

Division of Multidisciplinary Chemistry - Polymer Materials Science -

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Prof
KANAYA, Toshiji
(D Eng)



Assoc Prof
NISHIDA, Koji
(D Eng)



Assist Prof
MATSUBA, Go
(D Eng)

Students

RAHMAN, Nelly (D3)
ASAKAWA, Harutoshi (D1)
ITO, Chie (M2)
OKADA, Kazuma (M2)
TANAKA, Kentaro (M2)

TOMOHISA, Hiroshi (M2)
KAWABATA, Jun (M1)
KAWASHIMA, Kazuko (M1)
MORITA, Hideyuki (M1)
ZHAO, Yunfeng (M1)

ANADA, Ryota (UG)
MATSUI, Kazuya (UG)
MATSUI, Tamito (UG)
MATSUMOTO, Norihiro (UG)
TERATANI, Makoto (UG)

Visitors

Prof MUKHERJEE, Manabendra
Prof GABRYS, Barbara J

Saha Institute of Nuclear Physics, India, 17–29 March 2008 / 2–14 December 2008
University of Oxford, UK, 12–30 May 2008

Scope of Research

The structure and molecular motion of polymer substances are studied using mainly scattering methods such as neutron, X-ray and light with intension of solving fundamentally important problems in polymer science. The main projects are the mechanism of structural development in crystalline polymers from the glassy or molten state to spherulites; the dynamics in disordered polymer materials including low-energy excitation or excess heat capacity at low temperatures, glass transition and local segmental motions; formation processes and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.

Research Activities (Year 2008)

Publication

Ogawa H, Kanaya T, Nishida K, Matsuba G: Composition Fluctuations before Dewetting in Polystyrent/Poly(vinyl methyl ether) Blend Thin Films, *Polymer*, **49**, 2553-2559 (2008).

Presentations

Temperature Effects on Poly (L-lactic acid) Crystallization, Uchida H, Kawai T, Rahman N, Matsuba G, Nishida K, Kanaya T, The 57th SPSJ Annual Meeting, Yokohama, 28–30 May 2008.

Rapid Temperature Jump Stage for Optical Microscope, Nishida K, The Polymer Processing Society 24th Annual Meeting, Salerno, Italy, 15–19 June 2008.

Structure Formation of Polyethylene under Drawing with Small Angle Neutron Scattering Measurements, Ito C, Matsuba G, Nishida K, Kanaya T, 17th Autumn Meeting in Combined Societies about Fibers in Japan, Nara,

28–29 August 2008.

Effects of Surface Flatness of Glass Substrates on the Orientation and Size of the Grains of Colloidal Crystals Obtained by Centrifugation, Asakawa H, Suzuki Y, Summer Seminar of Society of Fiber Science and Technology in Japan, Oumi-hachiman, 10–12 September 2008.

Inelastic Neutron Scattering from Polystyrene Thin Films, Kanaya T, *Advances in Polymer Science & Neutron Scattering*, London, UK, 14–15 September 2008.

Crystallization Process of Polyesters under Shear Flow, Tomohisa H, Matsuba G, Nishida K, Kanaya T, The 57th SPSJ Discussion (Autumn) Meeting, Osaka, 24–26 September 2008.

Annealing of Mesomorphic Phase of Isotactic Polypropylene, Okada K, Nishida K, Matsuba G, Konishi T, Kanaya T, The 57th SPSJ Discussion (Autumn) Meeting, Osaka, 24–26 September 2008.

Critical Dissolution Ionic Strength of Aqueous Chito-

Precursor of Shish-kebab in Isotactic Polystyrene under Shear Flow

The polarized optical microscope (POM), depolarized light scattering (DPLS) and small-angle X-ray scattering measurements were performed on the structure formation process or the crystallization process of isotactic polystyrene (iPS) under shear flow below and above the nominal melting temperature T_m . It was found that an anisotropic oriented structure termed here as a string-like object was formed in μm scale even above the nominal melting temperature and stable for more than 24 hours, but melted at around 270 °C far above T_m in Figure 1. The string-like object acts as a nucleation agent for the folded chain lamella crystal (or the kebab), and was assigned to a precursor of the shish-kebab from small angle x-ray scattering measurements. Based on the results we have discussed two possible structures for the string-like object: one is fringed micelle type structure including partially extended chain crystals and the other is liquid crystal-like structure formed through extended network of entangled polymer chains.

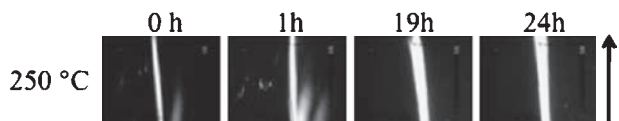


Figure 1. Time evolution of POM pictures of iPS during the annealing process at various temperatures after applying a pulse shear with shear rate 30s^{-1} and shear strain 12000 % at 250 °C up to 24 h. Note that the nominal melting temperature of iPS is 223 °C.

Heterogeneous Dynamics of Polymer Thin Films

In the last decade many studies have been performed on polymer thin films to reveal very interesting but unusual properties. One of the most interesting findings is that the glass transition temperature T_g decreases with film thickness in the thickness range below about 400 Å. It is be-

lieved that one of the most important key issues to solve the unusual properties of polymer thin films is heterogeneous dynamics of polymer thin films [1]. We therefore studied the dynamic heterogeneity of polystyrene thin films in glassy state in terms of non-Gaussian parameter A_0 , which is a measure of dynamic heterogeneity, using inelastic neutron scattering [2]. It was found that the non-Gaussian parameter increased with decreasing the film thickness, suggesting the increase in the dynamic heterogeneity. Assuming a simple two layer model consisting of an interface hard layer and a bulk-like layer we analyzed the thickness dependence of the non-Gaussian parameter A_0 and the mean square displacement $\langle u^2 \rangle$ to find that the hard layer has the thickness of ~ 130 Å and the mean square displacement of ~ 0.018 Å² at 230 K as shown in Figures 1 and 2, suggesting dynamic heterogeneity of polymer thin films.

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- [1] Inoue R, Kanaya T, Nishida K, Tsukushi I, Shibata K, *Phys. Rev. E* **77**, 032801-1-032801-4 (2008).
 [2] Inoue R, Kanaya T, Nishida K, Tsukushi I, Taylor J, Levett S, *Eur. Phys. J., E* **24**, 55-60 (2007).

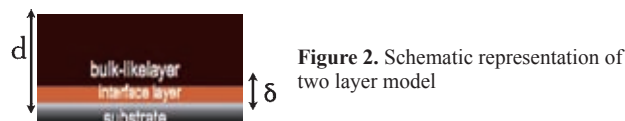


Figure 2. Schematic representation of two layer model

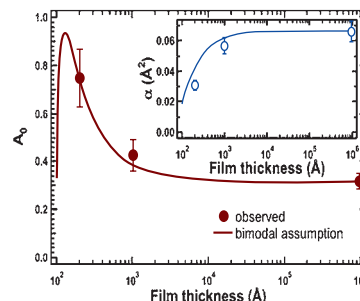


Figure 3. Non-Gaussian parameter A_0 at 230 K as a function of film thickness. Inset shows mean square displacement $\langle u^2 \rangle$. Solid curves are the results of fits with two layer model.

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san, Tanaka K, Nishida K, Gabrys BJ, Lawrence MJ, Kanaya T, The 57th SPSJ Discussion (Autumn) Meeting, Osaka, 24–26 September 2008.
 Formation Process of Shish-kebab Structure under Shear Flow, Matsuba G, The 3rd International Symposium on Polymer Science (NIST-JAPAN), Nagoya, 10–11 November 2008.

Distribution of Glass Transition Temperature in Polystyrene Multilayered films, Kawashima K, Inoue R, Matsuba G, Nishida K, Kanaya T, IUMRS-ICA, Nagoya, 9–14 December 2008.

Grants

Kanaya T, Higher Order Structure Formation in Induction Period of PLA Crystallization and External Fields, Collaboration Research with Toyota Motor Corporation and Toyota CRDL., INC, 15 January 2003–30 September 2009.

Nishida K, Kanaya T, Matsuba G, Control of Higher Order Structure by Crystallization via Mesomorphic Phase, Grant-in-Aid for Scientific Research (C), 1 April 2007–31 March 2009.

Matsuba G, Correlation between Phase Separation and Crystallization of Polyolefins, Grant-in-aid for Young Scientists (B), 1 April 2007–31 March 2009.