Benzyl Bromide Functionalized Poly(phenyleneethynylene)s: A Novel Approach toward Conjugated Polymers with a Well-Defined Chemical Reactivity

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ABSTRACT: The palladium(0)-copper(I)-catalyzed polymerization of 1,4-diethynyl-2,5-bis(decyloxy)benzene (I), 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene (IIA), 1-(6-(4-(hydroxymethyl)phenoxy)hexyloxy)-2,5-diiodo-4-methoxybenzene (III), and iodobenzene (IV) yielded a highly soluble, exclusively para-linked poly(phenyleneethynylene) (**PPE2A**). Thereby, statistically every fourth phenyleneethynylene unit bore a benzyl alcohol group predetermined by the molar ratio of the monomers. The monofunctional monomer IV was used as molar mass limiter, since preliminary investigations on the polymerization of I and IIA had revealed that the solubility of alkoxy-substituted poly(phenyleneethynylene)s consisting of more than 40 phenyleneethynylene units decreases drastically. The maximum effective conjugation length was attained at approximately 12 phenyleneethynylene repeating units. Furthermore, a partially meta-linked benzyl alcohol functionalized poly(phenyleneethynylene) (**PPE2B**) was synthesized employing 1,3diiodobenzene (IIB) instead of IIA. Both conjugated polymers (**PPE2A** and **PPE2B**) could be converted quantitatively into benzyl bromide functionalized poly(phenyleneethynylene)s (**PPE3A** and **PPE3B** applying triphenylphosphine and tetrabromomethane. Comparison of the polymers by means of GPC and UV/vis spectroscopy before and after the bromination showed no significant differences and thus no impairment of the delocalized π -electron system.

Introduction

The exceptional properties of conjugated polymers are reflected in a variety of potential applications.^{1,2} Because of their electrical conductivity, these materials might be used in field effect transistors³ as well as conductivity agents and antistatic coatings.⁴ Another field of application, represents the shielding of electromagnetic radiation,⁵ especially the absorption of radar beams. The UV/ vis absorption and fluorescence behavior of conjugated polymers enables their use in solid-state lasers^{6,7} as well as chemical sensors.^{8,9} In particular, conjugated polymers attract a great deal of attention as emitting layers in organic light-emitting diodes.^{10–12} Furthermore, investigations on the suitability of conjugated polymers in photovoltaic cells^{13,14} and microactuators¹⁵ are published.

The properties of conjugated polymers can be adjusted by means of various substituents attached to their main chains; e.g., their solubility was increased by fixing long alkoxy chains onto the skeletal structure,^{1,2} or the helical conformation of conjugated polymers was in-duced by chiral groups.^{16,17} Improved photo- and electroluminescent properties of a triphenylamine-bearing poly(phenylenevinylene)¹⁸ as well as the application of a cyclophane-substituted poly(phenyleneethynylene) as chemical sensor⁹ are described. Usually, substituents are already introduced into the monomers. An alternative procedure would be the linkage of substituents to conjugated polymers after the polymerization step. This method would allow not only the introduction of functionalities which are incompatible with the polymerization system but also the synthesis of different substituted conjugated polymers featuring identical

molecular weight distributions, a precondition to the comparability of such materials. However, such proceeding requires conjugated polymers with a defined chemical reactivity in order to successfully achieve the controlled polymer analogous conversion.

In this contribution the synthesis and characterization of benzyl bromide functionalized poly(phenyleneethynylene)s are presented. The use of poly(phenyleneethynylene)s should ensure the straightforward preparation as well as interesting properties of the products.^{19,20} The benzyl bromide groups should provide defined reaction centers, which might be employed to modify these materials by polymer analogous methods.

Results and Discussion

One important precondition for the successful polymer analogous modification of poly(phenyleneethynylene)s is their complete solubility, which is known to be considerably increased by means of flexible side chains at the skeletal structure.¹⁹⁻²¹ Hence, the use of decyloxy and 2-ethylhexyloxy side chains should provide sufficient solubility of the desired benzyl bromide functionalized poly(phenyleneethynylene)s. Additionally, the solubility of poly(phenylenethynylene)s is strongly influenced by the degree of polymerization.²² Therefore, the targeted conjugated polymers should consist of just as many repetition units as necessary to attain the maximum effective conjugation length. The appropriate number of phenyleneethynylene units was determined by means of the palladium(0)-copper(I)-catalyzed polymerization of 1,4-diethynyl-2,5-bis(decyloxy)benzene (I) and 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene (IIA) (Scheme 1). The syntheses of the monomers as well as the polymerization were accomplished according to the literature.23,24

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During the course of the polymerization samples were taken from the solution in time intervals of 3 h and subsequently investigated by GPC vs polystyrene calibration as well as UV/vis spectroscopy. However, it must be considered that the molar mass determination of poly(phenyleneethynylene)s via polystyrene calibrations results in an overestimation by a factor of approximately 2 in most cases due to the different hydrodynamic behavior of the flexible, coiled polystyrene and the rigid, rodlike conjugated polymer.^{25–27} The UV/vis absorption of conjugated polymers correlates directly with their effective conjugation length: The expansion of the delocalized π -electron system leads to a shift of the absorption maximum toward lower energy. Thus, the correlation between the UV/vis absorption maximum and the degree of polymerization of the poly(phenyleneethynylene)s provides their maximum effective conjugation length. Usually, the UV/vis absorption behavior is characterized by the wavelength of the intensity maximum at lowest energy (λ_{max}). However, this variable did not prove to be suitable for the abovedescribed purpose, since the UV/vis absorption spectra changed their shape on the transition from monomer to oligomer to polymer (Figure 1). Besides, the broad and oblate absorption maxima made the assignment of λ_{max} difficult. Hence, the variable $\lambda_{20\%}$ was defined: $\lambda_{20\%}$ corresponds to the wavelength at lowest energy, which attains 20% of the intensity at λ_{max} . The plot of $\lambda_{20\%}$ vs the molar mass and the number of phenyleneethynylene units respectively shows at the beginning of the polym-



Figure 1. Correlation between the UV/vis absorption and the degree of polymerization of the alkoxy-substituted poly(phe-nyleneethynylene) (**PPE1**).

erization of 1,4-diethynyl-2,5-bis(decyloxy)benzene (**I**) and 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene (**IIA**) a steep increase of the effective conjugation length (Figure 1). At approximately 24 phenyleneethynylene units $(M_n^{GPC/PS} = 10\ 000\ g\ mol^{-1})$ the correlation curve converges to $\lambda_{20\%} = 476\ nm$, indicating the achievement of the maximum effective conjugation length. In consideration of the molar mass overestimation by GPC, the real number of phenyleneethynylene units amounted to approximately 12. Gelation of the alkoxy-substituted poly(phenyleneethynylene) (**PPE1**) was observed on exceeding $M_n^{GPC/PS} = 30\ 000\ g\ mol^{-1}$.

The solubility of poly(phenyleneethynylene)s is also affected by the type of linkage between the phenyleneethynylene units (para, meta, ortho) due to the influence of this parameter on the symmetry of the conjugated polymer.²² Therefore, it was intended to synthesize the desired functionalized poly(phenyleneethynylene)s not only exclusively para-linked leading to the largest maximum effective conjugation length but also partly meta-bridged increasing solubility.

The benzyl bromide functionalized poly(phenyleneethynylene)s should be prepared on the basis of the synthesis of **PPE1**. A further monomer was required in order to introduce functional groups into the polymer. For this purpose, 1-(6-(4-(hydroxymethyl)phenoxy)hexyloxy)-2,5-diiodo-4-methoxybenzene (III) was chosen, as the benzyl alcohol group can easily be converted into a benzyl bromide (Scheme 2). This additional step was necessary because the auxiliary base (triethylamine) of the palladium(0)-copper(I)-catalyzed polymerization reaction was incompatible with benzyl bromides. The hexamethylene spacer ensured the decoupling of the functional groups from the delocalized π -electron system in the conjugated polymer. The benzyl alcohol substituted monomer (III) was synthesized in three steps. The starting material was 4-methoxyphenol, which was etherified with 1,6-dibromohexane to obtain 1-(6-bromohexyloxy)-4-methoxybenzene (78%). This intermediate was treated with iodine in the presence of an oxidant, resulting in 1-(6-bromohexyloxy)-2,5-diiodo-4methoxybenzene (82%). The subsequent etherification with 4-hydroxybenzyl alcohol gave 1-(6-(4-(hydroxymethyl)phenoxy)hexyloxy)-2,5-diiodo-4-methoxybenzene (III) in 86% yield.

The synthesis of the functionalized poly(phenyleneethynylene)s is summarized in Scheme 2. Initially, the monomers 1,4-diethynyl-2,5-bis(decyloxy)benzene (I), 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene (IIA) (and 1,3-diiodobenzene (IIB)), 1-(6-(4-(hydroxymethyl)phenoxy)hexyloxy)-2,5-diiodo-4-methoxybenzene (III), and iodobenzene (IV) as molar mass limiter were polymerized using tetrakis(triphenylphosphine)palladium(0), copper(I) iodide, and triethylamine in toluene at 60 °C for 24 h. The molar ratio of I:IIA/IIB:III:IV was adjusted to 1:0.45:0.45:0.2. Assuming quantitative conversion, these conditions should result in an average number of phenyleneethynylene units of 16,^{28,29} ensuring high solubility as well as the maximum effective conjugation length. Furthermore, the molar ratio of the monomers led to the benzyl alcohol functionalization of every forth phenyleneethynylene unit in PPE2A and **PPE2B**. A too large content of the polar hydroxy groups in the conjugated polymers was supposed to cause insolubility²³ and was therefore avoided. After termination the obtained benzyl alcohol functionalized poly-(phenyleneethynylene)s PPE2A and PPE2B were pu-

Scheme 2. Two-Stage Synthesis of Benzyl Bromide Functionalized Poly(phenyleneethynylene)s (PPE3A, PPE3b) via Benzyl Alcohol Substituted Poly(phenyleneethynylene)s (PPE2A, PPE2b) as Intermediates



rified by GPC followed by freeze-drying from benzene. Cutouts of the ¹H NMR spectra of **PPE2A** and **PPE2B** are shown in Figure 2. The average number of phenyleneethynylene units of these polymers was calculated from the intensity ratio of the resonances pertaining to the end-capping phenyl group and the aromatic repetition units. Thus, **PPE2A** consisted of 16 phenyleneethynylene units at an average corresponding with the requirement. In the case of the partly meta-linked poly-(phenyleneethynylene) **PPE2B** the average number of phenyleneethynylene units amounted to 12. This value was slightly lower than expected. However, superimposition of further signals in the resonance range of the end-group protons may result in an underestimation.

In a second step, the benzyl bromide functionalized poly(phenyleneethynylene)s **PPE3A** and **PPE3B** were prepared from **PPE2A** and **PPE2B** by means of tetrabromomethane and triphenylphosphine in dichloromethane at room temperature for 1.5 h (Appel reaction).^{30,31} This method allows the conversion of alcohols into bromides to the exclusion of Bronsted acids, which would affect the conjugated system. The purification of **PPE3A** and **PPE3B** occurred by GPC (removal of molecules < 1000 g mol⁻¹). The exchange of the hydroxy group by the bromine atom resulted in an only slight shift of the benzylic protones from $\delta = 4.56$ ppm to $\delta =$ 4.49 ppm in the ¹H NMR spectra of the functionalized poly(phenyleneethynylene)s. However, the benzylic carbon of **PPE2A** and **PPE2B** corresponds to the ¹³C NMR resonance at $\delta = 64.8$ ppm, which completely disappeared after the bromination reaction, indicating quantitative conversion. The benzylic carbon of the benzyl bromide functionlized polymers **PPE3A** and **PPE3B** was unambiguously assigned to the ¹³C NMR signal at $\delta = 34.5$ ppm (Figure 3).

The analysis of the benzyl alcohol functionalized poly-(phenyleneethynylene)s by GPC vs polystyrene calibration led to $M_n^{\text{GPC/PS}} = 8200 \text{ g mol}^{-1}$ (**PPE2A**) and $M_n^{\text{GPC/PS}} = 9800 \text{ g mol}^{-1}$ (**PPE2B**) (Table 1, Figure 4). The average number of phenyleneethynylene units (**PPE2A**: 20; **PPE2B**: 28) derived from these data shows the molar mass overestimation of this GPC method as mentioned before. Comparison of the GPC traces before and after the hydroxy-bromine exchange did not reveal any significant alteration (Table 1, Figure 4).

The UV/vis absorption behavior of the synthesized polymers is summarized in Table 1 and Figure 5. The wavelength $\lambda_{20\%} = 475.5$ nm of the exclusively paralinked **PPE2A** corresponds to the range of the convergence value, indicating maximum effective conjugation length (Figure 1). In the case of **PPE2B** the replacement of **IIA** by the meta-substituted monomer **IIB** resulted



Figure 2. ¹H NMR spectra of the benzyl alcohol functionalized poly(phenyleneethynylene)s PPE2A and PPE2B.



Figure 3. Cutouts of the ¹³C NMR spectra before (**PPE2A**) and after (**PPE3A**) the hydroxy–bromine exchange.

Table 1. Characterization of the Benzyl Alcohol and
Benzyl Bromide FunctionalizedPoly(phenyleneethynylene)s Concerning Molar Masses
and UV/vis Absorption

polymer	$M_{ m n}^{ m NMR}$, g mol $^{-1}$ (PE units) a	$M_{ m n}^{ m GPC/PS}, \ { m g\ mol^{-1}} \ ({ m PE\ units})^b$	PDIGPC/PS b	λ _{20%} , ^c nm	λ_{\max}, c nm
PPE2A	6700 (16)	8200 (20)	2.0	475.5	445.0
PPE3A		8800 (20)	2.2	475.5	443.0
PPE2B	4400 (12)	9800 (28)	2.0	465.0	418.0
PPE3B		10000 (28)	2.7	465.0	418.0

^{*a*} Determined by ¹H NMR. ^{*b*} Determined by GPC in CHCl₃ vs polystyrene calibration. ^{*c*} Determined by UV/vis spectroscopy in CHCl₃.

in 10 nm shifted wavelength $\lambda_{20\%} = 465.0$ nm. Both polymers did not change their $\lambda_{20\%}$ after the bromination. The absorption maximum λ_{max} of **PPE2A** amounts to 445.0 nm, in contrast to the 27 nm lower λ_{max} of **PPE2B**. Furthermore, the absorption maximum of the partly meta-linked polymer is considerably broader compared to those of the linear poly(phenyleneeth-ynylene)s. Although the UV/vis spectra of **PPE2A** and **PPE3A** seems to be congruent, λ_{max} diverges about 2 nm. emphasizing the difficult assignment of λ_{max} due to the oblate absorption maxima.



Figure 4. Molar mass distributions of the poly(phenyleneethynylene)s before (**PPE2A**, **PPE2B**) and after (**PPE3A**, **PPE3B**) the hydroxy-bromine exchange (GPC in CHCl₃ vs polystyrene calibration).



Figure 5. UV/vis absorption of the poly(phenyleneethynylene)s before (**PPE2A**, **PPE2B**) and after (**PPE3A**, **PPE3B**) the hydroxy–bromine exchange (UV/vis spectroscopy in CHCl₃).

Conclusion

The exclusively para-linked and the partly metalinked benzyl bromide functionalized poly(phenyleneethynylene) were prepared in a two-stage synthesis via benzyl alcohol functionalized poly(phenyleneethynylene)s. This additional step was necessary because the auxiliary base of the palladium(0)-copper(I)-catalyzed polymerization reaction is incompatible with benzyl bromides. The structure and the degree of polymerization of the poly(phenyleneethynylene)s were adjusted to ensure high solubility. Investigations of the conjugated polymers by GPC and UV/vis spectroscopy did not reveal any impairment of the delocalized π -electron system, resulting from the hydroxy-bromine exchange. The benzyl groups might be used as starting point for further modifications of these conjugated polymers.

Experimental Section

Materials and Instrumentation. All reagents and solvents were purchased from Sigma-Aldrich or Deutero in analytical grade (except for toluene: puriss. over molecular sieve, $H_2O < 0.005\%$, under Ar) and used as received except triethylamine, which was dried over CaH₂ and distilled under a N₂ atmosphere. Cross-linked polystyrene (Bio-Beads S-X1) for the preparative gel permeation chromatography (GPC) was acquired from Bio-Rad. NMR spectra were recorded on a Bruker ARX300 (¹H/300 MHz, ¹³C/75 MHz). UV/vis spectra were obtained from a Varian Cary 3. Elemental analysis was performed on an Elementar Vario EL. Analytical GPC was obtained from a Waters 510 equipped with a Waters 410 differential refractometer and Polymer Laboratories Gel Mixed B columns. CHCl₃ was used as eluent, and the calibration occurred by means of polysytrene (PS) standards.

Monomer Synthesis: 1,4-Bis(2-ethylhexyloxy)-2,5-diiodobenzene (I) and 1,4-diethynyl-2,5-bis(decyloxy)benzene (IIA) were prepared according to the literature.²³

1-(6-Bromohexyloxy)-4-methoxybenzene. 4-Methoxyphenol (12.4 g, 100 mmol), 1,6-dibromohexane (73.2 g, 300 mmol), potassium carbonate (19.8 g, 150 mmol), and DMSO (300 mL) were stirred at room temperature for 16 h. Subsequently, the reaction mixture was poured into ice water (1000 mL) and extracted with diethyl ether (500 mL). The organic layer was collected, and the solvent was removed by means of a rotary evaporator. The residue was taken up in toluene, and the solution was passed through a short plug of neutral aluminum oxide using toluene as eluent. After evaporation of the solvent, excess 1,6-dibromohexane still remaining in the product was removed by vacuum distillation. The residue was recrystallized from hexane/toluene (20:1) to yield colorless crystals (22.4 g, 78.0 mmol, 78%). ¹H NMR (CDCl₃): $\delta = 6.81$ (s, 4H, CH^{ar}), 3.89 (t, ${}^{3}J_{H,H} = 6.4$ Hz, 2H, OCH₂), 3.75 (s, 3H, OCH₃), 3.40 (t, ${}^{3}J_{\rm H,H} = 6.7$ Hz, 2H, CH₂Br), 1.95–1.83 (m, 2H, CH₂CH₂Br), 1.83-1.70 (m, 2H, CH₂CH₂O), 1.60-1.42 ppm (m, 4H, CH₂). ¹³C{¹H} NMR (CDCl₃): $\delta = 153.72$ (*C*^{ar}OCH₃), 153.19 (*C*^{ar}OCH₂), 115.42 (CarHCarOCH₃), 114.62 (CarHCarOCH₂), 68.36 (OCH₂), 55.72 (OCH₃), 33.76 (CH₂CH₂Br), 32.67 (CH₂Br), 29.18 (CH₂-CH2O), 27.91 (CH2CH2CH2Br), 25.29 ppm (CH2CH2CH2O). C13H19BrO2 (287.19): Calcd (%) C, 54.37; H, 6.67. Found (%): C, 55.28; H, 6,73.

1-(6-Bromohexyloxy)-2,5-diiodo-4-methoxybenzene. Water (40 mL), acetic acid (300 mL), concentrated sulfuric acid (8 mL), 1-(6-bromohexyloxy)-4-methoxybenzene (21.5 g, 75 mmol), potassium iodate (6.4 g, 30 mmol), and iodine (19.0 g, 75 mmol) were stirred at reflux for 3 h. After cooling to room temperature, the excess of iodine was destroyed using an aqueous sodium sulfite solution (10%), and the reaction mixture was poured into ice water (1000 mL). The aqueous phase was extracted with diethyl ether (2 \times 300 mL), and the solvent of the combined organic layers was evaporated. Purification of the residue by means of column chromatography (silica gel, hexane/toluene 3:1, $R_f = 0.5$) resulted in a colorless solid (33.0 g, 61.2 mmol, 82%). ¹H NMR (CDCl₃): δ = 7.17 (s, 2H, CH^{ar}), 3.93 (t, ${}^{3}J_{H,H}$ = 6.1 Hz, 2H, OCH₂), 3.81 (s, 3H, OCH₃), 3.42 (t, ${}^{3}J_{H,H} = 6.7$ Hz, 2H, CH₂Br), 1.95–1.85 (m, 2H, CH₂CH₂Br), 1.85-1.75 (m, 2H, CH₂CH₂O), 1.62-1.43 ppm (m, 4H, CH₂). ¹³C{¹H} NMR (CDCl₃): $\delta = 153.32$ (CarOCH₃), 152.84 (CarOCH₂), 122.96 (CarHCarOCH₂), 121.48 (C^{ar}HC^{ar}OCH₃), 86.34 (C^{ar}IC^{ar}OCH₂), 85.42 (C^{ar}IC^{ar}OCH₃), 70.08 (OCH₂), 57.16 (OCH₃), 33.75 (CH₂CH₂Br), 32.65 (CH₂-Br), 28.94 (CH₂CH₂O), 27.80 (CH₂CH₂CH₂Br), 25.28 ppm (CH₂-CH₂CH₂O). C₁₃H₁₇BrI₂O₂ (538.98): Calcd (%) C, 28.97; H, 3.18. Found (%): C, 28.89; H, 3.21.

1-(6-(4-Hydroxymethyl)phenoxy)hexyloxy)-2,5-diiodo-4-methoxybenzene (III). 1-(6-Bromohexyloxy)-2,5-diiodo-4methoxybenzene (31.3 g, 58 mmol), 4-hydroxybenzyl alcohol (10.8 g, 87 mmol), potassium carbonate (11.5 g, 87 mmol), and DMSO (300 mL) were stirred at 60 °C for 12 h. Afterward, the reaction mixture was poured into ice water (1000 mL) and extracted with diethyl ether (2 \times 400 mL). The solvent of the combined organic layers was removed by means of a rotary evaporator, and the residue was purified using column chromatography (silica gel, toluene/ethyl acetate 4:1, $R_f = 0.5$) to yield a highly viscous, colorless liquid (29.1 g, 50.0 mmol, 86%). ¹H NMR (CDCl₃): $\delta = 7.26$ (pd, ³ $J_{HH} = 8.7$ Hz, 2H, C^{ar}HC^{ar}CH₂-OH), 7.17 (s, 2H, CH^{ar}C^{ar}I), 6.87 (pd, ${}^{3}J_{H,H} = 8.7$ Hz, 2H, C^{ar}*H*C^{ar}HC^{ar}OCH₂OH), 4.60 (s, 2H, C*H*₂OH), 4.02–3.89 (m, 4H, OCH₂), 3.81 (s, 3H, OCH₃), 1.90-1.75 (m, 4H, CH₂CH₂O), 1.66–1.48 ppm (m, 4H, CH₂). ¹³C{¹H} NMR (CDCl₃): $\delta =$ 158.72 (CH₂CH₂OC^{ar}C^{ar}HC^{ar}H), 153.28 (C^{ar}OCH₃), 152.88 (CarICarOCH₂), 132.94 (CarCH₂OH), 128.61 (CarHCarCH₂-OH), 122.94 (C^{ar}IC^{ar}HOC^{ar}CH₂), 121.48 (C^{ar}HOC^{ar}CH₃), 114.56 (C^{ar}HC^{ar}HC^{ar}OCH₂OH), 86.36 (C^{ar}IC^{ar}OCH₂), 85.42 (CarICarOCH₃), 70.16 (CH₂OCarCarHCarH), 67.82 (CH₂OCarCarI), 65.07 (CH₂OH), 57.16 (OCH₃), 29.14 and 29.04 (CH₂CH₂O), 25.79 and 25.68 ppm (CH2CH2CH2O). C20H24I2O4 (582.21): Calcd (%) C, 41.26; H, 4.15. Found (%): C, 41.70; H, 4.21.

Polymer Synthesis: PPE1. 1,4-Diethynyl-2,5-bis(decyloxy)benzene (**I**) (461 mg, 1.05 mmol), 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene (**IIA**) (586 mg, 1.00 mmol), tetrakis(triphenylphosphine)palladium(0) (46 mg, 0.04 mmol), copper(I) iodide (6 mg, 0.03 mmol), toluene (20 mL), and triethylamine (5 mL) were stirred at 60 °C to the exclusion of moisture and oxygen. Samples (1 mL) were taken from the reaction mixture every 3 h. Iodobenzene (0.1 mL) and CHCl₃ (2 mL) were added immediately to each sample followed by analysis using GPC vs polystyrene and UV/vis spectroscopy.

PPE2Ă. 1,4-Diethynyl-2,5-bis(decyloxy)benzene (I) (978 mg, 2.23 mmol), 1,4-bis(2-ethylhexyloxy)-2,5-diiodobenzene (IIA) (586 mg, 1.00 mmol), 1-(6-(4-hydroxmethyl)phenoxy)hexyloxy)-2,5-diiodo-4-methoxybenzene (III) (582 mg, 1.00 mmol), iodobenzene (IV) (92 mg, 0.45 mmol), tetrakis(triphenylphosphine)palladium(0) (92 mg, 0.08 mmol), copper(I) iodide (11 mg, 0.06 mmol), toluene (40 mL), and triethylamine (10 mL) were stirred at 60 °C for 24 h to the exclusion of moisture and oxygen. After addition of iodobenzene (1 mL) the reaction mixture was stirred at 60 °C for another 15 min. The precipitate that originated during the course of polymerization was filtered off, and the volume of the residual solution was reduced by means of a rotary evaporator. Subsequently, the polymer solution were purified using GPC (stationary phase: cross-linked polysytrene (Bio-Beads S-X1, Bio-Rad); height: 30 cm; diameter: 3 cm; eluent: toluene). The fraction from 105 to 165 mL eluent was collected, and the solvent was evaporated. Finally, the residue was taken up in benzene and freezedried to yield an orange solid (1.19 g, 70%). ¹H NMR (C_2D_2 -Cl₄): $\delta = 7.57 - 7.44$ (m, I = 1.17, C^{ar}H/end group), 7.41 - 7.32 (m, I = 1.32, C^{ar}H/end group), 7.24 (pd, ${}^{3}J_{H,H} = 7.8$ Hz, I =2.26, $C^{ar}HC^{ar}CH_2OH$), 7.11–6.93 (m, $\hat{I} = 8.00$, $C^{ar}HC^{ar}O$), 6.85 (pd, ${}^{3}J_{H,H} = 7.8$ Hz, I = 2.29, $C^{ar}HC^{ar}HC^{ar}OCH_{2}OH$), 4.56 (s, I $= 2.02, CH_2OH), 4.20-3.70 (m, I = 19.75, OCH_2, OCH_3), 2.00-$ 1.70 (m, I = 14.49, CH, CH₂CH₂O), 1.70–1.10 (m, I = 88.66, CH₂), 1.05–0.72 (m, I = 26.29, CH₃) ppm. UV/vis (CHCl₃): $\lambda_{20\%}$ = 475.5 nm, λ_{max} = 445.0 nm. GPC (CHCl₃, RI det, PS): M_n = 8240 g/mol, PDI = 2.0. Repeating unit: $C_{102}H_{148}O_{10}$ (1534.29).

PPE2B. This synthesis was accomplished as described for **PPE2A** using 1,3-diiodobenzene (**IIB**) instead of **IIA**. On purification by GPC the fraction from 90 to 150 mL eluent was collected. **PPE2B** was obtained as orange solid (1.37 g, 82%). ¹H NMR (C₂D₂Cl₄): $\delta = 7.73$ (s, I = 1.00, C^{ar}H/meta), 7.59– 7.45 (m, I = 3.22, C^{ar}H/meta, C^{ar}H/end group), 7.43–7.32 (m, I = 2.46, C^{ar}H/meta, C^{ar}H/end group), 7.24 (pd, ³J_{H,H} = 8.0 Hz, I = 2.04, C^{ar}H/erCH₂OH), 7.09–6.98 (m, I = 6.00, C^{ar}HC^{ar}O), 6.85 (pd, ³J_{H,H} = 8.0 Hz, I = 1.96, C^{ar}HC^{ar}OCH₂OH), 4.56 (s, I = 1.91, CH_2 OH, 4.15–3.85 (m, I = 15.12, OCH₂, OCH₃), 1.99–1.71 (m, I = 12.28, CH_2 CH₂O), 1.70–1.10 (m, I = 67.74, CH₂), 0.94–0.80 ppm (m, I = 13.26, CH₃). UV/vis (CHCl₃): $\lambda_{20\%}$ = 465.0 nm, λ_{max} = 418.0 nm. GPC (CHCl₃, RI det, PS): M_n =

9830 g/mol, PDI = 2.0. Repeating unit: C₈₆H₁₁₆O₈ (1277.86). PPE3A. Tetrabromomethane (265 mg, 0.8 mmol) and triphenylphosphine (210 mg, 0.8 mmol) were added to a solution consisting of PPE2A (833 mg, 0.5 mmol -CH₂OH) and CH₂Cl₂ (15 mL) to the exclusion of moisture. The reaction mixture was stirred at room temperature for 1.5 h and finally diluted with toluene (20 mL). After reducing the volume of the polymer solution by evaporation followed by filtration, the volume of the residual solution was diminished again. Subsequently, the solution was passed through a GPC column (stationary phase: cross-linked polysytrene (Bio-Beads S-X1, Bio-Rad); height: 30 cm; diameter: 3 cm; eluent: toluene). The fraction from 80 to 170 mL eluent was collected in order to remove only components with a molar mass lower than 1000 g/mol. Subsequently, the solvent was evaporated and the residue freezed-dried from benzene to yield an orange solid (827 mg, 96%). ¹H NMR (C₂D₂Cl₄): $\delta = 7.59 - 7.47$ (m, I = 1.14, C^{ar}H/end group), 7.40–7.32 (m, *I* = 1.28, C^{ar}H/end group), 7.29 $(pd, {}^{3}J_{H,H} = 8.4 \text{ Hz}, I = 2.38, C^{ar}HC^{ar}CH_{2}Br), 7.12-6.93 (m, I)$ = 8.00, C^{ar}HC^{ar}O), 6,82 (pd, ³J_{H,H} = 8.4 Hz, C^{ar}HC^{ar}HC^{ar}OCH₂-Br), 4.49 (s, I = 1.93, $C\hat{H}_2Br$), 4.20–3.70 (m, I = 19.63, OCH_2 , OCH₃), 1.98–1.70 (m, I = 14.30, CH, CH₂CH₂O), 1.70–1.10 (m, I = 88.36, CH₂), 1.05–0.75 ppm (m, I = 26.64, CH₃). UV/ vis (CHCl₃): $\lambda_{20\%} = 475.5$ nm, $\lambda_{max} = 443.0$ nm. GPC (CHCl₃, RI det, PS): $M_n = 8820$ g/mol, PDI = 2.2. Repeating unit: C₁₀₂H₁₄₇BrO₉ (1597.18).

PPE3B. This synthesis was carried out as described for **PPE3A** using **PPE2B** (708 mg, 0.5 mmol of $-CH_2OH$) instead of **PPE2A** to result in an orange solid (699 mg, 96%). ¹H NMR ($C_2D_2Cl_4$): $\delta = 7.73$ (s, I = 1.05, $C^{ar}H/meta$), 7.61-7.46 (m, I = 3.09, $C^{ar}H/meta$, $C^{ar}H/end$ group), 7.43-7.33 (m, I = 2.53, $C^{ar}H/meta$, $C^{ar}H/end$ group), 7.28 (pd, ${}^{3}J_{H,H} = 8.4$ Hz, I = 2.12, $C^{ar}HC^{ar}CH_2Br$), 7.12-6.96 (m, I = 6.00, $C^{ar}HC^{ar}O$), 6.82 (pd, ${}^{3}J_{H,H} = 8.4$ Hz, I = 2.02, $C^{ar}HC^{ar}OCH_2Br$), 4.49 (s, I = 1.91, CH_2Br), 4.15-3.80 (m, I = 15.26, OCH_2 , OCH_3), 2.00-1.70 (m, I = 12.24, CH_2CH_2O), 1.70-1.10 (m, I = 67.18, CH_2), 0.96-0.77 pm (m, I = 13.22, CH_3). UV/vis (CHCl_3): $\lambda_{20\%} = 465.0$ nm, $\lambda_{max} = 418.0$ nm. GPC (CHCl₃, RI det, PS): $M_n = 9960$ g/mol, PDI = 2.7. Repeating unit: $C_{86}H_{115}BrO_7$ (1340.72).

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