Division of Environmental Chemistry
- Molecular Materials Chemistry -

http://www.molmat.kuicr.kyoto-u.ac.jp/

Prof
HORII, Fumitaka
(D Eng)

Assoc Prof
KAJI, Hironori
(D Eng)

Assist Prof
HIRAI, Asako
(D Eng)

Techn
OHMINE, Kyoko

PD
LUO, Qing
(D Sc)

PD
JIA, Yinggang
(D Eng)

Students

SUZUKI, Shinji (D2)
YAMADA, Tomonori (D2)
FUKUSHIMA, Tatsuya (D1)
KUSAKA, Masafumi (M2)
IWATA, Daiki (M2)
SESEI, Takashi (M2)
IGARASHI, Yuki (M1)
KIUCHI, Yohei (M1)
YAMANE, Hiroaki (M1)
TAKAMI, Kosuke (UG)

Visitor

Prof LAUPRETRE, Francoise Laboratoire de Recherche sur les Polymeres CNRS, France, 9–16 June 2007

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 2007)

Presentations

Disordered Structure of Polymer Materials as Revealed by High-Resolution Solid-State NMR Spectroscopy, Horii F, ICR International Symposium (ICRIS)'07, 11–13 June 2007 (Invited).

Molecular and Electronic Structure Analyses of N,N'-diphenyl-N,N'-di(m-tolyl)benzidine by Solid-State NMR and Quantum Chemical Calculations, Yamada T, Kaji H, Horii F, ICRIS'07, 11–13 June 2007.

Honored Lecture: New Developments in Solid-State NMR, Horii F, 46th Annual Meeting of NMR Society of Japan, 12 September 2007 (Invited).

Assembled and Hierarchical Structure of Native Cellulose, Horii F, International Cellulose Conference (ICC), 23 October 2007 (Invited).

Origin of the Different Emission Wavelengths in Alq_3 Analyzed by Solid-State NMR, Kaji H, SPIE Symposium on Photonic Devices + Applications, "Organic Light-Emitting Materials and Devices XI", 26 August 2007 (Invited).

Future Vision and Roadmap of Organic and Molecular Electronics/Bioelectronics, Kaji H, Special Program Symposium, "Future Vision of the Japan Society of Applied Physics", The 68th Annual Meeting of the Japan Society of Applied Physics, 29 March 2007.

Degradation and Structure of Materials in Organic LEDs Analyzed by Solution and Solid-State NMR, Kaji H, ATP Symposium, The 87th Spring Meeting of the Chemical Society of Japan, 26 March 2007 (Invited).

Effects of Added Electrolyte on the Magnetic Alignment of Bacterial Cellulose Microfibril Suspensions, Hirai A, Inui O, Horii F, Yamamoto S, Tsuji M, 56th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 20 September 2007.

Investigation of Dynamics of Poly(dimethylsilane) in the Mesophase by Solid-State ^{29}Si NMR: Evidence for Rotator Phase[1]

The characterization of the dynamics of materials is an important fundamental to understand their properties. For polymers, intermediate states, called "mesophases" often appear between the crystalline and liquid (or amorphous) states. The dynamics in the mesophases is closely related to important problems in polymer science, such as chain folding and (ultra)drawability. However, the dynamics of polymers with Si-Si backbones are not well characterized. In this study, the dynamics of poly(dimethylsilane) (PDMS) in the mesophase was studied.

Figure 1 shows the ^{29}Si cross polarization/chemical shift anisotropy (CP/CSA) spectra of PDMS. Below the transition temperature of 166ºC, which was observed by DSC measurements, we can observe typical CSA line shapes. The simulated CSA spectrum, shown on the experimental CSA spectrum at 23ºC by a green curve, agrees well with the experimental spectrum. Above the transition temperature of 166ºC, the observed CSA line shapes are found to be different from the typical CSA line shapes. The intensity near the isotropic chemical shift becomes small compared to the typical CSA line shapes. This intensity "hole" is experimental evidence of uniaxial rotational motion of the PDMS chains. Under the uniaxial rotation, the ^{1}H-^{29}Si dipolar interaction averages to be parallel to the direction of the rotation axis (see Figure 2). The ^{1}H-^{29}Si dipolar vector is then always directed to the polymer chain axis. The angular-dependence of the dipolar interaction is described by the second-order Legendre polynomial, P_2. Therefore, the signal intensity attenuation occurs during the CP process for polymers whose rotation axis is oriented near along the magic angle relative to the applied magnetic field, $\boldsymbol{B}_0$. The theoretical simulation considering the orientation-dependence of the CP efficiency, as shown on the experimental CSA spectrum at 240ºC by a pink curve in Figure 1, successfully explains the experimental spectrum with the "magic angle hole." This concept is confirmed by the ^{29}Si direct polarization (DP)/CSA and ultra-slow magic angle spinning (MAS) CP/CSA experiments. The change in the interchain packing from a monoclinic to a hexagonal lattice at 166ºC, which is analyzed by electron diffraction experiments, is therefore found to originate from the chain rotation dynamics around the molecular chain axis. From an analytical point of view, we provide an easy way to detect the rotational motion in solid materials.

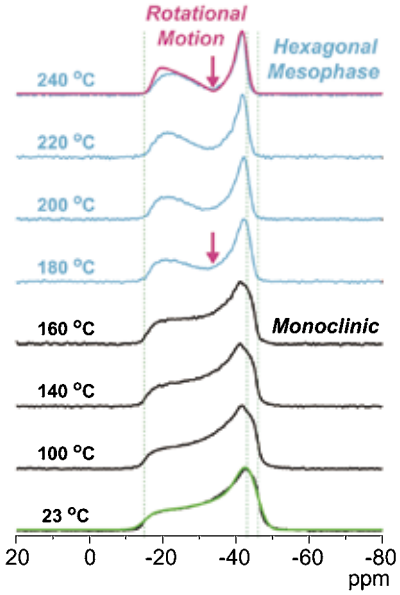

Figure 1. Temperature dependence of ^{29}Si CP/CSA spectra of PDMS from 23 to 240ºC. The arrow indicates the isotropic chemical shift, that is, the theoretical position of the magic angle hole. The simulated spectra for the experimental spectra of 23ºC and 240ºC are shown by the green curves.

[1] Kaji, H.; Horii, F. *Macromolecules* **2007**, *40*, 5420.

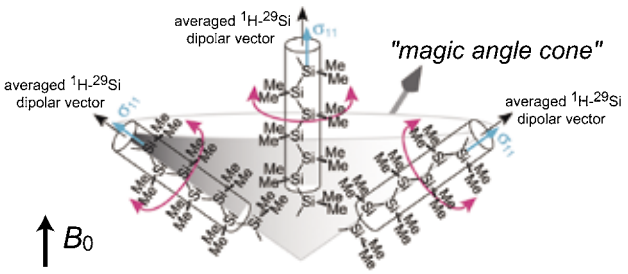

Figure 2. Rotational motion of PDMS in the mesophase.

Phase Separation Behavior of Aqueous Suspensions of Bacterial Cellulose Microfibrils, Hirai A, Inui O, Horii F, Tsuji M, 2nd International Cellulose Conference, 22 October 2007.

Grants

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

Kaji H, Electronic State Analysis of Organic Photoelectric Conversion Systems by Quantum Chemical Calculation and Nuclear Magnetic Resonance, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2007–31 March 2008.

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