Biaxial Molecular Arrangement of Rod−Disc Molecule under an Electric Field

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Since the first discovery of liquid crystalline (LC) materials in the 1880s, a large number of different LC phases have been observed from thousands of different LC molecular architectures. The discovery of new LC phases has continued to be driven by the novel design and synthesis of complex LC molecules.[1−4] Excellent examples of these complex LC phase structures include the twist grain boundary phases, blue phases, achiral banana phases, and biaxial nematic (N) LC phases.

In a biaxial nematic phase, there is orientational order not only for the long molecular axis but also with the short transverse molecular axis. Since Freiser first predicated the existence of the biaxial N phase in 1970,[5] it has been long sought after because of its unique dynamic and static physical properties and potential technological applications. The first observed biaxial nematic phase was in a complex lyotropic mixture of micellar aggregates.[6] More recently, biaxial nematic ordering was reported in a series of LC molecules with a bend at the center of the mesogen, so-called "bow-shaped" or "banana-shaped" molecules.[7−10]

There are two strategies to designing biaxial N LC molecules, the single-component and the double-component approaches, depending on the type of mesogens. In the single-component approach, the LC molecules must be board-shaped with D_{2h} symmetry. This type of molecule has been prepared by traditional molecular organic synthesis via covalent bonds as well as by molecular self-assembly via physical bonds.[11−15] Even though board-shaped molecules are elongated along the molecular long axis, they do not possess a free rotation around the molecular long axis because of geometric hindrance. Another type of single-component biaxial N LC molecule is the symmetric/asymmetric bent-core LC molecule with near-C_{2v} symmetry.[16−22] The stability of the biaxial N LC phase can be maximized by placing the molecular bend at the center of the mesogen.

Combining rodlike and disclike molecules is an example of the double-component strategy to the design and synthesis of biaxial N LC molecules.[23−29] Unlike common rodlike LCs, which exhibit uniaxial positive birefringence with the optical long axis parallel to the molecular long axis, disclike LCs possess intrinsically uniaxial negative birefringence with the optical long axis perpendicular to the disc plane. The competition between the excluded volumes of these two extremely different mesogenic shapes results in biaxial molecular orientation, wherein the rodlike and disclike molecules are oriented along mutually orthogonal molecular directors that correspond to the two optical directions.

We recently reported the phase structures and transition behaviors of a series of rod−disc LC molecules (RDn, where n is the number of carbon atoms between the rod and the disc mesogens, $n = 6−12$), which were prepared via the chemical attachment of six cyanobiphenyl calamitic (rod) mesogens (R) linked to the triphenyl discotic (disc) mesogen (D) by alkyl chains.[30] The chemical structure and its calculated geometric dimensions are shown in parts a and b of Figure 1, respectively. Specifically, for the RD12 molecule with 12 carbon atoms in each alkyl chain linkage between the rod and disc mesogens, three ordered phases have been observed below the isotropic (I) temperature: the N LC and

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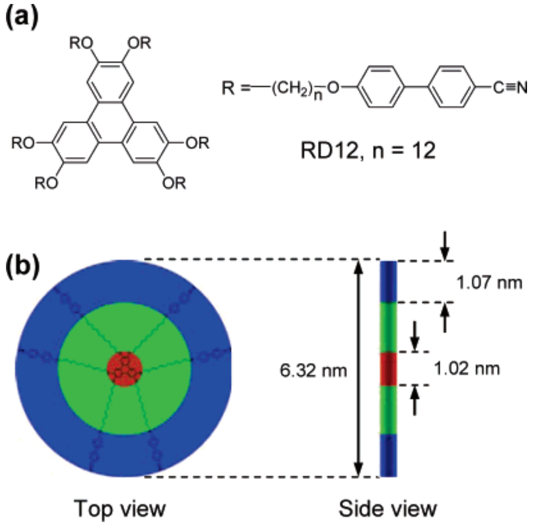

Figure 1. (a) Chemical structure and (b) calculated geometric dimensions of a RD12 molecule.

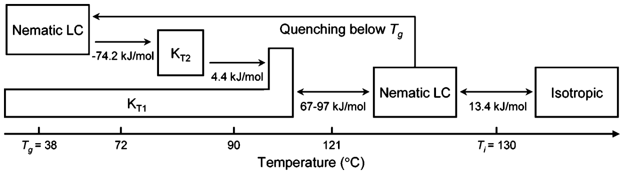

Figure 2. Phase-transition diagram of RD12 molecules.[30]

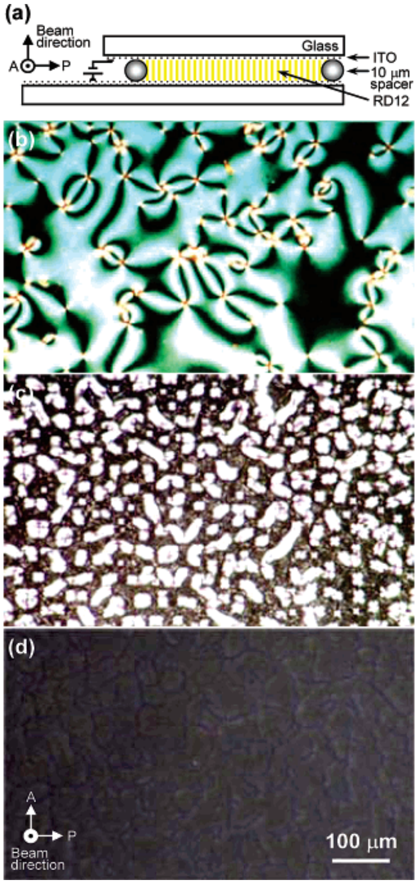

Figure 3. (a) Schematic illustration of an electro-optic cell filled with RD12 molecules. PLM textures at 125 °C at different electrical voltages: (b) 0 (without applying the electric field), (c) 80, and (d) 150 V.

the K_{T1} and K_{T2} crystalline phases, both of which possess triclinic unit cells.[30] The K_{T2} crystalline phase is formed by slowly heating the rapidly quenched sample from the N phase and is metastable with respect to the K_{T1} crystalline phase, which is formed by either slow cooling from the N LC phase or isothermal crystallization at relatively high temperatures. The phase relationships and corresponding transitions are illustrated in Figure 2. In the two crystalline phases, the RD12 molecular discs are intercalated. This leads to speculation that the low-ordered N LC phase could be biaxial, with the cyanobiphenyl calamitic rod director orthogonal to the triphenyl discotic core director. The question becomes can we generate this biaxial N LC phase and how do we identify the biaxial molecular orientation?

To determine the biaxial molecular orientation, we constructed an electro-optic LC cell filled with RD12 molecules using sealed indium thin oxide (ITO) glass slides as schematically illustrated in Figure 3a. A PZD350 Trek DC voltage generator, which could apply voltages between 0 and 200 V, was connected to the ITO junctions to apply an electric field across the electro-optic LC cell. The cell was first heated to the I melt of RD12, and gradually cooled to 125 °C, which is in the N LC phase. DC voltage was then applied to align the RD12 molecules. The difference between the RD12 discs and common discotic LC molecules is the presence of rodlike cyanobiphenyl mesogens located at the ends of each of the flexible tails of the triphenyl discotic core. On the basis of a combination of DSC and 2D WAXD experimental results for RD12, it was determined that the material exhibited a nematic phase between 121 and 130 °C. Because of the dielectric anisotropy, the long axis of the cyanobiphenyl calamitic mesogens and the in-plane direction of the triphenyl discotic core mesogens tend to align parallel to the direction of an electric field.[31−36] Furthermore, an electric field is more effective in the alignment of the cyanobiphenyl mesogens, because the cyanobiphenyl mesogens contain a strong antiparallel dipolar interaction.

The in situ optical textures of electrically oriented RD12 molecules under PLM are shown in Figure 3. The light was perpendicularly incident to the cell as illustrated in Figure 3a. Figure 3b−d is a set of RD12 optical textures in the N LC phase at 125 °C under different electric field voltages. Figure 3b shows the PLM texture without an electric field (at 0 V) and is a typical N Schlieren texture with 2-fold and 4-fold singularities with different signs.[37] As soon as the electric field is applied, the texture switches within less than 1 s. Figure 3c is a RD12 optical texture taken at 80 V under PLM. At this intermediate voltage, the electric field is not strong enough to completely align the mesogens homeotropically. Because of the different initial orientations of the mesogens, in some regions, the mesogens are more extensively aligned parallel to the electric field and thus appear dark, whereas in other regions, the mesogens are less

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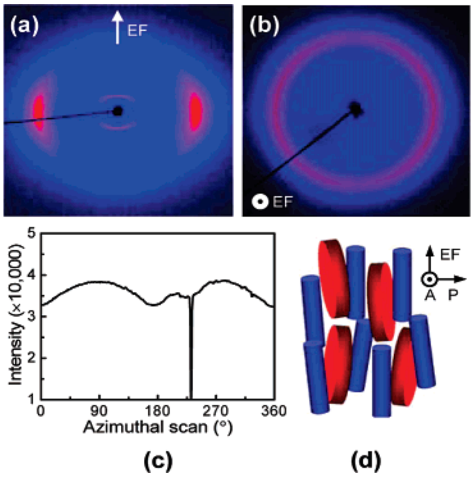

Figure 4. Two-dimensional WAXD patterns of the N LC phase at 30 °C when the incident X-ray beam is (a) perpendicular and (b) parallel to the ED. The RD12 molecules are oriented at 150 V in an electric field, and subsequently quenched to below its T_g. (c) Azimuthal scan of the 2θ angle between 18 and 24° in the parallel direction 2D WAXD pattern (Figure 4b). (d) Schematic biaxial molecular arrangement in the N LC phase at 150 V.

extensively aligned parallel to the electric field and thus appear bright. When the electric field is increased to 150 V, a darker PLM optical field with weak birefringence is observed (Figure 3d), which is not changed even in higher electric fields. This indicates that the long axis of the cyanobiphenyl mesogens and the in-plane direction of the triphenyl discotic cores are completely aligned parallel to the electric field direction, which is also parallel to the PLM optical beam direction. The weak birefringence is due possibly to the local N organization of triphenyl discotic cores perpendicular to the electric field directions.

The molecular orientation of this N LC phase under a high electric field can be characterized utilizing 2D WAXD experiments. The sample was prepared by quenching the cell (Figure 3d) into a dry ice/acetone mixture with the 150 V electric field still applied. As confirmed in our previous report, the N LC phase can be effectively frozen below the T_g of RD12.[30] The quenched sample with a 10 μm thickness was then peeled off for 2D WAXD experiments. Images a and b of Figure 4 show a set of 2D WAXD patterns for the quenched N LC phase along two different incident X-ray beam directions: perpendicular to the electric field and parallel to the electric field, respectively (the sample geometry has been shown in Figure 3a). When the incident X-ray beam direction is normal to the electric field direction as shown in Figure 4a, a pair of strong amorphous halos at $2\theta = 21.2°$ (d-spacing = 0.419 nm) are observed, with their maximum intensity on the equator. In the low-angle region, a pair of diffused halos were observed at $2\theta = 5.0°$ (d-spacing = 1.77 nm) with their maximum scattering intensity on the meridian. It is worth noting that the calculated diameter of the RD12 molecular disc is 6.32 nm on the basis of the assumption that the alkyl chains are in an all-trans conformation, the calculated diameter of the triphenyl discotic core is 1.02 nm, and the length of each cyanobiphenyl calamitic rod is 1.07 nm on the basis of the Cerius^2 (version 4.6) simulation software, as illustrated in Figure 1b. If the RD12 molecules are assumed to be packed without intercalation, the packing model would be hexagonal with a d-spacing of 5.37 nm. In the 2D WAXD pattern of Figure 4a, there is no pair of diffraction corresponding to this speculated d-spacing at 5.37 nm ($2\theta = 1.6°$). Additionally, a packing model without intercalation generates packing densities that are inconsistent with experimental results. This indicates that the triphenyl discotic mesogens and cyanobiphenyl calamitic mesogens are intercalated and mixed. The reflections at $2\theta = 5.0°$ (d-spacing = 1.77 nm) in Figure 4a could be generated by the creation of the intercalated antiparallel cyanobiphenyl mesogens even under the 150 V electric field because of the strong dipolar interactions. Under this strong DC electric field, the shape of the whole rod−disc RD12 molecule should be ribbonlike rather than disclike.

When the incident X-ray beam direction is parallel to the electric field direction, a pair of broad amorphous halos with a maximum intensity at 90 and 270° azimuthal angles was observed (panels b and c in Figure 4). This observation indicates that the uniaxial optical direction of triphenyl discotic mesogens is perpendicular to the long axis of cyanobiphenyl calamitic mesogens, even though these anisotropic biaxial molecular orientations are not perfect as schematically illustrated in Figure 4d. This supports the existence of a biaxial N LC phase. To macroscopically create a stable, uniform biaxial domain, another external force field perpendicular to the first force field is required to align the triphenyl discotic mesogens. This external force field must not affect the orientation of the cyanobiphenyl calamitic mesogens.

In summary, the rod−disc molecule, RD12, synthesized via the chemical attachment of six cyanobiphenyl rod mesogens (R) to the periphery of a triphenyl disc-like mesogen group (D) by alkyl chain linkages having 12 carbons in each linkage possibly exhibits a biaxial N molecular orientation under a DC electric field. On the basis of 2D WAXD experiments, the long axis of the cyanobiphenyl calamitic rods are in-plane with the triphenyl discotic cores. In this molecular arrangement, the optical directors of the rodlike and disklike mesogens are orthogonal to each other, creating a biaxial N phase. Newly designed and synthesized chemical structures that maximize the stability of the biaxial N molecular orientation are undergoing investigations via nuclear magnetic resonance and conoscopy experiments.

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Supporting Information Available: Experimental section (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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