h. A total of 20 mL of pyridine and 20 mL of a 20% KF solution were added, and the solution was stirred for 24 h at room temperature. A total of 200 mL of CH_2Cl_2 was added to the reaction mixture, and the organic phase was washed with NH_4OH, a 2 N HCl solution, and H_2O and dried over $MgSO_4$. The raw product was purified by column chromatography on silica gel with a *n*-hexane/CH_2Cl_2 mixture.

General Procedure for Radical Polymerization. Vinyl monomer **5** or **8** (1.0 mmol) was dissolved in 2 mL of benzene, the solution was degassed, and 0.01 mmol of AIBN was added under argon. The reaction mixture was stirred for 48 h at 80 °C. After cooling to room temperature, the solution was added to a 20-fold excess of methanol to precipitate the polymer. The raw product was reprecipitated from CH_2Cl_2 in *n*-hexane, washed with methanol, and dried in vacuo.

General Procedure for Cyclodehydrogenation. A total of 36 equiv of Cu(trifluoromethanesulfonate)$_2$ and 36 equiv of $AlCl_3$ per hexaphenylbenzene unit were suspended in 100 mL of CS_2 per 30 mg of polymer, and the resulting suspension was stirred for 5 min. The polymer was added under argon, and the suspension was stirred for 5 days at room temperature. The reaction was stopped by stirring with equal amounts of ethanol for 1 h. Afterward, equal amounts H_2O were added. The suspension was filtered and the residue washed extensively with H_2O, CS_2, concentrated HCl, a concentrated NH_3 solution, CH_2Cl_2, and THF and dried in vacuo.

4-Bromotolan (2). 4-Bromoiodobenzene, 22.63 g (80 mmol), and 8.98 g (88 mmol) of phenylacetylene were stirred for 16 h with 1.52 g (8 mmol) of CuI and 4.62 g (4 mmol) of $Pd(PPh_3)_4$ as catalysts in 100 mL of piperidine at room temperature for 24 h. The reaction mixture was acidified with 2 N HCl, and 600 mL of CH_2Cl_2 was added. The organic phase was washed twice with 2 N HCl and H_2O. The raw product was purified by column chromatography on silica gel with 1:1 CH_2Cl_2/*n*-hexane, yielding 16.9 g (82%) of **2** after evaporation of the solvent.

Mp: 87−88 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 403 K): δ 7.29−7.33 (3H, m, H-3′, H-4′), 7.36 (2H, d, ^3J = 8.4 Hz, H-2), 7.46 (2H, d, ^3J = 8.4 Hz, H-3), 7.47−7.52 (2H, m, H-2′). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 403 K): δ 88.66, 90.86 (acetylene C), 122.41, 122.71, 122.99 (quart *C*), 128.72, 128.89, 131.88, 131.91, 133.35 (tert *C*H). EI-MS: *m*/*z* 255.9 (M^+, 100%), 176.0 (M^+ − Br, 50%).

(4-Bromophenyl)pentaphenylbenzene (4). A total of 672 mg (2.6 mmol) of compound **2** and 1.15 g (3.0 mmol) of tetracyclone (**3**) were heated to 250 °C in 3 mL of diphenyl ether for 94 h. The raw product was washed with 20 mL of cold *n*-hexane and recrystallized from toluene, yielding 1.57 g (85%) of colorless prisms of a 1:1 adduct of **4** and toluene. Recrystallization from *n*-hexane yielded free (4-bromophenyl)-pentaphenylbenzene (**4**).

Mp: >300 °C (toluene complex). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 300 K): δ 6.71 (2H, d, ^3J = 8.2 Hz, H-2), 6.79−6.91 (25H, m, phenyl-H), 6.99 (2H, d, ^3J = 8.2 Hz, H-3). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 300 K, J-mod): δ 119.33 (C−Br), 125.27, 125.48, 126.78, 126.98, 129.86, 131.60, 131.63, 133.40, (tert C), 138.94, 140.20, 140.24, 140.54, 140.60, 140.72, 140.76 (quart C). FD-MS: *m*/*z* 612.2 (M^+). Elem anal. Found (calcd for $C_{49}H_{37}Br$ (705.7) (toluene complex)): C, 83.18 (83.39); H, 5.27 (5.28).

(4-Bromobiphenyl)pentaphenylbenzene (7). A total of 4.5 g (12.5 mmol) of compound **6** and 5.0 g (13 mmol) of tetracyclone (**3**) were heated to 250 °C in 15 mL of diphenyl ether for 94 h. The raw product was washed with 20 mL of cold *n*-hexane and recrystallized from *n*-hexane, yielding 8.2 g (95%) of colorless crystals.

Mp: >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 6.75−6.95 (27H, m, phenyl-H), 7.06 (2H, d, ^3J = 8.4 Hz, H-3), 7.27 (2H, d, ^3J = 8.6 Hz, H-2′), 7.42 (2H, d, ^3J = 8.6 Hz, H-3′). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 121.02 (*C*−Br), 124.92, 125.21, 126.58, 126.67, 128.32, 131.41, 131.57, 131.98, 136.22, 139.72, 140.32, 140.44, 140.54. FD-MS: *m*/*z*: 690.0 (M^+). Elem anal. Found (calcd for $C_{48}H_{33}Br$ (689.6)): C, 83.52 (83.59); H, 4.79 (4.82).

4′-Vinylhexaphenylbenzene (5). A total of 614 mg (1.0 mmol) of compound **4** and 349 mg (1.1 mmol) of tributylvinylstannane were reacted in 20 mL of toluene with 23 mg (0.02 mmol) of $Pd(PPh_3)_4$ and 5 mg of 2,6-di-*tert*-butyl-4-methylphenol according to the general conditions described above.

The raw product was purified by column chromatography on silica gel with 1:3 CH_2Cl_2/*n*-hexane as the eluent, resulting in 336 mg (60%) of colorless crystals after evaporation of the solvent.

Mp: 294 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 5.05 (1H, dd, ^3J = 10.9 Hz, ^2J = 1.0 Hz, H_a), 5.52 (1H, dd, ^3J = 17.6 Hz, ^2J = 1.0 Hz, H_b), 6.45 (1H, dd, ^3J = 17.6 Hz, ^3J = 10.9 Hz, H_c), 6.78 (2H, d, ^3J = 8.3 Hz, H-2), 6.80−6.87 (25H, m, phenyl-H), 6.90 (2H, d, ^3J = 8.3 Hz, H-3). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 112.64, 124.56, 125.17, 126.56, 126.64, 131.40, 131.56, 134.16, 136.80, 139.82, 140.32, 140.38, 140.59. FD-MS: *m*/*z* 560.4 (M^+). Elem anal. Found (calcd for $C_{44}H_{32}$ (560.7)): C, 94.23 (94.25); H, 5.69 (5.75).

4′-(4-Vinylphenylene)hexaphenylbenzene (8). (4-Bromobiphenylyl)pentaphenylbenzene (**7**), 3.44 g (5 mmol), and 1.90 g (6 mmol) of tributylvinylstannane were reacted in 200 mL of toluene with 115 mg (0.1 mmol) of $Pd(PPh_3)_4$ and 10 mg of 2,6-di-*tert*-butyl-4-methylphenol according to the general conditions described above.

The raw product was purified by column chromatography on silica gel with 1:4 CH_2Cl_2/*n*-hexane as the eluent, resulting in 2.16 g (68%) of colorless crystals after evaporation of the solvent.

Mp: 262 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 5.25 (1H, dd, ^3J = 10.9 Hz, ^2J = 0.77 Hz, H_a), 5.76 (1H, dd, ^3J = 17.6 Hz, ^2J = 0.77 Hz, H_b), 6.73 (1H, dd, ^3J = 17.6 Hz, ^3J = 10.9 Hz, H_c), 6.84−6.96 (27H, m, phenyl-H), 7.16 (2H, d, ^3J = 8.4 Hz, H-3), 7.40 (2H, d, ^3J = 8.4 Hz, H-2′), 7.43 (2H, d, ^3J = 8.4 Hz, H-3′). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 113.55, 124.91, 125.19, 125.24, 126.41, 126.57, 126.66, 126.73, 131.42, 131.43, 131.44, 131.87, 136.23, 136.44, 136.88, 139.89, 139.91, 140.14, 140.37, 140.41, 140.43, 140.58, 140.61. FD-MS: *m*/*z* 636.3 (M^+). Elem anal. Found (calcd for $C_{50}H_{36}$ (636.8)): C, 94.09 (94.30); H, 5.67 (5.70).

Poly(4′-vinylhexaphenylbenzene) (1a). A total of 1.12 g (2.0 mmol) of compound **5** was polymerized with 3.0 mg (0.02 mmol) of AIBN in 3 mL of benzene at 80 °C, yielding 0.84 g (75%) of **1a** by preparation according to the general procedure described above.

TGA: 456 °C (90%). DSC: no phase transitions were observed between −100 and +320 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 403 K): δ 1.0−1.9 (3H, b, aliphatic C−H), 5.5−5.9, 6.3−7.1 (29H, b, phenyl-H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 403 K, J-mod): δ 40.08 (−*C*H−CH_2−), 41.07 (−CH−*C*H_2−), 125.12, 126.52, 131.70 (tert aromatic *C*H), 140.71, 141.04 (quart aromatic *C*). GPC (THF, polystyrene): M_n, 11 100; M_w, 26 800; PDI, 2.42. MALDI-TOF-MS: *m*/*z* 2404 + *n* 560, 2421 + *n* 560 [(*n* + 4) repeat units + K^+ + 2 AIBN fragments)]. IR (ν [cm^{-1}]): 3081, 3057, 3023 (aromatic CH), 2920, 2853 (aliphatic CH), 1601, 1573, 1497, 1443, 1398, 1074, 1028, 909, 843, 812, 746, 733, 698. Elem anal. Found (calcd for $(C_{44}H_{32})_n$ $(560.7)_n$): C, 93.04 (94.25); H, 5.60 (5.75) (incomplete combustion due to formation of soot).

Poly[4′-(4-Vinylphenylene)hexaphenylbenzene] (1b). A total of 1.28 g (2.0 mmol) of compound **8** was polymerized with 3.0 mg (0.02 mmol) of AIBN in 3 mL of benzene at 80 °C, yielding 0.96 g (76%) of **1b** by preparation according to the general reaction procedure described above.

TGA: 459 °C (79%). T_g: 262.5 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 403 K): δ 0.9−1.9 (3H, b, aliphatic C−H), 6.1−7.1 (33H, b, phenyl-H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 403 K, J-mod): δ 40.01 (−*C*H−CH_2−), 40.77, 41.00 (−CH−*C*H_2−), 124.91, 125.39, 125.57, 126.80, 126.94, 128.21, 131.85, 132.19 (tert aromatic *C*H), 137.68, 139.77, 140.36, 140.90, 141.11, 141.22 (quart aromatic *C*). GPC (THF, polystyrene): M_n, 14 800; M_w, 27 200; PDI, 1.84. MALDI-TOF MS: *m*/*z* 3347 + *n* 637, 3364 + *n* 637 [(*n* + 5) repeat units + K^+ + 2 AIBN

fragments)]. IR (ν [cm^{-1}]): 3083, 3055, 3021 (aromatic CH), 2917, 2852 (aliphatic CH), 1600, 1495, 1442, 1398, 1073, 1023, 1004, 909, 829, 808, 732, 698. Elem anal. Found (calcd for $(C_{50}H_{38})_n$ (636.8)$_n$): C, 93.43 (94.30); H, 5.50 (5.70) (incomplete combustion due to formation of soot).

Poly(4′-vinylhexaphenylbenzene-*r*-MMA) (9a). A total of 1.12 g (2.0 mmol) of compound **5** and 2.0 g (20.0 mmol) of MMA were polymerized with 18 mg (0.11 mmol) of AIBN in 10 mL of benzene at 80 °C for 65 h. After workup according to the general conditions, 2.72 g (87%) of a white polymer was obtained.

TGA: 212 °C (6.8%), 283 °C (17.1%), 405 °C (68.8%). T_g: 145.2 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 403 K): δ 0.887, 0.920, 1.050, 1.211 (3H, α-CH_3), 1.348, 1.390, 1.433, 1.463, 1.826, 1.861, 1.892, 1.906, 1.959, 1.982, 2.051, 2.093 (2H, CH_2), 2.7−2.9 (4.5%), 3.525, 3.596 (95.5%) (3H, s, COOCH_3), 6.49 (2H 7.45%, d, ^3J = 6.2 Hz, H-3), 6.65−6.9 (27H 7.45%, b, phenyl-H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 403 K, J-mod): δ 18.11, 18.83, 19.82, 19.98, 22.04 (C−*C*H$_3$), 45.35, 45.56, 45.85, 46.34, 46.64, 46.96 (α-*C*), 52.96, 53.24, 54.02, 54.48, 54.71, 55.12, 55.20 (CH$_2$), 51.56 (O-*C*H$_3$), 125.34, 126.72, 126.81, 126.98, 131.86 (tert aromatic *C*H), 139.10, 140.28, 140.67, 140.84, 141.16, 141.27 (quart aromatic *C*), 176.32, 176.72, 176.98, 177.18, 177.65, 177.89, 178.14 (carbonyl *C*). GPC (THF, polystyrene): M_n, 19 800; M_w, 35 000; PDI, 1.76. IR (ν [cm^{-1}]): 3000−3100 (aromatic CH), 2850−2950 (aliphatic CH), 1732 (carbonyl), 1601, 1483, 1443, 1388, 1270, 1240, 1193, 1145, 1073, 987, 964, 841, 811, 750, 731, 720, 697. Elem anal. Found (calcd for $((C_{44}H_{32})(C_5H_8O_2)_{13.3})_n$ (1892)$_n$): C, 69.73 (70.11); H, 7.35 (7.42).

Poly[4′-(4-vinylphenylene)hexaphenylbenzene-*r*-MMA] (9b). A total of 1.27 g (2.0 mmol) of compound **8** and 2.0 g (20.0 mmol) of MMA were polymerized with 18 mg (0.11 mmol) of AIBN in 10 mL of benzene at 80 °C for 65 h. After workup according to the general conditions, 2.81 g (86%) of a white polymer was obtained.

TGA: 202 °C (5.2%), 295 °C (15.9%), 408 °C (72.0%). T_g: 158.3 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 403 K): δ 0.877, 0.891, 0.909, 1.056, 1.305 (3H, CH_3), 1.305 (2H, 10.4%, CH_2), 1.438, 1.468, 1.832, 1.903, 1.963, 2.063, 2.102 (2H, CH_2), 2.9−3.1 (5.5%), 3.508, 3.596 (94.5%) (3H, s, COOCH_3), 6.7−6.9, 7.01, 7.21 (33H 9.8%, b, phenyl-H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 403 K, J-mod): δ 17.96, 18.26, 19.43, 19.66, 19.84, 22.41 (C−*C*H$_3$), 45.41, 45.70, 46.18, (α-*C*), 52.81, 54.32, 54.56, 54.79, 54.96 (CH$_2$), 51.59 (O-*C*H3), 124.93, 125.00, 125.23, 126.61, 126.66, 131.78, 132.18 (tert aromatic *C*H), 137.62, 139.98, 140.08, 140.67, 141.03, (quart aromatic *C*), 176.40, 176.83, 177.03, 177.49, 177.74, 177.98 (carbonyl *C*). GPC (THF, polystyrene): M_n, 16 300; M_w, 30 300; PDI. 1.86. Elem anal. Found (calcd for $((C_{50}H_{36})(C_5H_8O_2)_{10.2})_n$ (1658)$_n$): C, 72.83 (73.16); H, 7.10 (7.15).

Poly(4′-vinylhexaphenylbenzene-*r*-styrene) (10a). A total of 561 mg (1.0 mmol) of compound **5** and 2.08 g (20.0 mmol) of styrene were polymerized with 17 mg (0.1 mmol) of AIBN in 5 mL of benzene at 80 °C for 65 h. After workup according to the reaction conditions, 1.55 g (59%) of a white polymer was obtained.

TGA: 419 °C (98.5%). T_g: 115.7 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 373 K): δ 0.9−2.3 (3H, b, aliphatic C−H), 5.7−6.0, 6.2−7.3 (5.6H, b, phenyl-H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 373 K, J-mod): δ 41.00, 41.22, 41.34 (alphatic *C*H), 43.0−46.7 (aliphatic *C*H$_2$), 125.20, 125.55, 125.70, 125.86, 126.68, 127.61, 127.74, 127.97, 128.12, 128.19, 128.25, 131.86 (tert aromatic *C*H), 140.45, 140.64, 141.19, 145.53, 145.71, 145.79, 146.03, 146.28, 146.46 (quart aromatic *C*). GPC (THF, polystyrene): M_n, 18 800; M_w, 30 100; PDI, 1.60. Elem anal. Found (calcd for $((C_{44}H_{32})(C_8H_8)_{38.5})_n$ (4570)$_n$): C, 92.32 (92.51); H, 7.28 (7.50).

Poly[4′-(4-vinylphenylene)hexaphenylbenzene-*r*-styrene] (10b). A total of 637 mg (1.0 mmol) of compound **8** and 2.08 g (20.0 mmol) of styrene were polymerized with 17 mg (0.1 mmol) of AIBN in 5 mL of benzene at 80 °C for 65 h. After workup according to the general conditions, 1.76 g (65%) of a white polymer was obtained.

TGA: 422 °C (95.0%). T_g: 118.8 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 373 K): δ 0.9−2.3 (3H, b, aliphatic C−H), 6.2−7.4 (6.3H, b, phenyl-H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 373 K, J-mod): δ 41.01, 41.26, 41.35 (alphatic *C*H), 43.0−46.5 (aliphatic *C*H$_2$), 124.94, 125.27, 125.37, 125.53, 125.69, 125.85, 126.70, 126.78, 127.61, 127.97, 128.18, 127.25, 128.43, 131.83, 132.18 (tert aromatic *C*H), 140.67, 141.09, 145.1−146.8 (quart aromatic *C*). GPC (THF, polystyrene): M_n, 19 100; M_w, 30 400; PDI, 1.60. Elem anal. Found (calcd for $((C_{50}H_{36})(C_8H_8)_{21.3})_n$ (2855)$_n$): C, 92.42 (92.71); H, 7.16 (7.29).

Poly(4′-vinylhexaphenylbenzene-*r*-vinylhexa-*peri*-hexabenzocoronene) (11a). A total of 100 mg (0.178 mmol) of polymer **1a** was cyclodehydrogenated according to the general procedure, yielding 98% of a dark brown, insoluble material. Cyclodehydrogenation occurred in about 90% yield.

TGA: 475 °C (5.7%), 500−800 °C (4.9%). X-ray powder diffraction diagram: broad peaks at 13.1, 6.1, and 3.62. LD-TOF MS [I]: *m*/*z* 523 (HBC, 15%), 536 (HBC−CH, 15%), 549 (HBC−(CH)$_2$, 100%), 562 (HBC−(CH)$_3$, 10%), 1089 (HBC−(CH)$_3$−HBC, 8%), ca. 1640 (1%), ca. 2190 (1%). IR (ν [cm^{-1}]): 3071, 3052, 3014 (aromatic CH), 2920, 2843 (aliphatic CH), 1607, 1584, 1493, 1443, 1375, 1225, 1090, 868, 827, 783, 762, 738, 698. Elem anal. Found (calcd for $(C_{44}H_{20-32})_n$ (548.6−560.7)$_n$): C, 91.63 (96.31−94.25); H, 3.72 (3.67−5.75) (incomplete combustion due to formation of soot).

Poly[4′-(4-vinylphenylene)hexaphenylbenzene-*r*-4-(hexa-*peri*-hexabenzocoronenyl)styrene] (11b). A total of 100 mg (0.157 mmol) of polymer **1b** was cyclodehydrogenated according to the general procedure, yielding 98% of a dark brown, insoluble material. Cyclodehydrogenation occurred in about 85% yield.

TGA: 420−600 °C (6.1%). X-ray powder diffraction: broad peaks at 14.3 and 3.76. IR (ν [cm^{-1}]): 3073, 3051, 3013 (aromatic CH), 2917, 2842 (aliphatic CH), 1600, 1581, 1558, 1496, 1435, 1378, 1365, 1221, 1088, 871, 824, 784, 764, 742, 698. Elem anal. Found (calcd for $(C_{50}H_{24-36})_n$ (624.7−636.8)$_n$): C, 90.04 (96.13−94.30); H, 4.24 (3.87−5.70) (incomplete combustion due to soot formation).

Poly(4′-vinylhexaphenylbenzene-*r*-vinylhexa-*peri*-hexabenzocoronene-*r*-MMA) (12). A total of 200 mg (0.108 mmol) of polymer **9a** was cyclodehydrogenated according to the general conditions, yielding 15 mg of $C_2H_2Cl_4$-soluble and 170 mg of insoluble brown product.

TGA: 403 °C (92.7%). T_g: 139.1 °C. UV/vis ($C_2H_2Cl_4$, λ [nm] (ϵ [L g^{-1} cm^{-1}]): 342 (3.13), 357 (3.91), 389 (1.50). IR (ν [cm^{-1}]): 2850−3100 (aromatic, aliphatic CH), 1733 (carbonyl), 1601, 1473, 1458, 1436, 1388, 1268, 1240, 1192, 1148, 988, 751, 720, 698, 669. Elem anal. Found (calcd for $[(C_{50}H_{24-36})_1(C_5H_8O_2)_{13.4}]_n$ $(C_{127}H_{131.2-143.2}O_{26.8})_n$ (2086.3−2098.4)$_n$): C, 68.32 (73.1−72.6); H, 6.77 (6.4−6.9) (incomplete combustion due to formation of soot).

Acknowledgment. This work was financially supported by Bundesministerium für Bildung und Forschung. We thank Dr. M. Steenbock for his work on the TEMPO-controlled polymerization of vinylhexaphenylbenzene. C.K. thanks Fonds der Chemischen Industrie for a scholarship.

References and Notes

(1) (a) Inagaki, M. *J. Mater. Res.* **1989**, *4*, 1560−1568. (b) Werner, W. *Adv. Mater. Lightweight Struct., Int. Symp.* **1992**, 185−190. (c) Manocha, L. M. *Mater. Sci. Forum* **1996**, *223−224*, 117−126. (d) Marchand, A. *Polycyclic Aromatic Hydrocarbons Astrophys.* **1987**, 31−54. (e) Minot, C. *J. Phys. Chem.* **1987**, *81*, 6380−6385. (f) Ostermay, G. *Freiberg. Forschungsh. A* **1987**, *A759*, 7−13.

(2) (a) Oberlin, A. High-Resolution TEM Studies of Carbonization and Graphitization. In *Chemistry and Physics of Carbon*; Thrower, P. A., Eds.; Marcel Dekker: New York, 1989; Vol. 22, p 1. (b) Oberlin, A.; Bonnamy, S.; Baurrat, X.; Monthioux, M.; Rouzaud, J. N. *ACS Symp. Ser.* **1986**, 85−98. (c) Oberlin, A. *Carbon* **1984**, *22*, 521−541. (d) Zander, M. *Fuel* **1987**, *66*, 1536−1548.

(3) (a) Marsh, H.; Diez, M. A. Mesophase of Graphitizable Carbons. In *Liquid Crystalline and Mesomorphic Polymers*; Shibaev, V. P., Lam, L., Eds.; Springer-Verlag: New York, 1993; p 231.

(4) (a) Müller, M.; Mauermann-Düll, H.; Wagner, M.; Enkelmann, V.; Müllen, K. *Angew. Chem.* **1995**, *107*, 1751−1754. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1583−1586. (b) Stabel, A.; Herwig, P.; Müllen, K.; Rabe, J. P. *Angew. Chem.* **1995**, *107*, 1768−1770; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1609−1611. (c) Herwig, P.; Kayser, C.; Müllen, K.; Spiess, H. W. *Adv. Mater.* **1996**, *8*, 510−513. (d) Iyer, V. S.; Wehmeier, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem.* **1997**, *109*, 1676−1679; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1604−1607. (e) Müller, M.; Iyer, V. S.; Kübel, C.; Enkelmann, V.; Müllen, K. *Angew. Chem.* **1997**, *109*, 1679−1682; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1607−1610.

(5) (a) Kovacic, P.; Kyriakis, A. *J. Am. Chem. Soc.* **1963**, *85*, 454−458. (b) Speight, J. G.; Kovacic, P.; Koch, F. W. *Macromol. Rev.* **1971**, 295−386. (c) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357−379. (d) Kovacic, P.; Wu, C. *J. Polym. Sci.* **1960**, *47*, 45−54.

(6) (a) Reck, B.; Ringsdorf, H. *Liq. Cryst.* **1990**, *8*, 247−262. (b) Kaufhold, W.; Finkelmann, H.; Brand, H. R. *Macromol. Chem. Phys.* **1991**, *192*, 2555−2579. (c) Messner, B.; Finkelmann, H. *Macromol. Chem. Phys.* **1991**, *192*, 2383−2390.

(7) (a) Stille, J. K. *Angew. Chem.* **1986**, *98*, 504−519; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−523. (b) Bochmann, M.; Kelly, K. *J. Chem. Soc., Chem. Commun.* **1989**, 532−534. (c) Farina, V.; Krishnamuthy, V.; Scott, W. J. *Stille-Reaction* in *Organic Reactions*; Paquelte, P. A., et al., Eds.; John Wiley & Sons: New York, 1997; Vol. 50.

(8) (a) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630. (b) Sanchika, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 752−755. (c) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253−257. (d) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259−263.

(9) Trial, T. T.; Khanna, R. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (2), 818−819.

(10) (a) Inoue, K.; Nishikawa, Y.; Tanigaki, T. *Macromolecules* **1991**, *24*, 3464−3465. (b) Inoue, K.; Takagi, M.; Nakano, M.; Nakamura, H.; Tanigaki, T. *Makromol. Chem., Rapid. Commun.* **1988**, *9*, 345−349. (c) Kajiwara, A.; Aramata, K.; Kamachi, M.; Sumi, K. *Polym. J.* **1994**, *26*, 215−223.

(11) The polymer was deposited in a dithranol/K^+-matrix (polymer:dithranol:K^+ = 1:1000:5) from a THF solution and ionized by a laser at 330 nm.

(12) The peak intensity in MALDI-TOF MS does not allow a direct correlation with the relative amount of the polymer because of the lower probability of ionization for high molecular weight polymers and fragmentation reactions in MALDI-TOF MS.

(13) Zammit, M. D.; Davis, T. P.; Haddleton, D. M.; Suddaby, K. G. *Macromolecules* **1997**, *30*, 1915−1920.

(14) (a) Torsion angle in crystalline state: 62 − 71°. Bart, J. *Acta Crystallogr.* **1967**, *B24*, 1277−1287. (b) Torsion angle in vapor: 90 ± 10°. Almenning, A.; Bastiansen, O.; Skancke, P. *Acta Chem. Scand.* **1958**, *12*, 1215−1223.

(15) A longer MMA sequence has to be observed due to the composition of the polymer with 90 mol % MMA units.

(16) (a) Steenbock, M.; Klapper, M.; Müllen, K.; Pinhal, N.; Hubrich, M. *Acta Polym.* **1996**, *47*, 276−279. (b) Georges, M. K.; Veregin, R. P. N.; Kazmaeier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987−2988. (c) Hamker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185−11189.

(17) Elemental analysis of carbon-rich materials often suffers from soot formation during the combustion of the sample. This results in a lower carbon content, but the hydrogen content of the remaining soot is low; thus, the hydrogen content of the sample should not be changed drastically.

(18) The reduced hydrogen content could, in principle, be due to either intermolecular or intramolecular reactions. The analytical data give no possibility of excluding either one of these reactions, but for monomeric HBC and even larger PAHs, we never observed any intermolecular reactions.[4]

(19) The quantitative analysis was carried out using a mixture of the polymers **1a/b** and **11a/b** with 5,5-dimethyl-1,3-cyclohexadione, which shows no absorption between 600 and 800 cm^{-1}. The carbonyl vibration was used as an internal standard to calibrate the absorption intensities, and the reduced intensity of the C−H deformation vibration at 696 cm^{-1} in **11** compared to **1** was used to calculate the yield of the cyclodehydrogenation reaction.

MA971707H