Division of Environmental Chemistry
- Molecular Materials Chemistry -

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Visitors

Prof MACDONALD, Peter M — University of Toronto, Canada, 13–18 October 2006
Prof BECKHAM, Haskell W — Georgia Institute of Technology, USA, 24–29 November 2006

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 2006)

Presentations

Noncrystalline Structure of Polymers Observed by High-Resolution Solid-State NMR, Horii F, Research Group of Fiber Materials, Soc. Polym Sci., Jpn., 1 March, (Invited).

Ordered and Disordered Structure of Native Cellulose Revealed by Solid-State NMR, Horii F, ACS Annual Meeting, 27 March, (Invited).

New Developments of the Characterization of Polymer Materials by High Magnetic-Field NMR, Horii F, 55th Symposium on Macromolecules, Soc. Polym Sci., Jpn., 21 September, (Invited).

From Simple to Advanced Solid-State NMR: the Analysis of Structure and Dynamics of Materials in Organic Devices, Kaji H, The 45th Annual Meeting of the NMR Society of Japan, 22 November (Invited).

Theoretical Study of Chemical Shift Changes by Cationization of TPD, a Hole Transport Material in Organic LEDs, Yamada T, Tsukamoto N, Kusaka Y, Kaji H, Horii, F, 55th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 21 September.

Solid-State ^{2}H NMR Detection of *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)benzidine Thin Films, a Hole-Transport Material in Organic LEDs, Sesei T, Mino A, Kaji H, Horii F, 55th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 20 September.

Preparation and Structure of Nanocomposites Composed of Cellulose Microfibrils and Imogolite Nanotubes, Hirai A, Ikuno M, Horii F, Donkai N, Tsuji M, Polychar-14, 21 April.

Phase Behavior of Aqueous Suspensions of Tunicate Cellulose Nanofibers, Hirai A, Inui O, Ikuno M, Horii F,

Super-High Field Solid-State NMR Characterization of Hydrogen Bonding of Native Cellulose

We are developing new high-resolution solid-state ^{1}H NMR methods to characterize hydrogen bonding by using the world-highest 930 MHz solid-state NMR spectrometer in NIMS at Tsukuba. One method is ^{1}H homonuclear dipolar decoupling under relatively high magic angle spinning (MAS). Phase-modulated Lee-Goldburg (PM-LG) and eDUMB pulses were evaluated in detail but the resolution of the spectra thus obtained was found not to be very high compared to the ^{1}H combined rotation and multiple pulse spectroscopy (CRAMPS) spectra measured at 400 MHz. A new 2 mm MAS probe is now being developed to enhance the spectral resolution. Nevertheless, the ^{13}C-^{1}H heteronuclear correlation (HETCOR) spectrum revealed that possible OH protons are well correlated with the corresponding C2, C3, and C6 carbons for tunicate cellulose as shown in Fig. 1 and the OH resonance lines in the ^{1}H CRAMPS spectrum are successfully assigned by using these correlations.

Another method is CP/MAS ^{2}H NMR spectroscopy newly developed by Mizuno et al. We successfully applied this method to the characterization of OH-deuterated tunicate and *Glaucocystis* celluloses which preferentially contain cellulose I_{β} and I_{α} crystals, respectively.

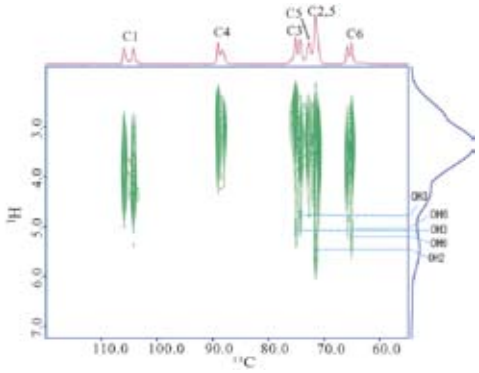

Figure 1. ^{13}C-^{1}H HETCOR spectrum for tunicate cellulose.

Formation and Structure of Liquid Crystal in Aqueous Suspensions of Tunicate Cellulose Nanofibers

Effective utilization of cellulose is a subject of great importance. Tunicate cellulose nanofibers prepared by sulfuric acid hydrolysis of purified mantles of tunicin are rodlike in appearance, 1-3 μm long and 15-30 nm wide. Aqueous suspensions of nanofibers separate into an isotropic and liquid crystalline phases above the concentration of 0.3 wt%. In particular, suspensions ranging in a cellulose concentration from 1 to 3 wt% are separated into three layers (Figure 2). The upper layer is the isotropic phase. The bottom layer exhibits a fingerprint-like pattern characteristic of the chiral nematic phase. Upon application of the horizontal field of 10T for 48h, the fingerprint texture in the bottom layer aligns with its helical axis being parallel to the applied magnetic field. The middle layer is also an anisotropic phase, but a fingerprint pattern is not observed. The distributions of the size of the nanofibers investigated by TEM are not different between the middle and bottom layers. However, a significant difference in ζ-potential is observed between them. Hence, it is concluded that surface charge density is the main factor to exhibit the different textures between the middle and bottom layers.

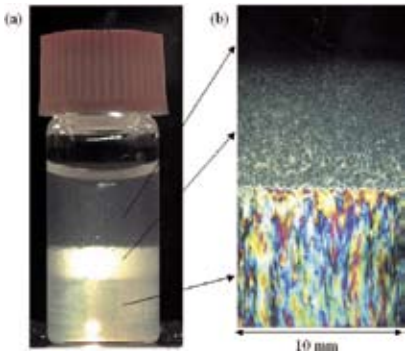

Figure 2. (a) Aqueous suspension of tunicate cellulose microfibrils with a concentration of 2.0 wt%. Three layers are formed. (b) Crossed-polar images of three layers of panel a.

Tsuji M, 55th Annual Meeting, Soc. Polym. Sci., Jpn., 24 May.

Formation and Structure of Liquid Crystal in Aqueous Suspensions of Sulfuric Acid Hydrolyzed Cellulose, Hirai A, Inui O, Ikuno M, Horii F, Tsuji M, 55th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 21 September.

Grants

Horii F, Precise Solid-State NMR Analyses of Noncrystalline Organized Structure and Dynamics of Polymer Functional Materials, Grant-in-Aid for Scientific Research (B) (2), 1 April 2004–31 April 2006.

Horii F, Hybridization Utilizing Hierarchical Structure of Microbial Cellulose by a Newly Developed Microbiosystem, Grant-in-Aid for Scientific Research, 1 April 2004–31 April 2006.

Kaji H, Science and Functions of Organic Amorphous Materials, Grant-in-Aid for Scientific Research (A), 1 April 2005–31 March 2008.

Kaji H, Development of Sublimation NMR Method, Grant-in-Aid for Scientific Research, 1 April 2005–31 March 2007.