

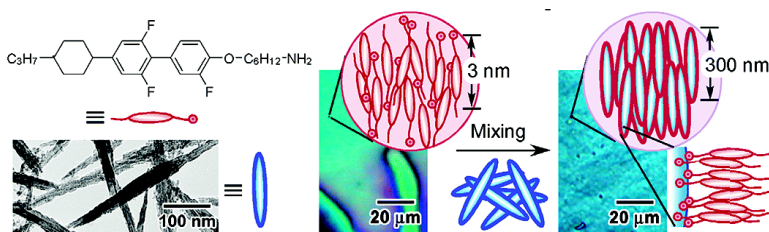
Communication

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Organic–Inorganic Hybrid Liquid Crystals: Hybridization of Calamitic Liquid-Crystalline Amines with Monodispersed Anisotropic TiO₂ Nanoparticles

Kiyoshi Kanie and Tadao Sugimoto*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

Received April 24, 2003; E-mail: sugimoto@tagen.tohoku.ac.jp

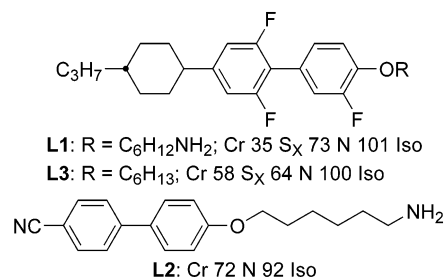
Organic–inorganic hybrid materials have attracted a great deal of interest, especially in the fields of materials science and nanotechnology, because it is not rare to find unexpected super-additive properties with such materials.¹ The present report pertains to the study of new hybrids of organic liquid crystal (LC) materials with an amino group and monodispersed anisotropic nanoparticles of anatase TiO₂. LCs are anisotropic organic materials having an enormous variety of dynamic and self-assembling functions,² and thus the introduction of such functions of LCs into organic materials has been a useful technique in materials science.^{3–12} On the other hand, we have developed the “gel–sol method” for the preparation of monodispersed particles precisely controlled in size and morphology in large quantities, and have produced many kinds of uniform particles of metal oxides, sulfides, pure metals, etc.¹³ On the basis of this method, we have reported a facile procedure for the preparation of ellipsoidal monodispersed anatase TiO₂ nanoparticles by using ammonia or primary amines as shape controllers.¹⁴ The key to shape control is the selective adsorption of these amines to the specific crystal planes parallel to the *c*-axis of tetragonal anatase titania particles during their growth. The strong adsorption of amines suggests that we would obtain novel organic–inorganic hybrid LCs by the adsorption of amino-substituted mesogenic organic LC molecules to the surfaces of the anisotropic TiO₂ nanoparticles.

We designed and synthesized amino-substituted **L1** and **L2**, as well as **L3**, the same as **L1** but without an amino group, as shown in Chart 1. The phase transition temperatures and LC phases of **L1–3** were determined by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) with a hot stage. On the other hand, anisotropic TiO₂ particles different in morphology, as shown in the transmission electron micrographs of Figure 1, were prepared by the gel–sol method and thoroughly washed with 2 M HNO₃, 0.01 M NaOH, and distilled water by centrifugation to completely remove the shape controllers. The rather polydispersed and irregular-shaped particles **T4** were prepared by mixing uniform TiO₂ particles of different shapes.

All TiO₂ powders were confirmed to be anatase-type titania by X-ray diffraction analysis, and their surfaces were all those of pure anatase titania, as revealed by X-ray photoelectron spectroscopy.

Hybridization of **L1/T1,2,3,4** and **L2,3/T1** was carried out as follows. Twenty milligrams of **L** and the same weight of **T** were mixed together and dispersed in 2 mL of methanol by ultrasonication for 30 min. The solvent was then removed by evaporation at 50 °C and subsequent suction under a reduced pressure. Figure 2 exhibits POM images of a hybrid **L1** and **T1** (**L1/T1**) at different temperatures. The hybrid melted at 48 °C, and a mesophase with strong birefringence was formed, as shown in Figure 2a. Phase transition of the mesophase occurred at 73 °C, as revealed from DSC, and a schlieren texture as a characteristic of a nematic (N)

Chart 1. Structures of Thermotropic LCs for Hybridization with TiO₂ Particles^a



^a Cr, crystal; S_X, higher order smectic; N, nematic; Iso, isotropic phases. The figures in between are transition temperatures in °C.

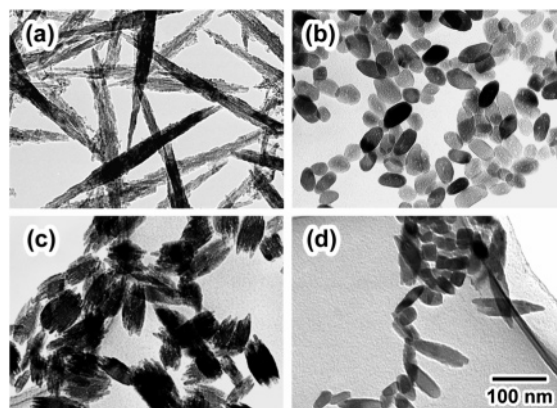


Figure 1. TEM images of TiO₂ particles **T1–3** prepared by the gel–sol method and irregularly shaped **T4** obtained by mixing different particles: (a) **T1**, (b) **T2**, (c) **T3**, and (d) **T4**.

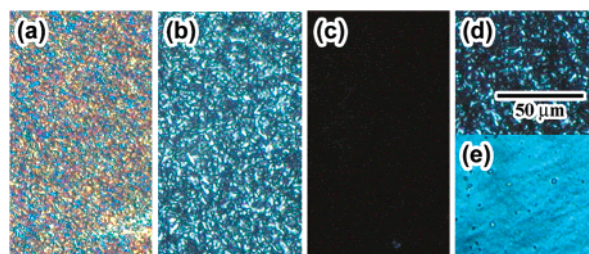


Figure 2. Polarized photomicrographs of thermotropic hybrid LC phases of hybrid **L1/T1** on heating: (a) 70, (b) 100, (c) 120, and (d) 140 °C, polydomain and (e) 140 °C, sheared monodomain.

phase was observed up to 113 °C (Figure 2b). On reaching 113 °C, the schlieren texture disappeared and an optically isotropic mesophase was seen up to ca. 130 °C (Figure 2c), at which a schlieren texture in a fluidized state was formed again (Figure 2d). The mesophase was readily transformed to a uniaxially aligned

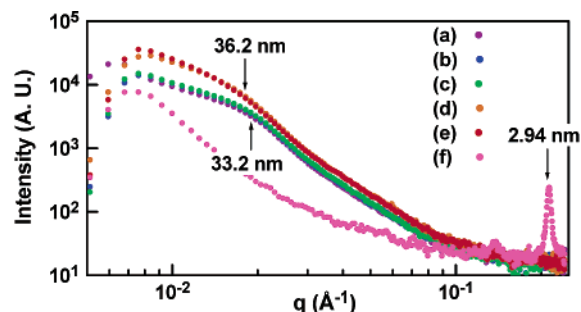


Figure 3. SAXS profiles of **L1/T1** and **L1**. **L1/T1**: (a) 70, (b) 90, (c) 110, (d) 130, and (e) 150 °C; (f) **L1** at 70 °C.

monodomain by shearing, as shown in Figure 2e. The birefringence was observed up to 250 °C. Interestingly, such liquid crystallinity owing to the hybridization was not observed at all with hybrids **L1/T2,3,4**. Thus, the aspect ratio of the anisotropic particles and their uniformity in morphology are decisive factors for the formation of the LCs of the hybrids. None of the mesomorphic phenomena was seen with hybrid **L2/T1** until **L2** of the **L2/T1** hybrid was decomposed (ca. 240 °C). Hence, in this case, the original liquid crystallinity of **L2** was lost by the hybridization with **T1**. Furthermore, since the phase separation was observed only with the hybrid **L3/T1** through POM, the amino group of **L1** was likely to play an essential role for the formation of the hybrid LC of **L1** with the anisotropic titania particles. The definite interaction between the amino group of **L1** and the surfaces of **T1** was confirmed by variable-temperature infrared spectroscopy.

The structural transitions of LC phases of hybrid **L1/T1** were examined by small-angle X-ray scattering (SAXS) measurements.¹⁵ Figure 3 shows the SAXS profiles of hybrid **L1/T1** and of a single component of **L1**. The scattering profiles of **L1/T1** at 70, 90, and 110 °C (Figure 3a–c) suggested the existence of periodic particle interactions at an interval of 33.2 nm, corresponding to the total width of a **T1** particle covered with LC molecules. Therefore, the mesomorphic phase seems to have a nematic-like one-dimensional order in the direction of the long axis of the acicular particles. Figure 3f shows a profile of the single component of **L1** at 70 °C, in which the sharp peak at 2.94 nm corresponds to the thickness of a layer unit of the smectic multilayer structure. Wide-angle X-ray diffraction (WAXD) measurements of **L1** at 70 °C revealed the presence of a peak at 0.45 nm, corresponding to the intermolecular center-to-center distance in a smectic monolayer of **L1**. On the other hand, the characteristic multilayer structure of **L1** was not observed from SAXS measurement on hybrid **L1/T1** at 70 °C. Nevertheless, a peak at 0.48 nm due to the intermolecular center-to-center distance among **L1** was still observed by WAXD measurement. These results indicate that a kind of N order was formed with hybrid **L1/T1**, in place of the original smectic multilayer order of **L1**, as a result of the adsorption of **L1** to the surfaces of **T1** through the amino group of **L1**. There was an additional phase transition between 110 and 130 °C, as revealed from the jump of the profile from (c) to (d) in Figure 3. The enlarged distance from 33.2 to 36.2 nm may correspond to the relaxation, or fluidization, of the bridging between the molecular layers of **L1** on the TiO₂ particles. The optically isotropic mesophase in Figure 2c seems to show a passing stage of the N–N phase transition. Since the BET surface area of **T1** was 214 m²/g, the surface density of **L1** on **T1** was calculated as 5.9 molecules/nm² on the assumption of full adsorption. This adsorption density is somewhat greater than that calculated from the occupation area of an **L1** molecule standing perpendicular to the surfaces of **T1** particles (ca. 0.2 nm²). However, since there was no sign of the LC formation of independent **L1** molecules, it seemed that most

of the **L1** molecules were densely adsorbed perpendicular to the surfaces of **T1** particles. As a consequence, the acicular TiO₂ particles are deemed to be bridged together through the hydrophobic interaction between the alkyl chains of the **L1** molecule layers on their surfaces, leading to an N structure of the TiO₂ particles linked together by a kind of smectic bilayers of the adsorbed **L1** molecules.

To date, LC behaviors are known for some inorganic anisotropic particles in a highly dilute aqueous dispersions.^{16–18} In such systems, the liquid-crystalline performance is governed by the balance of the repulsive and attractive forces among the anisotropic particles themselves. Kanayama et al.¹⁹ has observed an optically isotropic mesophase with a composite of a thiol derivative of an LC compound and gold nanospheres of ca. 3 nm. However, the details were unknown, and the optical anisotropy characteristic of LCs was not observed either. Hence, to the best of our knowledge, the present paper is the first report on new optically anisotropic LC phases with a novel organic–inorganic hybrid of a liquid-crystalline compound and monodispersed anisotropic inorganic particles. In view of the almost infinite possibilities in the combination of organic and inorganic matters, such hybrid materials may have unfathomable potential as one of the most advanced functional materials in the future.

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Supporting Information Available: Experimental details for the synthesis of **L1–3**, preparation of **T1–4**, and characterization of thermotropic hybrid liquid crystalline behavior (PDF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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