



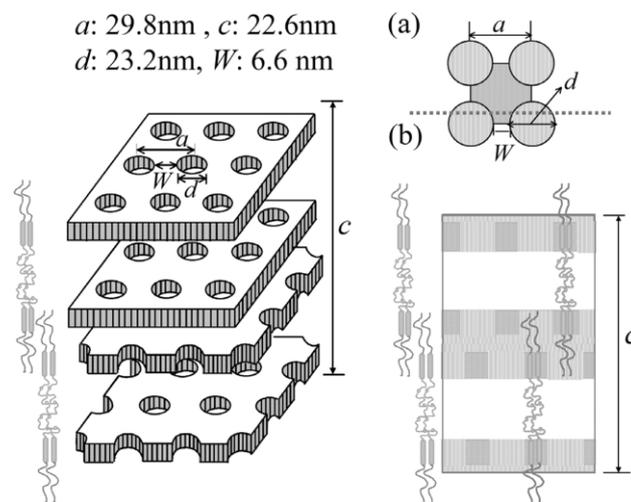
monomer and tetramer in the crystalline phases display three reflections in the spacing ratio of 1:2:3 in the small-angle region, whereas a number of sharp reflections are observed in the wide-angle region, indicative of a lamellar crystalline structure [Fig. 2(b)]. The small-angle peak broadening may arise from the effect of a small crystal size induced by the formation of a large number of nuclei of rod crystals on cooling. The lattice parameters measured from the small-angle XRD experiments indicate that both molecules crystallize into a bilayered lamellar structure. The rod building blocks within the aromatic domains are considered to pack into a monoclinic symmetry, as confirmed by wide-angle XRD patterns.† In the melt state of a rod block, both molecules display a non-lamellar liquid crystalline phase. Previously, XRD studies have demonstrated that the monomer exhibits a hexagonal columnar mesophase with a lattice parameter of 12.2 nm.<sup>4</sup> This molecule also exhibits a random micellar mesophase with a diameter of 12.3 nm as a higher temperature mesophase.<sup>4</sup>

In great contrast, the rod segments of the tetramer self-assemble into a tetragonally perforated layered structure upon melting of the rod segment, in which perforations are filled by hydrophobic docosyl chains. The small-angle XRD pattern of the tetramer at 97 °C shows a number of well-resolved reflections, which indicate the existence of a highly ordered structure as shown in Fig. 2(b). On heating, the tetragonally ordered structure transforms into a 2-D hexagonal columnar structure with a lattice constant  $a = 12.1$  nm. This phase identification is further supported by polarized optical microscopic observations, showing a characteristic pseudo-focal conic texture.† Thus, the tetragonal structure in these molecules exists as an intermediate structure between the lamellar and 2-D hexagonal columnar structures. This is in contrast to the thermal behavior of the tetragonal phase exhibited by other rod-coil systems reported previously. Another interesting point to be noted is that the peak intensity associated with the (002) reflection appears to be the most intense [see Fig. 2(b)], implying that the fundamental structure is lamellar. This is also in opposition to that of the tetragonal structure based on discrete bundles exhibited by other rod-coil molecules.

Taking into account the facts described above and the thermal behavior exhibited for an intermediate structure between the lamellar and columnar structures, this 3-D structure can be best described as a system of perforated rod layers with in-plane tetragonal packing of coil perforations. Based on the lattice parameters, the calculated rod length of 2.2 nm by Materials Studio Software, and the molecular densities, the perforation size diameter is estimated to be 23.2 nm.

Fig. 3 illustrates the possible model responsible for the formation of the tetragonally perforated lamellar structure ( $I4/mmm$  space group symmetry). The supramolecular structure consists of liquid crystalline rod layers with in-plane tetragonally ordered coil perforations stacked in an AB-BA sequence. The perforations are likely to be filled by docosyl chains, most probably due to the large chemical difference between the rod and poly(ethylene oxide) coil segments. The 3-D lattice is built up of two interpenetrating centred 3-D lattices. The small-angle XRD pattern at the optically isotropic phase at high temperature above the hexagonal columnar structure exhibits a strong reflection together with a weak reflection at about 1.8 relative to the primary peak position, similar to that of monomer. Considering liquid-like micelles, the diameter of the sphere can be calculated to be 11.9 nm. The tendency of the lamellar or columnar structures to split into smaller domains on heating is consistent with the results described previously.<sup>4</sup>

These results, together with the DSC scans, demonstrate that the tetramer self-assembles into successively lamellar crystalline, tetragonally perforated lamellar, hexagonal columnar, and discrete micellar phases in a reversible way as a function of temperature. In



**Fig. 3** Schematic representation of the 3-D tetragonally perforated lamellar ( $I4/mmm$  space group symmetry) structure of the tetramer: (a) top view, and (b) cross-sectional (along the dotted line) side view.

comparison with the phase behavior of the monomer, the remarkable feature of the tetramer investigated here is that attachment of coil-rod-coil molecules into a central point induces a perforated lamellar liquid crystalline phase with a 3-D tetragonal symmetry that is thermodynamically stable. Upon melting of rod segments in the monomer, there is adequate free volume for the poly(ethylene oxide) to form a 2-D hexagonal columnar mesophase. Attachment of four poly(ethylene oxide) chains to a central point, however, has the effect of reducing the freedom of movement for the flexible chains, which in turn suppresses the ability of the rod segments to form a columnar mesophase with a larger interfacial area. Consequently, certain supramolecular structures with reduced interfacial area such as a perforated lamellar structure are preferred over the columnar phase exhibited by the monomer.

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