Division of Environmental Chemistry
- Molecular Materials Chemistry -

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Visitors

Prof MARCHESSAULT, Robert H — R H, Xerox Research Centre of Canada, Canada, 26 - 27 October 2005
Dr SAMOSON, Ago — National Institute for Chemical Research and Biophysics, Estonia, 12 - 14 November 2005

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, and X-ray diffractometry in order to develop high- performance and high-functionality polymer materials such as organic thin films, 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 2005)

Presentations

Possible Origin of Disordered Structure in Bacterial Cellulose: Structure and Structural Evolution of Sub-Elementary Fibrils, Horii F, 229th ACS National Meeting, San Diego, March 13 - 15 (Invited).

Solid-State NMR Analyses of the Structure and Dynamics of Hydrogen-Bonded Polymers, Horii F, POLYCHAR-14 (Symposium U of ICMAT and ISPAT), Singapore, July 3 - 8 (invited).

Noncrystalline Structure of Native and Synthetic Polymer Materials, Horii F, Soc. Fiber Sci. Technol., June 8 - 10 (Invited).

Super-High Field Solid-State NMR Characterization of Polymer Materials, Horii F, PACIFICHEM 2005, 15 - 20 December (Invited).

The Disordered Structure of Native Cellulose and the Origin of the Formation, Horii F, PACIFICHEM 2005, 15-20 December (Invited).

Solid-State NMR Investigations of Materials in Organic Light-Emitting Diodes, Kaji H, PACIFICHEM 2005, 15 - 20 December (Invited).

Isomeric States and Molecular Packing in Alq_3 Polymorphs Studied by CP/MAS ^{13}C NMR, Kaji H, Third International Conference on Molecular Electronics and Bioelectronics (M&BE3), 3 - 4 March.

Conformational Analysis of TPD by Two-Dimensional Solid-State Double-Quantum NMR Spectroscopy and Quantum Chemical Calculations, Yamada T, Tsukamoto N, Kaji H, and Horii F, The 44th Annual Meeting of Japanese NMR Society and The 1st Asia-Pacific NMR Symposium, November 10, 2005.

Phase Behavior of Aqueous Mixtures of Cellulose Microfibrils and Imogolite Nanotubes and Preparation of Their Nanocomposites, Hirai A, PACIFICHEM 2005, 15 -

Relationships between Light-Emitting Properties and Isomeric States in Alq_3 Polymorphs Studied by Solid-State ^{27}Al NMR[1]

Tris-(8-hydroquinoline) aluminum (Alq_3) is one of the most widely used light-emitting and electron-transport materials in organic light emitting diodes (OLEDs). Recently, Brinkmann et al. found three crystalline forms, α-, β-, and γ-Alq_3, and the crystalline structures of α- and β-Alq_3, both are composed of only the meridional isomer, were determined. In contrast, the crystalline structure of γ-Alq_3 has been still unclear. More recently, Braun et al. found a new crystalline phase, δ-Alq_3. This shows interesting features; blue luminescence and a high photoluminescence quantum yield (51 %). Alq_3 is normally in the amorphous state in organic EL devices and the analysis of the amorphous structure is also crucial. In this study, isomeric states of Alq_3 in the different polymorphs, α-, γ-, δ-Alq_3, and in the amorphous state have been analyzed by solid-state NMR measurements.

Figure 1 shows the experimental ^{27}Al magic angle spinning (MAS) NMR spectra of Alq_3 in the different states. MAS technique eliminates the effect of chemical shift anisotropy and the spectra only reflect the quadrupolar interaction. Therefore, information on electric field gradient (EFG) tensors is obtained. For α-Alq_3 and amorphous Alq_3, broad spectral patterns are observed, whereas γ-Alq_3 and δ-Alq_3 give sharp spectral patterns. Qualitatively, these results show that the EFG tensors are more axially symmetric for γ- and δ-Alq_3 compared to α- and amorphous Alq_3. The quantitative symmetry is obtained by the asymmetry parameters, η. Although the spectra of α- and amorphous Alq_3 are not well reproduced by simulations up to now, the values of η are considered to be 0.6 – 1.0, which suggest Alq_3 molecules in these samples are in the meridional form. The simulations for γ- and δ-Alq_3 well reproduce the experimental spectra, and from the best-fit simulations, the values of η are determined to be 0 and 0.24, respectively. The DFT calculation for a single facial Alq_3 molecule predicts the axially symmetric pattern with $\eta = 0$. The DFT calculated value is in excellent agreement with the experimentally determined value for γ-Alq_3 ($\eta = 0$) and we conclude that the γ-Alq_3 is composed of the facial isomer. The point charge model calculation for facial Alq_3 in the δ-crystalline form gives $\eta = 0.26$. This value agrees well with our ^{27}Al MAS NMR result, $\eta = 0.24$, indicating the non-zero η value for δ-Alq_3 is originated from the crystalline intermolecular packing. We can therefore conclude that α- and amorphous Alq_3 are composed of the meridional isomer, whereas γ- and δ-Alq_3 are composed of the facial isomer.

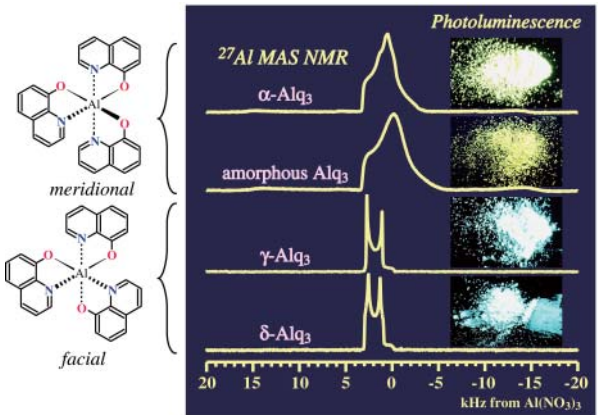

Figure 1. MAS ^{27}Al NMR spectra of α-, amorphous, γ-, and δ- Alq_3.

Our α- and amorphous Alq_3 samples show fluorescence spectra with maxima at 510 and 509 nm, respectively. In contrast, blue-shifted fluorescences are observed for γ- and δ-Alq_3 whose maxima are at 468 and 466 nm, respectively. This clearly indicates a close relation between the isomeric states and the light-emitting properties.

[1] H. Kaji, Y. Kusaka, G. Onoyama, F. Horii, Jpn. J. Appl. Phys., 2005, 44, 3706.

20 December (Invited).

Liquid Crystal Structure of Nanocomposites of Cellulose Microfibrils and Imogolite Nanotubes, Ikuno M, Hirai A, Horii F, Donkai N, Tsuji M, 54th Annual Meeting, Soc. Polym. Sci., Jpn., 25 May.

Grants

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

Horii F, Hybridization Utilizing Hierarchical Structure of Microbial Cellulose by a Newly Developed Microbio-system, Grand-in-Aid for Scientific Research, 1 April 2004 - 31 March 2006.

Kaji H, Higher Order Structures and Optical Properties of Light-Emitting Polymeric Materials, PRESTO, Japan Science and Technology Agency, 1 November 2002 - 31 March 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.