Generation dependent mesophase behavior in extended amphiphilic dendrons in the shape of macromolecular dumbbells

Byoung-Ki Cho,†[a] Anurag Jain,[a] Sol M. Gruner[b] and Ulrich Wiesner*[a]

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Small angle X-ray scattering studies of 2nd and 3rd generation based extended amphiphilic dendrons in the shape of macromolecular dumbbells with identical hydrophilic volume fractions suggest 2-D hexagonal columnar and *Pm*$\bar{3}$*n* micellar cubic mesophases, respectively, elucidating the role of shape induced interface curvature in mesophase formation.

Macromolecular architecture is a crucial parameter that influences morphological behavior. Beyond studies of simple linear block copolymers, structure–morphology correlations have been investigated theoretically and experimentally, *e.g.*, for "miktoarm star" block copolymers, where the center of a star-like block is connected to the chain end of a chemically different linear block.[1,2] For about a decade dendritic structures have also been employed as branched blocks in asymmetric molecular hybrids.[3–7] Dendrons, segments of dendrimers, offer a direct route to engineer the interface curvature in self-assembled microstructures. Furthermore, molecular features such as core and periphery chemistries as well as the nature of the junction (focal) point of the dendritic segments can be modulated independently, thus providing a rich tool box for molecular design.[8] We have recently devised extended amphiphilic dendrons where a 3rd generation hydrophilic aliphatic ether based dendron with a hydrophobic aliphatic docosyl periphery is extended at its focal point by a linear hydrophilic poly(ethylene oxide) (PEO) chain. Unique mesophase structure–mechanical and ionic transport correlations are observed for this system by keeping the dendron generation constant but changing the hydrophilic volume fraction through simple variation of the linear PEO chain length.[9] The present communication describes the opposite approach to tailor morphology. We report on the influence of dendron generation upon the phase behavior of this extended amphiphilic dendron system. To this end, extended amphiphilic dendrons in the shape of macromolecular dumbbells **1** and **2** were designed to have equal hydrophilic volume fractions, f = 0.48, but different branched segments, *i.e.*, 2nd and 3rd generation dendrons, respectively (Fig. 1). In this way for a constant volume fraction the influence of interface curvature on mesophase behavior can be elucidated. The interface in the condensed state is expected at the boundary between docosyl peripheries and the PEO-like dendritic core. It is interesting to note that so far only a few dumbbell shaped dendron-based molecules have been studied.[10,11] To the best of our knowledge, however, the present system constitutes the first example of a dendron-linear coil-dendron (ABA-type) architecture exhibiting well-defined mesophase behavior.

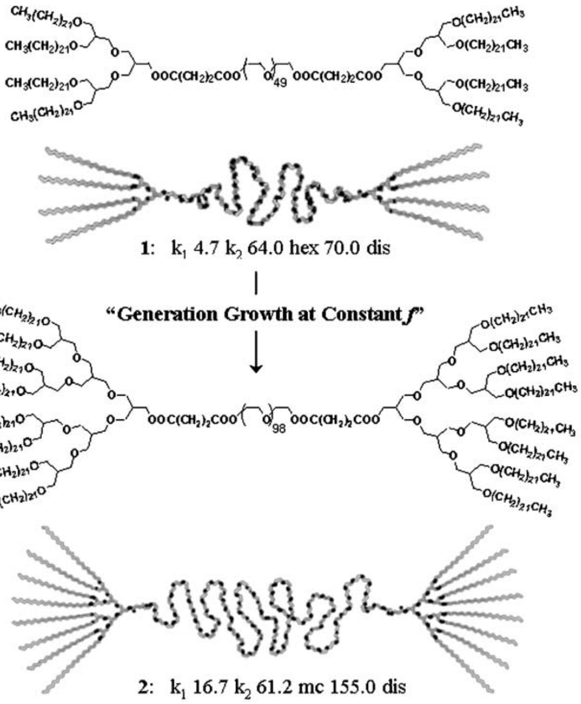

Fig. 1 Molecular structures/models and phase transition temperatures of ABA-type extended amphiphilic dendrons **1** and **2**. Temperatures are given in °C; k_1: crystalline in docosyl peripheries and PEO chains; k_2: crystalline only in docosyl peripheries; hex: hexagonal columnar; mc: *Pm*$\bar{3}$*n* micellar cubic; dis: disordered.

The synthesis was performed by following a procedure described elsewhere.[12,13] PEO molar masses (MWs) were determined to be 2170 and 4330 g mol^{-1} in **1** and **2**, respectively, calculated on the basis of the ratio of the area for the dendritic core plus PEO backbone proton signals to the area of the docosyl group signals in ^{1}H-NMR spectra. Molecular weight dispersities (M_w/M_n) from gel permeation chromatography (GPC) were found to be less than 1.06 for both compounds. Their thermal behavior was determined by differential scanning calorimetry (data not shown) and temperature dependent small angle X-ray scattering (SAXS) measurements as summarized in Fig. 1. In the solid state microphase-separation between hydrophobic docosyl groups and hydrophilic parts leads to two crystalline melting transitions. Melting of the docosyl peripheries was observed at nearly constant temperatures (~63 °C). The PEO melting transitions of **1** and **2** occurred at 5 and 17 °C, respectively. They are significantly lower

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† Current address: Department of Chemistry, Dankook University, 147, Hannam-ro, Yongsan-gu, Seoul 140-714, Korea
*ubw1@cornell.edu

than the melting temperatures of homo PEOs with similar MWs (52 and 59 °C for MW = 2000 and 4000 g mol^{-1}, respectively),[14] strongly suggesting that PEO chains are plasticized by the all-amorphous hydrophilic dendritic core due to the similarity in chemical composition.[15]

Upon melting of the docosyl peripheries, extended amphiphilic dendrons **1** and **2** both exhibit a single well-defined mesophase (liquid crystalline phase) before disordering into an isotropic liquid at 70 and 155 °C, respectively. The microstructures in the liquid crystalline states were characterized by temperature-variable SAXS measurements. In Fig. 2a the SAXS pattern of **1** at 68 °C exhibits three reflections with peak position ratios of $1 : \sqrt{3} : \sqrt{4}$, consistent with a 2-dimensional hexagonal columnar structure. Based on the primary peak, the inter-column distance was calculated to be $\boldsymbol{a}$ = 7.7 nm. The transition into the isotropic liquid at 70 °C is evident from the temperature dependent SAXS patterns of this compound in Fig. 2a. Contrary to **1**, the SAXS pattern of **2** at 70 °C shows a considerably larger number of reflections (Fig. 2b). They can be indexed as the (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (420), (421) and (332) reflections, indicative of a $Pm\bar{3}n$ cubic symmetry. From the dimension of the (200) reflection, the cubic lattice parameter can be estimated as $\boldsymbol{b}$ = 22.8 nm. A phase with $Pm\bar{3}n$ cubic symmetry has recently been predicted theoretically to be an equilibrium micellar phase stabilized over a relatively large volume fraction range in linear-branched hybrid block systems.[16,17] The insensitivity of the lattice size with temperature additionally argues for a micellar phase (Fig. 2b). Furthermore, our recent ion-conductivity experiments on a lithium doped homologous AB-type extended amphiphilic dendron with similar volume fraction (f = 0.41) also suggested that the observed $Pm\bar{3}n$ cubic phase is micellar.[9] These considerations suggest that the microstructure of the current $Pm\bar{3}n$ cubic phase of compound **2** is micellar.

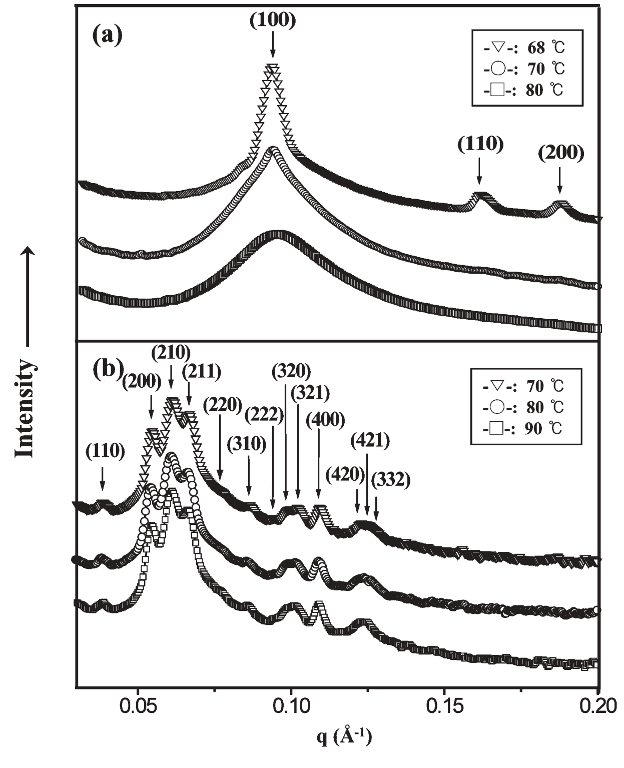

Fig. 2 Small angle X-ray scattering diffractograms of (a) **1** at 68, 70, and 80 °C and (b) **2** at 70, 80, and 90 °C. The expected positions of the Bragg peaks for the assigned lattices are indicated by ticks.

The different self-assembly behavior of **1** and **2** with identical f = 0.48 points towards a marked difference in how phase behavior can be controlled in the current highly branched *versus* conventional linear block copolymer systems. While in the latter the essential control parameter is volume fraction, in the former dendron generation can additionally be used as an independent parameter to control interface curvature.[18,19] The SAXS results for **1** are consistent with a twin taper shape with 1-D interfacial curvature, self-organizing into cylinders of a hexagonal columnar structure (Fig. 3a). In contrast, results for **2** are consistent with a twin conical shape with 2-D interfacial curvature constructing micelles in a $Pm\bar{3}n$ cubic structure (Fig. 3b).

The suggested dendron shape change from taper to cone with generation can be rationalized by considering the chain stretching penalty associated with the spatially crowded peripheries.[20] Compared to the tetra-branches of the 2nd generation based compound **1**, intuitively the bulkier octa-branches of the 3rd generation based compound **2** lead to more stretching for a given interface curvature. Since chain stretching is energetically unfavourable, **2** rather adopts a conical shape with larger interfacial curvature than what is induced in **1** with its taper shape. It should be noted that this simple interfacial curvature argument explains that the phase boundaries in the present linear-branched hybrid system are significantly shifted towards larger volume fractions of the linear chain containing hydrophilic part when compared to conventional linear block copolymers.[1,16]

In summary, we have prepared extended amphiphilic dendrons in the shape of macromolecular dumbbells with identical hydrophilic volume fractions but with branched 2nd and 3rd generation dendritic architectures, respectively. Structural data for the 2nd generation based species are consistent with a 2-D hexagonal columnar mesophase, while those of the 3rd generation based compounds are consistent with a $Pm\bar{3}n$ micellar cubic mesophase. These results demonstrate that compared to linear block copolymers, self-assembly can be fine-tuned in more detail

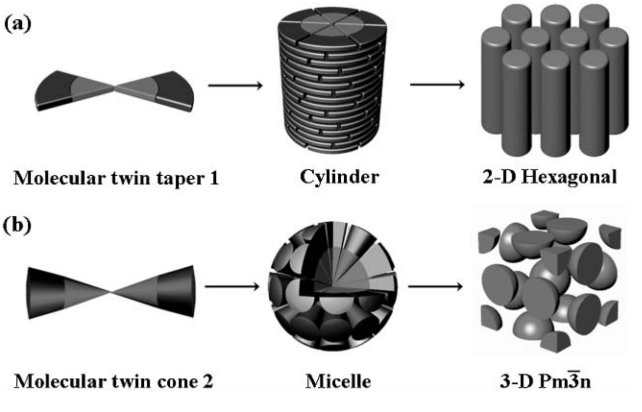

Fig. 3 Schematic sketches of molecular building blocks and self-assembly behavior of ABA-type extended amphiphilic dendrons. (a) 2-D hexagonal columnar assembly of molecular taper **1**; (b) 3-D $Pm\bar{3}n$ micellar cubic assembly of molecular cone **2**. The grey and dark parts represent the hydrophilic domains (PEO chains and dendritic cores) and hydrophobic matrix (docosyl peripheries), respectively. For clarity, structural models on the far right in (a) and (b) omit the hydrophobic parts.

since, in addition to volume fraction, generation dependent molecular shape is an independent parameter to tailor bulk supramolecular architecture.

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Byoung-Ki Cho,†[a] Anurag Jain,[a] Sol M. Gruner[b] and Ulrich Wiesner*[a]
[a]*Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA. E-mail: ubw1@cornell.edu*
[b]*Department of Physics, Cornell University, Ithaca, NY 14853, USA. E-mail: smg26@cornell.edu*

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