Division of Environmental Chemistry
- Molecular Materials Chemistry -

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Visitor

Dr OHIRA, Shino   School of Chemistry and Biochemistry, Georgia Institute of Technology, USA, 27–29 Octover 2009

Scope of Research

The research activities in this subdivision cover structural studies and molecular motion analyses of highly organized polymer materials in the different states by high-resolution solid-state NMR, electron microscopy, X-ray diffractometry, and so on, in order to develop high-performance and high-functionality polymer materials such as organic electron luminiscence devices and different molecular hybrid materials. The structure formation process of bacterial cellulose is also characterized in detail and environmentally friendly cellulosic nanohybrid materials are examined to develop in different stages of the biosynthesis.

Research Activities (Year 2009)

Presentations

Solid-State NMR Analysis of Amorphous Materials and its Application for Organic Light-Emitting Diodes, Kaji H, The 7th International OLED and PLED Materials Work-shop, 2009 Asian Symposium on Organic Materials for Electronics and Photonics (ASOMP 2009), Taipei, 15 December 2009 (Invited).

Solid-State NMR Analysis of Materials for Organic Light-Emitting Diodes and Organic Solar Cells, Kaji H, IMR Workshop on Organic Light-Emitting Devices, Sendai, 23 January 2009 (Invited).

Analysis of Carrier-Transports in Organic LEDs, Kaji H, ATP Symposium, Annual Meeting of the Chem. Soc. Jpn, Chiba, 28 March 2009 (Invited).

Synthesis of Phosphorus-Containing Materials and the Application to Electron-Transport Layers in Organic Light-Emitting Diodes, Fukushima T, Kaji H, 70th Annual Meeting, Jap. Soc. Appl. Phys., Toyama, 10 September 2009.

Simulation of Charge-Transports in TPD, a Hole-Transport Material, Kawaguchi H, Yamada T, Kaji H, 70th Annual Meeting, Jap. Soc. Appl. Phys., Toyama, 10 September 2009.

Solid-State NMR Analysis of Structure and Dynamics of Polyfuluorene, Shimahara Y, Fukushima T, Kiuchi Y, Kaji H, 9th Organic EL Symposium, Uji, 12 November 2009.

Analysis of Charge Transfer Integrals and Charge Transport Paths in CBP and TPD by Marcus Theory, Suzuki F, Yamada T, Sato T, Tanaka K, Kaji H, 9th Organic EL Symposium, Uji, 12 November 2009.

Formation of Liquid Crystals and the Magnetic Alignment of Tunicate Cellulose Nanofiber Suspensions, Hirai A, Nomura A, Tsujii Y, Tsuji M, Tosaka M, Kaji H, 58th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., Kumamoto, 17 September 2009.

Grants

Kaji H, Fabrication of High-Performance Polymer EL Devices Having Covalently-Bonded Interfaces, Grant-in-Aid for Scientific Research (A), 1 April 2009–31 March 2012.

Kaji H, Development of Solid-State NMR Methodology

Effects of Added Electrolytes on the Phase Separation Behavior in Aqueous Suspensions of Bacterial Cellulose Nanocrystals and on the Magnetic Alignment of the Chiral Nematic Phase

Effective utilization of cellulose as nano-materials is an important subject to create a sustainable society for the 21st century. Bacterial cellulose (BC) is produced by a gram-negative bacterium called *Gluconacetobacter xylinus* cultured in an aqueous medium containing carbon and nitrogen sources. The phase separation behavior in water suspensions has been studied for BC nanocrystals prepared by hydrolysis of BC with 60 wt% sulfuric acid at 51 °C for 1 h.[1] The suspensions separated into the upper isotropic and lower chiral nematic phases above 0.42 wt% of BC nanocrystals. The shape and size distributions of BC nanocrystals in both the phases were determined by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The average size of the BC nanocrystals in the isotropic phase was 8.5 nm × 40 nm × 800 nm and the aspect ratio was 44. On the other hand, the average size of the BC nanocrystals in the chiral nematic phase was 9.8 nm × 54 nm × 1670 nm and the aspect ratio was 73. The surface charge densities were 0.051 and 0.055 e·nm^{-2} for the isotropic and chiral nematic phases, respectively.

The effects of added NaCl (0–5.0 mM) on the phase separation behavior of the aqueous suspensions were investigated for a fixed total cellulose concentration of 3 wt% as shown in Figure 1.[1] The volume fraction of the chiral nematic phase had a minimum value at an NaCl concentration of ca. 1.0 mM. At NaCl concentrations ranging from 2.0 to 5.0 mM, the suspensions did not separate into two phases, but became entirely liquid crystalline, yet not chiral nematic. Figure 2 shows optical polarization micrographs of the anisotropic phase with the addition of NaCl. The size of the ordered domains in the anisotropic phase decreased with an increase in the NaCl concentration from 0 to 2.75 mM. At 2.75 mM, only tactoids were observed in the entire region. At 5.0 mM, chiral nematic domains were no longer observed. The chiral nematic pitch decreased with increasing concentration of added NaCl, reached a minimum value at approximately 0.75 mM, and then increased sharply with the NaCl concentration up to 2.0 mM.

The effects of added sodium chloride on the magnetic alignment of the chiral nematic phase of the suspensions are shown in Figure 3. Under a magnetic field of 9T at 20 °C for 24h, the helical axis of the chiral nematic phase of the suspensions without NaCl aligned parallel to the applied field. At 0.75 mM the helical axis of the chiral nematic phase aligned almost parallel to the applied field. However, the added NaCl moe than 1.0 mM prevented the helical axis of the chiral nematic regions from aligning parallel to the field.

[1] Hirai A, Inui O, Horii F, Tsuji M: *Langmuir*, **25**, 497-502 (2009).

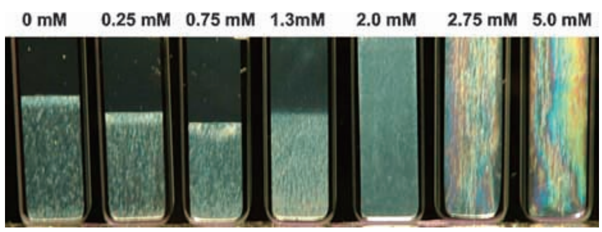

Figure 1. Effect of added NaCl on the phase separation behavior of the BC nanocrystals suspensions for a fixed total cellulose concentration of 3 wt% after 25 days of standing.

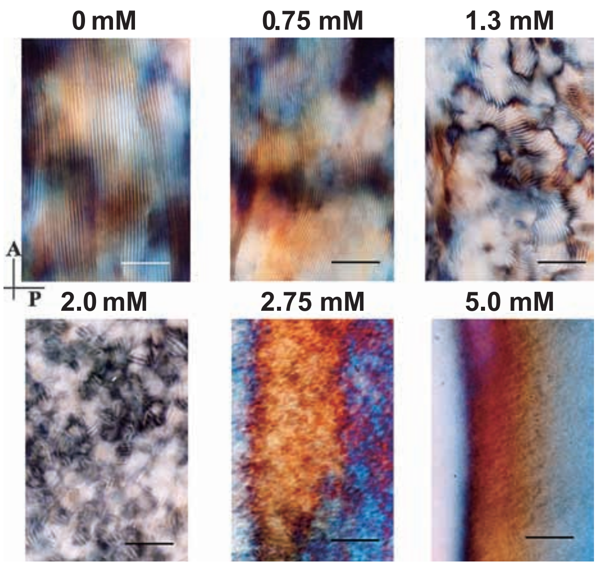

Figure 2. Optical polarization micrographs of the anisotropic phase with the addition of NaCl. The scale bars indicate 0.1 mm. Crossed polarizers are vertical and horizontal.

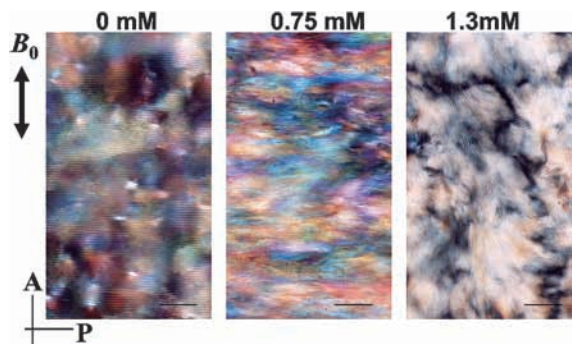

Figure 3. Effect of added NaCl on the magnetic alignment of the anisotropic phase of the suspensions with a total concentration of 3.0 wt%. A static magnetic field of 9T was applied to the samples at 20 °C for 24h. Scale bars indicate 0.1 mm.

for the Structure Analysis of Donor-Acceptor Supramolecules, Grant-in-Aid for Challenging Exploratory Research, 1 April 2009–31 March 2010.

Hirai A, Structure Control of Native Polymer Nano-Assemblies by Magnetic Field, Grant-in-Aid for Scientific Research, 1 April 2007–31 March 2010.