A New Level of Hierarchical Structure Control by Use of Supramolecular Self-Assembled Dendronized Block Copolymers

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Block copolymers, in which microphase segregation between two chemically incompatible blocks can be combined with supramolecular attachment of side chains or mesogens to one block, constitute very appealing systems to design hierarchically self-assembled macromolecular materials.[1,2] Self-organization of these systems is achieved typically at two length scales: that of the side chains ($\sim 10^0$ nm) and that of the block copolymers ($\sim 10^1$–10^2 nm). Advanced materials with tunable nanoporosity,[3] switchable proton conductivity,[4] and photonic properties [5] have been successfully prepared using diblock copolymers in which one block is inert, while the other is supramolecularly "hosting" side chain surfactants. The design of self-assembled materials with complex 3D structures can be further expanded when colloidal particles are introduced. This has allowed, for example, the design of electron semiconductors in which the hierarchical control of building blocks spans as much as 0.5 to 500 nm,[6] or the design of ordered organic/inorganic hybrid materials with metal-like conductivity.[7] Finally, the flexibility of this bottom-up process can be fully stretched when the multiple possibilities offered by non-covalent supramolecular interactions to bind together the polymer and the side-chain surfactants, such as ionic interactions,[8–11] hydrogen bonding,[12–14] π-π stacking,[15] and metal–ligand complexation,[16–21] are all considered.

This approach proves to be highly versatile for the control of structure on large length scales: varying the volume fractions of the blocks or swelling the inert block by the presence of colloidal entities can lead to a multitude of morphologies in the $\sim 10^1$–10^2 nm range. However, due to the linear nature of the supramolecular active blocks, the only possibility to control the structure at small length scales is the variation of the type of surfactants or mesogens supramolecularly attached, with the result of observing essentially lamellar phases at these length scales.[2–5]

Recently we have demonstrated that alkyl tail-dendronized polymer supramolecular complexes offer a very valuable alternative to surfactant-linear polymer complexes. They are characterized by a very rich phase diagram including liquid crystalline phases not accessible with linear macromolecules, such as columnar-rectangular, columnar-hexagonal and columnar-tetragonal phases.[22–24] The complexity of these phase diagrams is the consequence of an additional degree of freedom in the design of the bulk structure, that is, the dendronized-polymer generation.

In the present work, we show that by replacing, in a block copolymer, the linear polymer block with a dendronized polymer capable of participating in supramolecular interactions, the additional degree of freedom arising from the varying generation of the dendronized polymer allows engineering the self-assembly into unprecedented hierarchically ordered bulk structures. Not only does this allow control of the structures at the smaller length scale beyond current possibilities with the introduction, for example, of new columnar-rectangular, -hexagonal and -tetragonal phases, but it may also lead to new functional template materials with increased 3D topological complexity for advanced technologies.

In order to demonstrate this new hierarchical self-assembly concept, we have synthesized diblock copolymers in which one block is a dendronized polymer, while the other is a spacer block that can further act as a stimuli-responsive polymer (see Supporting Information).

The molecular structures of the first and second generation dendronized homopolymers (PG1 and PG2, respectively) and their ionic complexes with sulfate alkyl tails of various lengths are shown in Figure 1, together with the signature of their liquid-crystalline structures as observed by wide-angle X-ray scattering (WAXS). Figure 1b gives the WAXS profiles for the first generation dendronized polymer complexed with sulfate alkyl tails of lengths comprised between C12 and C18 (Figure 1a). The complex with C8 surfactant (not shown here) is characterized by a single broad peak, indicating an amorphous isotropic phase. However, as soon as the length of the alkyl tail is increased to C12 or more, multiple sharp peaks appear, demonstrating the presence of ordered structures. The complexes with C12 and C14 show, respectively,

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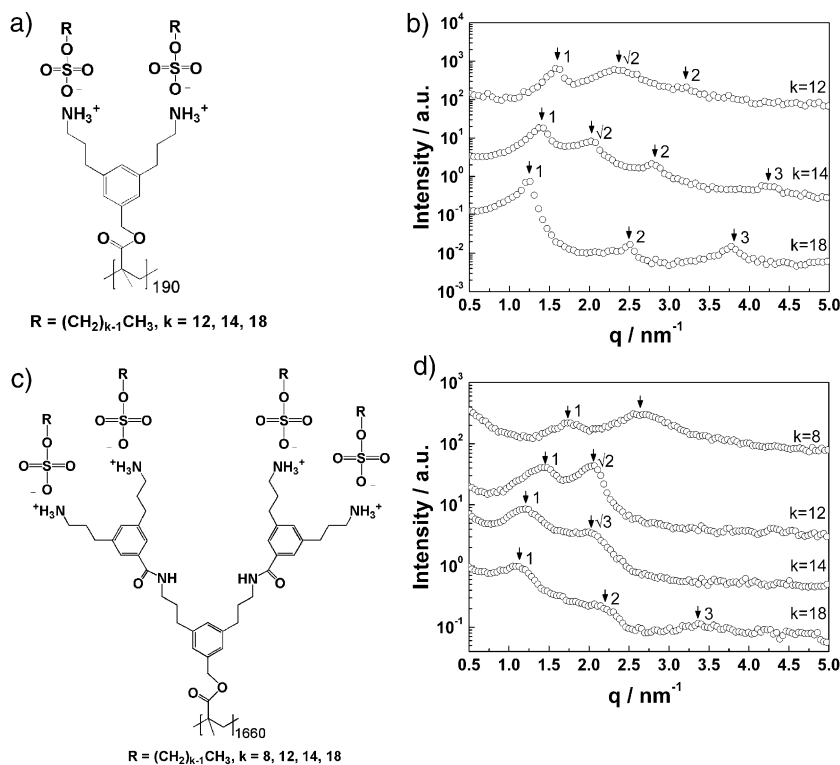1000 Lausanne 26 (Switzerland)

Figure 1. Chemical structures and WAXS profiles of the dendronized homopolymers complexed with sulfate alkyl tails. a) Scheme of $PG1_{190}$-SO_4C_k complexes and b) their corresponding WAXS profiles. c) Scheme of $PG2_{1660}$-SO_4C_k complexes and d) their corresponding WAXS profiles.

three and four reflections whose positions follow the ratios $1 : 2^{1/2} : 2$ and $1 : 2^{1/2} : 2 : 3$, respectively, which are indicative in both cases, of well ordered columnar square phases.[22–26] By further increasing the alkyl tail to C18, three reflections spaced as 1:2:3 appear, characteristic of a lamellar structure. Clearly, increasing alkyl length leads to an order-to-order transition from the columnar-tetragonal to lamellar structure, as we have previously observed in similar dendronized polymer/alkyl tail complexes.[22–24] Consistently with expectations, the periodicity increased with the alkyl chain length from 3.9 to 4.2 nm, and to 4.8 nm when going from C12 to C14, and to C18, which directly correlates with the alkyl length of the side chains.

Figure 1c shows the second generation dendronized homopolymer complexed with the surfactants with alkyl tails ranging from C8 to C18, and Figure 1d gives the corresponding WAXS profiles. The tendency is similar to the first generation analogs, with the main difference that already at C8 two reflections appear spaced as 1:1.52, indicative of a rectangular-columnar phase, as we previously observed in similar dendronized polymer/alkyl tails complexes.[24] This is the result of the increased tendency of the surfactants to microphase separate and an increasingly "thicker" polymer cross section. A tetragonal phase is observed with the C12 alkyl tail, while at C14, three reflections spaced as $1 : 3^{1/2} : 2$ indicate the presence of a columnar-hexagonal phase. Finally, upon further increasing to C18, a lamellar phase is observed.

Compared to Figure 1b, the peaks are systematically shifted towards lower scattering vector q, reflecting an increased lattice period, as a result of the increased dendronized polymer generation.

Figure 2 shows the chemical structures of the same dendronized polymers as in Figure 1 complexed with the same surfactants but extended into block copolymers by a contiguous block of varying length and chemical nature. Figures 2a and c illustrate the first and second generation dendronized block copolymers, respectively, in which the inert block is a low glass transition temperature ($-27.1\,°C$) poly(methoxy diethylene glycol methacrylate) (PMeDEG), while Figures 2b and d show the corresponding small- and wide-angle X-ray scattering (SWAXS) profiles. PMeDEG was selected as a possible stimuli-responsive block as it has a lower critical solution temperature (LCST) in water, $24.3\,°C$, accompanied by great chain conformation and volume changes. The positions of the reflections observed by WAXS for both these dendronized block copolymers locate exactly at the same q as for the homopolymers (Fig. 1), revealing that the same microphase-separated liquid-crystalline morphologies at the 10^0 nm length scale are preserved in the block copolymers. This fact suggests microphase separation taking place between the complexed alkyl tail/dendronized block and the PMeDEG, although no reflections at the accessible lower q region appear in the SAXS profile, possibly due to the overlap with the X-ray detector beamstop, settled at corresponding real space length scales larger than 58 nm.

Figures 2e and f give the chemical structure and SWAXS profile for a first generation dendronized block polymer extended by a poly(N-isopropylacrylates) (PNiPAM) block, whose well known LCST in water is $32\,°C$. The first order diffraction peaks for its complexes with C12, C14, and C18 surfactants are located at the same q as in Figure 1b, demonstrating the same liquid-crystalline structures at the 10^0 nm length scale are maintained. Furthermore, in this case a peak at $q = 0.23\,nm^{-1}$ occurs, indicating the presence of a microphase-separated morphology with periodicity of 27 nm.

Transmission electron microscopy (TEM) was further used to confirm the finding shown in Figure 2 and assess the hierarchical organization of the complexed dendronized block polymers in real space. All of the block copolymer complexes reported in Figure 2 show microphase-separation between the complexed dendronized block and the other block. Figure 3 gives TEM micrographs of the microstructures of some selected combinations of alkyl tails, dendronized polymers, and spacer blocks. Each individual image illustrates the large length scale structures observed at low magnification, while
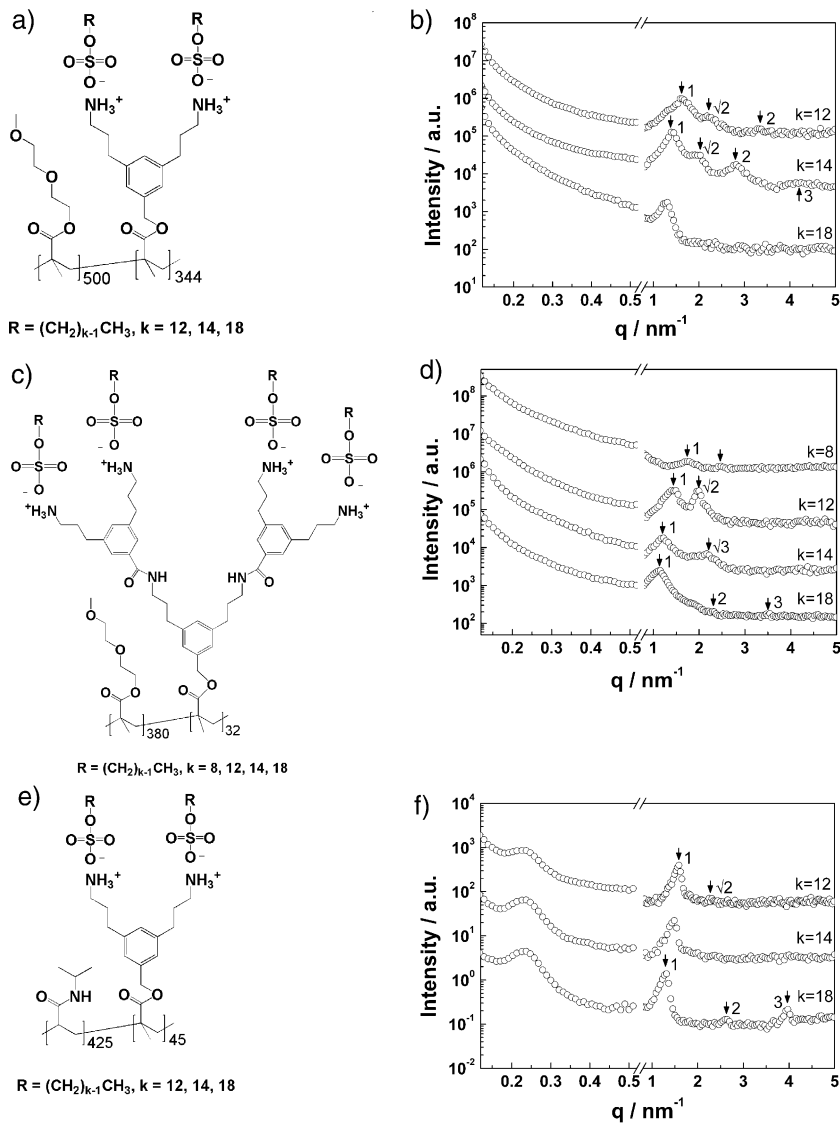
a)

R = (CH$_2$)$_{k-1}$CH$_3$, k = 12, 14, 18

b)

c)

R = (CH$_2$)$_{k-1}$CH$_3$, k = 8, 12, 14, 18

d)

e)

R = (CH$_2$)$_{k-1}$CH$_3$, k = 12, 14, 18

f)

Figure 2. Chemical structures and SWAXS profiles of the dendronized block copolymers complexed with sulfate alkyl tails. a) Scheme of PMeDEG$_{500}$PG1$_{344}$-SO$_4$C$_k$ complex and b) corresponding SWAXS profile. c) Scheme of PMeDEG$_{380}$PG2$_{32}$-SO$_4$C$_k$ complex and d) corresponding SWAXS profile. e) Scheme of PNiPAM$_{425}$PG1$_{45}$-SO$_4$C$_k$ complex and f) corresponding SWAXS profile.

(Figure 2f) is found. The length of the inert block in these systems can also be varied to change the large length scale structures to spheres or cylinders of bicontinuous gyroid phases without affecting the low length scale structure (see Supporting Information).

In these original hierarchical structures, because the liquid-crystalline structures are confined within the dendronized block domains, the influence of microphase-segregated domains on the orientation of the liquid-crystalline structures is a subject of remarkable interest itself. Indeed, studies of block copolymer structures confined within geometric constraints, such as thin films and nanometer pores, have demonstrated a strong effect of the confining surfaces/interfaces.[27,28] In the present study, orientation of the liquid-crystalline structures can be expected to directly depend on: i) interfaces among microphase-separated block copolymer domains, ii) the relative orientation of alkyl tails to the polymer backbones and iii) the difference in periodicity between the length scales of the two main structures. Nonetheless, in all the insets of Figure 3, the lipid columns or lamellae appear to orient normally to microphase-segregated domain interfaces, irrespective of the liquid-crystalline structure considered.

The orthogonal orientation of the lipid columns or lamellae with respect to microphase-segregated domain interfaces is in agreement with the topological connectivity among different chemical components in complexed dendronized block copolymers, as sketched in Figure 4a. These observations on the orientation of alkyl tail domains together with our previous findings on cylinders formed by alkyl tails in this class of liquid-crystalline polymers[22–24] allow identification of the topological models sketched in Figure 4b for the main hierarchical structures presented here, namely rectangular-within-lamellar, tetragonal-within-lamellar, hexagonal-within-lamellar, and lamellar-within-lamellar structures. Among these structures, only lamellar-within-lamellar (highlighted by a dashed box) has previously been accessible using linear macromolecular templates.[29] The systematic orthogonal orientation of alkyl tail domains with respect to the microphase-separated domain interfaces in a lamellar-within-lamellar structure for the PNiPAM$_{425}$PG1$_{45}$-SO$_4$C$_{18}$ system is further highlighted in Figure 4c by a medium-high magnification TEM micrograph.

In summary, we have presented a new general approach to the hierarchical self-assembly of block copolymers in which
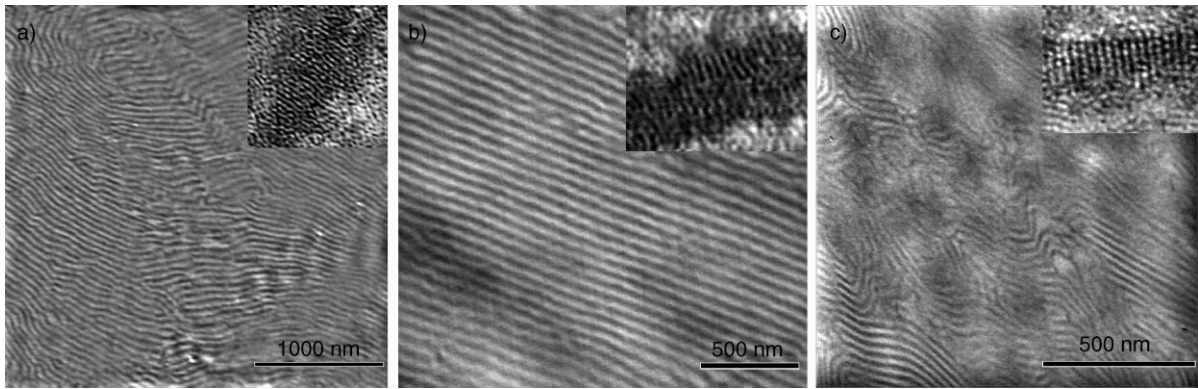
each inset is a zoom-in on the corresponding liquid-crystalline structure observed at low length scale and high magnification within the segregated dendronized blocks. RuO$_4$ was used to stain the aromatic groups in the dendronized polymers. Thus, at large length scales, the dark domains represent the dendronized polymers and the white domains represent the other block; at low length scales, the alkyl tail domains appear white. Therefore, the TEM images in Figure 3 together with their insets clearly demonstrate in real space the hierarchical self-assembly of the alkyl tails/dendronized block copolymers in structures other than lamellar-within structure. In the case of Figure 3c, a perfect agreement of the large length scale periodicity observed (27 nm) and that measured by SWAXS

Figure 3. TEM images of dendronized block copolymers complexed with sulfate alkyl tails. The low magnification large images give the structure observed at large length scales, while the high magnification insets (horizontal edge window is 60 nm in (a) and (b) and 40 nm in (c) give the corresponding liquid-crystalline structure observed at low length scales. a) Columnar tetragonal-within-lamellar structure observed for $PMeDEG_{380}PG2_{32}$-SO_4C_{12}. b) Columnar hexagonal-within-lamellar structure observed for $PMeDEG_{380}PG2_{32}$-SO_4C_{14}. c) Lamellar-within-lamellar structure observed for $PNiPAM_{425}PG1_{45}$-SO_4C_{18}. In inset c, the white lamellae formed by the alkyl tails are entirely traversing the dendronized polymer lamellae (in black), indicating that their orientation orthogonal to the image is maintained at least over the TEM section film thickness ($\sim$50 nm). In the case of cylinders (insets in (a) and (b)), discontinuities of the white alkyl tail cylinders throughout the black lamellae occur due to tilting of the black lamellae (and white cylinders) with respect to the image plane.

substituting the conventional linear supramolecular active block with dendronized polymers gives rise to increased topological complexities and morphologies not otherwise accessible with linear block copolymers. More specifically, we were able to design, for the first time, 3D hierarchically organized structures with columnar phases at the small length scales, and to engineer these approximately nanometer-scaled phases into square, rectangular, and hexagonal lattices. The

novel liquid-crystalline morphologies, which can be designed at the low length scale in these systems, are expected to provide the final materials not only with unprecedented structural complexity, but also with tunable physical properties. For example, lyotropic liquid-crystalline systems with different space groups are known to be characterized by very different rheological properties,[30] which should also be reflected in the present systems. More in general, these findings may be used to
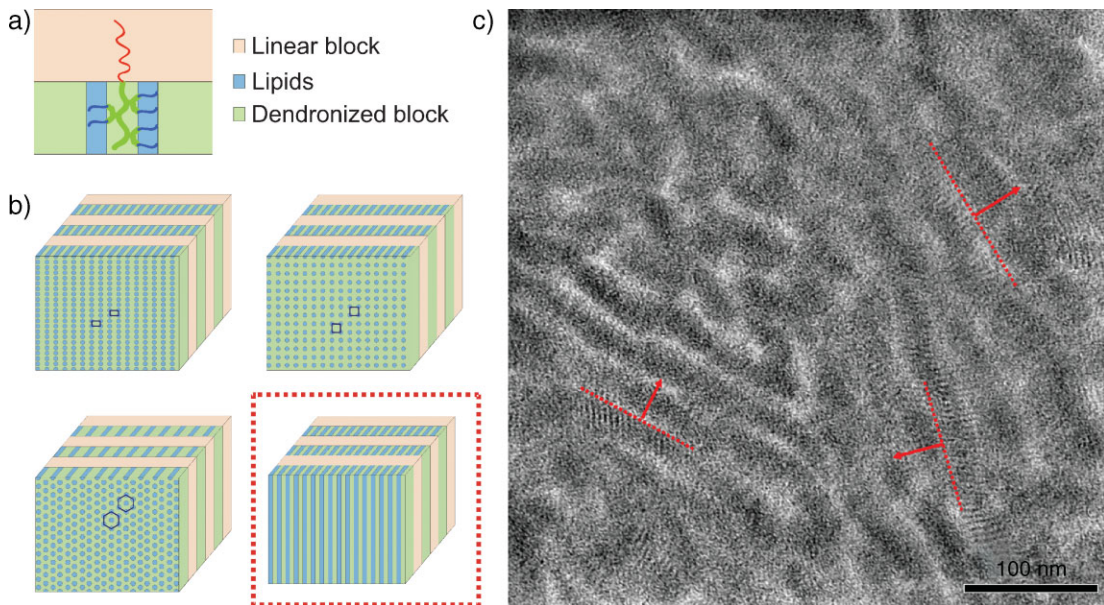

Figure 4. Schematic representation of hierarchical nanostructures obtained by self-assembly of sulfate alkyl tail/dendronized block copolymer complexes. a) Topological chemical connectivity of dendronized block copolymer components in the microphase-separated state. b) Relative domain orientation of rectangular-within-lamellar, tetragonal-within-lamellar, hexagonal-within-lamellar, and lamellar-within-lamellar structures. c) Medium-high magnification TEM micrograph of $PNiPAM_{425}PG1_{45}$-SO_4C_{18}. The red arrows indicate the average orientation of alkyl tail domains and the dashed red lines indicate the interfaces among the micro-segregated blocks.

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provide the resulting self-assembled materials with tunable electron and proton conductivities, optical properties, and unexplored templating possibilities.

Experimental

Materials: Dendronized homopolymers ($PG1_{190}$ and $PG2_{1660}$) and block copolymer $PNiPAM_{425}PG1_{45}$ were prepared according to previous reports [31,32], while block copolymers $PMeDEG_{500}PG1_{344}$ and $PMeDEG_{380}PG2_{32}$ were synthesized by atom transfer radical polymerization (see Supporting Information).

Complexation: Individual aqueous solutions (1 wt%) of polymers and lipid surfactants were prepared, and their respective pH values were adjusted to 3.5 by HCl. Thereafter, the polymer solution was dropped slowly and under continuous stirring into the corresponding surfactant solution by maintaining a stoichiometric ratio of positive ammonium and negative sulfate charges. The mixtures were further stirred for 12 h and then centrifuged at 40 °C, which is higher than the LCSTs in water of both PNiPAM and PMeDEG. To remove eventual excess unbound surfactants, the precipitated samples were reiteratively washed by water (typically twice with water at pH = 3.5). Finally, the samples were dried in ultra high vacuum (10^{-7} mbar) for 48 h before characterization.

Instrumentation: TEM images were obtained with a Philips TEM (CM 100) instrument operating at 80 kV. Samples were cryo-sectioned at −60 °C on a Leica Ultracut UCT ultramicrotome. Sections of ∼50 nm thick were collected on 600-mesh copper grids and then stained by RuO_4 for 20 min. SWAXS measurements were performed at the Elettra Synchrotron facility (Trieste, Italy). A sample-to-detector distance of 176 cm together with a fixed wavelength ($\lambda = 1.54$ Å) provides an effective q-range of 0.1∼7 nm^{-1}. Here q is the scattering vector defined as $q = 4\pi\sin(\theta)/\lambda$, with a scattering angle of 2θ. A 1D gas-filled detector (Gabriel type) was used to collect the scattered X-rays, whose q-scale is calibrated by Ag behenate.

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