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Comparative TEM Studies of Liquid Crystals: Freeze Fracture, Plunge Freezing of Thin Films, and Cryosectioning of Bulk Samples

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The fascinating liquid crystals (LCs) [1], uniquely combining order and mobility and having tremendous impacts (e.g., liquid crystal display, the so-called LCD), impose great challenges for direct TEM studies due to the difficulties in specimen preparation and the severe radiation damage. Recently, we demonstrated that a widely available cryo-TEM, a high sensitivity CCD camera and a modified low-dose imaging procedure provided a ready combination for direct subnanometer resolution imaging of challenging LC materials [2, 3]. In this paper, we present a series of specimen preparation routines for LCs, aiming to set up a comprehensive yet easily accessible toolbox for TEM imaging especially high resolution direct cryo-TEM observation of the majority of LC materials.

Organic LCs can be categorized into thermotropic and lyotropic LCs, with the phase transition (change in the amount of order) mainly driven by temperature and concentration, respectively. The most common mesophases in thermotropic LCs are nematics and smectics. Simply speaking, a nematic phase has only orientational order but no long-range positional order. Besides the orientational order, a smectic phase also has a degree of positional order, as the molecules tend to form layers stacked on top of each other. Lyotropic LCs are formed by mixing LC molecules with solvent (most often, water). The lyotropic chromonic LCs used in this study consist of mesogens with disk-like aromatic central core and ionic outer groups. While in water, the molecules self-assemble into columnar aggregates by face-to-face stacking to minimize the contact area with water.

The understanding of detailed LC behaviors at the molecular level is surprisingly limited, partly attributed to the lack of effective structural probe for organic liquids at nanometer and subnanometer scale. Currently, a replica TEM technique, namely freeze fracture TEM (FFTEM) providing a typical resolution of a few nanometers, is the dominant high resolution imaging tool of LCs. At the current stage, it is common to use cryo-TEM to observe plunge-frozen thin films of fluid-like materials. However, among other challenges, the molecular alignment in LCs is highly sensitive to the presence of surfaces and interfaces due to the so-called surface anchoring phenomenon. As a result, thin specimens may show structures very different from the bulk LC structures. On the other hand, to freeze a thick sample with minimized influence of the surface forces is often not practical because of the insufficient cooling rate, especially for lyotropic LCs with high water content.

In addition to adopting and modifying a few of the previous practices, some new concepts are introduced in this study, e.g., suspended thermotropic LC thin films, cryo-electron microscopy of vitreous section (CEMOVIS) of high pressure frozen lyotropic LCs, and complementary combination of direct cryo-TEM and replica FFTEM. We have studied a wide range of LCs comparatively by plunge freezing of thin films, cryosectioning of plunge or high pressure frozen bulks, and FFTEM. Figures 1 and 2 show results of a cholesteric thermotropic LC and a lyotropic chromonic LC, respectively.

In general, the very convenient-to-use thin film approach allows the best imaging quality for both thermotropic (Fig. 1a) and lyotropic (Fig. 2a) LCs due to the high cooling rate and no further specimen

processing after the freezing. However, complicated surface effects can often be observed, and the specimen preparation can be difficult for viscous lyotropic liquid crystals. On the other hand, FFTEM can effectively avoid the surface effect and irradiation damage, but its application is limited by the relatively poor resolution. For example, FFTEM failed to resolve the columnar aggregates in Fig. 2 which are separated from each other by 2 - 2.4 nm.

Cryosectioning combines the advantages of both thin film technique and FFTEM. Compared to FFTEM, cryosectioning allows subnanometer resolution direct imaging, and the processing-induced artifacts (e.g., knife marks, crevasses, and compression) are considerably easier to identify. On the other hand, the surface effects are minimized and more reliable results can be obtained. For example, the application of CEMOVIS in the high pressure frozen lyotropic LC (Figs. 2b&c) reveals large orientation variation of the aggregates, while due to the confinement of the holes in the carbon film, the aggregates in thin film approach normally orient uniformly along the long direction of the holes (Fig. 2a).

Direct TEM observation opens ways to a variety of TEM techniques, e.g., diffraction, STEM, and spectroscopies. Our initial results suggest that direct TEM (cryo and in situ techniques such as liquid cell), in general, is a promising part of the solution to the lack of effective high resolution structural probe in LC studies and can be essential to understand LC behaviors at the molecular scale.

References:

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[4] The LC samples were provided by the research groups of Dr. Oleg D. Lavrentovich, Dr. Quan Li, Dr. Georg H. Mehl, Dr. Wolfgang Weissflog, Dr. Daniela Pucci andewa gorecka.

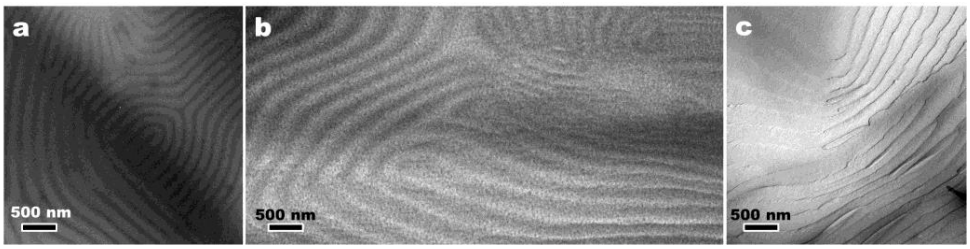

Figure 1. (a) and (b) Cryo-TEM images of a cholesteric thermotropic LC. Specimens prepared by plunge-freezing of a LC thin film (a) and cryosectioning of a plunge-frozen LC bulk (b). The bright and dark regions are caused by the variation in molecular orientation. (c) FFTEM image of the same LC.

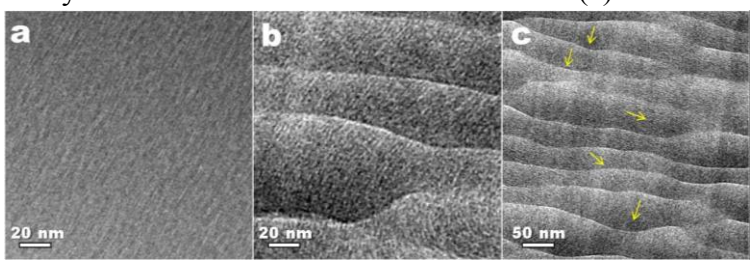

Figure 2. Cryo-TEM images of a lyotropic chromonic LC (~65% water) using thin film plunge freezing (a) and bulk high pressure freezing (Leica EM PACT2) and cryo-sectioning (Diatome cryo immuno diamond knife and Leica UC7/FC7 cryo-ultramicrotome) (b and c). In the low magnification Fig. 2c, the arrows point to the local orientations of the columnar aggregates.

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