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Confinement induced relaxations and phase behavior of a nanoconfined ionic liquid crystal

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Liquid crystalline mesophases in nanoconfinement exhibit intriguing phase transition behaviors and relaxation dynamics. Here in, we investigate the molecular dynamics and electrical conductivity of a linear shaped guanidinium based ILC confined in self-ordered nano porous alumina oxide membranes of pore size ranging from 180nm down to 25nm by employing broadband dielectric spectroscopy (BDS) and calorimetry. Calorimetric investigation reveals a complete suppression of the columnar – isotropic transition, while the plastic crystalline – columnar transition temperature decreases with inverse pore size and deviates from the Gibbs – Thomson equation.

For the bulk case, BDS detects two relaxation modes in the crystalline phase, the ▯ relaxation and the $\alpha 1$ relaxation, and two relaxation modes in the columnar phase, the $\alpha 2$ and $\alpha 3$ relaxation. For the confined case, all relaxation modes slow down compared to the bulk. However, for the least pore size (25 nm), the $\alpha 2$ relaxation is absent. We discuss the possible molecular origins of the different relaxation modes observed. For the bulk ILC, a clear jump of 4 orders of magnitude in the absolute values of DC conductivity occurs at the transition from the plastic crystalline to hexagonal columnar phase, for the confined ILC, this transition is smooth. DC conductivity is reduced for the confined case, except for the 25nm, where the values is similar to the bulk.

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