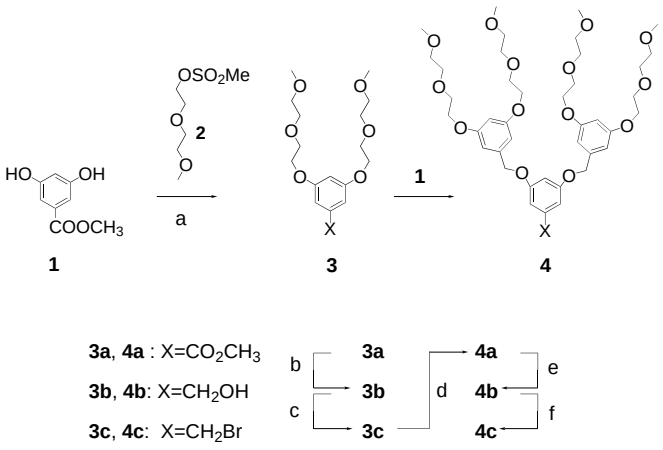
A Poly(*para*-phenylene) with Hydrophobic and Hydrophilic Dendrons: Prototype of an Amphiphilic Cylinder with the Potential to Segregate Lengthwise**

Zhishan Bo, Jürgen P. Rabe, and A. Dieter Schlüter*

Two subclasses of dendrimers[1] have recently been developed intensively, namely those with on the one hand dotlike cores and amphiphilic character and on the other polymeric cores and homophilic character. Interest in the first class arises mainly from their representatives' unusual size and shape that complements the array of commonly known much smaller amphiphiles.[2] The representatives of the second subclass are interesting because of their unprecedented mesophase behavior[3] and the finding that some of them can be considered as cylindrical, shape-persistant nano objects with lengths in the range of 30–100 nm and diameters of 2–5 nm.[4] In view of these important developments for both supramolecular and nano chemistry, we decided to merge these subclasses by providing access to amphiphilic cylinders, which, depending on the surrounding medium, could segregate lengthwise into two different halves (see schematic representation **A**). This structural motif is rather unique. In nature it can be found in some ion-channel membrane proteins. The targeted macromolecules, therefore, attracted our interest as models for such proteins.[5] They may also serve as novel and giant constituents of self-aggregated assemblies and should show interesting behavior at interfaces. Thus, a polymer was required, preferentially of the rigid-rod type, whose repeating units are equipped with two sterically demanding substituents, one of which being hydrophobic and the other hydrophilic. The synthetic strategy for this target should be flexible in regard to the achievable hydrophilicity/hydrophobicity ratio, as this ratio is well known to have a strong impact on the aggregation behavior of amphiphiles.[6] Here we describe the synthesis of the Suzuki-type monomer **8** equipped with unlike dendrons and its polycondensation with diboronic acid **9** to give the prototype amphiphile **10**. The behavior of **8** and **10** at the air/water interface is also described.

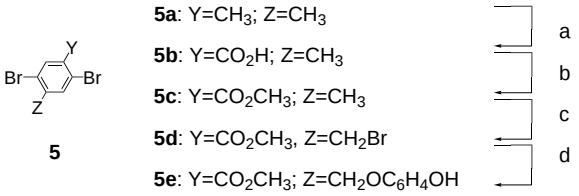
A

The synthesis of **8** and **10** are described in Schemes 1–4. Dendron **4c** was prepared by standard procedures (Scheme 1). Despite the required purification by repeated column chromatography it was obtained on the 10 g scale. The substitution of **8** with unlike dendrons was brought about by



Scheme 1. Synthesis of the hydrophilic dendron **4c**: a) K_2CO_3, DMF, 90 °C, 24 h, 68 %; b) $LiAlH_4$, THF, RT, 24 h, 86 %; c) CBr_4, PPh_3, THF, RT, 76 %; d) methyl-3,5-dihydroxybenzoate, K_2CO_3, acetone, reflux, 24 h, 99 %; e) same as b), 88 %; f) same as c), 61 %.

the selective oxidation of one methyl group of **5a** with nitric acid[7, 8] to give **5b** (Scheme 2). Esterification and bromination afforded **5d** whose conversion into **5e** was done with hydroquinone in tenfold excess. After purification by filtering through a short column followed by recrystallization the yield reached 78 %. The coupling of Fréchet dendron **6**[9] with **5e**



Scheme 2. Synthesis of the unsymmetrically substituted dibromobenzene **5e**: a) 45 % HNO_3, 7 d, 100 °C, 92 %; b) CH_3OH, H_2SO_4, reflux, 16 h, 87 %; c) CH_2Cl_2, Br_2, 15 °C, UV, 66 %; d) hydroquinone (10 equiv), K_2CO_3, acetone, [18]crown-6, reflux, 24 h, 78 %.

gave **7a** whose ester group was converted into the hydroxyphenyloxymethyl substituent in **7d** through a short sequence (Scheme 3).[10] The final attachment of hydrophilic dendron **4c** to monodendronized dibromide **7d** gave the amphiphilic monomer **8**[11] on the 3 g scale.

A purity of over 98 % was estimated for **8** from its 500 MHz proton NMR spectrum. This high purity is further backed by analytical gel permeation chromatography (GPC; UV and refractive index detection), which shows only one, fully symmetrical trace with a polydispersity of less than 1.01.

Suzuki polycondensation of **8** with diboronic acid ester **9** [12] was done under standard conditions[13] in 2 N $NaHCO_3$ and THF with $[Pd\{P(p\text{-tolyl})_3\}_3]$ as the catalyst precusor (Scheme 4). Standard work-up afforded **10**[11] as a white amorphous material in a yield of 95–98 % and in quantities exceeding 1 g. Its molecular weight was determined by GPC versus a polystyrene standard as $M_n = 38000$ ($P_n = 20$), $M_w = 85000$ ($P_w = 45$), and $M_w/M_n = 2.3$. It should be noted that according to molecular weight determinations of various

[*] Prof. Dr. A. D. Schlüter, Dr. Z. Bo
Institut für Organische Chemie der Freien Universität
Takustrasse 3, D-14195 Berlin (Germany)
Fax: (+49) 30-838-3357
E-mail: adschlue@chemie.fu-berlin.de
Prof. Dr. J. P. Rabe
Institut für Physik der Humboldt Universität
Invalidenstrasse 110, D-10115 Berlin (Germany)

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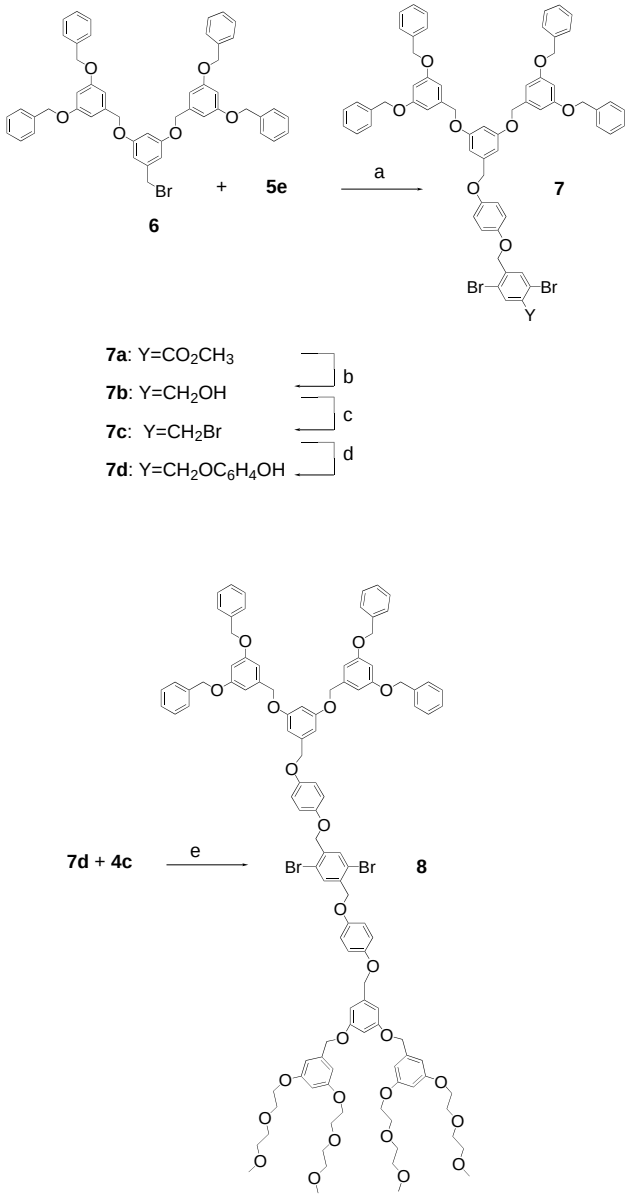
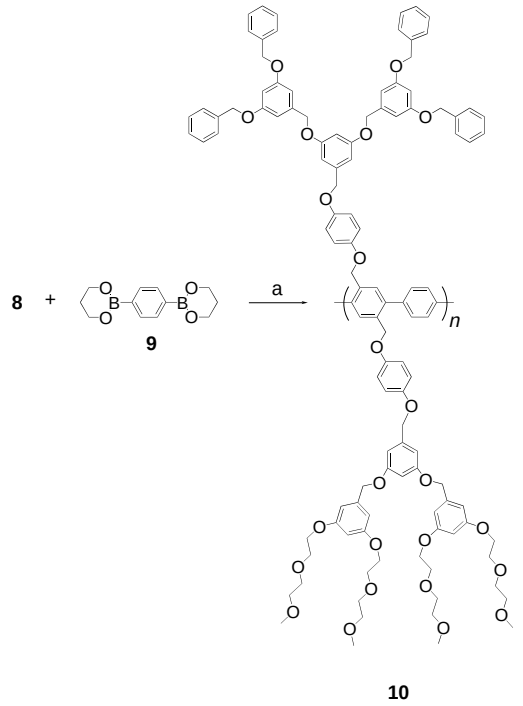


Scheme 3. Synthesis of **8**: a) K_2CO_3, acetone, [18]crown-6, reflux, 24 h, 86 %; b) $LiBH_4$, THF, reflux, 8 h, 97 %; c) CBr_4, PPh_3, THF, RT, 42 %; d) hydroquinone (20 equiv), K_2CO_3, acetone, [18]crown-6, reflux, 24 h, 78 %; e) K_2CO_3, acetone, [18]crown-6, reflux, 24 h, 63 %.



Scheme 4. Polycondensation of monomers **8** and **9**: a) $NaHCO_3$, THF, H_2O, 1 – 1.5 mol % $[Pd\{(P(p\text{-tolyl})_3\}_3]$, reflux for 3 d.

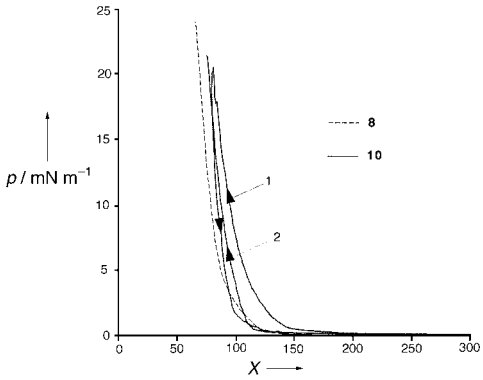


Figure 1. Surface pressure – area isotherm of **8** and **10** (X in Å^2 per r.u.; 1 and 2 indicate the first and second compression).

other dendronized polymers by small angle neutron scattering (SANS) GPC tends to underestimate the actual molecular weights. Typical factors by which molecular weights determined by GPC versus the polystyrene (PS) standard should be multiplied to get the actual ones lie in the range of 1.5 – 4.[14, 15]

Langmuir monolayers of **8** and **10** have been prepared at the air/water interface. Surface pressure – area isotherms (Figure 1) at room temperature reveal stable monolayers (area change is less than 1 % during 20 min) at pressures of more than 20 mN m^{-1}. The monolayers of **8** exhibit very good reversibility for compression, decompression, and repeating cycles, with an area per molecule of about 0.73 nm^2 per molecule at 20 mN m^{-1}. This is consistent with a monolayer structure in which the four ethyleneoxy chains per water soluble dendron are close packed and oriented perpendicularly to the monolayer,[16] thereby defining a minimum area per molecule. In comparison, **10** exhibits a 10 % larger area per repeat unit (0.82 nm^2 per r.u.) upon the first compression with a hysteresis in the first decompression and a shift to a more reversible isotherm and a smaller area per r.u. in the second cycle (0.77 nm^2 per repeat unit (r.u.)). The good agreement between the areas per molecule of **8** and per r.u. of **10** indicates a structure of the polymer monolayer in which the rodlike polymer molecules are oriented with their long axes within the monolayer plane and close packed. Moreover, the hydrophilic ethyleneoxy chains are on that side of the polymer that faces the water subphase, while the more hydrophobic dendron faces the air side of the polymer. This picture is supported by a control experiment on a closely related polymer in which the hydrophilic dendron of **10** is replaced by another G2 Fréchet dendron.[17] Under the same conditions this polymer does not form a stable monolayer at the air/water

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interface.[18] Monolayers of **10** can be transferred on to mica to give homogenous films of 3.3 nm thickness with a transfer efficiency greater than 96%.

In conclusion, we have synthesized a new type of Suzuki monomer that carries G2 hydrophobic and hydrophilic dendrons and shown that it can be polymerized to give the first length-wise (not block-wise) amphiphilically equipped poly(*para*-phenylene) **10**. Polymer **10** differs from known amphiphiles in that it consists of a linear, covalently bound sequence of "little" amphiphiles. It differs from common "polysoaps" because it is much more rigid, which should increase its potential to aggregate, for example, into channels. Langmuir–Blodgett experiments provide the first evidence that the dendritic substituents of **10** segregate lengthwise into hydrophobic and hydrophilic domains (see schematic representation **A**).

Experimental Section

Langmuir monolayers were prepared by spreading 100 μL of solution in $CHCl_3$ (1 g mL^{-1}) on a distilled water subphase in a Langmuir–Blodgett trough (NIMA Ltd.) at room temperature. Compression rates were on the order of one percent per minute. The stability of the monolayers was checked by compressing them to 20 mN m^{-1} and monitoring the area for 20 min.

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[11] **8**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.38$ (12H, s), 3.67 (8H, t), 3.71 (8H, t), 3.83 (8H, t), 4.13 (8H, t), 4.94–5.01 (24H, seven partially overlapping s), 6.45–6.67 (18H, eight partially overlapping s), 6.91 (8H, narrow AA′BB′), 7.31–7.47 (20H, m), 7.77 (1H, s), 7.78 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 58.98$, 67.29, 69.11, 69.55, 69.79, 69.92, 70.30, 70.59, 71.79, 100.92, 101.35, 105.90, 106.18, 115.68, 115.71, 120.85, 127.46, 127.91, 128.47, 132.08, 136.59, 137.53, 138.93, 139.08, 139.49, 139.53, 152.35, 153.23, 153.26, 159.91, 159.99; elemental analysis calcd for $C_{110}H_{116}O_{24}Br_2$: C 66.66, H 5.90; found: C 65.97, H, 5.78. **10**: ^{1}H NMR (500 MHz, $CDCl_3$): all signals are broad, $\delta = 3.31$ (12H), 3.50 (8H), 3.65 (8H), 3.77 (8H), 4.03 (8H), 4.82–5.01 (24H), 6.40–6.63 (20H), 6.80–6.82 (8H), 7.28–7.38 (20H), 7.53–7.68 (4H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 59.00$, 67.30, 68.55, 69.56, 69.76, 69.89, 70.34, 70.59, 71.81, 100.95, 101.38, 105.95, 106.21, 115.59, 115.77, 127.49, 127.91, 128.48, 129.16, 131.38, 134.17, 136.64, 138.98, 139.14, 139.49, 139.59, 140.76, 152.86, 153.07, 159.89, 159.93, 159.99; elemental analysis calcd for $(C_{116}H_{120}O_{24})_n$: C 73.40, H 6.37; found: C 72.49, H 6.28.
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The First Efficient Hydroaminomethylation with Ammonia: With Dual Metal Catalysts and Two-Phase Catalysis to Primary Amines**

Burkhard Zimmermann, Jürgen Herwig,* and Matthias Beller*

Dedicated to Professor Rüdiger Selke on the occasion of his 65th birthday

Aliphatic amines are amongst the most important bulk and fine chemicals in the chemical and pharmaceutical industries.[1] Alongside hydroamination,[2] hydroaminomethylation of olefins to amines represents an atom-economic efficient

[*] Dr. J. Herwig
Celanese GmbH – Werk Ruhrchemie
D-46128 Oberhausen (Germany)
Prof. Dr. M. Beller
Institut für Organische Katalyseforschung
an der Universität Rostock e.V.
Buchbinderstrasse 5–6, D-18055 Rostock (Germany)
Fax: (+49) 381-466-9324
E-mail: matthias.beller@ifok.uni-rostock.de
Dipl.-Chem. B. Zimmermann
Technische Universität München
Lichtenbergstrasse 4, D-85747 Garching (Germany)

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