Contribution to the Study of the Biaxial Nematic Phase in Termotropic Liquid Crystal Dendrimers

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Extended Abstract

This thesis is a contribution to the study of the biaxial nematic phase of organosiloxane tetrapodes (a zero generation dendrimer), as there have been found organosiloxane tetrapodes that exhibit biaxial nematic phases. This work tries to evaluate whether the biaxial nematic phase has its origin manly due to the structure of the molecules and the structure of the exhibited nematic phases or due to the composition of each molecule. The current study, that tries to contribute to the understanding of the origin of the biaxial nematic phase, was based on structural studies of the nematic phases of these materials and molecular order investigations by NMR in the nematic phases of the corresponding monomers.

In this framework, two organosiloxane tetrapodes, that exhibit liquid-crystalline phases, were studied by means of X-ray diffraction (XRD) in aligned samples. The aim of this analysis was the study of the structures of the mesophases exhibited by the tetrapodes with related molecular structures. The compounds present liquid-crystalline phases; one of the compounds, Ts, exhibits a smectic C phase and a nematic phase, the other compound, Tas, exhibits only one nematic phase. One of these compounds, Tas, presents a biaxial nematic phase confirmed by optical techniques and NMR spectroscopy.

Based on the XRD results, there have been proposed packing models for the studied mesophases. The results point towards interdigitation between different molecules, as the average distance between consecutive molecules was found to be significantly smaller than the length of the molecules. It was noticed that the pattern obtained for the nematic phase, of both compounds, had a similar pattern of a smectic C phase. That pattern denotes the present of cibotatic clusters within the nematic phase, where the molecules adopt locally a configuration like in a chevron smectic C phase (within all the temperature range of the nematic phase).

Two monomers of the tetrapode Ts were analysed through deuterium NMR spectroscopy in order to investigate the relationship between the molecular structure of the tetrapodes and the biaxial ordering in the nematic phase. The key aim of this study was to verify the existence (or inexistence) of biaxial nematic order in the monomers’ nematic phase. The
samples used in this analysis were mixtures of the monomers with a deuterated probe. The probe was selected considering that it must take the same alignment of the monomers without inducing additional order to the system. Considering those constraints, the chosen probe (7CBαD2) presents only a nematic uniaxial phase, with a molecular structure that will, most probably, make the probe assume the same kind of order as the one presented by the monomers.

The samples were put into rotation, with the rotating axis aligned with the magnetic field of an NMR experiment, which causes them to form a two-dimension powder in the plane orthogonal to the axis or rotation. The signature of a two-dimension powder of a nematic uniaxial phase is characterized by the fact that the ratio between the splittings of the inner and the outer peaks of the spectrogram is equal to 1/2, but if that ratio is different from one, it means the nematic phase is biaxial. This ratio was found to be 1/2. From this study, no evidence of biaxial nematic order was found, in the nematic phase of the monomers. This result means that the biaxial behaviour found in the monomers should not have its origin in the monomers, when taken individually, but rather in the way they are linked to form the tetrapode.

The results obtained from NMR, together with the structural studies, support the hypothesis that the biaxial order in the nematic phase is related to the structural specificity of the linkage between mesogenic units and the dendritic core of the tetrapodes and its effect in the peculiar structure of the resulting nematic phase.

The fact that nematic phases formed by the monomers present only uniaxial nematic order, differently from what happens with the tetrapodes, is compatible with the hypothesis that the nematic biaxial order results from orientational constrains of the mesogenic units, caused by their linkage to the central core of the dendrimers. The difference on this behaviour from the monomers to the tetrapodes must probably be related to the reduction of some freedom degree in rotation movements in the tetrapodes, because of the interdigitated structure of the nematic phase.

The behaviour found for the tetrapodes compared to the monomers is similar to that associated with some liquid-crystalline polymers which present nematic biaxial phases, but their mesogenic units do not. The behaviour of systems composed by the linkage of simple mesogenic units to form more complex systems cannot be described only by the behaviour of the units taken alone.

These systems of tetrapodes can be interesting in the future for their possible technological applications as they have more than one axis in which the molecules can align, considering in particular the fact that the orientation towards a secondary axis is significantly faster than what happens in the principal axis, allowing faster response times of the liquid-crystal displays. There is still plenty of work in this area, to try to understand the mechanisms associated to the nematic biaxial phase.