

Division of Multidisciplinary Chemistry - Polymer Materials Science -

<http://www.scl.kyoto-u.ac.jp/~kanaya2/index.html>



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University of Rostock, Germany, 18 February 2005
The Hebrew University of Jerusalem, Israel, 28 April 2005
Instituto de Estructura de la Materia, CSIC, Spain, 31 May 2005
University of Akron, United States, 9 September 2005
Korea University, Korea, 1 April - 30 September 2005

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 2005)

Presentations

Effect of Charge Density on Phase Separation of Aqueous Solutions of Hetero Polyelectrolytes, Tsubouchi T, Takahashi N, Nishida K, Kanaya T, Annual Meeting, the Society of Polymer Science, Japan, Yokohama, 26 May.

Effect of Ultra-high Molecular Weight Component in Crystallization of Polyethylene under Shear Flow (I) - SAXS Measurements, Sakamoto S, Ogino Y, Matsuba G, Nishida K, Kanaya T, Annual Meeting, the Society of Fiber Science and Technology, Gifu, 9 June.

Structural Analysis of Shish-kebab with X-ray and Neutron Scattering Measurements, Matsuba G, Ogino Y, Nishida K, Kanaya T, 230th ACS National Meeting, Washington DC, USA, 29 August.

Crystallization of Isotactic Polypropylene under Shear Flow -Effect of Shear Rate-, Ogino Y, Matsuba G, Nishida K, Kanaya T, 230th ACS National Meeting, Washington

DC, USA, 30 August.

Phase Separation of Hetero Polyelectrolyte Solutions, Nishida K, Tsubouchi T, Kanaya T, 54th Symposium on Macromolecules, Yamagata, 21 September.

Crystallization of Poly(L-lactic acid), Kawai T, Kanaya T, European Discussion Meeting on Polymer Physics, Polymer Crystallization, Waldau, Germany, 7 October.

Crystallization from Mesomorphic Phase of Isotactic Polypropylene, Konishi T, Nishida K, Matsuba G, Kanaya T, European Discussion Meeting on Polymer Physics, Polymer Crystallization, Waldau, Germany, 7 October.

Neutron Scattering Researches on Soft Condensed Matter, Kanaya T (invited), International Conference on Neutron Scattering, Sydney, Australia, 28 November.

Grants

Kanaya T, Collaboratory on Electron Correlation toward

Phase Inversion in Blend of Aqueous Polyelectrolytes Due to Imbalanced Charge Densities

Most of polymeric materials of different kind or their solutions are difficult to dissolve each other. Even in an exceptional case, such a blend usually shows upper critical solution temperature (UCST) type phase behavior, i.e. the blend is in one phase region and in two phase region above and below the critical temperature, respectively. It is still more rare that the blend shows lower critical solution temperature (LCST) type one, since the entropy loss by demixing in the higher temperature region causes a great penalty for the free energy. We have found that a blend of aqueous solutions of different polyelectrolytes (PSSNa/PVSNa/water) having imbalanced charge densities is a promising system to show the LCST type behavior. When the charge densities of different polyelectrolytes are balanced, normal UCST type behavior is observed. However, as the charge densities of different polyelectrolytes become imbalanced, the phase behavior suddenly changed from the UCST to LCST type (Fig. 1). It is considered that the entropy loss in the higher temperature region is compensated by special repulsive interaction that stabilizes the structure between different polymers.

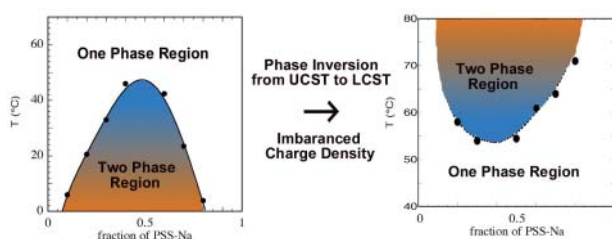


Figure 1. Phase diagrams for blends of aqueous solutions of different polyelectrolytes. Phase inversion occurs when the charge densities of different polyelectrolytes becomes imbalanced.

Crystallization of Poly(L-lactic acid)

Poly (L-lactic acid), PLLA, is one of environmentally friendly polymers that attracted significant interest in recent years. We found novel crystalline form of PLLA (α' phase). In Fig. 2, wide angle X-ray diffraction (WAXD)

profiles at higher crystallization temperatures, T_c s, above 120 °C are assigned to be of α' -form (10_3 helix, *pseudo-orthorhombic*, $a=10.05\text{\AA}$, $b=6.1\text{\AA}$, $c=28.8\text{\AA}$), while some reflections including (1 0 10) are absent in lower T_c s below 90°C. The results strongly suggest that the disordered α' phase, which has hexagonal lattice (10_3 helix, $a=6.2\text{\AA}$, $c=28.8\text{\AA}$), is formed at lower temperatures. The disordered α' phase is transformed into the ordered α phase upon heating (Fig. 3). One can see clearly in the WAXD profiles that phase transformation takes place at 150°C. Each reflection shifts to higher q as well as the increase in the number of reflections, which are due to the change in the lattice size and the space group, respectively. The profiles above 150°C were obviously the same as that of high T_c samples (ordered α phase). Moreover, two-step decrease in diffraction intensity has been observed during the melting process. It is reasonable, therefore, to consider that ordered α phase grows through the melting–reorganization or melting–recrystallization mechanism.

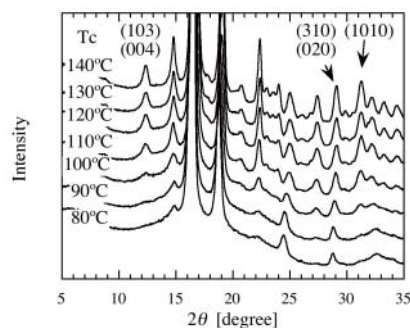


Figure 2. WAXD profiles of PLLA crystallized at various T_c s from the melt.

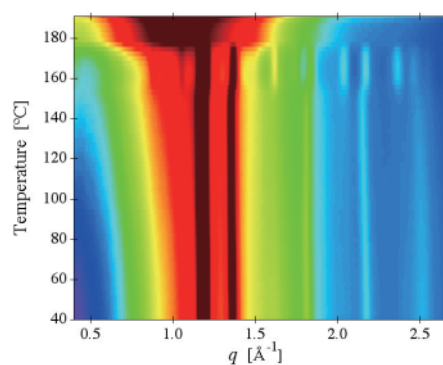


Figure 3. 2D WAXD profiles upon heating at 10°C/min. The sample was pre-crystallized at 80°C.

a New Research Network between Physics and Chemistry, Grand in-Aid for Creative Scientific Research, 1 April 2004 - 31 March 2006.

Kanaya T, Higher Order Structure Formation in Induction Period of PLA Crystallization and in External Fields, Collaboration Research with Toyota Motor Corporation

and Toyota CRDL., INC, 15 January 2003 - 31 March 2006.

Matsuba G, Observation of Shish-kebab Structural Formation Processes of Polymers with Neutron Scattering Technique, Grant-in-Aid for Young Scientists (B), April 2005 - March 2007.