

## Fundamental Material Properties -Polymer Materials Science-



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## 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 intention 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 2001)

### Presentations

*In situ* microscopic observation of crystallization process of PET by a rapid temperature jump method, Nishida K, Matsuba G, Kaji K, Kanaya T, Polymer Symposium (Kobe), Soc. Polym. Sci. Jpn., 6 July.

Microscopic observation of frozen structure of melt-crystallization process of PET, Okuyama T, Nishida K, Kaji K, Kanaya T, Polymer Symposium (Kobe), Soc. Polym. Sci. Jpn., 6 July.

Microscopic observation of glass-crystallization process of PET, Konishi T, Nishida K, Kaji K, Kanaya T, Polymer Symposium (Kobe), Soc. Polym. Sci. Jpn., 6 July.

A novel concept in mechanism of polymer crystallization and its application for the control of higher order structure of polymer materials, Nishida K, Kaji K, Kanaya T, Matsuba G, Okuyama T, Konishi T, Meeting of the POVAL COMMITTEE, 7 July.

Self organization in polymer crystallization - Microphase separation during the induction period and structure control - (invited), Kaji K, the 32nd Joint Autumn Meeting, General Association for Chubu Branches of Chemistry-Related Societies, Jpn., 6 October.

Fast process in glass-forming polymers (invited), Kanaya T, Tsukushi I, Kaji K, The Fourth International Discussion Meeting of Relaxations in Complex Systems, Crete, Greece, 20 June.

Hierarchic structure of polymer gels revealed by

WANS, SANS and USANS (invited), Kanaya T, International Symposium on Advanced Utilization of Research Reactor, Kumatori, Japan, 28 February.

Spinodal decomposition and syneresis of gels, Takahashi N, Takeshita H, Kanaya T, Nishida K, Kaji K, Autumn Meeting, Soc. Polym. Sci. Jpn., 13 September.

Phase diagram of polyelectrolyte solutions, Nishida K, Kaji K, Kanaya T, Autumn Meeting, Soc. Polym. Sci. Jpn., 14 September.

Structure and dynamics of polymer micelles as studied by small-angle neutron scattering and neutron spin-echo techniques, Kanaya T, Watanabe H, Nagao M, Kaji K, Monkenbusch M, Richter D, Autumn Meeting, Soc. Polym. Sci. Jpn., 14 September.

### Grants

Kaji K, Kanaya T, Fukao K, Imai M, Preparatory mechanism of polymer crystallization, Grant-in-Aid for Scientific Research (B) (2), 1 April 2000 - 31 March 2002.

Kanaya T, Ebisawa T, Tasaki S, Glass transition mechanism of polymers, Grant-in-Aid for Scientific Research (C) (2), 1 April 2001 - 31 March 2003.

Nishida K, Control of higher order structures of polymer materials by a rapid temperature jump method, Industrial Technology Research Grant Program by New Energy and Industrial Technology Development Organization (NEDO) of Japan, 1 April 2001 - 31 March 2003.

## Topics

### A finding of spinodal decomposition-assisted crystal nucleation in polymers

About ten years ago we found a surprising phenomenon that a spinodal decomposition (SD) type phase separation due to the orientation fluctuations of rigid segments occurs prior to crystal nucleation. Recently it has been revealed that this is a new type of crystal nucleation. The well-known homogeneous crystal nucleation occurs at high temperatures above the binodal  $T_b$  directly from the melt in the liquid-crystal coexistence domain, while the SD-assisted crystal nucleation does below spinodal temperature  $T_s$ . The figure shows the optical micrographs for crystallization of poly(ethylene terephthalate) where a sudden change of morphology from an SD pattern to a spherulitic or nucleation-and-growth pattern is seen above  $T_s = 213^\circ\text{C}$  [1].

1. K. Nishida, K. Kaji, T. Kanaya, G. Matsuba, T. Okuyama and T. Konishi, *Meeting Report of the Poval Committee*, No.118, 55 (2001).

### Evidence for localization of the Boson peak in glassy PMMA

One of the most important but controversial problems in dynamics of glassy materials is the origin of the boson peak and the picosecond fast process observed in many glass-forming materials [1]. In this work [2], we carried out coherent inelastic neutron scattering measurements on glassy poly(methyl methacrylate) (PMMA) to elucidate the spatial scale of the boson peak and the fast process. Comparing the observed  $Q$  dependence of the inelastic scattering intensity at various excitation energies  $\Delta E$  with that of the elastic scattering (see figure), we found that the boson peak and the fast process modes do not move in phase at a length scale of  $\sim 7\text{\AA}$ , suggesting that they are localized modes on two monomers within a PMMA chain.

1. T. Kanaya, K. Kaji, *Adv. Polym. Sci.*, **154**, 87 (2001).
2. T. Kanaya, I. Tsukushi K. Kaji, B. J. Gabrys, S. M. Bennington, H. Furuya, *Phys. Rev.* **B64**, 144202 (2001).

### Phase diagram of polyelectrolyte solutions

We have presented an improved phase diagram of polyelectrolyte solutions as functions of the degree of polymerization and the concentration [1]. This new phase diagram was drawn for salt-free solutions of vinyl-type polyelectrolytes, and the main improved points are the dilute-semidilute crossover concentrations, which were determined from the recent experimental data on the polyion persistence length. The concentrated regime and the swollen regime were newly introduced according to our findings. Furthermore, the degrees of orderliness in the dilute regime were specified according to the ratio  $\delta/\xi_{\text{cent}}$  of the amplitude of thermal fluctuations to the mean intermolecular distance. Thus, the new phase diagram considerably well describes the realistic structure of polyelectrolyte solutions.

1. K. Nishida, K. Kaji and T. Kanaya, *J. Chem. Phys.*, **115**, 8217 (2001).

