Fundamental Material Properties
- Molecular Dynamic Characteristics -

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Visitors

Prof HU, Shaohua	DonghuaUniversity, China, 15 January–23 March, 2002
Dr AMORNSAKCHAI, Taweechai	Mahidol University, Thailand, 1 April–31 May, 2002
Dr SCHELER, Ulrich	Institut fuer Polymerforshung, Doresden e. V., Germany, 27–28 November, 2002

Scope of Research

The research activities in this subdivision cover structural studies and molecular motion analyses of polymers and related low molecular weight compounds in the crystalline, glassy, liquid crystalline, solution, and frozen solution states by high-resolution solid-state NMR, dynamic light scattering, electron microscopy, X-ray diffractometry, and so on, in order to obtain basic theories for the development of high-performance polymer materials. The processes of biosynthesis, crystallization, and higher-ordered structure formation are also studied for bacterial cellulose.

Research Activities (Year 2002)

Presentations

Structural Study of Microbial Poly(ε-lysine) in the Different States, Horii F, Masuda K, Nakamura H et al., 224th ACS Annual Meeting, 20 August.

Critical Fluctuations and Dissipative Structure Formation in Solution of Cellulose Acetates in Couette Flow (Paris, France), International Conference on Theor. Phys., Tsunashima Y, International Union for Pure and Appl. Phys., 24 July.

Chain Dynamics and Structure Transition of Cellulose Acetates in Dilute Solution (Kyoto), IUPAC Polym. Conference, Tsunashima Y, Soc. Polym. Sci., Jpn., 4 December.

Structure of Band-like Cellulose Assemblies Produced by *Acetobacter Xylinum*, Hirai A, Tsuji M, Horii F, 1st International Cellulose Conference, 6 November.

Structure and Dynamics of Disordered Polymers and their Properties, Kaji H, 1st RIKEN Symposium “Structural and Functional Aspects of Polymer Crystals”, 19 July.

Dynamic Assemblies of Cellulose Acetates in Polar Solvents, Tsunashima Y, Kawanishi H, Mizuno M, Onodera G, Horii F; Structure of Band-like Cellulose Assemblies Produced by *Acetobacter Xylinum* as Revealed by TEM and X-Ray Diffraction Analysis, Hirai A, Tsuji M, Horii F; Characterization of Specific Interactions in Polymers by an MAS NMR Method Without Irradiating Passive Spins, Kaji H, Horii F, 6th International Conference of ICRIS’02 (Kyoto), 31 January.

Solid-Phase Reaction and Microfibiril Structure of Bacterial Cellulose, Yamamoto H, Horii F, Hirai A, Annual meeting, Cellulose Soc. Jpn, 11 July.

Studies on Unique Thermal Changes in Conformation for Atactic Polypropylenes, Nishimura T, Kuwabara K, Kaji H, and Horii F, Annual Meeting, Soc. Polym. Sci., Jpn., 29 May.

The Analysis of Dynamics in Amorphous Super-Engineering Plastics by Two-Dimensional Solid-State NMR Spectroscopy, Kaji H, Okazaki H, Fuke K, Horii F, Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 4 October.

Topics

Selective Observation and Quantification of Amorphous Trans Conformers in PET by Zero-Quantum MAS Solid-State NMR

We present a new NMR method for identifying and quantifying conformations of ^{13}C-labeled polymers under magic-angle spinning (MAS). The experiment is based on zero-quantum (ZQ) dephasing under the recoupled chemical-shift anisotropy (CSA), and the observed magnetization is dephased by the relative orientation of relevant two ^{13}C sites. This method is applied to the O-$^{13}CH_2$-$^{13}CH_2$-O moieties in amorphous poly(ethylene terephthalate) (PET). Signals of near-trans conformations decay more slowly than those near gauche, which permits the determination of trans : gauche ratio and torsion angles of respective components. This experiment also enables selective observation of amorphous trans component, which cannot be detected by traditional CP/MAS experiments due to complete overlap with dominant gauche signal. The angular resolution is especially high for near-trans conformations. From the decay curves (see Fig. 1), it is determined that the trans fraction is $12 \pm 3\%$ and the torsion angle is distributed with a standard deviation $\sigma_\psi = 16^o$ around the ideal trans state $\psi_{ave} = 180^o$ for amorphous PET.

In semicrystalline PET (not shown here), the crystalline trans :crystalline gauche : amorphous trans : amorphous gauche = 23 : 0 : 20 : 57 (± 5) %. The trans fraction in the amorphous regions of semicrystalline PET, 26 ± 5 %, is found to be significantly higher than 12 ± 3 % in amorphous PET.

The technique presented here opens the possibility of characterizing the conformations of various kinds of ordered and disordered materials, including organic, inorganic, and bio-materials.

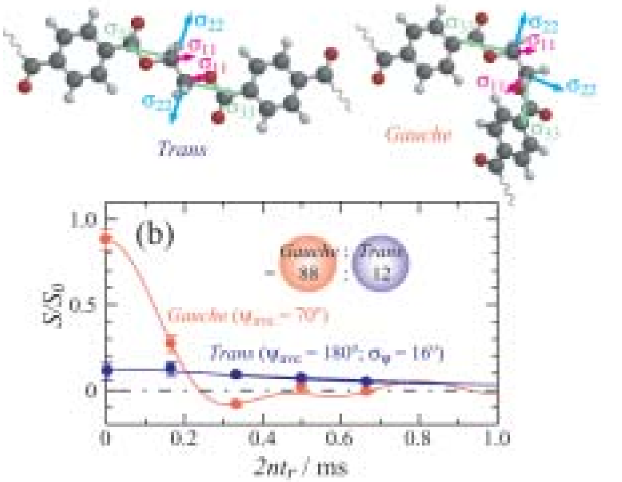

Fig. 1. ZQ-CSA-dephasing curves of amorphous PET. The quantitative torsion angles are determined from the curves.

Hierarchical Structure of Cellulose Produced by *Acetobacter Xylinum*

We have been studying the hierarchical structure formation process of cellulose produced by *Acetobacter xylinum* under various culture conditions. Under standard culture conditions, bacteria produce cellulose gels which are composed of thin ribbon assemblies. A ribbon-like assembly is extruded parallel to the long axis of the cell and twisted in a right-handed manner. In contrast, at 4 °C a band-like cellulose assembly, which consists of strand-like cellulose entities, is extruded perpendicularly to the long axis of the bacterial cell. We have been clarifying the role of extensive hydrogen bonding of cellulose and its hydrophobicity on the hierarchical structure formation process of bacterial cellulose. Together with this vital information we are trying to design hybrids based on cellulose at molecular level. This new and revolutionary material, it is hoped, will solve the recent energy and environmental problems facing today's world.

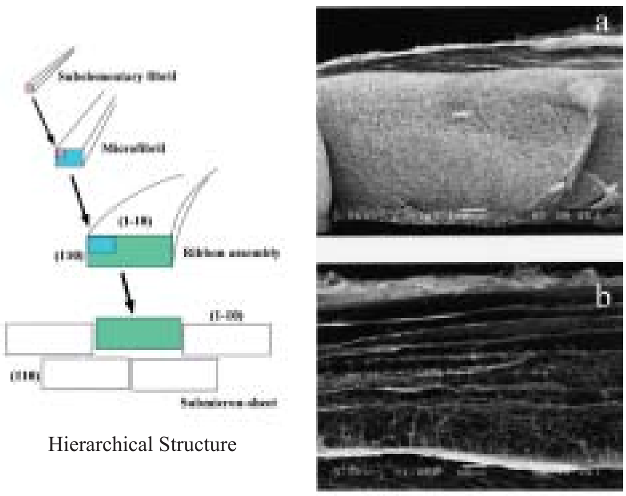

Fig. 2. (a) SEM photo of a freeze-dried cellulose gel sample. (b) Magnified image near the surface of (a). Stacked submicron sheets (see the left model) are observed.

Analyses of Local Structures in Glassy Polymers by Multiple-Quantum NMR Methods, Kaji H, Horii F, Schmidt-Rohr K (Iowa State Univ.), NMR Conf. Jpn., 8 November.

Grants

Horii F, Multi-Dimensional Structure Control of Microbial Polymers in the Biosynthesis Process and Precise Analysis of their Structure and Functionality, Grant-in-Aid for Scientific Research (C)(1), 1 April 2002 - 31 March 2003.

Hirai A, Molecularly Aggregated State of Bacteria-Produced Cellulose Made Through Nano-Spinning, Grant-in Aid for Scientific Research (C)(2), 1 April 2001 - 31 March 2003.

Kaji H, Precise Analyses of Polyamorphous Structure and Dynamics by Advanced Solid-State NMR, Grant-in Aid for Young Scientists (A), 1 April 2001 - 31 March 2003.

Kaji H, Higher Order Structures and Optical Properties of Light-Emitting Polymeric Materials, PRESTO, Japan Science and Technology Corporation, 1 November 2002 - 31 October 2005.

Award

Masuda K, Award for the Outstanding Paper, The Society of Polymer Science, Japan, 30 May.