A New Soluble Poly(*p*-phenylene) with Tetrahydropyrene Repeating Units

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ABSTRACT: The first poly(*p*-phenylene) (PPP) based on repeating 4,5,9,10-tetrahydropyrene units has been synthesized starting from 2,7-dibromo-4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene (**3a**) as the monomer in a polycondensation reaction. The new polymer is soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, THF, and toluene. By contrast with other PPP's, the solubilizing alkyl substituents do not induce torsion about the aryl−aryl single bonds. GPC analysis indicates a monomodal molecular weight distribution, and the average degree of polymerization, based on tetrahydropyrene units, is 40 (polystyrene standards), corresponding to 80 phenylene rings. The NMR spectra reveal that the poly(tetrahydropyrene) (PTHPy, **4**) obtained possesses a regular structure. The fluorescence spectrum measured in THF solution shows an emission maximum at 425 nm, while for the film, the maximum is shifted to 457 nm. The above characteristics qualify the new PPP as an attractive material for use in light-emitting diodes.

Introduction

In recent years, considerable attention has been directed toward the synthesis of poly(*p*-phenylenes) (PPP) and their derivatives. Their good thermal and chemical stability,[1] electrical conductivity upon doping,[2] and optical properties[3] make these rigid-rod polymers attractive candidates for scientific and industrial applications.

A major problem in attempts toward the synthesis of high molecular weight PPP is the insolubility of even small oligophenylenes and, therefore, the difficulty to reach high degrees of polymerization. The most important approach to PPP is the so-called "direct method"[4] which starts from benzene or its derivatives. Typical examples are the oxidative polymerization according to Kovacic,[5] dehalogenation polycondensation with alkali metals[6] or copper,[7] and the method in which nitrogen is extruded from diazonium compounds.[8] The materials produced by these methods show structural irregularities such as ortho-, meta-, and cross-linkages and tend to be low molecular weight polymers.

Higher molecular weight PPP can be synthesized using "precursor routes"[9] which provide a well-defined, soluble prepolymer capable of being aromatized to PPP in a final step. The polymer produced in this way is still insoluble and possesses structural defects as a result of the difficulty in controlling the aromatization step.

Recently, a long-chain and soluble PPP derivative (**7**) has been synthesized via palladium-catalyzed coupling of 4-bromo-2,5-di-*n*-hexylphenylboronic acid or via a mixed coupling of the corresponding diboronic acid and the dibromo compound.[10] The steric demand of the alkyl chains, however, leads to a considerable torsion about the phenyl−phenyl bonds which seriously inhibits the conjugative interaction along the polymer chain.

More recent approaches have tried to avoid these problems by chemical or electrochemical[12] coupling of 2,7-dibromo-9,10-dihydrophenanthrene.[11] The methylene bridges do not increase the solubility of the material; hence, the average degree of polymerization is still on the order of only five repeating units.

A more successful approach is the oxidative polymerization of 9-alkyl- or 9,9-dialkylfluorenes affording materials with approximately 10 repeating units but still containing defects along the polymer chain due to undesirable coupling at positions 3 and 6.[13]

A novel and particularly promising approach toward the planarization of the PPP backbone is its incorporation into a ladder-type structure (**8**).[14] When solubilizing alkyl groups are present, a polymer with about 50 1,4-coupled benzene rings can be produced.

In this paper, we report on the synthesis of a new PPP derivative (**4**) which is based on 2,7-coupled 4,9-dialkyl-4,5,9,10-tetrahydropyrene. The fundamental idea using 2,7-dibromo-4,9-dialkyl-4,5,9,10-tetrahydropyrene (**3**) as a monomer for the synthesis of a new PPP derivative is based on the following: (i) the solubility of the polymer will be brought about by the presence of ethanediyl bridges and the attachment of alkyl groups at the 4- and 9-positions which do not disturb the conjugation interaction along the π-chain; (ii) it can be deduced from the crystal structure of 2,7-dibromo-4,9-di-*n*-octyl-4,5,9,-10-tetrahydropyrene (**3a**) that the angle of torsion within the biphenyl system is 20°.[15] In comparison with PPP, wherein the angle of torsion between each phenylene ring is about 23°,[16] PTHPy shows a twist angle that alternates between a maximum of 20° within the biphenyl system and a higher value among two tetrahydropyrene units. This improved $\pi-\pi$ overlap in **4** is proven by an electron absorption spectrum.

It is well-known that the yields of aryl coupling reactions with Ni(0) complexes are strongly dependent on the sterical influence of side groups located next to the coupling position. We were able to polymerize **3** using the Yamamoto reaction. In contrast to previous examples, there is no steric hindrance produced by neighboring alkyl groups.

Results and Discussion

We recently synthesized 2,7-difunctionalized pyrenes carrying solubilizing alkyl substituents at their 4,9-positions. These species serve as building blocks for the synthesis of 2,7-linked oligopyrenes which exhibit quite unusual physical properties.[17]

On the basis of these results, we designed a new poly(*p*-phenylene) derivative possessing 4,5,9,10-tetrahydropyrene building blocks.

According to Scheme 1, 2,2′-bis(alk-1″-enyl)biphenyl (**1**), synthesized by a Wittig reaction[18] of either biphenyl 2,2′-dialdehyde and an alkylphosphonium salt or of an *n*-alkyl aldehyde and 2,2′-bis(triphenylphosphoniometh-

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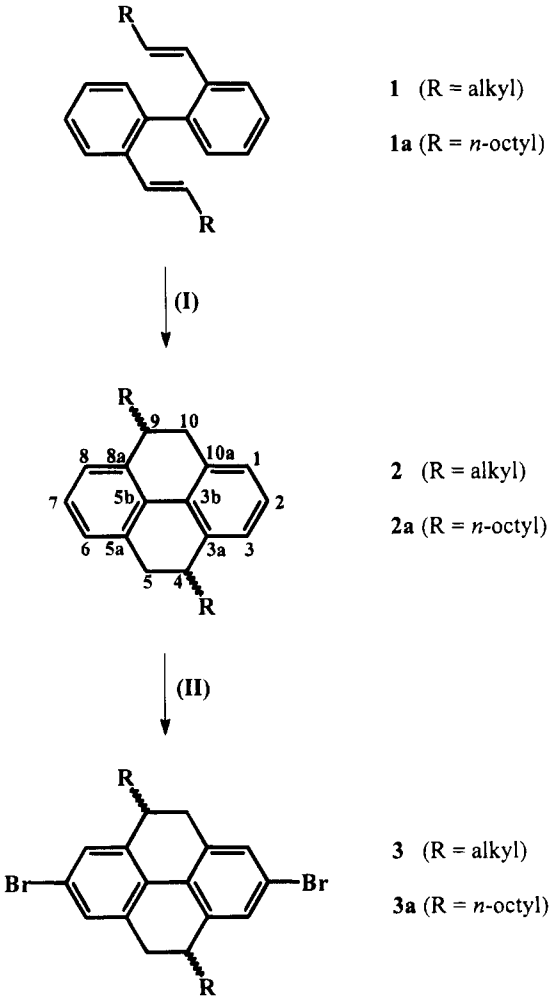
Scheme 1. Synthesis of Monomer 3[a]



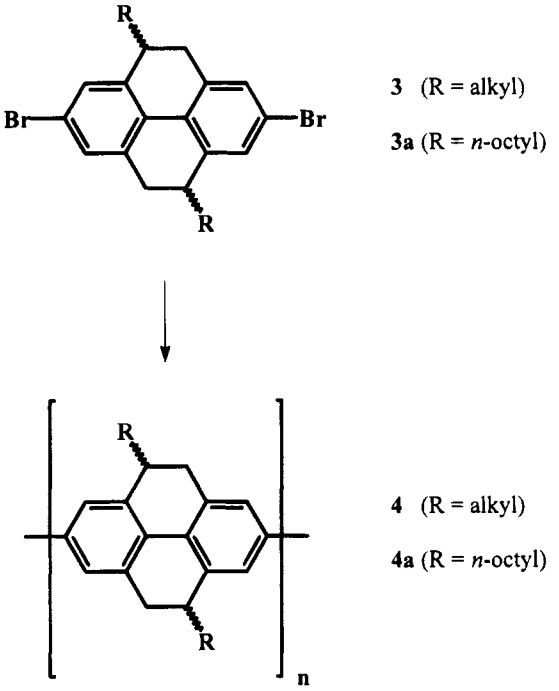
[a] (I) *hv*, *n*-hexane, 85%. (II) Br_2/DMF, Pd on C 5%, 85%.

yl)biphenyl dibromide, was photocyclized to 4,9-dialkyl-4,5,9,10-tetrahydropyrene (**2**) in 85% yield. Compound **2** was obtained as a mixture of cis-/trans-isomers, since the alkyl chains at the 4- and 9-positions can each be arranged either above or below the tetrahydropyrene plane.

The bromination of **2**, catalyzed by 5% palladium or platinum on activated charcoal afforded, after purification by column chromatography, 2,7-dibromo-4,9-dialkyl-4,5,9,10-tetrahydropyrenes (**3**) as colorless oils in70−80% yield. Although the cis-/trans-isomers of **3** can be separated by multiple column chromatography with low-boiling petroleum ether, we decided to use the isomeric mixtures for the polymerization of 2,7-dibromo-4,9-dialkyl-4,5,9,10-tetrahydropyrenes (**3**). While the presence of both *cis*- and *trans*-alkyl groups within the repeating units is expected to further increase the solubility of the polymer (**4**), it should not affect the electronic properties of the conjugated polymer. For the polymerization of **3**, we used a complex of nickel(0) cyclooctadiene and 2,2′-bipyridyl in toluene/dimethylformamide, according to the method described by Yamamoto[11b] (Scheme 2). Herein we describe the synthesis of a PTHPy polymer with octyl side chains as a representative example.

2,7-Poly(4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene) (**4a**) was obtained as a light yellow solid in 96% yield after precipitation from acetone. The residual bromine end groups were removed by dropwise addition of a solution of the polymer in toluene to a suspension of $LiAlH_4$ in THF. The reaction mixture was then heated under

Scheme 2. Synthesis of Polymer 4[a]



[a] $Ni(COD)_2$, 2,2′-Bipyridyl, COD, toluene/DMF, 75%.

reflux for 24 h. After further purification procedures, as described in the Experimental Part, **4a** was obtained in 75% yield. The good solubility of PTHPy (**4a**) in common solvents such as $CHCl_3$, toluene, THF, and CH_2Cl_2 allowed for a full characterization of this rigid-rod polymer. X-ray fluorescence analysis gave evidence that there are no considerable traces of nickel remaining (Ni contamination <20 ppm). Films formed from **4a** are transparent and homogeneous. The molecular weight determination of the polymer will be discussed below.

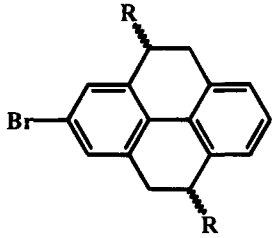
As a model compound, to assist in the structure elucidation of the polymer, the dimer 2,2′-bis(4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene) (**6**) was synthesized starting from 2-bromo-4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene (**5**)[17] according to the Yamamoto method[11b] (Scheme 3).

Figure 1b shows the ^1H NMR spectrum of PTHPy (**4a**) which is almost identical to that of dimer **6** (Figure 1a). The broad signal between δ 7.47 and 7.43 is due to the H-atoms 1x, 3x, 6x, 8x in the polymer chain. In the dimer **6**, a doublet of doublets at δ 7.41 can be assigned to the H-atoms 1 and 3 and the two signals at δ 7.12 and 7.19 to the H-atoms 6, 7, and 8. In the polymer, a very small signal at δ 7.19 can still be observed, characterizing the H-atoms 6, 8, 6z, and 8z. The protons attached to the C-atoms 4x, 5x, 9x, and 10x appear between δ 2.79 and 3.18 in accordance with dimer **6**. The signals between δ 0.89 and 1.88 can be ascribed to the aliphatic protons of the octyl chains.

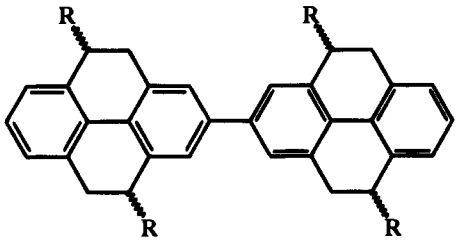
Further evidence for the structure of PTHPy **4a** can be obtained by comparing the ^{13}C NMR spectra of 4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene (**2a**), 2,2′-bis(4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene) (**6**), and 2,7-poly(4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene) (**4a**).

Table 1 shows the ^{13}C NMR chemical shifts of **2a**, **4a**, and **6**. By comparison, six signals in the aromatic region of **4a** could clearly be assigned to the C-atoms in the tetrahydropyrene system of the polymer. Ten signals in the aliphatic region are almost identical in all three compounds and therefore not listed in Table 1. The absence of end-group signals in the ^{13}C NMR spectrum

Scheme 3. Synthesis of Dimer 6[a]



5 (R = *n*-octyl)



6 (R = *n*-octyl)

[a] Ni(COD)$_2$, 2,2′-bipyridyl, COD, toluene/DMF, 99%.

Table 1. ^{13}C NMR Chemical Shifts (ppm) of Monomer 2a, Dimer 6, and Polymer 4a ($CDCl_3$, 125 MHz)

monomer **2a**	C-atoms	dimer **6**	C-atoms	polymer **4a**	C-atoms
		140.1, 140.3	C_2, $C_{2'}$	140.2	C_{2x}
139.2	C_{3b}, C_{5b}	139.7	C_{3b}, $C_{3b'}$	139.6	C_{3bx}, C_{5bx}
		139.2	C_{5b}, $C_{5b'}$		
		135.3	C_{10a}, $C_{10a'}$	135.3	C_{5ax}, C_{10ax}
134.9	C_{5a}, C_{10a}	134.7	C_{5a}, $C_{5a'}$		
130.0	C_{3a}, C_{8a}	129.3	C_{3a}, $C_{3a'}$		
127.0	C_1, C_6	129.1	C_{8a}, $C_{8a'}$	129.1	C_{3ax}, C_{8ax}
126.2	C_3, C_8	127.0	C_8, $C_{8'}$		
		126.2	C_6, $C_{6'}$		
		124.8, 124.9	C_3, $C_{3'}$	124.9	C_{3x}, C_{8x}
124.2	C7	124.3	C_7, $C_{7'}$		
		123.1, 123.2	C_1, $C_{1'}$	123.2	C_{1x}, C_{6x}

of PTHPy (**4a**) indicates that a true polymer has been formed, rather than telomers.

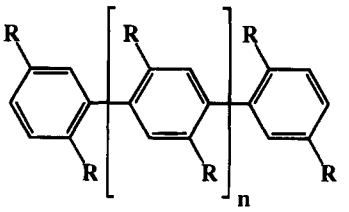
Polymer Molecular Weight Analysis

The gel permeation chromatography (GPC) analysis (polyester standards) of 2,7-poly(4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene) (PTHPy, **4a**), performed after the first precipitation in acetone, shows a monomodal distribution with a weight-average molecular weight (M_w) of approximately 35 000 and a number-average molecular weight (M_n) of 17 400. The number-average molecular weight corresponds to a degree of polymerization on the order of 40, which is equal to approximately 80 linearly coupled benzene rings. The polydispersity (M_w/M_n) is 2.01. Since it is well-known that a GPC analysis of rigid-rod polymers using polystyrene standards as calibration can overestimate the value of the degree of polymerization, we checked the correctness of the molecular weight determination by calibrating with oligomer standards[19] with up to 10 tetrahydropyrene units. The molecular weight obtained in this way is approximately 25% lower than the value achieved by polystyrene calibration.

A second GPC, performed after the debromination and purification of **4a**, shows identical values for M_w and M_n; hence, it follows that no decomposition or fractionation took place.

Remarkably enough we succeeded to separate a very high molecular weight fraction from PTHPy (**4a**) in an amount of 20% with M_w of 55 000 and a number-average weight M_n of 33 300. This is equal to 150 coupled benzene rings.

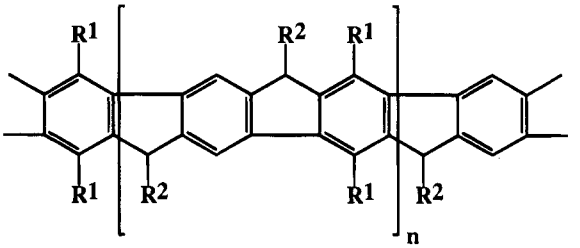
Chart 1. PPP with Solubilizing Alkyl Groups (7)[10a,b] and Ladder-Type PPP (8)[14b]



R = *n*-hexyl

7

λ_{max} = 330 nm



R^1 = alkyl, R^2 = aryl

8

λ_{max} = 440 nm

The TGA curve of PTHPy(**4a**) indicates a 5% weight loss at 310 °C. Main decomposition can be observed between 280 and 420 °C (maximum: 367 °C, 55%) which is due to the extrusion of the octyl groups. Another weight loss maximum (480 °C, 13%) indicates further decomposition of the polymer structure.

Absorption and Fluorescence Properties

The absorption spectrum of the monomer **2a** shows a wavelength maximum at λ_{max} = 295 nm. The extended π-delocalization of polymer **4a** is revealed in a considerable bathochromic shift of its absorption maximum (Figure 2; λ_{max} = 385 nm, cyclohexane). The same value is obtained for the UV spectrum of a PTHPy film on a quartz plate.

A good case can be made when comparing the λ_{max} values of different PPP's (Chart 1): The PPP **7** in which the solubilizing alkyl groups seriously inhibit the π–π interaction possesses an absorption at a short wavelength (λ_{max} = 330 nm)[10a,b] while the fully planarized ladder-type PPP **8** shows a significant bathochromic shift (λ_{max} = 440 nm).[14] Accordingly, the title polymer PTHPy (**4a**, λ_{max} = 385 nm) is intermediate between both of these extremes.

Figure 3 shows the fluorescence emission spectrum (curve a, λ_{max} = 425 nm, excitation wavelength 385 nm) of **4a** plotted against its fluorescence excitation spectrum (curve b, λ_{max} = 409 nm, observation wavelength 470 nm). The small Stokes shift provides further evidence for the rigid geometry of the polymer.[14]

The fluorescence emission spectrum (λ_{max} = 457 nm, excitation wavelength 385 nm) measured using a thin film on a quartz plate is shown as curve c. Here, a

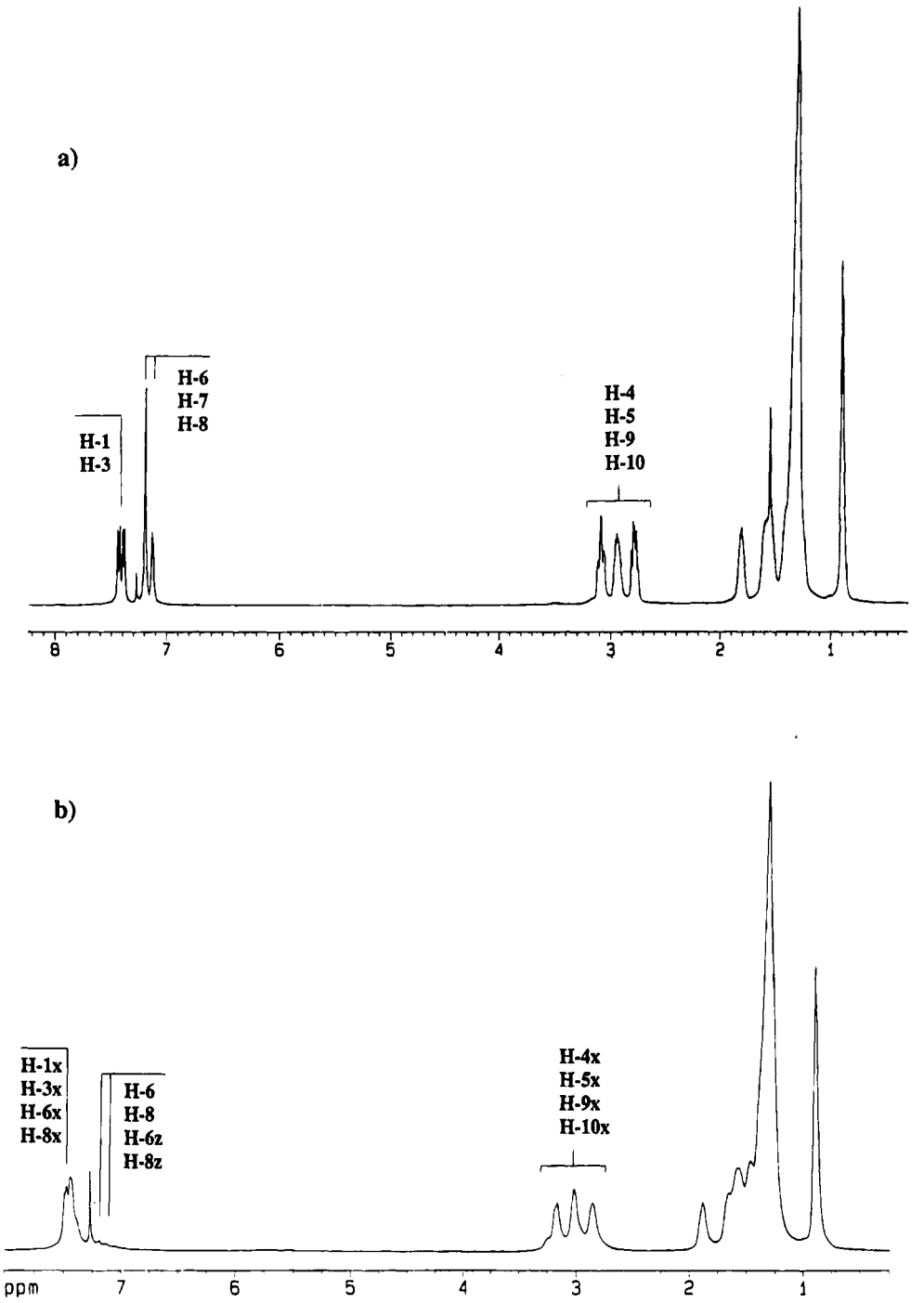


Figure 1. (a) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of dimer **6**. (b) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of polymer **4a**.

bathochromic shift of nearly 30 nm to a value of 457 nm is observed.

The emission maximum of the film is located in the blue. The sterically regular structure, the good solubility, the film-forming attributes, and the wavelength domain of absorption and emission qualify PTHPy as an active component in light-emitting diodes.

Conclusion

The synthesis of a PPP derivative derived from 4,9-dialkylated 4,5,9,10-tetrahydropyrenes produces a well soluble and characterizable, high molecular weight PPP derivative. The structural regularity has been convincingly proven by NMR on comparison with the building block **2a**, the dimer **6a**, and the polymer **4a**. The absorption and fluorescence spectra demonstrate the unique structure of this polymer. The improved $\pi-\pi$ orbital interaction and structural purity, as compared to alkylated or Kovacic-type PPP, make this polymer attractive for further physical studies.

Finally, we mention that the cis- and trans-isomers of 2,7-dibromo-4,9-dialkyl-4,5,9,10-tetrahydropyrene (**3**) can be separated. Further studies will then include the polymerization of each isomer in combination with the variation of the alkyl side-chain length. This is important because isomeric PTHPy polymers are expected to adopt different packing behavior in the solid state.

Experimental Part

General Procedures. 2,2′-Bis(*n*-dec-1″-enyl)biphenyl (**1a**) was synthesized according to the general procedures already described.[17]

The photocyclization was carried out in a Graentzel photoreactor, no. 12, equipped with a UV low-pressure mercury lamp (80 W, length 1 m, ϕ 14 mm).

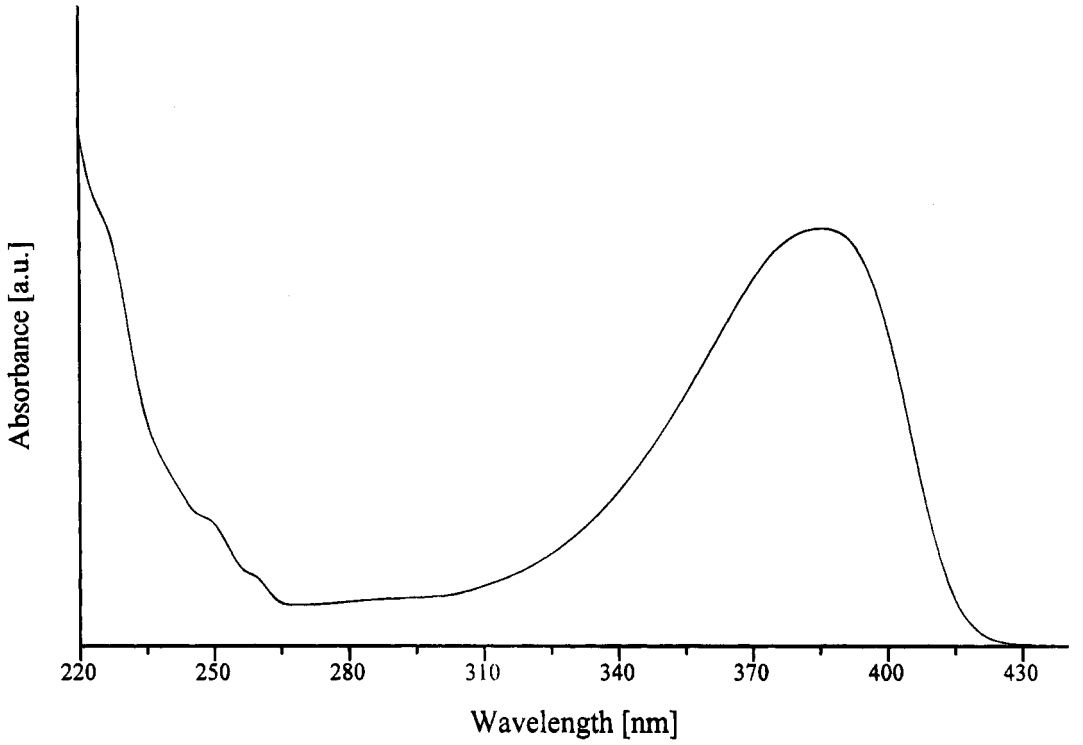


Figure 2. UV spectrum of polymer **4a**.

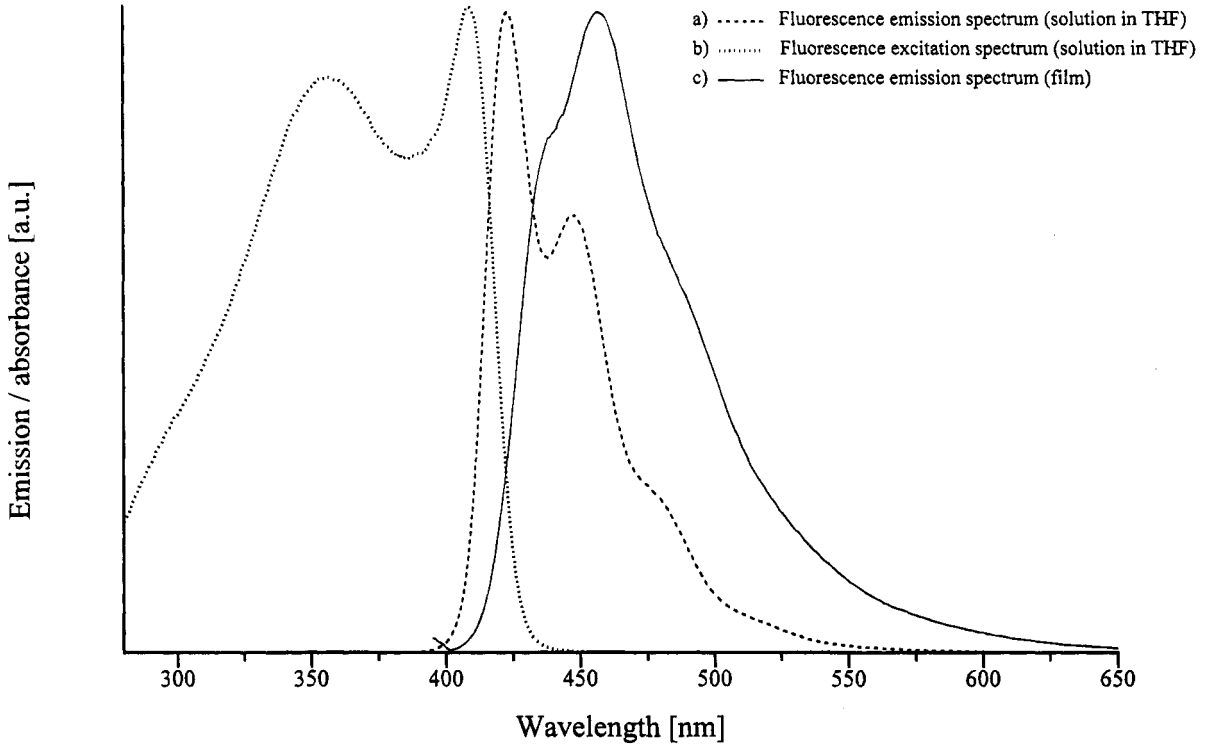


Figure 3. Fluorescence spectra of polymer **4a**.

The solvents used were of commercial p.a. quality; toluene was distilled from sodium, *N,N*-dimethylformamide (DMF) was distilled from calcium hydride, and tetrahydrofuran (THF) was distilled from potassium. ^{1}H NMR: Varian Gemini 200 (200 MHz), Bruker AMX 500 (500 MHz). ^{13}C NMR: Bruker AMX 500 (125 MHz). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS), and ^{13}C resonances were recorded using the 77.0 ppm $CDCl_3$ resonance of the solvent as an internal reference and are reported in ppm downfield from TMS. UV–Vis: Perkin-Elmer Lambda 9. The fluorescence spectrum was recorded on a spectrograph using a Xe arc lamp XBO 450 W, a double monochromator Fluorolog 2 type F212, SPEX USA, and an emission detector PMT R928, Hamamatsu. The fluorescence was stimulated with a wavelength of 385 nm. Gel permeation chromatography (GPC) analysis was performed with PL-gel columns (10^3- and 10^4-Å pore widths) connected to a UV–vis detector. The calibration was based on polystyrene standards with narrow weight distribution. TGA analysis was performed on a Mettler 500 thermogravimetric analyzer (heating rate 10 °C/min, N_2 atmosphere). The infrared (IR) spectrum was obtained from a Nicolet FT-IR 320.

4,9-Di-*n*-octyl-4,5,9,10-tetrahydropyrene (Mixture of Cis-/Trans-Isomers) (2a). 2,2′-Bis(*n*-dec-1″-enyl)biphenyl (**1a**) (2.15 g, 5.0 mmol) was dissolved in *n*-hexane (300 mL) and transferred into the described photoreactor. An argon

stream was passed through the stirred solution over 30 min to remove the remaining oxygen. The solution was then irradiated at a wavelength of 254 nm (80 W) for 6 h. The end of the photoreaction was detected by ^{1}H NMR. Removal of the solvent *in vacuo* gave a pale yellow oil. Purification by column chromatography [silica gel, petroleum ether (low boiling)/ether (20:1)] afforded 1.83 g (85%) of **2a** as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.04–7.21 (m, 6 H), 2.64–3.06 (m, 6 H), 1.21–1.73 (m, 28 H), 0.79–0.96 (m, 6 H).

2,7-Dibromo-4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene (Mixture of Cis-/Trans-Isomers) (3a). To a stirred solution of **2a** (10.75 g, 25.0 mmol) in DMF (200 mL) was added palladium (100 mg, 5% on activated charcoal). Bromine (75 mmol) in DMF (40 mL) was then added dropwise at room temperature over 2 h. After the addition was completed, the reaction mixture was allowed to stir for 12–16 h. A 15% aqueous solution of NaOH was then added to remove any excess of bromine. After the addition of water (200 mL), the organic layer was separated and the aqueous portion extracted with methylene chloride (3×). The combined organic layers were filtered through Celite to remove the remaining traces of the palladium catalyst and then dried over magnesium sulfate. Evaporation of the solvent gave a yellow oil. Purification by column chromatography [silica gel, petroleum ether (low boiling); alumina, petroleum ether (low boiling)] afforded 12.5 g (85%) of **3a** as a colorless oil. The cis/trans isomeric ratio is 3:1. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.24 (s, 1.5 H), 7.22 (s, 1.5 H), 7.18 (s, 0.5 H), 7.15 (s, 0.5 H), 2.59–3.12 (m, 6 H), 1.21–1.66 (m, 28 H), 0.94 (t, 6 H). ^{13}C NMR (cis-isomer, $CDCl_3$, 50 MHz): δ 141.2, 136.2, 128.3, 129.1, 127.6, 121.1, 37.1, 33.3, 32.6, 31.9, 29.7, 29.5, 29.3, 27.1, 22.7, 14.0. Anal. Calcd for $C_{32}H_{44}Br_2$: C, 65.30; H, 7.54; Br, 27.16. Found: C, 65.26; H, 7.51; Br, 27.23.

2,7-Poly(4,9-di-*n*-octyl-4,5,9,10-tetrahydropyrene) (4a).[11b] To a 100-mL Schlenk flask equipped with a stirring bar and containing bis(1,5-cyclooctadiene)nickel(0) (1.10 g, 3.77 mmol), 2,2′-bipyridyl (0.65 g, 4.36 mmol), and 1,5-cyclooctadiene (0.43 g, 4.01 mmol) under an argon atmosphere was added DMF (7 mL) and toluene (10 mL) via a syringe. The ensuing deep blue/lilac solution was stirred at 70 °C for 30 min, and then a solution of **3a** (1.49 g, 2.54 mmol) in toluene (12 mL) was added, upon which the color of the reaction mixture turned to red/brown. The reaction mixture was then stirred at 75 °C under exclusion of light for 5 days. The mixture was cooled to room temperature, filtered through Celite, and washed with 5 N aqueous HCl. The organic layer was separated and the aqueous portion extracted with chloroform (3×). The combined organic layers were successively washed with an aqueous solution of *N,N,N′,N′*-ethylenediaminetetraacetic acid (EDTA; pH = 3.8), an aqueous solution of EDTA (pH = 9), and water (3×). The organic layer was dried over magnesium sulfate and the solvent evaporated. To remove the bromine end groups, the residue was then dissolved in toluene (70 mL) and added dropwise, at room temperature, to a suspension of lithium aluminum hydride (1.00 g, 26.32 mmol) in THF (20 mL) under an argon atmosphere. The ensuing mixture was then heated under reflux for 24 h. After cooling to room temperature, the reaction mixture was quenched with 2 N aqueous H_2SO_4 (25 mL) and water (200 mL).

The organic layer was separated and the aqueous portion extracted with chloroform (3×). The combined organic layers were dried over magnesium sulfate. After evaporating the solvent, purification by column chromatography [alumina, chloroform] afforded a solution of **4a** in chloroform, which was concentrated *in vacuo* to 10 mL. Then **4a** was precipitated by adding the ensuing solution dropwise to acetone. Filtration and removal of the solvent under reduced pressure afforded 0.81 g (75%) of **4a** as a light yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43–7.47 (m, 4n H), 2.86–3.16 (m, 6n H), 1.30–1.88 (m, 28n H), 0.90 (bs, 6n H). FTIR (KBr): ν 2954.3, 2923.9, 2854.3, 1607.2, 1465.9, 1455.5, 1444.6, 871.4, 764.8, 742.7, 486.7, 477.4, 458.9.

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