7974 *Macromolecules* **2009**, *42*, 7974–7978
DOI: 10.1021/ma901155d

Macromolecules
NOTE

Defined Oligo(*p*-phenylene−butadiynylene) Rods

Dennis Mössinger, Stefan-Sven Jester, Eva Sigmund, Ute Müller, and Sigurd Höger*

Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Received May 28, 2009

Introduction

Molecularly defined linear oligomers have been drawn on as model compounds for the corresponding (polydisperse) polymers. Polymer physical properties such as persistence length and effective conjugation length can be successfully extrapolated from defined oligomer data.[1−6] The often-quoted counter-argument of a rather tedious incremental synthesis becomes anchorless for "rigid rod" applications that demand specific, easily tailorable dimensions. Linear molecular rods based on phenylene and ethynylene subunits have been widely used as spacers for metal chelate ligands,[7] as enzyme transporters,[8] for ESR[9] and redox[10] studies, for molecular electronics,[11−15] in surface studies,[16−18] and for the construction of large shape-persistent superstructures.[19,20]

Some of the widely investigated systems are oligo(phenylene−ethynylene)s (OPEs),[21] since they can be obtained by high-yield Pd-catalyzed Sonogashira−Hagihara coupling[22] or by alkyne metathesis with molybdenum hexacarbonyl as precatalyst.[23] Oddly, oligo(phenylene−butadiynylenes)s (OPBs) have been less intensely investigated. Standard routes to butadiynylene units are either the Cadiot−Chodkiewicz coupling for asymmetrical butadiynes[24] or the oxidative dimerization of identical terminal acetylenes.[25,26] The latter method can be performed in high yields either by palladium catalysis[27] or, more commonly, with copper(I)-mediated protocols such as Glaser−Hay[28,29] and Glaser−Eglinton[30] or with the sole use of copper(II) acetate in polar solvents.[31]

First experiments on a statistical, copper-mediated polymerization of diethynylbenzene have been performed by Hay.[32] More recent examples show that polymers obtained under copper-mediated polymerization conditions are of low molecular weight (M_n = 3000−11 000 g mol^{-1}), yet overestimated by PS-calibrated GPC.[33−36] In palladium-catalyzed polymerizations, molecular weights up to 14 000 (M_n) for homopolymers were obtained.[37] Compared to the original set of reagents for acetylene dimerizations,[27] iodine had been replaced by benzoquinone as reoxidant. Solubility as a molecular weight limiting factor could be overcome with 2-ethylhexyl side groups (Cu(I), $M_n \leq 23\,000$),[38] by block copolymerization (Cu(I), $M_n \leq 40\,000$),[39] or by random copolymerization of different monomers (Pd(0), $M_n \leq 150\,000$).[37] Recently, a Pd-catalyzed synthesis of linear PPBs and triangular networks[40] leading to solid microporous materials was reported. Moreover, bisacetylenes can be polymerized and characterized inside copper(II)-functionalized alumina and silica channels.[41] Some more sophisticated OPBs and oligo(phenylene−ethynylene−butadiynylene)s (OPEBs) have been applied as encapsulated wires,[15,42] in one case with light-harvesting properties.[43]

While the butadiyne bridge as a structural unit can be frequently found in dimerized oligo(arlyene−ethynylene)s,[7,9−11,13,17,44,45] only a small number of publications actually deal with the stepwise synthesis of defined OPBs. For example, aryl dihalogenides were coupled with two monoprotected butadiynyl units up to the trimer using 2-hydroxy-2-propyl as protective group.[46] In principle, defined oligomers can be obtained by separation of statistical oligomeric mixtures, e.g., by preparative recycling GPC,[47] as demonstrated for bulky dendronized oligomers.[15]

We employed both methods, the stepwise synthesis via protective groups and the separation of a statistical oligomeric mixture, to receive a set of oligo(*p*-phenylene−butadiynylene) rods of defined length. Their optical properties can be extrapolated to determine effective conjugation lengths of dialkyl OPBs. GPC elution volumes of the separated oligomers can be used to determine PS-OPB conversion factors for the corresponding relative GPC calibration.

Stepwise Synthesis

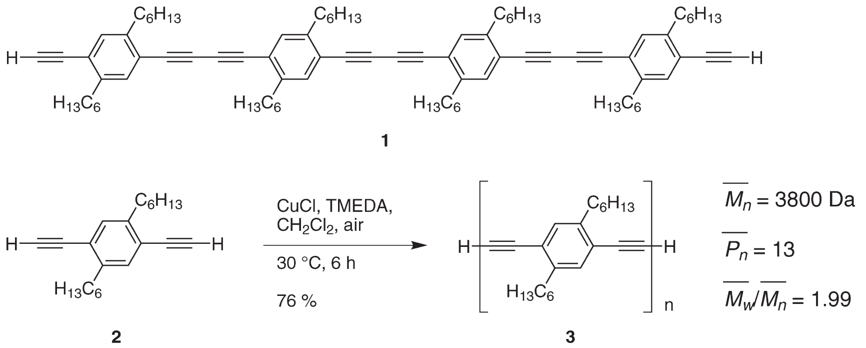
Defined oligo(*p*-phenylene−butadiynylene)s up to the tetramer **1** (Scheme 1) can be obtained from 1,4-diethynyl-2,5-dihexylbenzene **2** by an efficient sequence relying on the polar (3-cyanopropyl)dimethylsilyl (CPDMS) protective group.[48] The bisacetylene monomer **2** was received in an overall yield of 63% via Kumada alkylation of *p*-dichlorobenzene **4**,[49] diiodination of 1,4-dihexylbenzene **5** with iodine/iodic acid,[44] Sonogashira−Hagihara coupling of **6** with ethinyltrimethylsilane (TMSA), and subsequent deprotection of **7** under mild basic conditions (Scheme 2).

As illustrated in Scheme 3, the stepwise synthesis toward defined oligomers is a repetition of monoprotection, dimerization, and complete deprotection steps. The iteration starts with the statistical monoprotection of the bisacetylene monomer **2** with 1 equiv of (3-cyanopropyl)dimethylsilyl chloride (CPDMSCl).[48,50] The CPDMS group—as a polar analogue of the trimethylsilyl group—simplifies the chromatographic separation of the monoprotected product **8** (61%) from both the nonprotected starting material (18%) and the diprotected side product (15%).[51] In the subsequent Glaser coupling step, the length of the oligomer is doubled. **8** is dimerized in a CuCl/TMEDA (1 equiv each) mediated Hay reaction in dichloromethane forming the diprotected bisacetylene **9**. Again, traces of the starting material could be easily separated due to the CPDMS-induced difference in polarity. At the end of the first iteration loop, the polar bisacetylene dimer **9** was deprotected with potassium carbonate and purified by column chromatography in petroleum ether. The consecutive polarity shift during the "complete deprotection/statistical monoprotection" sequence guarantees one nonpolar work-up per iteration. This leads to pure, copper-free bisacetylenes that can be stored for several months, even if exposed to air. The overall yield of the first loop toward the nonprotected bisacetylene dimer **10** was 56%. In the second loop, the bisacetylene tetramer **1** was obtained under

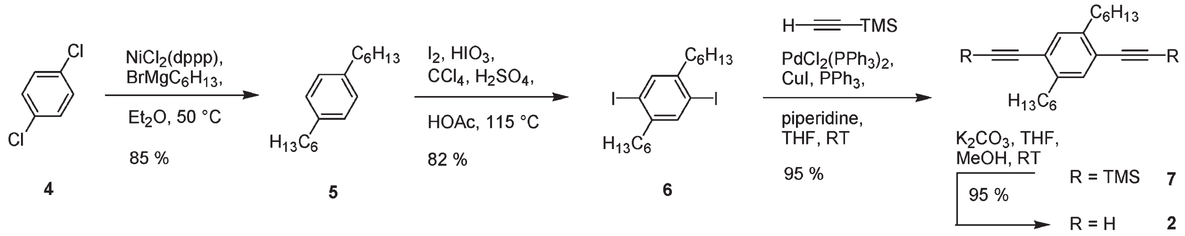
---

*Corresponding author. E-mail: hoeger@uni-bonn.de.

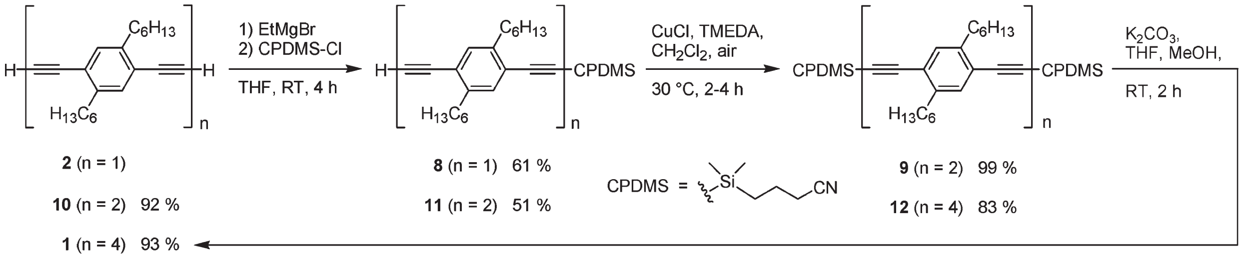
Scheme 1. Tetramer and Statistical Oligomer (GPC Data vs PS)



Scheme 2. Monomer Synthesis



Scheme 3. Iterative Oligomer Synthesis



analogue conditions in comparable, but slightly lower, yields (39%; for the full characterization of all compounds see the Supporting Information). A similar strategy is possible with the more stable (3-cyanopropyl)diisopropylsilyl (CPDIPS) protective group. In that case, the iteration starts from the diprotected bisacetylene with repetitive monodeprotection and dimerization steps.[52]

Polymer Parameters

For comparison, the above dimerization conditions were applied to a statistical polymerization of **2** without major changes except for a longer reaction time. As expected, the produced oligomers precipitated from the reaction medium, leading to a heterogeneous mixture. Low solubilities state a general problem of PPBs if not substituted with branched side groups like 2-ethylhexyl or dendrons[34,53] because intermediate oligomers precipitate prior to high conversion. This tendency has already been indicated by the dimerization yields toward the tetramer **1** (83%) compared to the dimer **10** (99%). Even though our conditions were suboptimal for the synthesis of high-molecular-weight samples, they ideally suited the desired oligomerization. Thus, in dichloromethane, we received a canary yellow oligomeric mixture **3** which is soluble in toluene and chloroform as well as in THF upon gentle heating (Scheme 1). Polymer parameters from GPC analysis (in THF vs PS) are $\overline{P}_n = 13$, $\overline{M}_n = 3800$ g mol^{-1} (GPC vs PS), and a polydispersity of $\overline{M}_w/\overline{M}_n = 1.99$.[33]

Figure 1 displays the MWD of **3** taken from GPC analysis. The peak of tetramer **1** has been superimposed as a "reference" to assign the peaks of the distribution and to demonstrate the overestimation of molecular weight obtained from the PS calibration even at small molecular weights. GPC analysis (vs PS standard) interprets the molecular weight of **1** as M_w = 1950 g mol^{-1}, but its actual molar mass is 1171.9 g mol^{-1}. This means an overestimation of nearly 70% for this molecule. However, for higher molecular weights this deviation is not necessarily constant. For this purpose, we separated **3**[54] up to the heptadecamer by recycling GPC (see Supporting Information for elugrams and mass spectra).[55] Comparison of GPC-interpreted $M_{p,i}$ values[56] of each separated oligomer P_i with its actual molar mass gives a nonlinear set of PS-OPB conversion factors f_i (Figure 2 and Table S1). These increasing, size-dependent conversion factors specify the degree of overestimation (in terms of molecular weight) of our PB oligomers by a PS-calibrated GPC system.[57] Extrapolation of the conversion factors f_i (by an exponential fit) results in a limit of $f_\infty = 3.8 \pm 0.2$ (see Supporting Information). Assuming that this approach is correct, the theoretical limit f_∞ is met at the utter tip of the MWD tail (e.g., 80 kDa, vs PS), which can be estimated at 21 ± 1 kDa (vs OPB), i.e., a degree of polymerization of about 72 ± 4.

As molecular weight distributions change as soon as their components are corrected with a nonlinear set of conversion factors, this oligomer-based evaluation cannot produce reliable average values of MWDs, such as $\overline{P}_n$. For this reason, we carried out an end-group analysis based on the ^{1}H NMR spectrum of **3** (see Supporting Information). Integration of terminal acetylene and aromatic protons reveals a theoretical end-group conversion ratio of about 86%,[58] corresponding to an average degree of

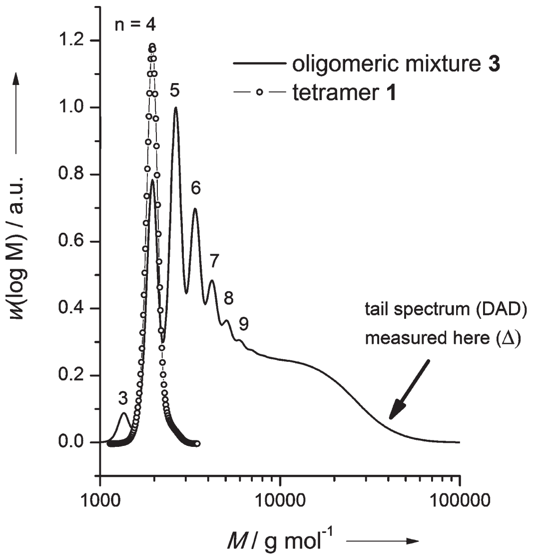


Figure 1. GPC analyses (in THF vs PS) of the tetramer **1** (circles) and the oligomeric mixture **3** (black curve). Low molecular weight oligomers of **3** (n = 3−10) are well-resolved and can be assigned by comparison with **1**. Absorption spectra measured at the tail of the MWD by online diode array detection (DAD, see Figure 3) cannot be assigned to specific degrees of polymerization but give a hint at the absorption limit $\lambda_{\mathrm{abs},\infty}$.

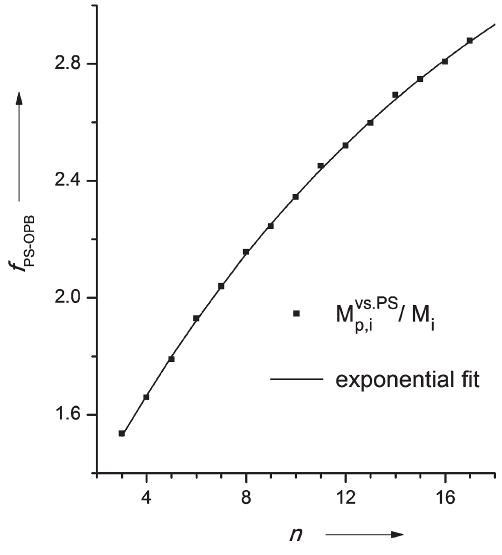


Figure 2. PS-OPB conversion factors f_i (for n = 3−17). GPC analyses of the separated oligomers of **3** give a set of maxima $M_{\mathrm{p},i}$ (vs PS) which can be divided by the actual molecular masses M_i giving size-dependent conversion factors f_i. The growth of the factors with increasing molecular weight can be fitted and extrapolated to a limit of f_∞ = 3.8 ± 0.2 (approximately met at $n \geq 70$).

polymerization of about 7 ± 0.5,[59] whereas GPC analysis (vs PS) suggested a $\overline{P}_\mathrm{n}$ of 13. This means an overestimation by PS-calibrated GPC by a factor of 1.8.

Optical Properties

The UV−vis absorption spectrum of the tetramer **1** in THF reveals a single maximum at 379 nm and a shoulder at around 396 nm (Figure 3, circles). Because of the extension of the conjugation length, we found a red-shifted spectrum for **3** with a different band shape and two maxima at 382 and 399 nm (Figure 3, black curve). Obviously, these data are not consistent with a literature value of 409 nm for the same polymer.[34] Monitoring the analytical GPC elution of the oligomer mixture **3** with a diode array detector (DAD), one finds yet another absorption spectrum at low retention times, i.e., high molecular weight. Again, the band is red-shifted and the shape changed further to a faint shoulder around 400 nm and a maximum at 413 nm (Figure 1, arrow; Figure 3, triangles). Obviously, with increasing conjugation length the initial shoulder of the tetramer at 396 nm gradually shifts to the red and turns out as the main band for $n \geq 7$. These findings are nicely illustrated by the spectra of the separated oligomers (Figure 3, gray curves). Band shape and absorption maxima of **3** are similar to those of the hexamer and heptamer, which is another hint at the average degree of polymerization.

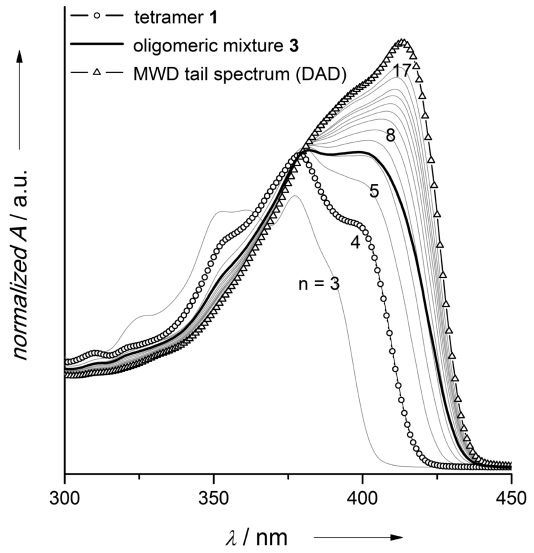


Figure 3. UV−vis absorption spectra of **1** (circles), **3** (black curve), at the MWD tail of **3** (triangles), and of the separated oligomers (n = 3−17, gray curves). Normalized at 250 nm (in THF).

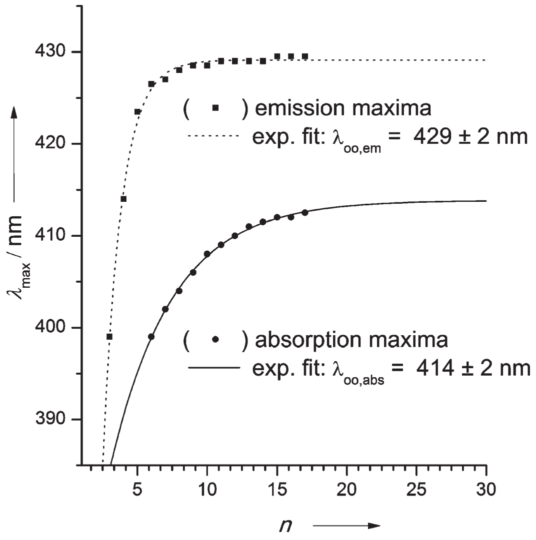


Figure 4. Separated oligomers of **3**: plot of $\lambda_{i,\mathrm{abs}}$ and $\lambda_{i,\mathrm{em}}$ vs number of repeating units n. Exponential fit and extrapolation of the absorption and emission maxima gives the corresponding limits $\lambda_{\infty,\mathrm{abs}}$ and $\lambda_{\infty,\mathrm{em}}$.

Plotting the absorption maxima $\lambda_{\mathrm{i,abs}}$ (in THF) against n gives a nonlinear curve[2,4,5] which can be fitted by Meier's exponential function (see Supporting Information).[60] Extrapolation suggests a saturation value of $\lambda_{\infty,\mathrm{abs}}$ = 414 ± 2 nm, which is already met at a conjugation length corresponding to less than 20 monomer units (Figure 4 and Supporting Information). The deviation of **3**'s emission maximum (428 nm, in THF) from the literature value

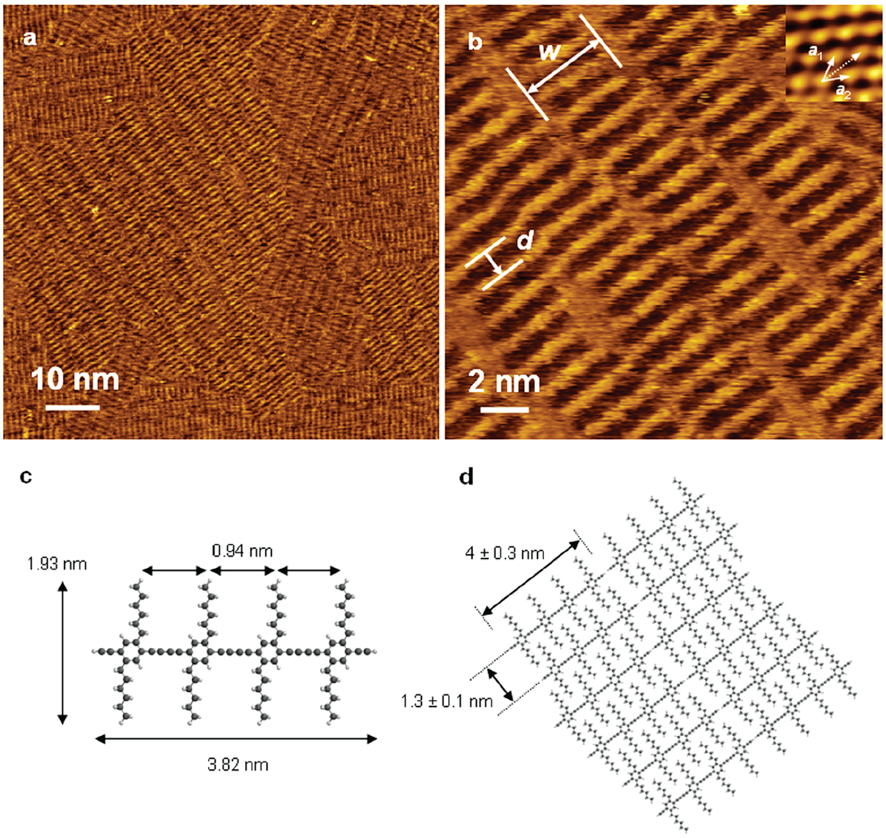


Figure 5. (a) STM overview image of **1** on HOPG, obtained from a 10^{-4} M solution. Image size 80 × 80 nm^2, $V_s = -1.00$ V, $I = 6$ pA. (b) High-resolution STM image of **1** on HOPG. Image size 20 × 20 nm^2. $V_s = -0.80$ V, $I = 10$ pA; inset: atomic structure of HOPG, obtained at the center position of (b) after switching the tunneling parameters to $V_s = -0.05$ V, $I = 0.1$ nA. (c) Calculated molecular structure of **1**. (d) Proposed molecular packing model for **1** on HOPG.

(432 nm, in $CHCl_3$)[34] can partly be explained by solvatochromism.[61] But in fact—as deduced from the emission spectra of the separated oligomers, exponential fit, and extrapolation[60]—the emission maximum (in THF) quickly meets a limit at $\lambda_{\infty,em} = 429 \pm 2$ nm at a conjugation length of less than 10 monomer units (Figure 4 and Supporting Information). The fluorescence spectra of the separated oligomers exhibit similar band shapes and narrow Stokes shifts due to the constraint linear geometry of the macromolecules. Tables S4 and S5 summarize the data plotted above (Supporting Information).

Adsorption on HOPG

As already mentioned above, there is a great interest in the self-organization of rigid oligomers on solid surfaces.[16−18] Figure 5 displays STM images of ordered monolayers of **1**. Rod molecule **1** forms domains of several tens of nanometers size, as observed in the large area scan. A domain angle of 60°/120° with respect to the backbone is observed. The molecular backbones are aligned parallel to the nearest-neighbor direction of the carbon atoms in the HOPG substrate surface. The inlay of Figure 5b represents the STM measurement of the graphite substrate at the center position of Figure 5b after changing the tunneling parameters, a_1 and a_2 being the unit vectors of HOPG. The molecular backbone, consisting of a conjugated π-electron system and thus appearing bright, can be clearly identified, whereas the alkyl chain regions appear as darker stripes. Although individual alkyl chains could not be resolved, we conclude from the unit cell parameters that parallel rods must pack with their alkyl groups staggered. As illustrated by a model in Figure 5d, this packing leads to an irregular lateral offset and voids between the lamellae consistent with weak end-group interaction. Since tetramer **1** is available in large quantities, systematic reactions toward linear and kinked coupling products, end-capped molecular rods, and more complex rigid superstructures are currently under investigation. A detailed discussion on self-assembled monolayers of derivatives of **1** will be published separately.

Conclusion

We presented an efficient stepwise route toward defined oligo(*p*-phenylene−butadiynylene)s up to the tetramer starting from 1,4-diethynyl-2,5-dihexylbenzene. We used the polar (3-cyanopropyl)dimethylsilyl (CPDMS) protective group for the construction of defined linear rods. In a comparative approach we separated the respective statistical oligomer by recycling GPC in semipreparative quantities. The separated homologues of known molar mass could be used to determine a nonlinear set of conversion factors for an OPB-specific GPC calibration. Extrapolation of defined oligomer properties permits conclusions regarding the maximum effective conjugation lengths of dialkyl-substituted OPBs and PPBs. Self-assembled monolayers of the tetramer **1** have been prepared and investigated by STM at the solid/liquid interface. The smooth syntheses of defined rigid rods such as **2**, **10**, and **1** allow them to be used as building blocks for complex superstructures.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft (DFG), the SFB 624, and the VolkswagenStiftung is gratefully acknowledged.

Supporting Information Available: Data summaries in table form, recycling GPC elugrams of **3**, DSC thermograms of **1** and **3**, the ^1H NMR end-group analysis of **3**, and experimental procedures for all products and intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, 1998.

(2) Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. *Chem.—Eur. J.* **2004**, *10*, 2681–2688.

(3) Meier, H. Defined-Length Carbon-Rich Conjugated Oligomers. In *Carbon-Rich Compounds*; Haley, M. M. T., Rik, R., Eds.; Wiley-VCH: Weinheim, 2006; pp 476−528.

(4) Ickenroth, D.; Weissmann, S.; Rumpf, N.; Meier, H. *Eur. J. Org. Chem.* **2002**, 2808–2814.

(5) Pilzak, G. S.; van Lagen, B.; Hendrikx, C. C. J.; Sudhölter, E. J. R.; Zuilhof, H. *Chem.—Eur. J.* **2008**, *14*, 7939–7950.

(6) Godt, A.; Schulte, M.; Zimmermann, H.; Jeschke, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7560–7564.

(7) Khatyr, A.; Ziessel, R. *J. Org. Chem.* **2000**, *65*, 3126–3134.

(8) Malolanarasimhan, K.; Kedei, N.; Sigano, D. M.; Kelley, J. A.; Lai, C. C.; Lewin, N. E.; Surawski, R. J.; Pavlyukovets, V. A.; Garfield, S. H.; Wincovitch, S.; Blumberg, P. M.; Marquez, V. E. *J. Med. Chem.* **2007**, *50*, 962–978.

(9) Godt, A.; Franzen, C.; Veit, S.; Enkelmann, V.; Pannier, M.; Jeschke, G. *J. Org. Chem.* **2000**, *65*, 7575–7582.

(10) Heckmann, A.; Amthor, S.; Lambert, C. *Chem. Commun.* **2006**, 2959–2961.

(11) González-Cabello, A.; Vázquez, P.; Torres, T. *J. Organomet. Chem.* **2001**, *637−639*, 751–756.

(12) Wang, C.; Palsson, L.-O.; Batsanov, A. S.; Bryce, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 3789–3799.

(13) Wielopolski, M.; Atienza, C.; Clark, T.; Guldi, D. M.; Martín, N. *Chem.—Eur. J.* **2008**, *14*, 6379–6390.

(14) Wei, Q.; Galoppini, E. *Tetrahedron* **2004**, *60*, 8497–8508.

(15) Li, W.-S.; Jiang, D.-L.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 2943–2947.

(16) Gesquiere, A.; Jonkheijm, P.; Hoeben, F. J. M.; Schenning, A. P. H. J.; De Feyter, S.; De Schryver, F. C.; Meijer, E. W. *Nano Lett.* **2004**, *4*, 1175–1179.

(17) Mu, Z.; Yang, X.; Wang, Z.; Zhang, X.; Zhao, J.; Bo, Z. *Langmuir* **2004**, *20*, 8892–8896.

(18) Gong, J.-R.; Zhao, J.-L.; Lei, S.-B.; Wan, L.-J.; Bo, Z.-S.; Fan, X.-L.; Bai, C.-L. *Langmuir* **2003**, *19*, 10128–10131.

(19) Johnson, C. A.; Lu, Y.; Haley, M. M. *Org. Lett.* **2007**, *9*, 3725–3728.

(20) Mössinger, D.; Hornung, J.; Lei, S.; De Feyter, S.; Höger, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 6802–6806.

(21) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644.

(22) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470.

(23) Steffen, W.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 9518–9521.

(24) Chodkiewicz, W.; Cadiot, C. R. *Hebd. Seances Acad. Sci.* **1955**, *241*, 1055–1057.

(25) Glaser, C. *Ber. Dt. Chem. Ges.* **1869**, *2*, 422–424.

(26) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632–2657.

(27) Liu, Q.; Burton, D. J. *Tetrahedron Lett.* **1997**, *38*, 4371–4374.

(28) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275–1276.

(29) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321.

(30) Eglinton, G.; McRae, W. *Adv. Org. Chem.* **1963**, *4*, 225–328.

(31) Berscheid, R.; Vögtle, F. *Synthesis* **1992**, 58–62.

(32) Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1969**, *7*, 1625–1634.

(33) Nishihara, Y.; Kato, T.; Ando, J.-i.; Mori, A.; Hiyama, T. *Chem. Lett.* **2001**, *30*, 950–951.

(34) Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Müllen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571–580.

(35) Bunz, U. H. F.; Enkelmann, V.; Kloppenburg, L.; Jones, D.; Shimizu, K. D.; Claridge, J. B.; zur Loye, H.-C.; Lieser, G. *Chem. Mater.* **1999**, *11*, 1416–1424.

(36) Kijima, M.; Kinoshita, I.; Shirakawa, H. *J. Mol. Struct.* **2000**, *521*, 279–283.

(37) Williams, V. E.; Swager, T. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4669–4676.

(38) Kijima, M.; Matsumoto, S.; Kinoshita, I. *Synth. Met.* **2003**, *135−136*, 391–392.

(39) Kinoshita, I.; Kijima, M.; Yoshikawa, K.; Mishima, Y.; Sasaki, N. *Synth. Met.* **2003**, *137*, 1059–1060.

(40) Jiang, J.-X.; Su, F.; Niu, H.; Wood, C. D.; Campbell, N. L.; Khimyak, Y. Z.; Cooper, A. I. *Chem. Commun.* **2008**, 486–488.

(41) Lin, V. S. Y.; Radu, D. R.; Han, M.-K.; Deng, W.; Kuroki, S.; Shanks, B. H.; Pruski, M. *J. Am. Chem. Soc.* **2002**, *124*, 9040–9041.

(42) McNeil, A. J.; Muller, P.; Whitten, J. E.; Swager, T. M. *J. Am. Chem. Soc.* **2006**, *128*, 12426–12427.

(43) Becker, K.; Lagoudakis, P. G.; Gaefke, G.; Höger, S.; Lupton, J. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3450–3455.

(44) Lei, S.; Ver Heyen, A.; De Feyter, S.; Surin, M.; Lazzaroni, R.; Rosenfeldt, S.; Ballauff, M.; Lindner, P.; Mössinger, D.; Höger, S. *Chem.—Eur. J.* **2009**, *15*, 2518–2535.

(45) Wang, C.; Batsanov, A. S.; Bryce, M. R. *J. Org. Chem.* **2006**, *71*, 108–116.

(46) West, K.; Wang, C.; Batsanov, A. S.; Bryce, M. R. *Org. Biomol. Chem.* **2008**, *6*, 1934–1937.

(47) Porath, J.; Bennich, H. *Arch. Biochem. Biophys.* **1962**, Suppl. I, 152−156.

(48) Höger, S.; Bonrad, K. *J. Org. Chem.* **2000**, *65*, 2243–2245.

(49) Rehahn, M.; Schlüter, A.-D.; Feast, W. J. *Synthesis* **1988**, 386–388.

(50) Lopez, S.; Fernandez-Trillo, F.; Midon, P.; Castedo, L.; Saa, C. *J. Org. Chem.* **2005**, *70*, 6346–6352.

(51) The starting material can be directly recycled, the diprotected species after deprotection with K_2CO_3.

(52) Gaefke, G.; Höger, S. *Synthesis* **2008**, 2155–2157.

(53) Though Swager et al. reported a better solubility for hexadecyloxy-substituted polymers than for the decyloxy derivatives,[37] we were not even able to purify the $C_{16}H_{33}$-substituted tetramer in our stepwise approach due to solubility problems.

(54) Another approach would be to synthesize higher analogues of **1** in a stepwise manner (analogous to Scheme 3) and perform a relative GPC calibration for these OPBs.

(55) Despite the state-of-the-art recycling GPC system, the preparative benefits are still poor for this kind of material. With our set of columns, one injection of a saturated solution of **3** in THF only yielded about 1.2 mg of the main fraction (pentamer) that took three cycles (75 min) to split up. The whole separation up to the heptadecamer took nine cycles (200 min; see Supporting Information). Hence, for multi-milligram quantities the stepwise synthesis of defined OPBs is more efficient.

(56) Since the separated oligomers are monodisperse by definition, we refer to the peak maximum of the GPC-interpreted MWD which is given by the M_p value.

(57) For the separated oligomers of **3** ($n = 3-17$), the Mark−Houwink−Sakurada relationship can be used to determine Mark−Houwink parameters for OPBs which are valid for $n \leq 20$: $K_{OPB}M_{OPB}{}^{a_{OPB}+1} = K_{PS}M_{PS}{}^{a_{PS}+1}$. If we use literature values for narrow PS samples in THF (*Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999; Vol. *2*, p 23) ($a = 0.714$, $K = 0.013\,63$ mL g^{-1}), we obtain the following values for our PB oligomers: $a = 1.374$ and $K = 3.084 \times 10^{-4}$ mL g^{-1} (see Supporting Information).

(58) From the ^{1}H NMR spectra of the defined, stepwise produced oligomers, we know that the “zg30” pulse sequence scarcely discriminates acetylenic protons. Integration and comparison with the aromatic region gives about 92% of the expected signal intensity (see Supporting Information).

(59) Simplified Carothers equation.

(60) Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379–384.

(61) For **3**, we measured an emission maximum of 430 nm in $CHCl_3$.