

Polymer and Colloid Highlights

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Dendrons, Dendrimers.... Octopus!

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Dendrons and dendrimers are a fascinating class of macromolecules which substantially differ from more traditional ones since their physical properties can be tuned by varying their generation. A unique property of these branched templates is their intrinsic curvature at the dendritic surface, which is 'concave' with respect to the focal point. In previous studies of liquid crystals produced by covalent or supramolecular attachment of pendant chains on dendron or dendrimer surfaces, it has been assumed that the concave dendrimer/pendant chain interface is preserved in the bulk self-assembled structures. Indeed, the current understanding and molecular models are based on X-ray and electron scattering data, which only provide the reciprocal space signature of the crystalline space group without allowing the direct identification of domains, a phenomenon known as the 'Babinet Principle'. The accepted self-assembly scheme of dendritic liquid crystals, which postulates interfaces concave towards the focal points of dendrons and dendrimers, can be 'frustrated' by a reduction in the volume fractions of the pendant chains. This would favour bending the interfaces in the opposite direction, conferring an 'inverted' configuration to the liquid crystalline polymers. In other terms, not only the intrinsic curvature of dendrons and dendrimers is important, but also the volume fraction of the pendant chains can play an important role in defining the final curvature of the domain interfaces.

We have recently demonstrated these conjectures by designing dendrons and dendrimers bearing functional ammonium groups on their periphery, and thus are capable to bind ionically to counter-charged sulphate-headed alkyl tails. These systems allow easy variation of the volume fraction of the pendant chains, by simply changing the length of the supramolecularly attached hydrocarbon tails. Fig. 1A shows typical small angle X-ray scattering (SAXS) profiles for a second-generation dendron, DG2, complexed to counter-charged alkyl tails of lengths varying between C8 and C18 carbon units. SAXS profile show that the systems organize into columnar rectangular (C8), columnar hexagonal (C12 and C14) and lamellar liquid crystalline phases. However, no information can be drawn on the packing mechanisms of the dendron-alkyl tail complexes. Fig. 1B shows transmission electron microscopy (TEM) images on the same complexes in which the dendrons are chemically stained by RuO₄ salts, and thus appear dark in the images, while the unstained alkyl tails appear white. Clearly, the pendant chains seem to be confined within discrete domains, leading to a microscopic curvature of the dendron-side chains' interfaces opposed to the intrinsic cur-

vature of the dendrons. Our findings mandate a reassessment of postulated self-assembly mechanisms in dendron and dendrimer-based liquid crystals. In order to confine pendant chains into cylinders, dendrons and especially dendrimers must fold back and assume an 'octopus'-like configuration (see Fig. 1C), with inverted curvature. This is far from the commonly accepted view of dendritic liquid crystals as 'core-shell' particles. In terms of applications, these novel structures may be used as structurally ideal templates for functional materials such as ultra-nanoporous materials, in which the density of the pores, upon chain removal, can be controlled to levels well beyond current alternatives.

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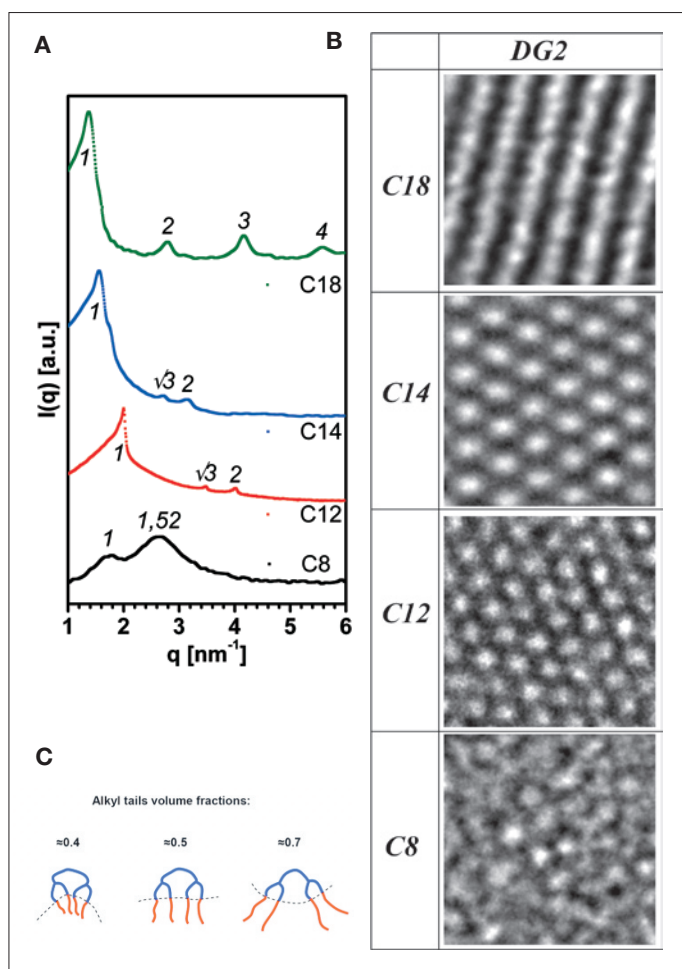


Fig. 1. (A) SAXS profile of a second-generation dendron ionically complexed with C8 to C18 alkyl tails surfactants. (B) TEM micrographs for the same complexes as (A) indicating unstained clear alkyl tail cylinders. (C) Inversion of the curvature of the pendant chains-dendrons by variations of the volume fraction of alkyl tails.

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