

Supramolecular Nano-Architectures Generated from Dendron Based Molecular Hybrids

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ABSTRACT

Novel molecular hybrid system based upon aliphatic polyether dendrons and linear coils is reviewed. The review article deals with their supramolecular self-assembly and charge transport behavior.

Key words : self-assembly, dendron, coil-coil block copolymer, molecular hybrid

Introduction

Supramolecular nano-structures generated by self-assembly of soft-materials are considered an exciting research field due to their peculiar functionalities which can't be realized in molecular level.¹ Thus, it is a great challenge to develop novel nano-structures and control their size and shape.

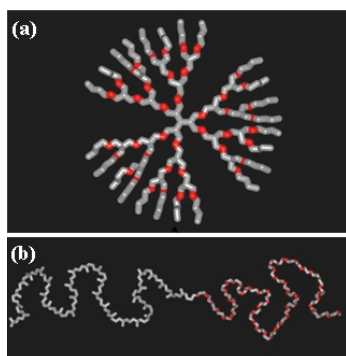


Fig. Schematic molecular architectures of (a) dendrimer and (b) coil-coil block copolymer.

Molecular architecture of an organic building block has

been considered a crucial factor to govern the final nano-structures. To this end, various molecular shapes such as disk,² rod,³ linear⁴ architectures have been employed. Very recently, tree-like molecules, i.e., dendrimers/dendrons, have begun to be utilized as fascinating molecular building units (Fig. 1a). Their regularly branched architecture leads to the intrinsic curvature at the edge of dendritic core that provides a powerful tool for the design of nano-structures with curved interface.⁵ In addition, the compartment of chemically distinct periphery and dendritic core offers a route to well-defined self-assembled nano-structures. However, their typical globule-like or wedge-like molecular structures resulted in only a few supramolecular architectures such as micellar and columnar structures in most cases.⁶

Coil-coil block copolymers have been studied extensively due to their structural simplicity (Fig. 1b). They consist of chemically different two blocks connected by a covalent linkage. Due to the irreversible covalent bonding, two immiscible blocks microphase-separate on nano-meter dimensions. Among a variety of molecular parameters to influence phase behavior, in particular, a volume fraction of a block is believed to be the most important factor regardless of molecular weight as long as microphase separation occurs.⁷ Lamellar, network cubic, columnar, micellar cubic (mostly body centered cubic) were theoretically predicted and ex-

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perimentally found as a function of volume fraction (ϕ).

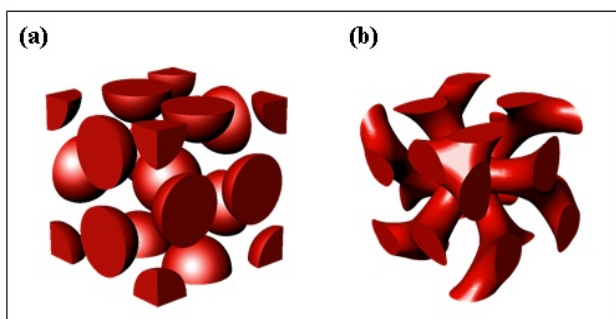


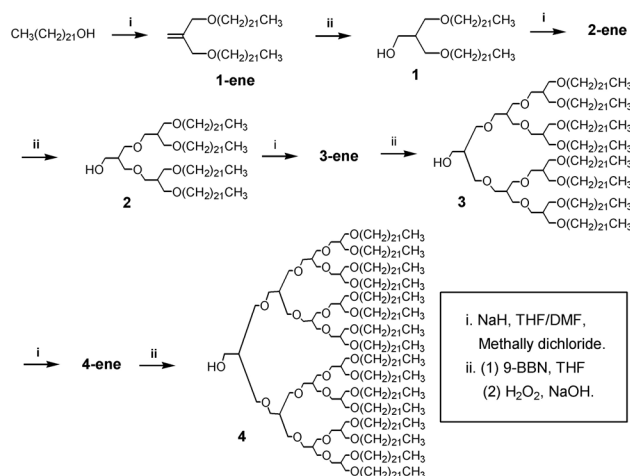
Fig 2. Schematic sketches of (a) A15 micellar and (b) continuous cubic structures. For clarity, only domain structures are represented.

In spite of rapid development of soft materials, dendrimers and coil-coil block copolymers were studied individually. Particularly, they showed different phase behavior. For example, an A15 micellar structure was common in dendrimer system, but it was not observed in coil-coil block copolymers (Fig. 2a). On the other hand, a continuous cubic structure was shown only in coil-coil block copolymers, not in dendrimers (Fig. 2b). Thus, hybrid molecular system to combine these distinct self-assembling soft materials was thought as an exciting research topic to be figured out. In this review, a novel molecular hybrid system which shares dendrimer's and coil-coil block copolymer's characteristics will be briefly introduced by dealing with amphiphilic dendrons based on hydrophilic aliphatic polyether dendritic cores.

I. Amphiphilic Dendrons Based on Aliphatic Polyether-Type Dendritic Cores

Aliphatic polyether type linear coils, e.g., poly(ethylene oxide) (PEO), have been widely used as hydrophilic components because of their high polarity, ion transporting ability and biocompatibility, resulting in self-assembling materials,⁸ ion-conducting polyelectrolytes⁹ and drug-delivery¹⁰ applications. Molecular architectural conversion of the hydrophilic aliphatic ether units from linear to dendritic structure has been tried. In 1998, Fréchet *et al.* reported on the synthesis of hydrophilic aliphatic polyether dendrons which have an almost

similar repeating unit to that of PEO.¹¹ Synthetic scheme consists of Williamson etherification as a generation growth step and hydroboration/oxidation as an activation step. By iteration of these two reactions, the hydrophilic polyether dendron was synthesized up to fifth generation.



Scheme 1. Synthesis of amphiphilic dendrons 1-4.

Amphiphilic character was able to be introduced to aliphatic polyether dendrons. Cho *et al.* attached hydrophobic docosyl chains at the peripheral sites of the polyether dendrons, resulting in amphiphilic dendrons up to generation 4 (Scheme 1).¹² The strong incompatibility between docosyl peripheries and dendritic core is believed to lead to micro-phase separated domain structures on nano-meter dimensions in their solid state. Supramolecular architectures were investigated as a function of dendron generation by using small angle x-ray scattering (SAXS) experiments. Generation 1, 2 and 3 dendrons exhibited lamellar structures with layer periodicities of 6.5, 6.8 and 7.0 nm, respectively. From the molecular modeling and layer thicknesses, the local packing of the hydrophilic and hydrophobic blocks in the lamellar structures was defined, where the docosyl peripheries pack in bilayer fashion and the dendritic cores are interdigitated (Fig. 3a). The local packing modes were elucidated by the minimization of the unfavorable interfacial area between the hydrophilic and hydrophobic blocks. In contrast, generation 4 showed a different supramolecular structure in its solid state. Based on the SAXS pattern, generation 4 was found to organize into a 2-dimensional oblique columnar structure

with lattice parameters $a = 10.2$ nm, $b = 7.1$ nm and $\gamma = 100.3^\circ$ (Fig. 3b). From the non-symmetrical oblique packing, the cross-section of the column is considered elliptical instead of circular. This distortion of the cross-section might be driven by the crystallization of docosyl peripheries along their longer axis.

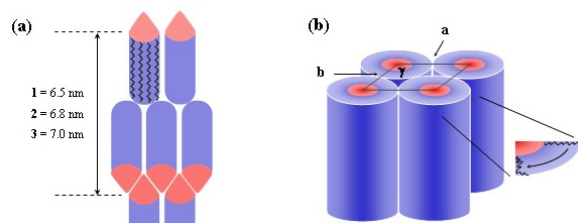


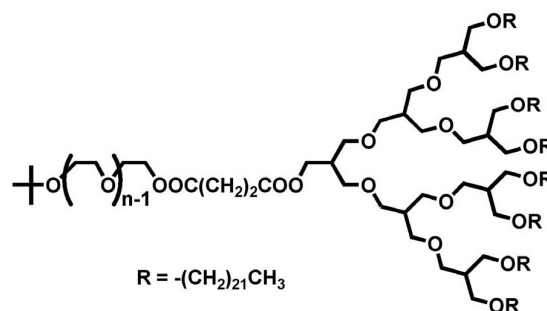
Fig 3. Schematics of (a) the bilayered lamellar structures of generation 1, 2, and 3 and (b) the 2-dimensional oblique columnar structure of generation 4.

As discussed, the dramatic supramolecular structural change was observed moving from generation 3 to 4. This is rationalized by the consideration of the molecular shape change from linear to taper. More curved interface designed in generation 4 inevitably is believed to force the building blocks to adopt the columnar rather than lamellar. The result demonstrated that the intrinsic curvature programmed by the molecular engineering significantly influences the self-assembled nanostructures.

II. Amphiphilic Dendrons Hybridized by Hydrophilic Linear Poly(ethylene oxide)

Early study on the hybridization of dendrons and linear chains was focused on the development of synthetic routes. Fréchet *et al.* reported on the synthesis of hybrid molecules based on benzyl ether dendrons combined by poly(styrene) or poly(ethylene oxide).^{13,14} They employed a variety of coupling reactions and polymerization methods to construct designed hybrid molecules. Besides the synthetic effort, several examples for the self-assembly of hybrid molecules have been studied. Hammond *et al.* have used poly(amidoamine) (PAMAM) as a hydrophobic dendritic block with linear PEOs in hybrid copolymers which can form ultrathin lay-

ered films.¹⁵ Meijer *et al.* employed poly(propylene imine) (PPI) functionalized by hydrophilic carboxylic acid groups onto the surface of PPI, which was connected with poly(styrene) coils.¹⁶ However, what they investigated were the self-assembly behavior in the solid state because the amine based dendrons are not strongly hydrophilic or hydrophobic. Thus, the segregation hardly occurred in the molten state.



5: n = 31	k ₁ 12	k ₂ 63	mc 93	dis
6: n = 96	k ₁ 45	k ₂ 63	hex 114	cc 190 lam 226 dis
7:	k ₁ 16	k ₂ 63	mc 139	dis
8:	k ₁ 44	k ₂ 63	hex 170	cc 190 dec

Scheme 2. Molecular structures of molecular hybrids (5 and 6) and phase behavior of them and their ion-doped samples (7 and 8). The transition temperatures are given in $^\circ\text{C}$; k: crystalline; mc: micellar; hex: hexagonal columnar; lam: lamellar; cc: continuous cubic; dis: disordered; dec: decomposition.

Very recently, Cho *et al.* devised a novel hybrid molecular system by a coupling reaction of the amphiphilic dendron (generation 3) with hydrophilic linear PEO chains (Scheme 2).¹⁷ They prepared two hybrid molecules which have 4600 and 7500 g/mol as molar masses, respectively. Compared to the amine based dendrons, the hydrophilicity of the aliphatic polyether dendritic core is much stronger due to the existence of more polar oxygens, thus the hydrophilic core can be readily miscible with hydrophilic PEO attached at the focal point of the dendron. Furthermore, the growth of the hydrophilic part increases the immiscibility between hydrophilic (dendritic core plus PEO) and hydrophobic (docosyl peripheries) parts. This reinforces the block segregation, finally induces ordered supramolecular structures in the molten state (liquid crystalline phase or mesophase). Cho *et al.*

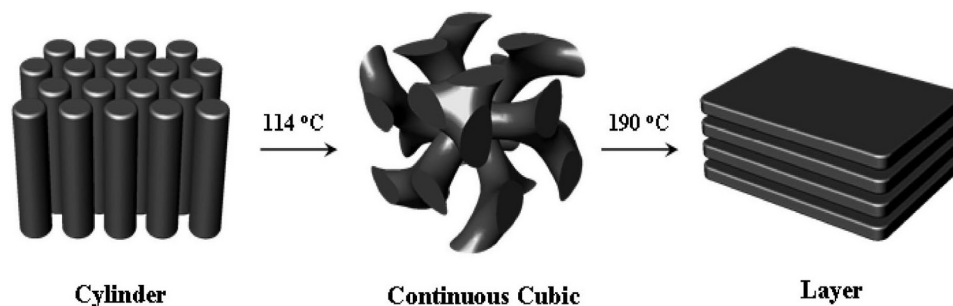


Fig 4. Unusual phase transformation of hybrid molecule 6 in the liquid crystalline state. Only hydrophilic domains in each structure are indicated.

investigated the morphological behavior of the hybrid molecules as a function of PEO length by temperature variable SAXS experiments. Hybrid molecule 5 with the shorter PEO chain showed an A15 micellar phase with $Pm\bar{3}n$ symmetry in the liquid crystalline state, which has been observed in only a few bulk systems with other molecular structures such as taper-shaped small amphiphiles and cone shaped dendrons,^{18,19} and have recently been predicted for branched block copolymer type systems.²⁰ With respect to the local core-shell structure of the micellar phase, the hydrophilic parts occupy the core encapsulated by the hydrophobic peripheries as expected from the inherent interfacial curvature.

In the case of hybrid molecule 6, three different liquid crystalline phases, i.e., hexagonal columnar, continuous cubic and lamellar, were observed upon heating (Fig 4). Most remarkably, the continuous cubic liquid crystalline phase with $Ia\bar{3}d$ symmetry at intermediate temperatures is the most notable feature because the continuous cubic structure has never been observed in dendrimer/dendron systems. In addition, the phase sequence shown in 6 is quite unusual compared to the conventional coil-coil block copolymers where lamellar, continuous cubic and hexagonal columnar were exhibited upon heating.⁴ They speculated that a larger expansion parallel to the interface as a function of temperature of the linear PEO/branched (dendritic) section of the molecules versus the hydrophobic docosyl section is the major driving force for that.

III. Charge Transport Behavior of Lithium ion Doped Hybrid Molecules

The study on charge transport behavior in ordered struc-

tures can provide in-depth microstructural information like dimensionality and connectivity as well as a pathway to materials applications. Cho *et al.* also prepared multi-domain ion-doped materials by complexation of hybrid molecules 5 and 6 with lithium ions and investigated their charge transport behavior as a function of structural dimensionality.¹⁷ In both doped samples, lithium ion concentrations per an ethylene oxide unit were chosen to be 0.02. Thermal stability of the liquid crystalline phases after lithium ion doping was found to be enhanced due to increase of immiscibility between hydrophobic and hydrophilic parts (Scheme 2).²¹ Ion doped sample 7 showed an A15 mesophase as similarly shown in hybrid molecule 5, while lithium ion doped sample 8 displayed hexagonal columnar and continuous cubic mesophases upon heating because of thermal degradation near 195 °C. The existence of the continuous cubic structure after lithium doping is in striking contrast to the case of

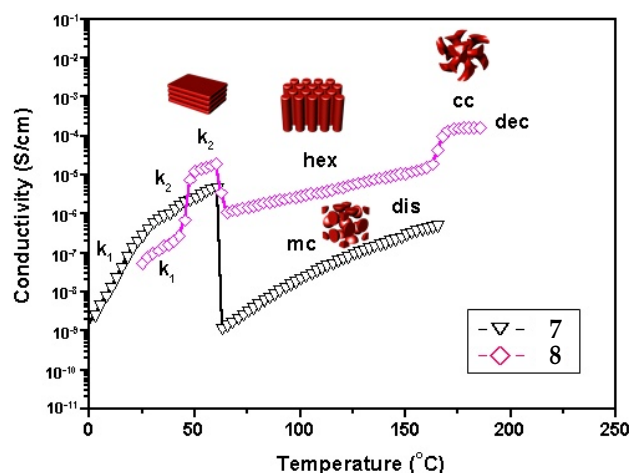


Fig 5. Ion conductivity curves as a function of temperature for 7 and 8.

coil-coil block copolymers where even small amounts of ions have been shown to cause a change from a continuous cubic phase to a hexagonal columnar mesophase.²²

For **7**, the most exciting feature in the conductivity data happened at the docosyl periphery melt transition where the conductivity (σ) drops from 4.6×10^{-6} to 1.2×10^{-9} S/cm (Fig 5 and 6). This significant reduction of the conductivity was interpreted by supramolecular structural change from a two-dimensional lamellar with the molten PEO and crystalline docosyl peripheries to a micellar structure in which hydrophilic micelles are imbedded in a hydrophobic matrix. Therefore, lithium ions are preferentially confined in micelles, inhibiting fast long-range transport. The conductivity transition can be ideally utilized as a supramolecular on-off switch for temperature sensing.

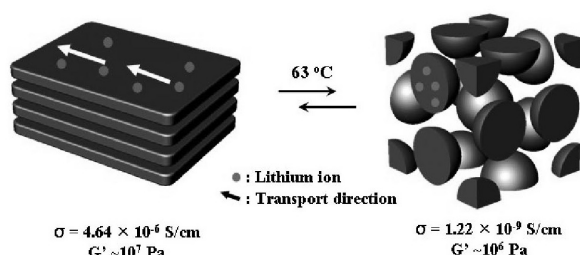


Fig 6. Schematic representation of the lamellar to micellar transition at 63 °C of ion doped sample **7**. Lithium ions are confined in micelles, preventing rapid long-range charge transport. σ and G' indicate the conductivity and elastic modulus values, respectively. Hydrophilic domains in each structure are indicated.

In the case of **8**, the charge transport behavior was more complicated by conforming to the phase transitions upon heating (Fig 5). At the PEO melting transition conductivity rises by 1-2 orders of magnitude due to the increase of PEO chain mobility while at the periphery melting it drops by about an order of magnitude going from the lamellar into the hexagonal mesophase. At the onset of the continuous cubic phase it rises again by an order of magnitude and finally reached values of about 1.5×10^{-4} S/cm at the highest temperatures measured. In particular, the conductivity values of the continuous cubic structure without macroscopic orientation efforts are comparable to those of aligned lamellar structures at similar temperatures and lithium concentrations studied

earlier.^{23,24} In particular, the cubic structures including A15 micellar and continuous cubic phases, they showed the robust mechanical properties ($G' \sim 10^6$ Pa in both phases) which encourage materials applications involving charge transport.

Conclusions

To intrigue the structural fusion of distinct molecular species, i.e., dendrons and linear coils, into single component hybrid molecular system can open possibility to create novel self-assembling functional materials. Through appropriate molecular engineering methods the hybrid molecules can be prepared and the understanding of molecular parameters such as molecularly designed curvature and linear coil length makes it possible to develop a variety of well-defined ordered nano-structures as platforms for functional materials. In the end, the advanced molecular design concept is expected to be applied to exciting research areas ranging from ion conductors, solar cells etc.

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(Received Feb 1, 2005; Accepted Feb 25, 2005)