Cyclodehydrogenation of Poly(perylene) to Poly(quaterrylene): Toward Poly(*peri*-naphthalene)

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ABSTRACT: Cyclodehydrogenation of soluble polyperylenes gives polymers containing predominantly quaterrylene units by spectral analysis. Evidence for larger rylene units is also seen. These polymers represent important intermediates toward a poly(*peri*-naphthalene) (PPN). Reactions on model compounds suggest that the insolubility of polymers with larger rylene units is predominantly due to the rigidity of the polymer backbone.

Introduction

Theoretical works conclude that poly(*peri*-naphthalene) (PPN) (**4a**) (Scheme 1) is expected to have a very small band gap and thus to be an intrinsic electrical conductor.[1] The origin of this behavior is the ladder-type conjugated structure leading to a more rigid backbone than those of other electroactive conjugated polymers such as poly(*p*-phenylenevinylene) (PPV) or poly(*p*-phenylene) (PPP). This rigidity leads to a greater degree of planarity and corresponding greater delocalization of electron wave functions. It also reduces the susceptibility of the structure to local distortions upon excitation by minimizing the degree of ring-rotational freedom and inhibiting Peierls distortion through bond length alteration by inclusion of all the CC bonds in aromatic rings.[2] Because of its insolubility, PPN has yet to be synthesized and characterized, and calculations could only be correlated with a series of oligorylenes **2a**−**d** (Scheme 1).[3−5] While the tetraalkylperylene **2a** is readily soluble in organic solvents, solubility decreases with increasing length so that the pentarylene **2d** is only slightly soluble even in boiling chlorobenzene.[3] The extrapolation of the longest wavelength absorption band of these oligomers with increasing chain length results in a theoretical optical band gap of 0.93−0.98 eV for the polymer PPN (**4a**).[3] This small gap is the reason for its expected intrinsic semiconductivity, making PPN a potentially extremely interesting polymer. Because of its expected insolubility, chemically regular PPN may not become available in the future; the choice of the right solubilizing groups might however permit preparation and characterization of a soluble polymer with a PPN backbone, hence possessing similar electronic properties as PPN. Our approach toward such a polymer is to synthesize a soluble poly(perylene) which could be converted to a PPN by a polymer analogous cyclodehydrogenation reaction. Such a reaction has previously been used by us for the conversion of bi(perylene) to quaterrylene **2c**.[3−5]

Poly(perylene) **3b** has been previously synthesized by Yamamoto polycoupling of a dibromoperylene monomer.[6] However, the low solubility of **3b** in DMF resulted in a low number-average molecular weight M_n of 10 540 (M_w = 27 220). It was therefore concluded that *tert*-butylphenoxy substituents did not introduce enough solubility to enable higher molecular weights.[6] Since *tert*-octylphenoxy substituents have proven to be much better solubilizing groups groups,[7] our approach was to repeat these experiments with the perylene monomer **10** which carries four solubilizing *tert*-octylphenoxy groups in the bay positions.

Results and Discussion

The synthesis of perylene **10** can be performed starting from 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (**5**) (Scheme 2). Reaction with cyclohexylamine gave the corresponding diimide **6** in 88% yield. The solubilizing phenoxy groups were then attached by reaction of the tetrachloride **6** with 4-(1′,1′,3′,3′-tetramethylbutyl)phenol in the presence of potassium carbonate in 65% yield. Hydrolysis of the diimide **7** under basic conditions produced the dianhydride **8** in 65% yield. Decarboxylation of the anhydride then afforded the perylene **9** (65% yield), which was then brominated resulting almost quantitatively in the perylene monomer 3,9-(3,10)-dibromo-1,6,7,12-tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene (**10**). This monomer is a 1:1 inseparable mixture of the 3,9- and 3,10-dibromo isomers. As has previously been shown,[6] the use of such a mixture presents no problems in polymerization as the two isomers are of equal reactivity. Polymerization of **10** under Yamamoto conditions led to the poly(perylene) **3a** which could be purified by precipitation from a solution of methanol/acetone/2 N HCl (5:5:1) to yield 73% of a yellow-greenish polymer. ^{1}H NMR investigation revealed broad signals at δ (ppm) 7.00, 6.84, 6.45, 1.40, 1.03, and 0.44. Gel permeation chromatography (GPC) using polystyrene calibration gave a number-average molecular weight (M_n) of 27 000 and a weight-average molecular weight (M_w) of 99 000 (Figure 5) corresponding to a degree of polymerization (P_n) of about 27. This molecular weight is about 3 times larger than that of the earlier poly(perylene) **3b,** due to the better solubilizing groups. Although less commonly used in the literature, the molecular weight of a rigid polymer as poly(perylene) **3a** with a poly(*p*-phenylene) (PPP) backbone can be expressed more accurately by application of a PPP calibration. This resulted for polymer **3a** in a M_n of 19 000 and a M_w of 51 000. The shape of the UV−vis spectrum of **3a** is similar to that of **3b**. The absorption maximum is however shifted to 489 nm (cf. **3b**: 443 nm). This bathochromic shift might be due to **3a** possesssing a longer conjugation length than **3b**. The bathochromic shift compared to perylene **2a** can be explained from the greater conjugation length

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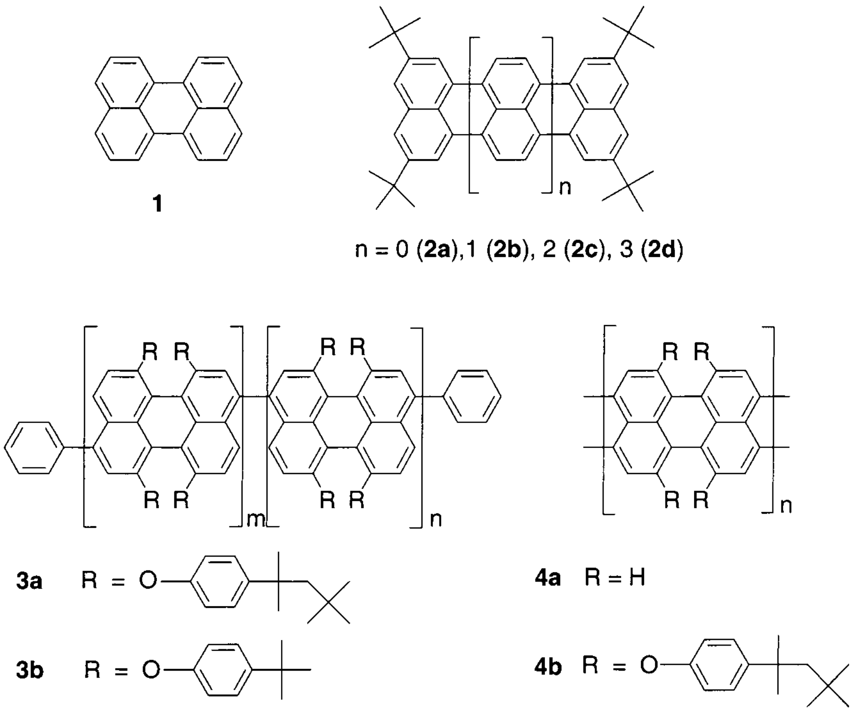
Scheme 1. Perylene (1), Oligorylenes 2a–d, Poly(perylene)s 3a,b, and PPNs 4a,b



and also from the electron pushing effect of the phenoxy groups.

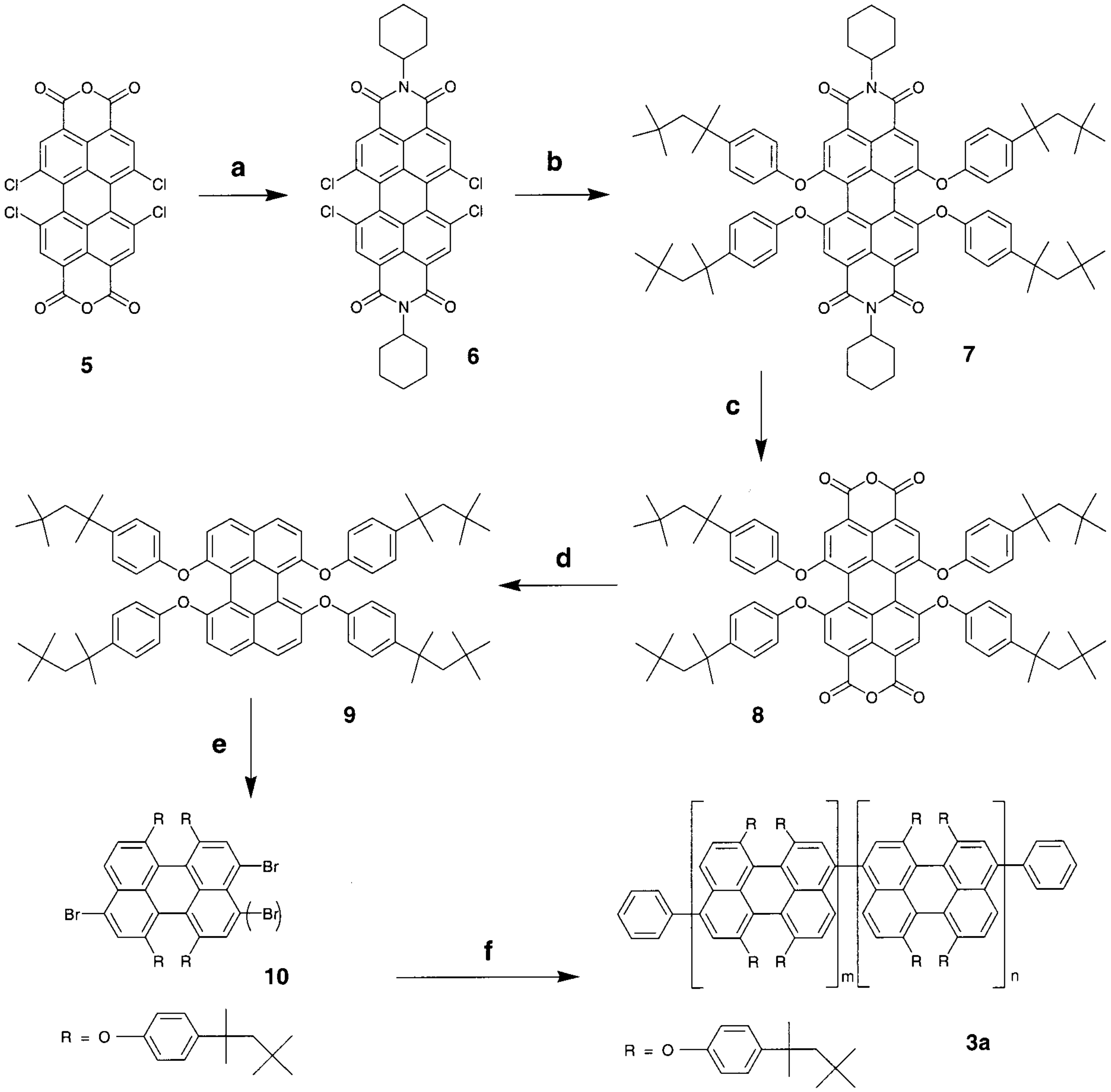
Compared to polynaphthalene, poly(perylene) **3a** constitutes a better precursor for achieving a polymer with extended rylene structure since every second naphthalene unit is already *peri*-condensed. To achieve PPN, (i) the availability of a dehydrogenation method as quantitative as possible and (ii) a sufficient solubility of the resulting PPN is crucial. We applied several methods that are well-known from the literature to obtain dehydrogenation: (i) sulfur in toluene (oxidation potential: +0.142 V[8]), (ii) aluminum chloride/copper(II) chloride in carbon disulfide (+0.153 V, Kovacic conditions[9]), (iii) iodine in toluene (+0.536 V[8]), (iv) *p*-benzoquinone in toluene (+0.699 V[8]), (v) iron(III) chloride in nitromethane–dichloromethane (+0.771 V[8]), and (vi) 5,6-dichloro-2,3-dicyano-*p*-benzoquinone in toluene (DDQ, ca. +1 V[10]). Kovacic conditions have previously been successfully used for the synthesis of oligo(*peri*-naphthylene)s **2a**–**d** starting from oligo(1,4-naphthylene)s.[3]

Treatment of **3b** with sulfur, *p*-benzoquinone and DDQ did not lead to any reaction. However, dehydrogenation occurred under Kovacic conditions as well as from the reaction with iodine and with iron(III) chloride as was shown by the color of the reaction mixtures becoming greenish. The isolated products were characterized by their UV absorption spectra. The reaction of **3b** with iron(III) chloride as well as with iodine led almost quantitatively to a poly(quaterrylene) **11** (Scheme 3). This was concluded from the loss of the typical perylene absorption band at 489 nm of **3b** (Figure 2) and the appearance of a typical quaterrylene absorption (Figure 3). The absorption maximum of 713 nm shows a bathochromic shift compared to quaterrylene **2c** (662 nm) (Figure 4). As in the case of **3a** and **2a**, this shift can be explained by a larger conjugation length and the electron-donating effect of the phenoxy groups.

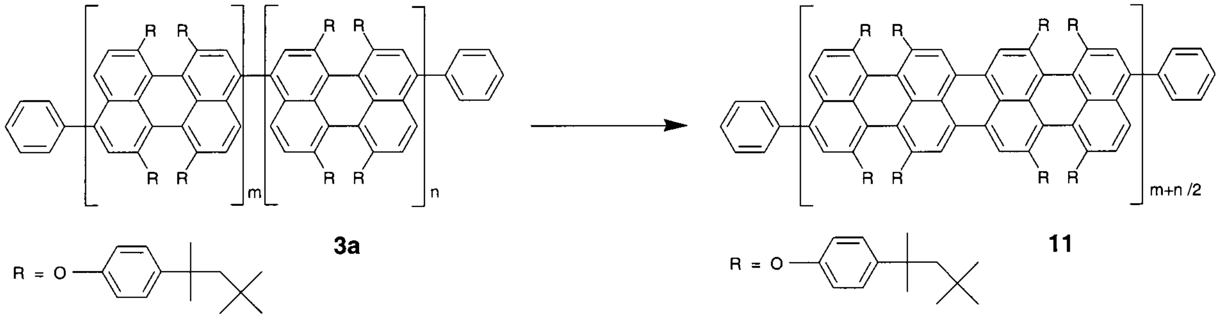
Remarkably, the dehydrogenation seems to stop at the stage of a quaterrylene. A further weak absorption with a maximum of 939 nm (Figure 3) can probably be assigned to a small amount of octarrylene units in the polymer which might be formed by *peri*-condensation of two quaterrylene units. Further evidence for this assignment can be found by relating the optical transition energies to the reciprocal chain length of the corresponding rylene units in the polymer chain. Extrapolation of oligomer properties to indefinite chain length is a commonly used approach to estimate polymer characteristics in order to compare the extrapolated results with the experimental values of a polymer and especially to forecast properties of polymers that are not accessible due to insolubility.[2] Karabunarliev et al.[2] investigated a series of oligorylenes **2a**–**d** (optical transition energies: 2.830, 2.209, 1.872, and 1.657 eV) and plotted the optical transition energies as a function of the reciprocal chain length. The experimental results are displayed together with calculated results (PPP-SCI calculation) and the absorption maxima of polyperylene **3a**, polyquaterrylene **11**, and the second absorption maximum of **11** in Figure 1. It is very probable that the latter can be assigned to octarylene blocks within the polymer chain because the corresponding data point is located exactly on the line extrapolated from the other data points. It is obvious that electronic transitions originating from the polymer occur at smaller energies compared to electronic transitions of the corresponding oligorylenes. Remarkably, extrapolation to infinite number of rylene units from these data gives the same value of 0.95 eV for the polymer as was obtained from the series of oligomers. This result is reasonable when considering that a difference in conjugation length between **4a** and **4b** is no longer seen for $1/n = 0$. Furthermore, this observation might suggest that electron-donating phenoxy groups would have a negligible effect on the band gap of a PPN **4b**.

The absorption, excitation, and fluorescence spectra of poly(perylene) **3a** and poly(quaterrylene) **11** are displayed in Figures 2 and 3, respectively. The absorption maxima of **3a** and **11** are found at 489 and 713 nm, respectively.

Scheme 2. Synthesis of the Poly(perylene) 3a: (a) NMP, CH_3COOH, Cyclohexylamine; (b) 4-(1′,1′,3′,3′-Tetramethylbutyl)phenol, K_2CO_3, NMP; (c) KOH, 2-Propanol, H_2O; (d) Cu_2O, Cu, quinoline; (e) NBS, DMF; (f) (1) $Ni(COD)_2$, 2,2′-Bipyridine, COD, DMF/Toluene, (2) Bromobenzene



Scheme 3. Oxidation of Poly(perylene) 3a to Poly(quaterrylene) 11 with Iodine in Toluene or with $FeCl_3$ in CH_3NO_2 and CH_2Cl_2



As can be seen from Figure 4, the absorption spectra for the polymers closely resemble those for the monomers, but with a bathochromic shift.

The GPC traces of poly(perylene) **3a** and poly(quaterrylene) **11** are displayed in Figure 5. Although **3a** and **11** should possess the same chain length, the number- and weight-average molecular weights of **11** ($M_n = 41\,000$, $M_w = 112\,000$) seem to be higher than the ones of the “precursor” **3a** ($M_n = 7000$, $M_w = 9000$). This is to be expected since **11** has a much more rigid backbone than **3a** and thus has an increased hydrodynamic volume for chains with the same chain length. The resulting shift of the GPC trace to shorter retention times of **11** compared to **3a** is visualized in Figure 5.

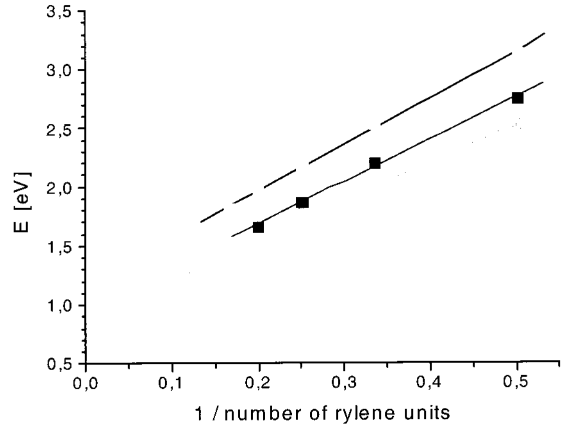


Figure 1. Band gap (eV) (calculated from UV absorption) as a function of the number of rylene units of oligorylenes **2a**−**d** (experimental (■) and calculated (□) values) and polymers **3a** and **11** (●).

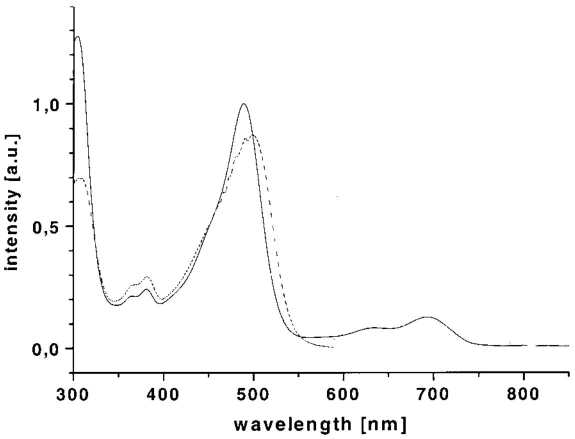


Figure 2. Absorption, excitation (dashes), and fluorescence spectra of poly(perylene) **3a**.

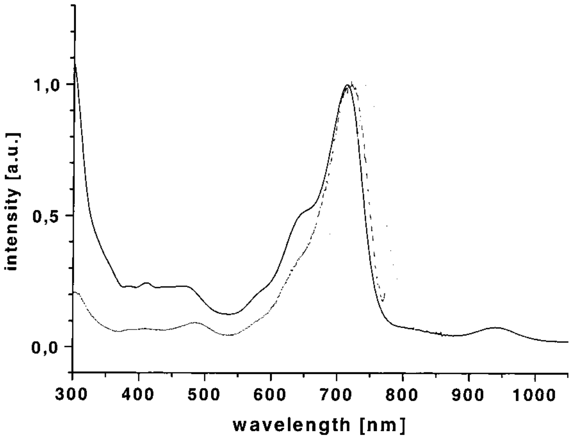


Figure 3. Absorption, excitation (dashes), and fluorescence spectra of poly(quaterrylene) **11**.

As mentioned above, for rigid polymer chains as **3a** and **11** GPC with poly(*p*-phenylene) calibration should lead to more accurate values. For **11** the number- and weight-average molecular weights are $M_n = 26\,000$ and $M_w = 57\,000$.

One might anticipate that more drastic reaction conditions would result in a further condensation of rylene blocks. However, when the reaction mixtures were refluxed for a longer time, the absorption of **11** at 939 nm did not increase. Instead, the reaction with iodine produced small insoluble fractions. Kovacic conditions resulted in a polymer that showed UV absorption originating from perylene and quaterrylene units in about equal intensities. Heating of the reaction mixture to 60 °C gave a clear solution with an insoluble fraction. This observation could be caused by two effects. On one hand, formation of further ring closures within poly(quaterrylene) **11** might result in insufficient solubility due to increased rigidity of the polymer. On the other hand, more drastic conditions might cause a loss of solubilizing phenoxy groups.

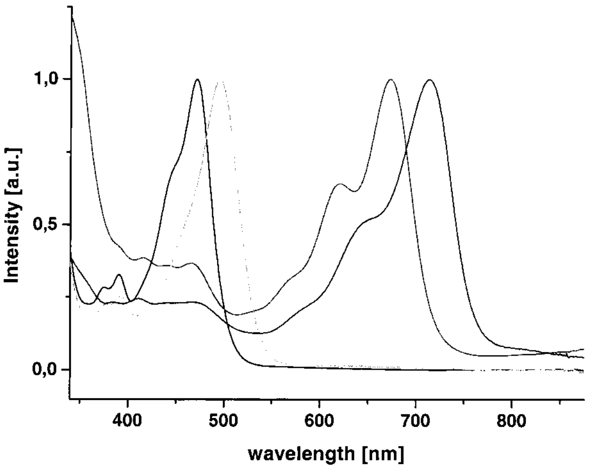


Figure 4. UV spectra (chloroform) of (from left to right) bisperylene **13**, poly(perylene) **3a**, quaterrylene **14**, and poly(quaterrylene) **11**.

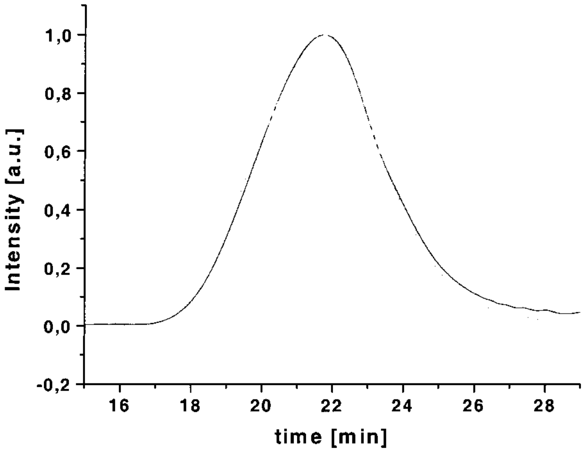
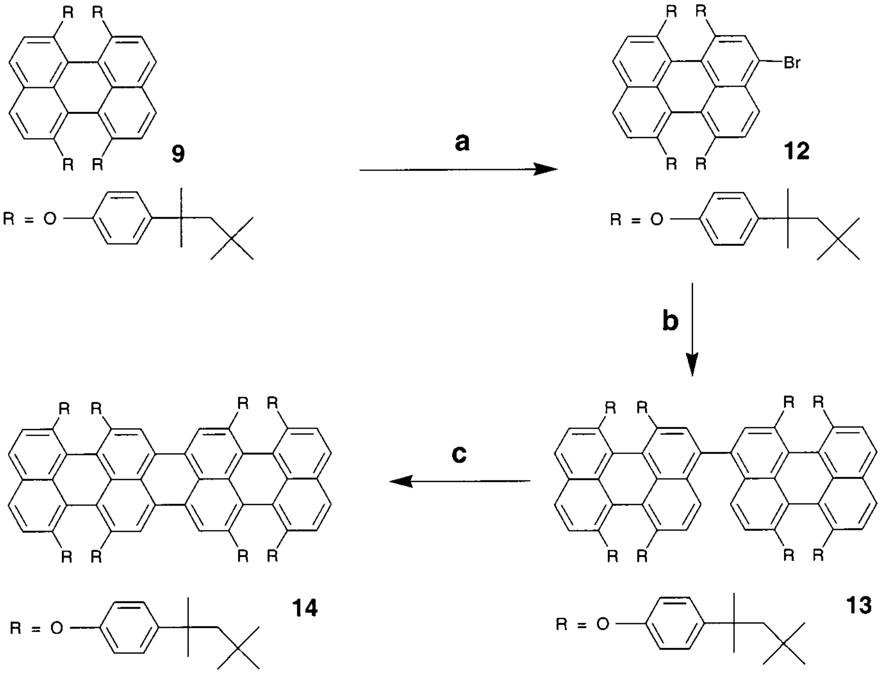


Figure 5. GPC traces (THF) of poly(perylene) **3a** (solid line) and poly(quaterrylene) **11** (dashed line).

To test this, we prepared the biperylene **13** and subjected it to the same reaction conditions. Bromination of **9** gave a crude product which field desorption mass spectrometry (FD-MS) revealed to be a mixture of perylene **9** (relative intensity 100), 3-bromo-1,5,7,12-tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene (**12**) (50), and 3,9-(3,10)-bromoperylene **10** (15), which was subjected to Yamamoto coupling without further purification. FD-MS of ther resulting crude product revealed a mixture of perylene **9** (relative intensity 100), ca. 60% (**13**) (60), and a triperylene (65). The desired product **13** was obtained in 4% overall yield by column chromatography on silica eluting with hexane/dichloromethane (8:1). Reaction of biperylene **13** with iodine in toluene at 60 °C or with iron(III) chloride produced the quaterrylene **14** (Scheme 4). Investigation of this quaterrylene **14** showed only a negligible loss of phenoxy groups. This

Scheme 4. Synthesis of Model Compounds 3,3′-Biperylene 13 and Quaterrylene 14: (a) NBS, DMF; (b) Yamamoto Coupling; (c) Iron(III) Chloride in CH_3NO_2/CH_2Cl_2



outcome suggests that stiffness of the polymer backbone is the dominant cause of insolubility of materials with PPN fragments larger than quaterrylene blocks within the polymer chains. Reaction of **13** under Kovacic conditions resulted in an unidentified insoluble product. These results suggest that prepartion of a PPN by this route may be infeasible unless the solubility can be further improved.

Conclusions

We have shown that by using superior solubilizing groups the molar mass of polyperylenes as potential intermediates in the synthesis of PPN can be improved significantly. These can be cyclodehydrogenated at every second perylene unit to give a poly(quaterrylene) in nearly quantitative yield. Some evidence for formation of longer rylene units was also seen. Application of stronger dehydration methods in attempts to get closer to a PPN structure produced insoluble materials. Reactions on model compounds suggest that the dominant cause of insolubility, when PPN fragments within the polymer chains become larger than quaterrylene blocks, is the rigidity of the backbone.

Experimental Section

1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride was obtained from BASF-AG, Ludwigshafen. Other reagents were purchased from Aldrich. GPC was performed in THF against polystyrene or functionalized poly(*p*-phenylene)[11] standards on a Waters 717 with autosampler.

***N,N’*-Dicyclohexyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic Acid Diimide (6).** 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (**5**) (20 g, 37.8 mmol) was dissolved in *N*-methyl-2-pyrrolidinone (NMP) (300 mL), and glacial acetic acid (14 g) was added to the stirred solution. Cyclohexylamine (11.11 g, 112 mmol) was then added slowly, and the solution was stirred under argon for 6 h at 90 °C. During this time a change of color to orange was observed. The solution was cooled to room temperature, and the orange-red solid product was isolated and washed with methanol. The yield was 22.9 g (87.7%).

6: mp >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.62 (s, 4H), 4.98 (m, 2H), 2.50 (m, 4H), 1.83 (m, 8H), 1.72 (m, 8H). ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 162.63 (C=O), 135.29, 132.87, 131.41, 128.39, 123.79, 123.34, 54.29, 26.48, 25.35. FD-MS: m/z (u e_0^{-1}) = 692.4 (100%, M^+) (calcd: 692.41). FT-IR: ν = 1700 ($\nu_{C=O}$); 1665 cm^{-1} ($\nu_{C=O}$). UV ($CHCl_3$): λ_{max} (ϵ) = 322 (3645); 426 (10231); 484 (26 883); 516 nm (35 024 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{36}H_{26}Cl_4N_2O_4$: C, 62.45; H, 3.78; N, 4.05. Found: C, 61.97; H, 3.75; N, 4.20.

***N,N′*-Dicyclohexyl-1,6,7,12-tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene-3,4,9,10-tetracarboxylic Acid Diimide (7).** *N,N′*-Dicyclohexyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid diimide (**6**) (10 g, 14.4 mmol), 4-(1′,1′,3′,3′-tetramethylbutyl)phenol (29.8 g, 14.4 mmol), and potassium carbonate (9.98 g, 72.2 mmol) were suspended in NMP (720 mL) under an argon atmosphere. The suspension was stirred at 120 °C. The conversion was controlled by monitoring the change in color from orange red to dark red violet and the disappearance of the insoluble fraction. After 8 h the reaction was complete; after cooling to room temperature the solution was poured into a stirred mixture of H_2O/concentrated HCl (11:1, 300 mL), and the precipitate was collected and washed with water. The dried product was purified by chromatography on silica column eluting with dichloromethane/hexane 1:1. The resulting dark red solid was dried under vacuum at 65 °C (yield: 12.84 g, 64.8%).

7: mp 241 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.07 (s, 4 H), 7.19 (d, ^3J = 8.77 Hz, 8 H), 6.78 (d, ^3J = 8.77 Hz, 8 H), 4.86 (m, 2 H), 2.42 (m, 4 H), 1.78 (m, 8 H), 1.65 (m, 8 H), 1.61 (s, 8 H, CH_2), 1.29 (s, 24 H, $(CH_3)_2$), 0.71 (s, 36 H, $(CH_3)_3$). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 162.78 (C=O), 155.10, 151.72, 145.58, 131.65, 126.61, 122.02, 119.29, 118.97, 118.66, 118.48, 56.09, 52.91, 37.35, 31.43, 30.87, 30.51, 28.14, 25.49, 24.42. FD-MS: m/z (u e_0^{-1}) = 1372.0 (100%, M^+) (calcd:1371.87). FT-IR: ν = 2953, 2872, 1700 ($\nu_{C=O}$), 1661 ($\nu_{C=O}$), 1588, 1503, 1412, 1337, 1296, 1217, 1176, 1148, 1015, 984, 873, 836, 806, 584 cm^{-1}. UV ($CHCl_3$): λ_{max} (ϵ) = 368 (4132); 449 (17 098); 540 (26 652); 578 nm (42 734 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{92}H_{110}N_2O_8$: C, 80.55; H, 8.08; N, 2.04. Found: C, 80.51; H, 8.09; N, 2.13.

1,6,7,12-Tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene-3,4,9,10-tetracarboxylic Acid Dianhydride (8). The diimide **7** (11.8 g, 8.6 mml), potassium hydroxide (250 g), 2-propanol (1.7 L), and water (170 mL) were heated under reflux in a 4 L flask for 12 h. During the reaction, the color changed from red to green due to the formation of the tetraanion of **8**. The solution was cooled to room temperature and poured into a mixture of H_2O/concentrated HCl (10:1, 2 L) which was accompanied by a change in color to red. After 2 h the precipitation was completed, and the product was washed with water and recrystallized from dichloromethane/methanol (1:1) (yield: 12.84 g, 64.8%).

8: mp 250 °C. ^1H NMR (250 MHz, $C_2D_2Cl_4$, 25 °C): δ (ppm) = 7.99 (s, 4 H), 7.23 (d, ^3J = 9.3 Hz, 8 H), 6.82 (d, ^3J = 9.2 Hz, 8 H), 1.68 (s, 8 H), 1.28 (s, 24 H), 0.68 (m, 36 H); FD-MS: *m/z* (u e_0^{-1}) = 1209.2 (100%, M^+) (calcd:1209.55). FT-IR: 3448, 2952, 1744 ($\nu_{C=O}$), 1588 ($\nu_{C=O}$), 1502, 1350, 1337, 1288, 1213, 1136, 1015, 820, 798, 737 cm^{-1}. Anal. Calcd for $C_{80}H_{88}O_{10}$: C, 79.44; H, 7.33. Found: C, 79.40; H, 7.51.

1,6,7,12-Tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]-perylene (9). A mixture of the anhydride **8** (15 g, 12.4 mmol), copper(I) oxide (10 g), copper powder (1 g), and quinoline (700 mL) was heated to 220 °C for 8 h under an argon atmosphere. Half of the solvent was removed under reduced pressure, and the residue was poured into a stirred mixture of H_2O/concentratedHCl (10:1, 2.5 L). The resulting yellow precipitate was washed with water and purified by chromatography on silica eluting with dichloromethane/*n*-hexane (1:2) (yield: 8.62 g, 65%).

9: mp 176−178 °C. ^1H NMR (500 MHz, THF, 306 K): δ (ppm) = 7.62 (d, ^3J = 5.5 Hz, 4 H), 7.24 (d, ^3J = 5.8 Hz, 8 H), 7.03 (d, ^3J = 5.5 Hz, 4 H), 6.79 (d, ^3J = 5.9 Hz, 8 H), 1.76 (s, 8 H), 1.35 (s, 24 H), 0.78 (s, 36 H). ^{13}C NMR (125 MHz, THF, 25 °C): δ (ppm) = 155.50 (arom q), 154.73 (arom q), 145.35 (arom q), 136.03 (arom q), 127.92 (arom CH), 127.83 (arom CH), 126.22 (arom CH), 119.84 (arom q), 118.25 (arom CH), 117.30 (arom q), 57.74 (aliph q), 38.90 (aliph q), 33.02 (CH_2), 32.31 ($(CH_3)_2$), 32.15 ($(CH_3)_3$). FD-MS: *m/z* (u e_0^{-1}) = 1068.7 (100%, M^+) (calcd:1069.5). FT-IR: ν = 2951, 2901, 1599 ($\nu_{C=O}$), 1490, 1384, 1364, 1249, 1220, 1172, 1014, 879, 828, 579 cm^{-1}. UV ($CHCl_3$): $\lambda_{max}(\epsilon)$ = 359 (6834); 376 (8707); 422 (16 019); 444 nm (18 452 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{76}H_{92}O_4$: C, 85.35; H, 8.67. Found: C, 85.36; H, 8.65.

3,9-(3,10)-Dibromo-1,6,7,12-tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene (10). A solution of 1,6,7,12-tetrakis[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]perylene (**9**) (5.7 g, 5.33 mmol) in DMF (700 mL) was heated to 60 °C. After addition of NBS (3.5 g, 19.1 mmol) the solution was stirred at 60 °C for 3 h, with the progress of the reaction being monitored by TLC. The solution was cooled to room temperature and poured into a stirred mixture of water/concentrated HCl (10:1). The product was extracted with dichloromethane, and the organic layer was washed with water and dried over magnesium sulfate. After evaporation of the solvent under vacuum the yellow solid was purified by column chromatography on silica eluting with dichloromethane/*n*-hexane (1:2) (yield: 6.15 g, 94%).

10: mp 133−134 °C. ^1H NMR (500 MHz, THF, 25 °C): δ (ppm) = 7.96 (d, ^3J = 2.4 Hz, 2 H), 7.29 (m, 10 H), 7.13 (d, ^3J = 2.4 Hz, 2 H), 6.82 (m, 8 H), 1.74 (d, ^3J = 4.6 Hz, 8 H), 1.34 (s, 24 H), 0.77 (tr, ^3J = 6.2 Hz, 36 H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 393 K): δ (ppm) = 127.47, 119.44, 103.06, 57.55, 38.55, 32.45, 32.03, 31.67.

Poly[1,5,7,12-Tetrakis{(1,1,3,3-tetramethylbutyl)-phenoxy}perylene-3,9(3,10)-diyl] (3a). A solution of bis-(cyclooctadiene)nickel(0) (158 mg, 0.58 mmol), 2,2′-bipyridine (90 mg, 0.58 mmol), and 1,5-cyclooctadiene (0.13 mL) in dimethylformamide (2.5 mL) was prepared in a Schlenk tube under glovebox conditions. The solution was heated to 80 °C for 20 min under argon, and then a solution of 336 mg (0.27 mmol) of the dibromide **10** (336 mg, 0.27 mmol) in dry toluene (5 mL) was added via syringe. The reaction mixture was stirred for 3 days at 90 °C. Then bromobenzene (253 mg, 1.62 mmol) and 158 mg (0.58 mmol) of bis(cyclooctadiene)nickel(0) (158 mg, 0.58 mmol) were added, and the solution was stirred for another 24 h at 90 °C. After cooling to room temperature toluene (80 mL) was added, and the organic phase was washed with a 10% aqueous HCl solution (100 mL). The solvent was removed under reduced pressure, and after dissolution of the residue in toluene (6 mL) the polymer was precipitated from a mixture of methanol/acetone/2 N HCl (5:5:1, 200 mL). The polymer was obtained as a brown-greenish powder (210 mg, 73%).

3a: ^1H NMR (500 MHz, THF, 25 °C): δ (ppm) = 7.00, 6.84, 6.45 (3 × m, 22 H), 1.40, 1.03, 0.44 (3 × m, 68 H). GPC (THF, 1 g/L, 30 °C): M_n 27 000, M_w 99 000 (polystyrene calibration), M_n 19 000, M_w 51 000 (poly(*p*-phenylene) calibration). UV abs-($CHCl_3$): $\lambda_{max}(\epsilon)$ = 489 nm (29 100 L/mol cm). UV fluor($CHCl_3$, exc at 470 nm): λ_{max} = 554 nm. DSC (20 K/min): glass transition at 208 °C (0.159 J/(g K)). TGA (20 K/min): 5% degradation at 376 °C, maximum degradation (29%) at 422 °C. Anal. Calcd for ($C_{76}H_{90}O_4$): C, 85.5; H, 8.5. Found: C, 80.7; H, 9.3.

Poly(quaterrylene) 11. The poly(perylene) **3a** (20 mg, 0.02 mmol) was placed in a Schlenk tube under an argon atmosphere and dissolved in dichloromethane (5 mL). After addition of iron(III) chloride (60 mg, 0.34 mmol) and nitromethane (0.3 mL) the solution was stirred at room temperature for 2 h and then refluxed for 7 days with monitoring by UV−vis spectroscopy. Methanol (10 mL), water (20 mL), and dichloromethane (50 mL) were added to the solution. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give the poly(quaterrylene) **11**.

Alternatively, **3a** was converted to **11** by oxidative dehydrogenation with iodine in toluene. Excess iodine was removed by addition of toluene and washing the organic layer with sodium thiosulfate solution. **11**: GPC (THF, 1 g/L, 30 °C) (Figure 5): M_n 41 000, M_w 112 000 (polystyrene calibration), M_n 26 000, M_w 57 000 (poly(*p*-phenylene) calibration). UV abs-($CHCl_3$): λ_{max} = 713 nm; UV fluor($CHCl_3$, exc at 700 nm): λ_{max} = 744 nm. Anal. Calcd for ($C_{152}H_{178}O_8$): C, 85.6; H, 8.4. Found: C, 78.8; H, 8.6.

3,3′-Biperylene 13. 1,6,7,12-Tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]perylene (**9**) (100 mg, 0.09 mmol) was dissolved in DMF (2 mL). After addition of NBS (18 mg, 0.09 mmol) the solution was stirred for 24 h at 70 °C to give a crude mixture of products which was used without further purification. Bis(cyclooctadiene)nickel(0) (17 mg, 0.06 mmol), 2,2′-bipyridine (10 mg, 0.06 mmol), and cyclooctadiene (0.03 mL) were dissolved in dimethylformamide (1.5 mL) in a Schlenk tube under glovebox conditions. The solution was heated to 80 °C for 20 min, and a solution of the above crude product mixture (70 mg) in toluene (1 mL) was added. The resulting crude product was then absorbed onto on silica. Elution with hexane/dichloromethane (8:1) gave the desired product **13** (8 mg, 4%).

13: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 7.39−7.04 (m, 46 H), 1.75, 1.40, 1.03, 0.95, 0.51 (5 × m, 136 H). UV ($CHCl_3$): λ_{max} = 471 nm. FD-MS: *m/z* (u e_0^{-1}) = 2136.7 (100%, M^+) (calcd for $C_{152}H_{182}O_8$: 2137.1), 1931.7 (7%, $M^+-O(C_6H_4)(C_8H_{17})$).

Quaterrylene 14. 3,3′-Biperylene **13** (2 mg) was placed in a Schlenk tube together with iron(III) chloride (5 mg), nitromethane (0.1 mL), and dichloromethane (1 mL). The solution was stirred for 24 h and then worked up as in the preparation of poly(quaterrylene) **11**.

14: ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.39−7.04 (m, 46 H), 1.60, 1.40, 1.02, 0.85, 0.35, 0.27 (6 × m, 136 H). UV ($CHCl_3$): λ_{max} 673 nm (100%) and 621 nm (67%). FD-MS: *m/z* = 2135.0 (100%, M^+) (calcd for $C_{152}H_{180}O_8$: 2135.1), 1931.6 (7%, $M^+-O(C_6H_4)(C_8H_{17})$).

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