Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

Horizontally and Vertically Aligned Helical Conjugated Polymers: Comprehensive Formation Mechanisms of Helical Fibrillar Morphologies in Orientation-Controlled Asymmetric Reaction Fields Consisting of Chiral Nematic Liquid Crystals

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[1] Observation of Grandjean texture

Figures 5 in the manuscript shows the fingerprint textures of the surface layer (I) and the intermediate layer (II) of system 3, but shows no texture corresponding the inner layer (III). There are some reasons why the Grandjean texture formed in the inner layer (III) of system 3 cannot be observed.

1. The Grandjean texture is a so-called planar texture (see Figure 4(B)) and has no characteristic texture compared with the fingerprint texture.

2. When the surface layer (I) has a fingerprint texture with a short helical pitch, the stripes of the fingerprint texture prevent us to observe the texture of the inner layer or to distinguish it with that of the surface layer.

3. When the thickness of the intermediate layer (II) is large, it is furthermore difficult to observe the texture of the inner layer (III) with a different texture.

Actually, the above situation occurs in the vertical N*-LC of system 3 [PCH506 : $(PCH50)_2$6 : (*R*)-$(PCH506)_4$-Binol = 100 : 5 : 0.5] with a helical pitch of 2.3 μm, as shown in Figure 5(A) and 5(B). The stripes of the texture are still clear in the intermediate layer (II), and the thickness of the intermediate layer (II) is large owing the effect of the vertical orientation inducer (see Figure 5(C)). As a consequence, it is hard to observe the optical texture of the inner layer (III) in system 3, even if the Grandjean texture is formed.

To examine the formation of the Grandjean texture in the inner layer of the vertical N*-LC, we subjected another vertical N*-LC, system 5 [PCH506 : $(PCH50)_2$6 : (*R*)-$(PCH506)_2$-Binol = 100 : 3 : 2]. System 5 has the same components of the parent LC molecule [PCH506] and the vertical orientation inducer [$(PCH50)_2$6] as those of system 3, except the chiral dopant. The chiral dopant used in system 5 is a *di*-substituted binaphthyl derivative, (*R*)-$(PCH506)_2$-Binol. This chiral dopant has a weaker helical twisting power than *tetra*-substituted binaphthyl derivative, (*R*)-$(PCH506)_4$-Binol that is used in system 3. Therefore, system 5 has a longer helical pitch of 3.6 μm and a thinner layer (II) to give a longer distance between the stripes in the fingerprint texture of the surface layer, than the case of system 3. At the same time, POM photographs of system 5 were taken from the side of glass substrate to cut off the fingerprint texture of the surface layer. As shown in Figure A1, the fingerprint and Grandjean textures are observed in the layer (I and II) and the inner layer (III), respectively, of system 5. We also confirmed that the system 5 gave the vertically aligned H-PA, as depicted in Figure A2 (see also ref. 13(c)). These results strongly suggest that the Grandjean texture might formed in the inner layer (III) of system 3 bearing the components essentially the same as system 5.

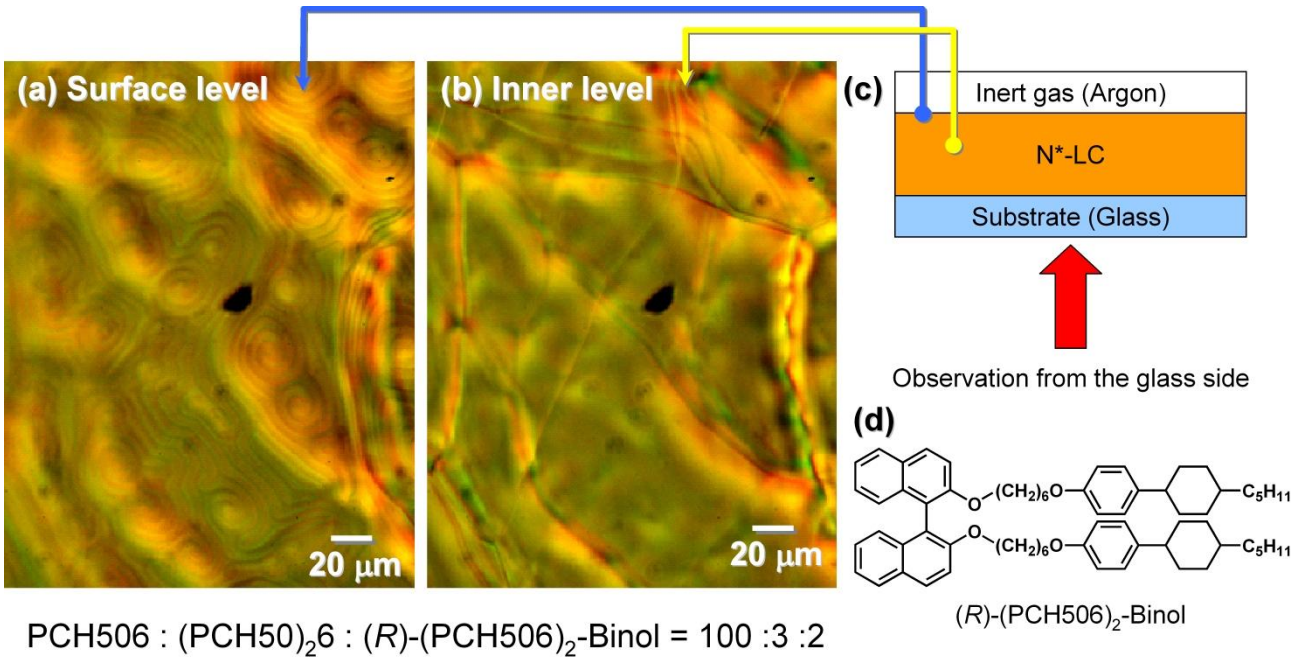

Fig. A1 Reflection POM photographs of (a) surface and (b) inner layers of the vertical N*-LC, system 5 [PCH506 : $(PCH50)_2$6 : (*R*)-$(PCH506)_2$-Binol = 100 : 3 : 2, helical pitch = 3.6 μm]. (c) Cross section image of the vertical N*-LC and (d) chemical structure of (*R*)-$(PCH506)_2$-Binol.

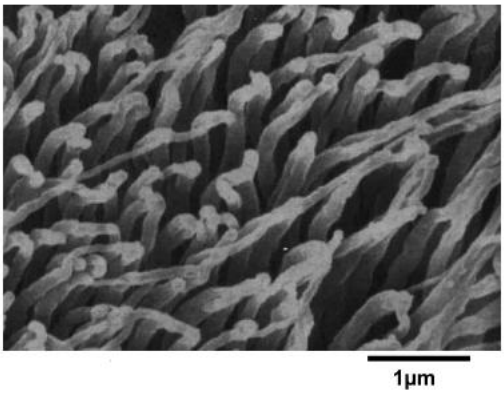

Fig. A2 SEM image of the surface of the vertically aligned H-PA film synthesized in the vertical N*-LC of system 5. See reference 13(c) of the manuscript [T. Mori, T. Sato, M. Kyotani, K. Akagi, *Synth. Met.* 2003, **135**, 83-84].

[2] Orientation direction of LC molecules to the substrate

When the structure of the N*-LC is known, it is possible to determine the orientation direction

of the N*-LC molecules to the substrate by rotating a polarizer towards an analyzer or a sample itself under POM. If a dark field remains unchanged upon the rotation of the polarizer, the LC molecules are perpendicular to the substrate. If bright and dark fields are repeatedly observed at every 45° in the rotation of the polarizer, the LC molecules are parallel to the substrate.

Fig. A3-(a) shows POM photograph of fingerprint texture of N*-LC with spiral morphology. The distance between the bright lines (or dark lines) corresponds to a half helical pitch of the N*-LC. Fig. A3-(b) and -(c) depict the model structures for the fingerprint texture of the N*-LC from (b) top and (c) side views, respectively. The LC molecules represented as yellow and red ellipsoids are parallel and perpendicular to the substrate, respectively, and they correspond to the bright and dark lines of POM, respectively.

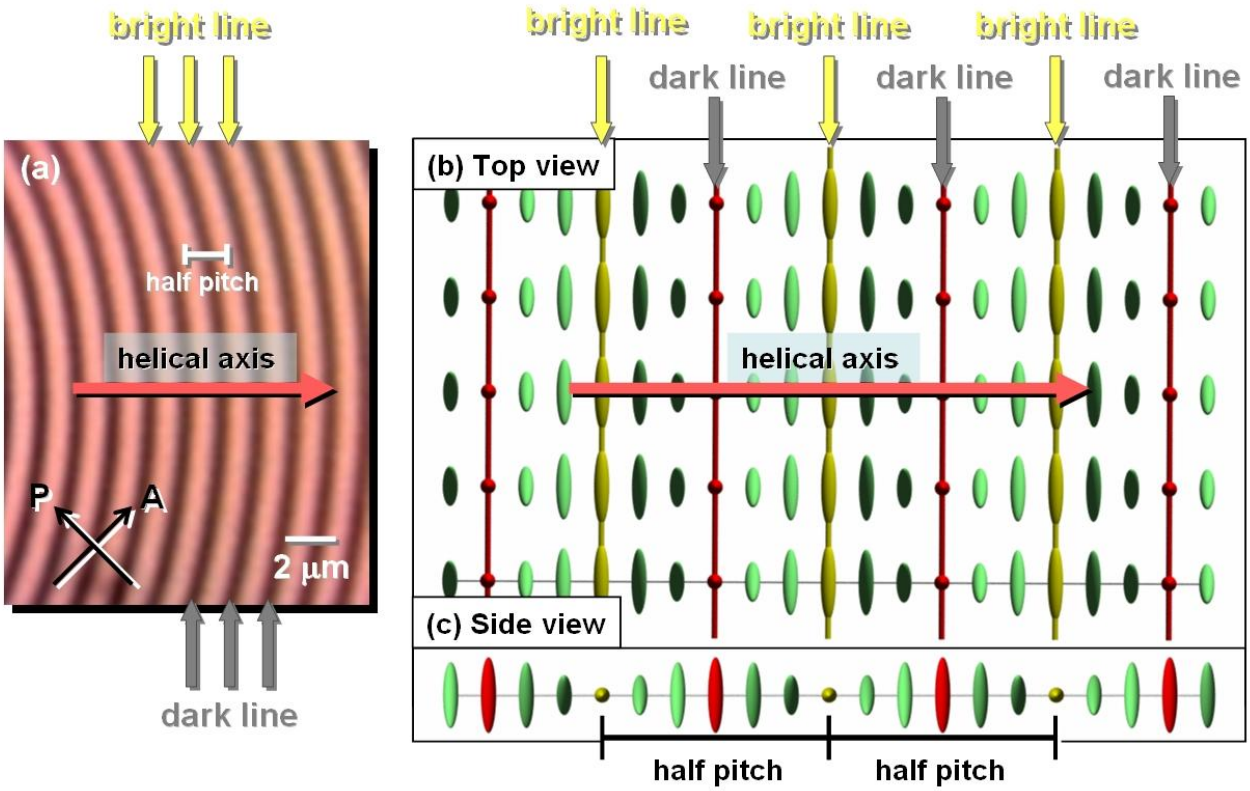

Fig. A3 (a) POM photograph of fingerprint texture of N*-LC. Model structures for the fingerprint texture of the N*-LC from (b) top and (c) side views. The LC molecules represented as yellow ellipsoids and red spheres are parallel and perpendicular to the substrate, respectively, and they correspond to the bright and dark lines of POM, respectively.