

Molecular dynamics of a liquid crystal with highly ordered smectic E phase under different forms of confinement

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Liquid crystals (LCs) confined in various host system have attracted great interest in recent years. New material properties originating from finite size of pores and interaction between molecules and pore surface have been reported, including optical properties, dynamic peculiarities and different phase diagram than in bulk. It was concluded that a change in the transition temperature originates from two competing effects: orientational order locally imposed by pore surface that increases the transition temperature and disordering effect resulting from the elastic forces and rearrangement of defect lines which cause the reduction of the transition temperature. One of our previous papers [1,2] discusses the dynamics and morphology of 4-heptyl-4'-isothiocyanatobiphenyl (7BT) confined in silica pores with average diameters of 4, 6, 7.5, 9.5 and 10.5 nm. While 7BT in bulk demonstrates a smectic E (SmE) phase characterized by an orthorhombic arrangement of molecules within the smectic layers, the order of 7BT molecules is imposed by a strong surface potential in nanopores. Consequently, molecular dynamics are significantly modified in nanopores compared to bulk. Two relaxation processes were detected by dielectric spectroscopy: one related to the "flip-flop" motions of molecules around their short axis, while the second was ascribed to the librational motions of molecules partially immobilized on pore walls. As the pore size decreases, the surface effect becomes more pronounced, with only librational motions observed in 4nm pores. An analysis of the temperature dependencies of specific IR absorption bands, in terms of their spectral position and integrated intensity, highlighted the varied influence of confinement on rigid and flexible molecular moieties: i.e. the gradual ordering of aromatic cores and amorphous-like behaviour of alkyl chains.

The purpose of this work is to examine the dynamic properties of 4-hexyl-4'-isothiocyanatobiphenyl (6BT) with a SmE phase experiencing different forms of confinement. Hard confinement was achieved by the infiltration of LCs into nanoporous aluminum oxide (AAO) templates with non-intersecting, cylindrical, channels. Other interesting, but as yet unexplored is soft confinement derived from the interactions between the polymer and guest liquid crystalline molecules. This was investigated on an example of electrospun polymer/liquid crystal composite fibers (see Fig. 1). We prepared composite fibers for three different mass ratios of polycaprolactone (PCL) and 6BT. By a combination of broadband dielectric spectroscopy and Fourier-Transform Infrared (FTIR), the microscopic picture of the influence of soft and hard confinement on molecular dynamics is obtained. In this talk, I will discuss similarities and differences in the impact of hard and soft confinement on dynamic properties and crystallization kinetics of 6BT liquid crystal.

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1 M. Jasiurkowska, W. Kossack, R. Ene, C. Iacob, W. K. Kipnusu, P. Papadopoulos, J. R. Sangoro, M. Massalska-Arodz, F. Kremer, *Soft Matter* 8 (19), 5194 (2012).

[2] W.K. Kipnusu, C. Iacob, M. Jasiurkowska-Delaporte, W. Kossack, J. R. Sangoro, F. Kremer; "Rotational diffusion of guest molecules confined in uni-directional nanopores" in: *Dynamics in Geometrical Confinement*, F. Kremer (Ed.), Springer-Verlag (2014)

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Summary

Topic

1. Amorphous and soft matter

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