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Supramolecular organization of block oligomers based on rod-shaped mesogen into liquid crystalline assembly

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The development of novel supramolecular materials with nanometer-scale architectures and the effect of these architectures on the materials' properties are presently of great interest in molecular design. Liquid crystalline assemblies of rod like mesogenic molecules containing flexible coils (rod-coil molecules) provide a facile entry into this area. Rod-coil molecules are demonstrated to self-assemble into a rich variety of different liquid crystalline structures of nanoscale dimensions through the combination of shape complementarity and repulsive interaction of rigid and flexible parts as an organizing force. The mesophases include smectic, hexagonal columnar, bicontinuous cubic, honeycomb like and discrete micellar phases. The unconventional mesophases are induced by changing the rod to coil volume fraction, by controlling the number of rod-coil repeating units and by increasing the rod-coil molecular length. Additionally, the liquid crystalline structures of rod-coil molecules are also discussed with respect to their manipulation by complexation of polyether chains with lithium cations or addition of polar solvent, from lamellar, bicontinuous cubic to hexagonal columnar mesophases.

Introduction

The development of new materials based on self-organizing systems has had a great deal of attention due to their potential in the construction of well-defined supramolecular nanostructures.[1] In particular, the construction of novel supramolecular architectures with well defined shape and size by using rod building blocks is one of the most important subjects in organic materials chemistry because these compounds can exhibit novel electronic and photonic properties as a result of both their discrete dimensions and three dimensional organization.[2]

Rod-coil systems consisting of rigid rod and flexible coil segments are excellent candidates for creating well defined supramolecular structures *via* a process of spontaneous organization.[3] The rod-coil molecular architecture imparts microphase separation of the rod and coil blocks into ordered periodic structures in nano-scale dimensions due to the mutual repulsion of the dissimilar blocks and the packing constraints imposed by the connectivity of each block, while the anisometric molecular shape and stiff rod like conformation of the rod segment imparts orientational organization. In order to balance these competing parameters, rod-coil molecules self-organize into a variety of supramolecular structures which can be controlled by variation of the rod to coil volume fraction.[4] Typical examples of the main types of rod-coil molecules forming supramolecular structures with mesophase are shown in Fig. 1. In contrast to coil-coil block molecules, microphase separated structures in rod-coil block molecules can form, even though the molecular weight of each block is very small, due to large chemical differences between each block. At the interface separation of the rod and coil domains, the relatively smaller area per junction favored by the rod block results in chain stretching of the coil block, which is energetically unfavorable. Considering the energetical penalties associated with chain stretching of the coil block and interfacial energy resulting from the interfaces separating the rod and coil domains, the theoretical works on rod-coil systems have predicted nematic–smectic A and smectic A–smectic C transitions in the melt.[4a,b] Other theoretical works have dealt more with the phase behavior of rod-coil diblocks in a selective solvent for the coil segment.[4d] These works have predicted various micellar structures for sufficiently large coil volume fraction, in addition to the familiar lamellar structures (Fig. 2). This article will present an overview of recent work in designing rod-coil systems based on flexible oligo(alkylene ether) coils and demonstrating their self-organization capability into a variety of liquid crystalline phases. In addition, lyotropic liquid crystalline phase behaviors of these rod-coil molecules will be discussed as well as the new opportunities they offer for materials applications.

1. Rod-coil diblock systems

It is well known that the connection of oligo(alkylene ether) chains into a calamitic rigid rod at the terminals destabilize the thermotropic mesophases.[5] However, mesomorphic properties

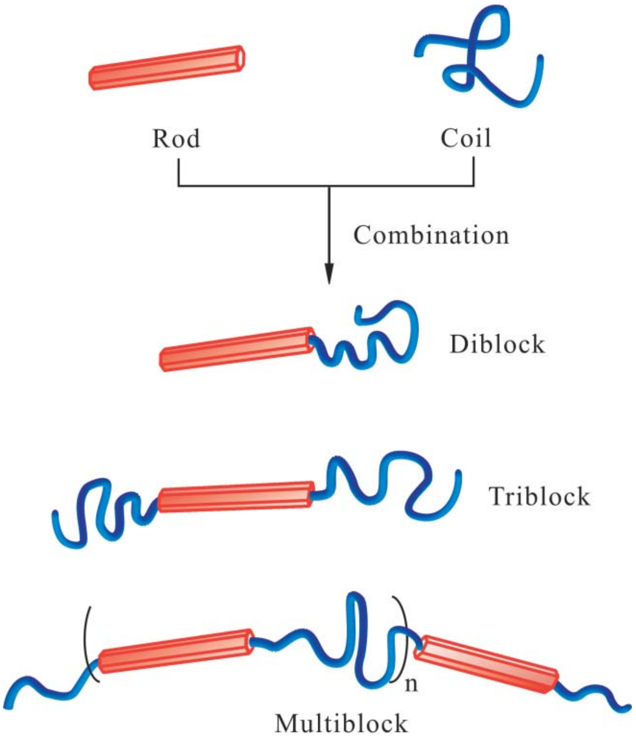

Fig. 1 Typical examples of rod-coil molecules.

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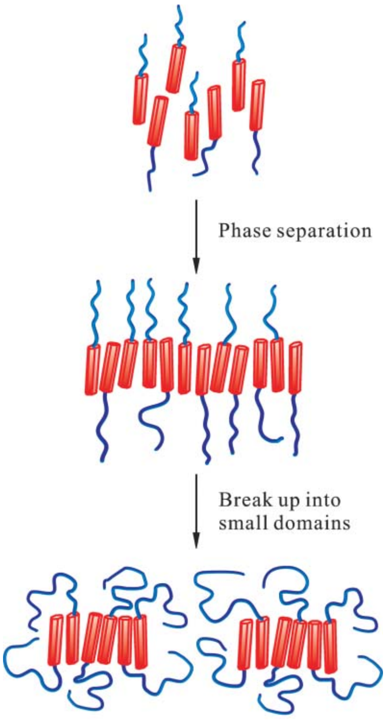
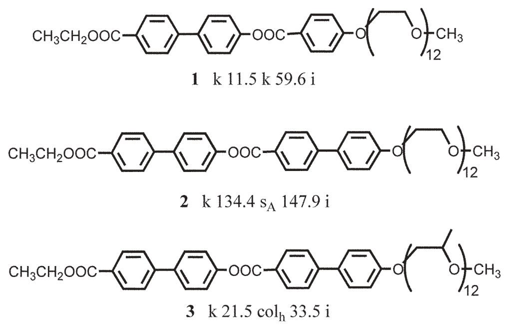


Fig. 2 Possible arrangements of the rod-coil molecules with increasing volume fraction of coil segments.

can be obtained by molecules with extended rigid rod segments as a result of the microphase segregation between the polar flexible oligo(alkylene oxide) ethers and rigid rod segments.[3a,6] The rod-coil molecules based on three phenyl units (**1**) as a rod segment, for example, exhibit only an isotropic phase after crystalline melting,[7] while the molecule **2** based on four phenyl units as a rod segment shows a smectic A mesophase.[6] In the case of a rod-coil molecule with short rod-length, the coil segment may couple with the anisotropic rod owing to the relatively high miscibility between coil and rod segments, which can disturb the anisotropic aggregation of rod blocks. However, as the rod-length increases, the immiscibility between chemically different flexible and rigid chains increases. This allows the increasing lateral intermolecular interactions of rigid segments. As a result, a layered smectic liquid crystalline phase can be induced, as exhibited by **2**. If the coil volume fraction increases, smectic ordering of rod segments becomes unstable due to a large space crowding; consequently, the lamellar structure will transform into cylindrical micelles which allows more volume for coils to explore. In contrast to the molecule **2**, the molecule **3** based on poly(propylene oxide) (PPO) coil shows a hexagonal columnar (col$_h$) structure.[8] This large structural variation between molecularly similar systems should be caused by the larger spatial requirement of the bulkier PPO coil in comparison with the poly(ethylene oxide) (PEO) (see Chart 1).



1 k 11.5 k 59.6 i

2 k 134.4 s$_A$ 147.9 i

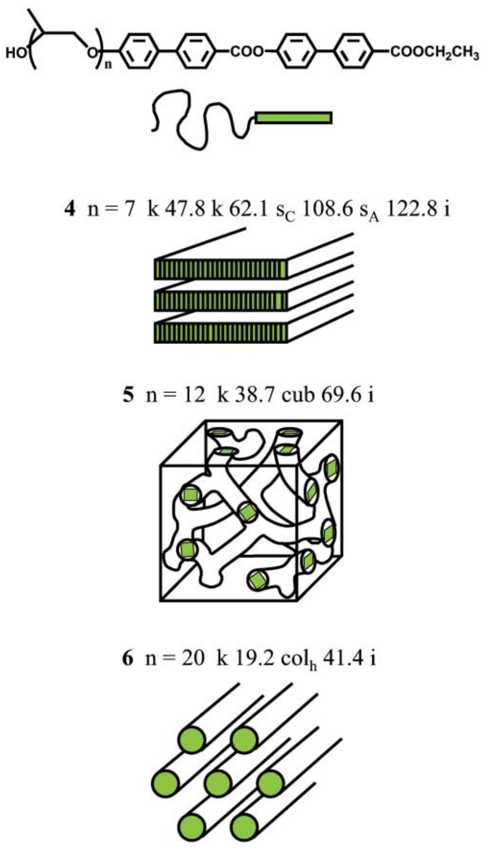
3 k 21.5 col$_h$ 33.5 i

Chart 1

In a more systematic work on the influence of the coil length on phase behavior, rod-coil molecules (**4–6**) with PPO having different degrees of polymerization but an identical rod segment were prepared.[9,10] A dramatic structural change in the mesophase of this rod-coil system was observed with variation in the coil length as determined by a combination of techniques consisting of differential scanning calorimetry (DSC), optical polarized microscopy and X-ray scattering. Rod-coil molecule (**4**) with 7 propylene oxide (PO) repeating units exhibits layered smectic C and smectic A phases, while rod-coil molecule (**5**) with 12 PO repeating units exhibits an optically isotropic cubic phase. This structure was identified by X-ray scattering method to be a bicontinuous cubic (cub) phase with *Ia3d* symmetry. Further increasing the coil length induces a hexagonal columnar mesophase as in the case of the molecule (**6**) with 20 PO repeating units (Fig. 3). Organization of the rod-coil molecules into a cross sectional slice of a cylinder for cubic and columnar phases gives rise to an aromatic core with approximately square cross section. The sizes and periods of these supramolecular structures are typically in a range of less than 10 nm. This structural variation can be explained by considering the fact that increasing coil volume fraction leads to the structure with larger interfacial area, similar to well known conventional diblock copolymer phase behaviors.[11]

2. Rod-coil triblock systems

If a chemically distinct hydrophobic chain is attached to the opposite end of the rod segment, segregation of incompatible chain ends takes place and leads to an ordered phase composed of three distinct sublayers.[12] In contrast to that of diblock molecules based on PEO coil which show isotropic or smectic phase depending on the coil length,[6,7] the ABC triblock molecule exhibits hexagonal columnar mesophases.[13] Molecule **8**



4 n = 7 k 47.8 k 62.1 s$_C$ 108.6 s$_A$ 122.8 i

5 n = 12 k 38.7 cub 69.6 i

6 n = 20 k 19.2 col$_h$ 41.4 i

Fig. 3 Schematic representation of liquid crystalline structures of the rod-coil diblock molecules. (k; crystalline, s$_C$; smectic C, s$_A$; smectic A, cub; bicontinuous cubic, col$_h$; hexagonal columnar, i; isotropic).

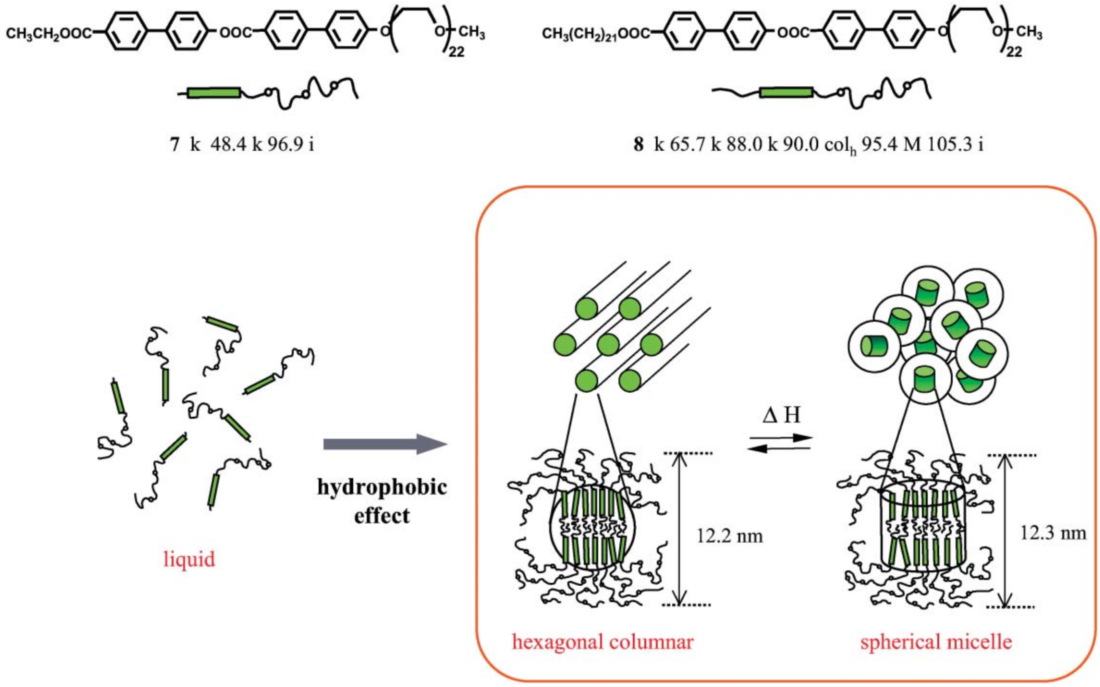


Fig. 4 Illustration of the induction of the mesophase in rod-coil molecules through hydrophobic force. (k; crystalline, col$_h$; hexagonal columnar, M; spherical micelle, i; isotropic).

with 22 ethylene oxide (EO) repeating units, for example, exhibits a hexagonal columnar mesophase which, in turn, undergoes transformation into a discrete spherical micellar structure in which rod segments are packed into discrete bilayer lamellar structure that is encapsulated with PEO coils (Fig. 4). Small-angle X-ray diffraction in the optically isotropic state revealed a strong primary peak together with a broad peak of weak intensity at about 1.8 relative to the primary peak position, indicating that the spatial distribution of centers of the spherical micelles has only liquid-like short range order, most probably due to random thermal motion of spherical micelles.[14] From the observed primary peak of X-ray diffraction, the diameter (d) of spheres was estimated to be approximately 12 nm. Considering that diblock rod-coil molecule **7** with 22 EO repeating units shows only an isotropic phase after crystalline melting,[15] it is likely that hydrophobic force plays an important role in the self-assembly of the molecules into discrete nanostructures.

In the case of a symmetric coil-rod-coil molecule, the rod segment is connected with coil segments at both ends. This gives rise to the formation of the liquid crystalline structure with higher interfacial area in comparison with rod-coil diblock systems at similar coil volume fraction. For example, the triblock molecule **9** with coil volume fraction, $f_{\text{coil}} = 0.47$ exhibits a bicontinuous cubic phase instead of a smectic phase.[16] Similar to diblock rod-coil systems, increasing the volume fraction induces a hexagonal columnar mesophase as in the case of **10**.

Remarkably, molecules with a longer length of coil (9–22 PO repeating units) assemble into discrete supramolecular aggregates that spontaneously organize into a 3D tetragonal phase with a body-centered symmetry in the solid state and mesophase as determined by small-angle X-ray scattering. Based on X-ray data and density measurement, the inner core of the supramolecular aggregate is constituted by the discrete rod bundle with a cylindrical shape 5 nm in diameter and 3 nm in length that is encapsulated with phase-separated PPO coils, and this gives rise to the formation of non-spherical oblate aggregates (Fig. 5). The supramolecular rod bundles subsequently organize into a 3D body-centered tetragonal symmetry. The oblate shape of supramolecular aggregates is believed to be responsible for the formation of unusual 3D tetragonal phases (M$_{\text{tet}}$). This unique phase behavior mainly originates from the anisotropic aggregation of rod segments with their long axes within microphase separated aromatic domains. Consequently, rod bundles with puck-like cylindrical shape would give rise to oblate micelles which can pack more densely into an optically anisotropic 3-dimensional tetragonal lattice, rather than an optically isotropic cubic lattice. These results

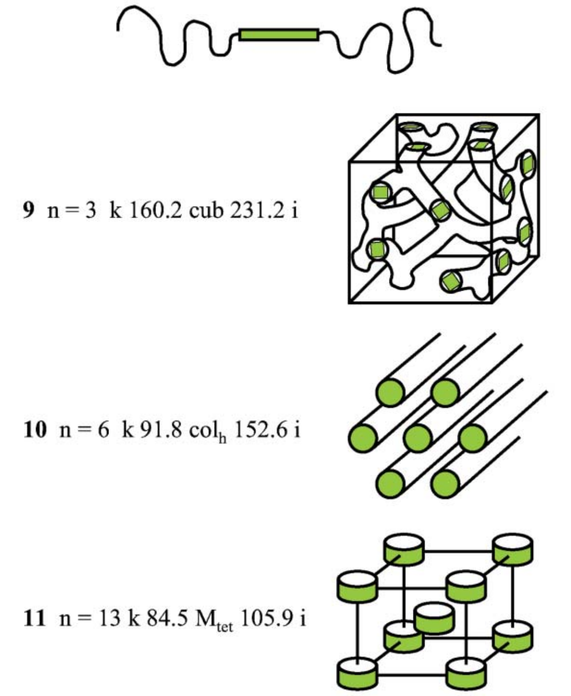
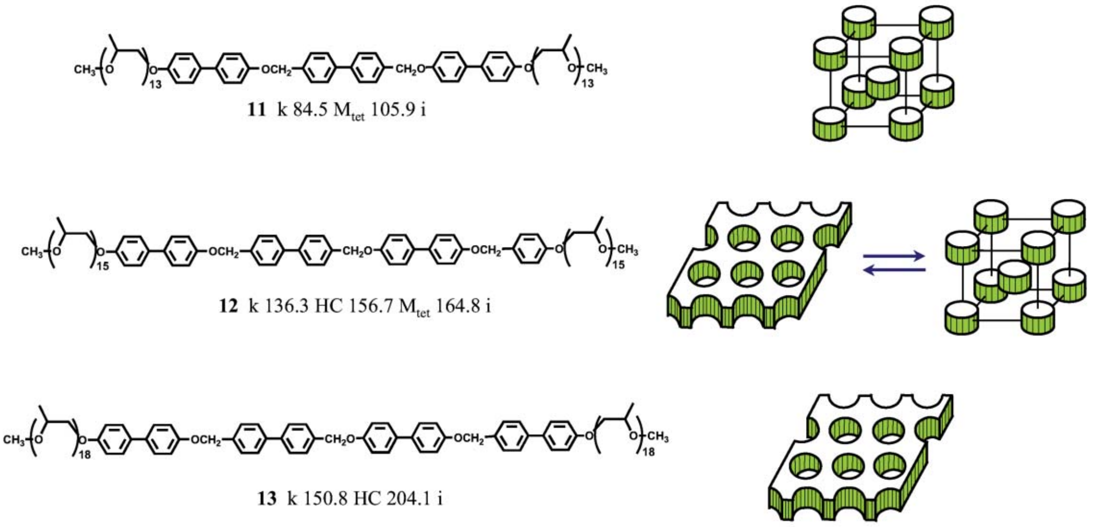


Fig. 5 Schematic representation of mesophases of the ABA coil-rod-coil triblock molecules. (k; crystalline, cub; bicontinuous cubic, col$_h$; hexagonal columnar, M$_{\text{tet}}$; body-centered tetragonal structure, i; isotropic).



11 k 84.5 M_{tet} 105.9 i

12 k 136.3 HC 156.7 M_{tet} 164.8 i

13 k 150.8 HC 204.1 i

Fig. 6 Structural variation of the coil-rod-coil triblock molecules with $f_{rod} = 0.22$ depending on the molecular length. (k; crystalline, HC; hexagonal perforated honeycomb like layered, M_{tet}; body-centered tetragonal, i; isotropic).

demonstrate that the linear combination of flexible coils at both terminals of the rod segment leads to discrete micellar aggregates which organize into a body centered tetragonal liquid crystalline phase above a certain coil volume fraction.

Another possible way to manipulate the liquid crystalline structure should be provided by systematic variation in the rod length at the constant rod to coil volume ratio. In particular, increasing the length of the rod segment should disturb the assembly of the rigid rod segments into discrete bundles due to larger rod to rod interactions. As mentioned above, the triblock molecule **11** based on three biphenyl units exhibits a tetragonal micellar liquid crystalline phase. In great contrast, the rod segment of **12** based on longer chain length self-assembles into a honeycomb like layered liquid crystalline phase (HC) as a lower temperature mesophase in which hexagonally ordered perforations within a layer are filled by coil segments (Fig. 6).[17] These layers, in turn, are stacked spontaneously in an ABAB fashion to generate a 3D hexagonal order. A DSC heating trace of **12** shows a crystalline melting transition at 136 °C, followed by a birefringent liquid crystalline phase that undergoes transformation into another liquid crystalline phase at 157 °C. On heating to 157 °C, the honeycomb like mesophase transforms into a 3D tetragonal micellar liquid crystalline phase. On slow cooling from the isotropic liquid, the formation of fern-like domains growing in four directions with an angle of approximately 90° which coalesce into a mosaic texture could be easily observed on the polarized optical microscopy, indicating the presence of a 3D tetragonal mesophase (Fig. 7a).[16,17]

Further increasing the length of rod segment suppresses the formation of a 3D tetragonal mesophase, and also induces only a honeycomb like liquid crystalline phase as in the case of the molecule **13**. On slow cooling from the isotropic liquid, dendritic domains with striations merge into an arced pseudofocal conic texture, indicative of a lamellar phase with in-plane hexagonal order (Fig. 7b).[17,18] These results indicate that the self-assembled 3D liquid crystalline phase changes significantly from organized rod-bundles in a coil matrix (tetragonal structure) to organized coil perforations in rod layers (honeycomb structure) on increasing the rod-length. This direct structural inversion is also accompanied by changing temperature. Therefore, changing temperature produces an effect similar to varying the molecular length. This example indicates that the molecular length in rod-coil systems also has a large impact on the organized structure formed by self-assembly of rod-coil molecules.

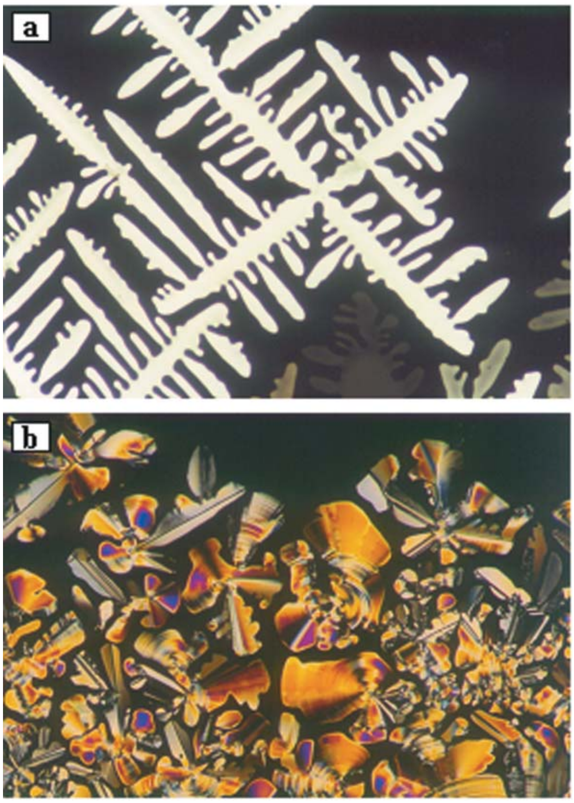
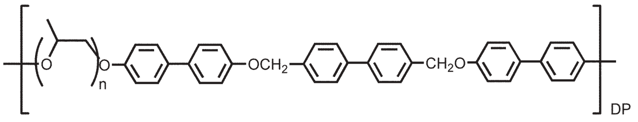


Fig. 7 Optical polarized micrographs (100 ×) of the textures by (a) the body centered tetragonal mesophase of **12** at 156 °C and (b) the honeycomb mesophase of **13** at 195 °C on the cooling scan.

3. Rod-coil multiblock systems

The rod-coil approach as a means to manipulate supramolecular structure as a function of rod volume fraction was reported to be extended to main chain multiblock copolymer systems which generate bicontinuous cubic and hexagonal columnar mesophases depending on the rod-to-coil volume fraction.[19] For example, rod-coil multiblock copolymer **14** based on short length of coil (rod volume fraction, $f_{rod} = 0.38$) exhibits a bicontinuous cubic mesophase, while copolymer **15** based on higher coil volume fraction ($f_{rod} = 0.29$) shows a hexagonal columnar mesophase (Chart 2).

In contrast to this, another strategy to manipulate the supramolecular structure at constant rod-to-coil volume ratio



14 n = 12 g -29.8 k 86.2 cub 136.5 i

15 n = 18 g -56.6 k 85.4 col_h 117.8 i

Chart 2

can also be accessible by varying the number of grafting sites per rod which might be closely related to the grafting density at the interface separating rod and coil segments. For this reason, **16**, **17** and **18** with rod-coil repeating units consisting of three biphenyl units connected by methylene ether linkages as the rod block and PPO with 13 PO repeating units as the coil block were prepared.[20]

All of the oligomers are self-organized into ordered supramolecular structures that differ significantly on variation of the number of repeating units as confirmed by X-ray scattering. The molecule **16** shows a bicontinuous cubic liquid crystalline structure. In contrast, the molecule **17** shows a 2D rectangular crystalline and a tetragonal columnar (col_t) liquid crystalline structure, while the molecule **18** displays a hexagonal columnar structure in both the solid state and mesophase (Fig. 8). These results show that self-assembled liquid crystalline structures, from 3D bicontinuous cubic, 2D tetragonal to 2D hexagonal lattices are formed by rod-coil structures that differ only in the number of repeating units.

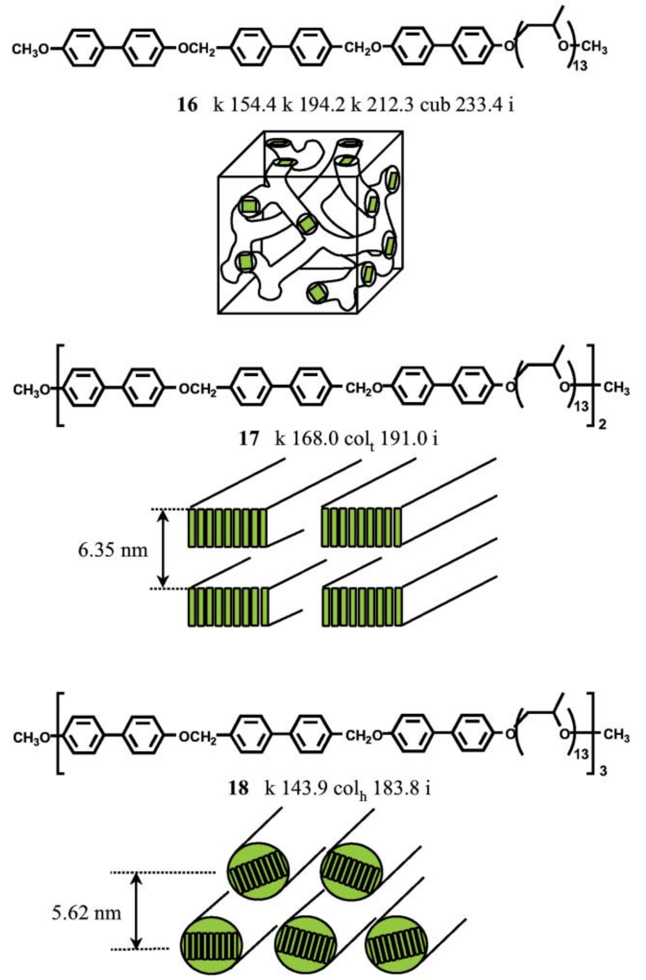


Fig. 8 Schematic representation of mesophases of the rod-coil multiblock molecules depending on the rod-coil repeating unit. (k; crystalline, cub; bicontinuous cubic, col_t; tetragonal columnar, col_h; hexagonal columnar, i; isotropic).

This interesting variation of self-assembled structures, at an identical rod to coil volume ratio, can be explained by considering the density of grafting sites at the interface separated by rod and coil. On increasing the number of rod-coil repeating units, the density of grafting sites at the interface will be increased due to an increase in the average number of coils grafted to a rod, which results in a strong entropic penalty associated with coil stretching at the rod-coil interface. To reduce this coil stretching, a bicontinuous cubic structure of the monomer would break up into 2D cylindrical domains in which less confinement and deformation of coil segments occur. These results demonstrate that systematic variation of the number of repeating units in the rod-coil multiblock oligomers can provide a strategy to regulate the liquid crystalline phase, from bicontinuous cubic, 2D tetragonal columnar to 2D hexagonal columnar structure.

4. Supramolecular structures from binary mixtures

Rod-coil block molecules are a type of amphiphile that can self-assemble into a variety of ordered nanostructures in a selective solvent.[21–23] In solvents that selectively dissolve only coil blocks, rod-coil molecules can form well-defined nanostructures with rod domain consisting of the insoluble block. This results in an increase of the relative volume fraction of the coil segment relative to the rod segments, which gives rise to various supramolecular structures. Particularly, poly(alkylene oxide) as the coil block of rod-coil molecule has additional advantages due to its complexation capability with alkali metal cations, which can provide an application potential for solid polyelectrolytes with various supramolecular structures.[24,25]

Control of the supramolecular structure in rod-coil molecular systems containing either PEO or PPO coils and induction of ordered structures are possible through selective complexation with lithium ions. For example, the complexes of **2** with 0.0–0.15 mol CF_3SO_3Li per ethylene oxide unit ($[Li^+]/[EO]$) exhibit only a smectic A mesophase, while the complex with $[Li^+]/[EO] = 0.20$ shows an optical isotropic cubic phase in addition to a high-temperature smectic A phase.[26] The complex with $[Li^+]/[EO] = 0.25$ exhibits only a bicontinuous cubic phase and the smectic A phase is suppressed for this complex. On melting of complexes with $[Li^+]/[EO] = 0.30$ and 0.35, a cubic phase is also formed, however, further heating gives rise to a 2D hexagonal columnar mesophase. Complexes with $[Li^+]/[EO] = 0.40$–0.70 exhibit only a columnar phase. As shown in the binary phase diagram of Fig. 9, the supramolecular structure in the mesophase changes successively from smectic A through bicontinuous cubic to hexagonal columnar structures as the salt concentration increases.

Complexation of ABC rod-coil block molecules with CF_3SO_3Li also induces liquid crystalline phases.[27] The coil-rod-coil triblock molecule (**19**) based on PPO and docosyl coil segments was observed to show only an isotropic liquid upon melting.[27] In contrast, the addition of greater than 0.10 mol CF_3SO_3Li per propylene oxide unit ($[Li^+]/[PO]$) induces the formation of a liquid crystalline order (Fig. 10). The complex with $[Li^+]/[PO] = 0.10$ exhibits a crystalline melting transition followed by a smectic A mesophase. By increasing salt concentration as in the case of complexes with $[Li^+]/[PO] = 0.15$–0.30, the smectic A phase is suppressed, instead, they exhibit a hexagonal columnar mesophase. The induction of ordered structure in the mesophase of the rod-coil molecule by complexation is most probably due to enhanced microphase separation between hydrophobic blocks and PPO block caused by transformation from a dipolar medium to an ionic medium in PPO coil segments.

The complexation of ABC coil-rod-coil triblock molecules with CF_3SO_3Li also induces oblique and rectangular columnar liquid crystalline structures (col_r) (Fig. 11). The ABC coil-rod-coil triblock molecule **20** exhibits only a smectic C liquid

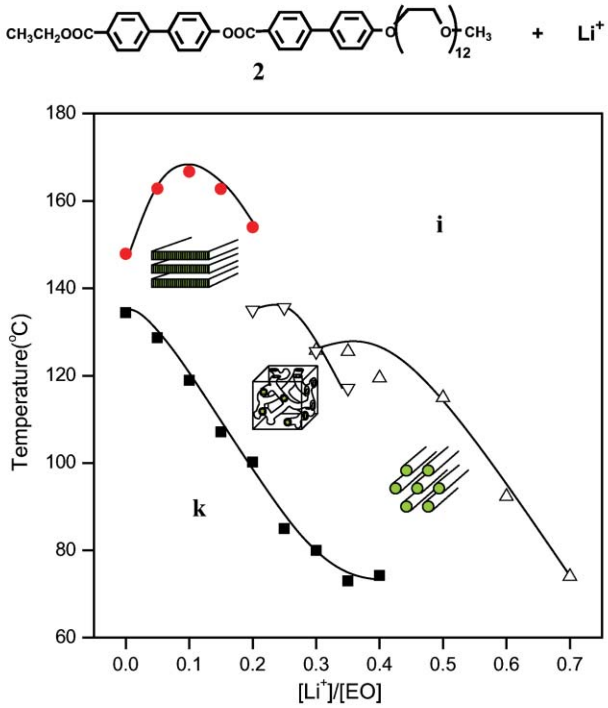


Fig. 9 Phase diagram of the complexes of **2** with CF_3SO_3Li.

crystalline phase.[28] On the contrary, the complexes with $[Li^+]/[PO] = 0.10–0.30$ exhibit successively oblique columnar, rectangular columnar and smectic A mesophase on heating. The lamellar structure observed in the smectic C phase of **20** is the most efficient packing of rods and grafted chains, similar to that of smectogens with long alkyl chains. The added CF_3SO_3Li will be selectively dissolved in the micro-separated PEO coil segments of **20** through ion-dipole interactions. Lamellar ordering of rods would confine junctions within a flat interface of rods and coils with a relatively high density of grafting sites, forcing a strong stretching of the coils away from the interface; the system then becomes entropically unfavorable. Consequently, the lamellar structure of ABC coil-rod-coil triblock molecules may break apart into a rectangular columnar phase in which coil stretching is reduced.

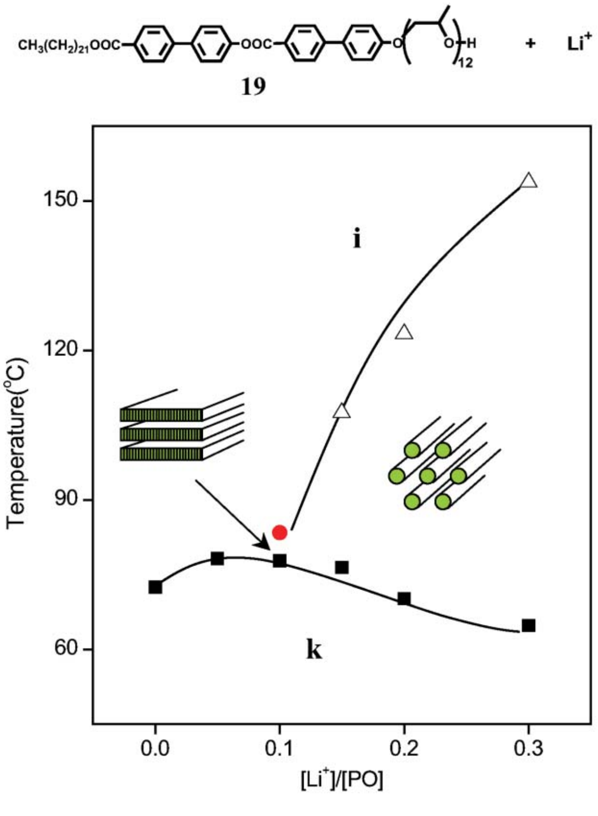


Fig. 10 Phase diagram of the complexes of **19** with CF_3SO_3Li.

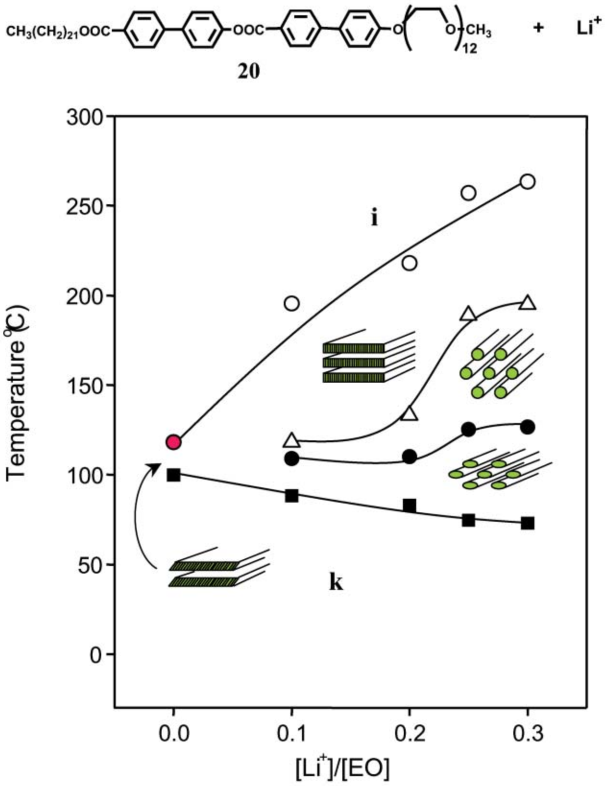


Fig. 11 Phase diagram of the complexes of **20** with CF_3SO_3Li.

These complexed ABC triblock molecules have another phase transition from a columnar to a smectic phase on heating. It is a somewhat striking result from the viewpoint of phase behavior of rod-coil molecules, because most rod-coil molecules show a lamellar to columnar phase transition with increasing temperature or with increasing coil length.[3a] The packing structure of complex with $[Li^+]/[EO] = 0.25$ in the rectangular columnar phase is a bilayered structure, as shown in Fig. 12, *i.e.* the inner core of the cylinder is composed of alkyl chains and two discrete aromatic cores with a rectangular cross-section, while the lithium complexed PEO chains fill the outer intercylinder matrix. On heating, this bilayered structure collapses, and a monolayered lamellar structure forms (Fig. 13). In this monolayer structure, alkyl chains, PEO chains and CF_3SO_3Li are mixed with one another. The free energy of mixing can be expressed as a sum of two contributions: enthalpy and entropy of mixing. At ambient temperature, the hydrophobic docosyl chain would not mix with hydrophilic PEO and polar CF_3SO_3Li. So the enthalpy of mixing should act unfavorably in this $col_r–s_A$ transition. On the other hand, this mixing generates entropies of various kinds: translational entropy of CF_3SO_3Li ion, rotational entropy (flipping) of **20**, and mixing entropy between the docosyl chains and CF_3SO_3Li. Because the entropy finally dominates with increasing temperature, this bilayered cylinder to monolayer smectic transition may be feasible. Thus, due to the added CF_3SO_3Li, a columnar to lamellar phase transition takes place in the complexed ABC triblock molecule.

Rod-coil molecular architecture containing PEO endows an amphiphilic character as discussed earlier, and thus hydrophilic solvents such as acrylamide would be selectively dissolved in the microphase-separated coil domains, which gives rise to a variety of supramolecular structures. Polymerization of

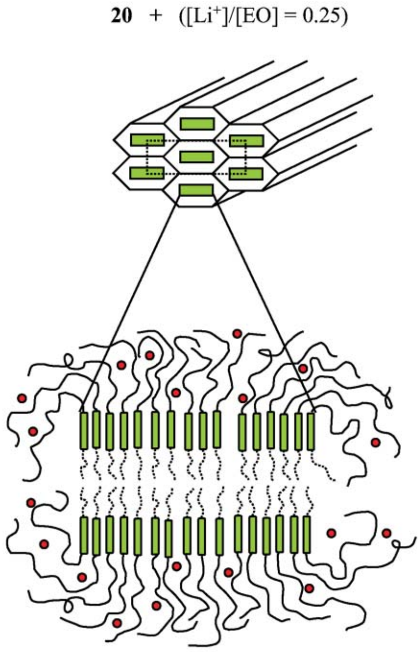


Fig. 12 Schematic representation of the formation of the rectangular columnar phase of the complex of **20** with $[Li^+]/[EO] = 0.25$.

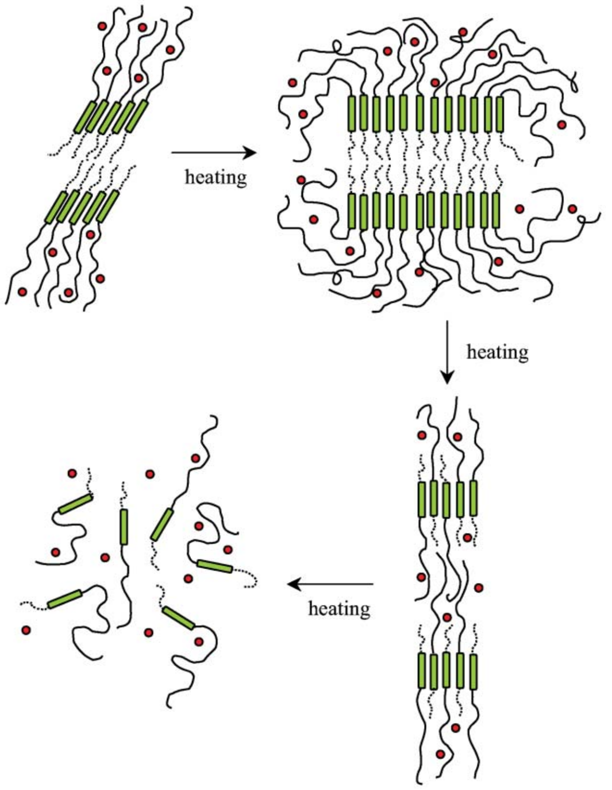


Fig. 13 Schematic representation of the transformation of the self-assembled structure of the complex of **20** with $[Li^+]/[EO] = 0.25$ on increasing temperature.

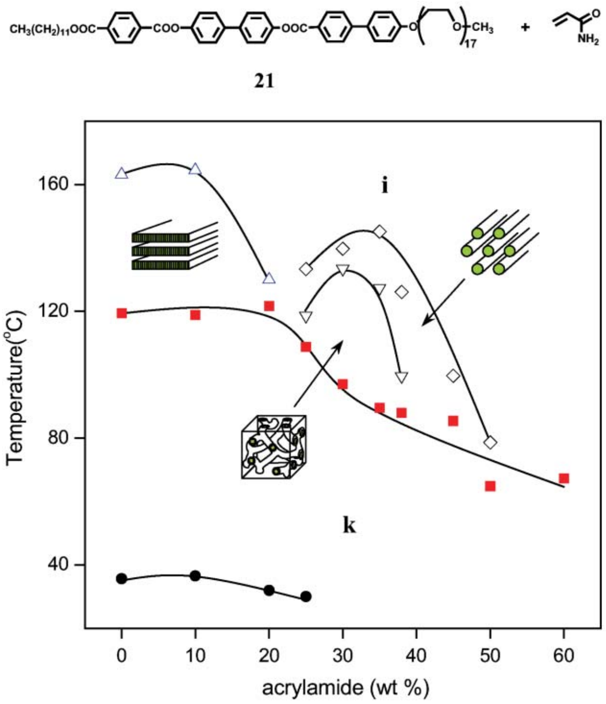


Fig. 14 Phase diagram of the complexes of **21** with acrylamide.

acrylamide solution in an ordered state can give rise to ordered nanocomposite materials. Similar to rod-coil complexes with CF_3SO_3Li, the acrylamide solution of a rod-coil molecule **21** shows a phase transition from layered smectic to columnar phase with a bicontinuous cubic phase as the intermediate regime with increasing acrylamide content (Fig. 14).[29] More importantly, this organized polymerizable solution can be used for construction of ordered aromatic–aliphatic nanocomposite materials. Thermal polymerization of the hexagonally ordered solution containing acrylamide and 0.5 mol% of 2,2′-azoisobutyronitrile with respect to acrylamide at 130 °C for 24 h produces a hexagonally ordered nanocomposite material with a primary spacing of 4.8 nm (Fig. 15).

Conclusions

This article shows a variety of different mesophases can be formed by self-assembly of mesogenic rod building blocks with terminally attached polyether coils. This unique phase behavior seems to originate from a combination of organizing forces including the mutual repulsion of the dissimilar blocks and

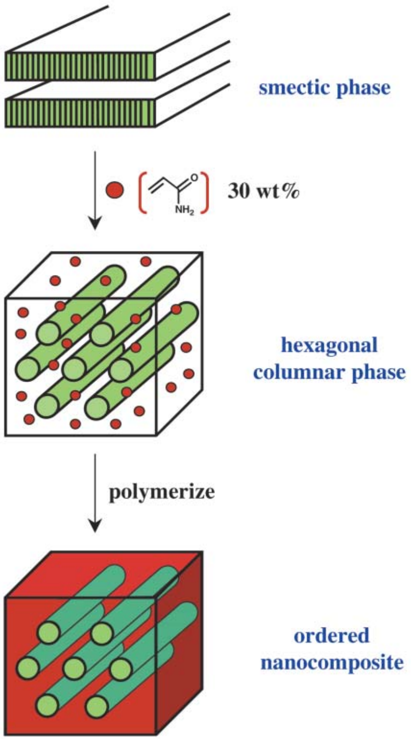


Fig. 15 Schematic representation for the induction of a hexagonal columnar phase by addition of acrylamide and subsequent formation of ordered nanocomposite through polymerization.

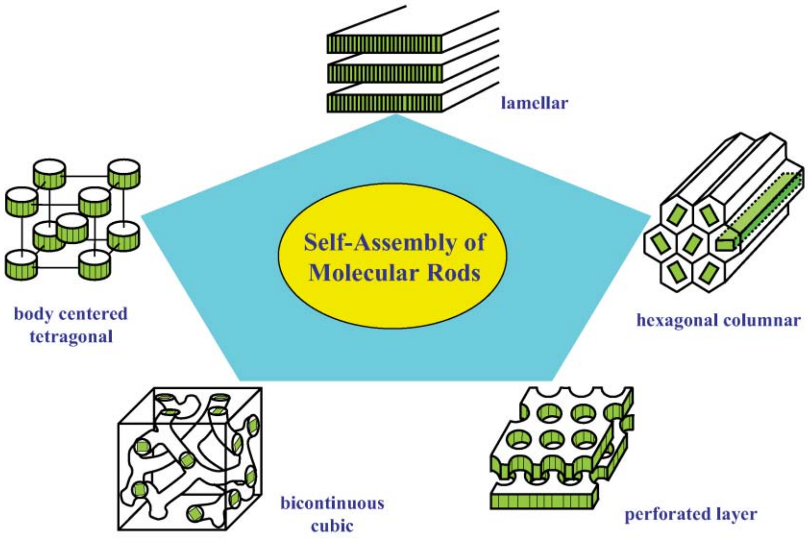


Fig. 16 Schematic representation of various liquid crystalline phases formed by self-assembly of rod-coil molecules.

packing constraints imposed by the connecting of each block, and the tendency of the rod block to form orientational order. The liquid crystalline phase formed by rod segments in rod-coil systems include 1D smectic, 2D columnar, 3D bicontinuous cubic, 3D micellar tetragonal and even 3D honeycomb phases (Fig. 16).

Another remarkable feature of rod-coil molecules is their amphiphilic characteristics that show the tendency of their lipophilic and lipophobic parts to segregate in space into distinct microdomains. Depending on the solvent content and polarity, rod-coil molecules self organize into a wide variety of different mesophases from lamellar, bicontinuous cubic to hexagonal columnar phases. It can also be expected that many more rod-coil systems which can assemble into novel supramolecular structures such as giant vesicles or artificial cells for possible applications as diverse as self-assembled materials for nanotechnology, periodic porous materials, biomimetic materials and optoelectronic nanomaterials will be developed in the near future.

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This Feature Article is dedicated to Professor Jung-Il Jin of Korea University on the occasion of his 60th birthday.

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