Bilayer gelation in nanoparticle-doped nCB-homologues

A. Lorenz, 1*D. M. Agra-Kooijman, 2 N. Zimmermann, 3 Heinz-S. Kitzerow, 3 D. R. Evans, 4 S. Kumar 2

1 Department of Chemistry, Berlin Institute of Technology, Berlin, Germany
2 Department of Physics, Kent State University, USA
3 Department of Chemistry, University of Paderborn, Paderborn, Germany
4 Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, Ohio, USA

Five members of the 4-n-alkyl-4’-cyanobiphenyl homologous series were dissolved in n-heptane and subsequently doped with a n-heptane/nanoparticle-dispersion of milled BaTiO₃ nanoparticles, which led to gelation.[1] X-ray scattering studies of the obtained gels revealed a characteristic smectic multilayer structure in all samples. Surprisingly, the same smectic layer spacing of 4.5 nm was measured for all of the five homologues. The multilayers were found to consist of molecular bilayers wherein the mesogens were arranged in a head-to-head assembly of the polar head-groups.

Doped samples of two of the homologues, 4-n-pentyl-4’-cyanobiphenyl and 4-n-octyl-4’-cyanobiphenyl, were studied with synchrotron[2] x-ray scattering; nine orders of the primary Bragg reflection could be observed in these experiments, which were used to calculate the electron density profiles of the multilayers by Fourier analysis.[3]

The figure shows intensity vs. scattering vector plots for doped-5CB (black line) and doped-8CB (gray line). Nine orders of the primary diffraction peak corresponding to 4.65 nm are indicated (1 – 9). A composite peak corresponding to the (1 1 0) and (1 0 1) reflections of BaTiO₃ nanoparticles is indicated by an arrow. Characteristic short-range correlations (SRC) for a soft phase were present. The inset shows a schematic of the observed nanostructure where polar nanoparticles (hatched filling) and non-polar nanoparticles (solid filling) are embedded in bilayers represented by encircling lines.

The dissolved nanoparticles clearly induced self-assembled nanostructure in which the rigid aromatic part, and not the entire molecule, defined the layer spacing. This experimental approach is suitable to test other mesogenic and even non-mesogenic soft materials to further understand the nature of molecular associations induced by the presence of nanoparticle.

References:
[2] X-ray investigations supported by the US Department of Energy, Basic Energy Sciences award No. DE-SC-0001412 were conducted at the Advanced Photon Source, an Office of Science User Facility, operated for the Argonne National Laboratory and supported by the U.S. DOE, BES award No. DE-AC02-06CH11357.

* presenting author; E-mail: a.lorenz@campus.tu-berlin.de