Dynamic Heterogeneity of Amorphous Polymers below and above T_g

Toshiji Kanaya and Keisuke Kaji

Dynamic heterogeneity has been investigated for amorphous polymers in terms of non-Gaussian parameter A_0, which is currently believed to be a key to reveal anomalous dynamics near the glass transition. This parameter A_0 was evaluated in incoherent elastic neutron scattering measurements in a wide range of Q (length of scattering vector). Combining the neutron data with the positron annihilation lifetime spectroscopy (PALS) data the spatial scale of the heterogeneous domain or the so-called *cooperatively rearranging region* (*CRR*) has been determined.

Keywords: heterogeneity/ amorphous polymers/ neutron scattering/ non-Gaussian parameter/ positron annihilation lifetime spectroscopy/ cooperatively rearranging region

The glass transition is one of the most important phenomena in condensed matter sciences, especially polymer materials science because polymer materials necessarily include amorphous regions and the properties such as mechanical and thermal properties drastically change at the glass transition temperature T_g. It is now elucidated that the glass transition is not a second order phase transition but a relaxation phenomenon. Therefore, extensive dynamical studies were carried out on amorphous materials using many kinds of techniques to reveal various anomalous but common features of them [1]. A huge amount of data implies that there exists the so-called *cooperatively rearranging region* (*CRR*) in amorphous materials near T_g where molecules or polymer segments must move cooperatively. The existence of *CRR* makes the amorphous materials dynamically very heterogeneous. It is therefore believed that the heterogeneity is a key to solve the anomalous dynamics near T_g.

In a series of works we studied the dynamic heterogeneity of some amorphous polymers below and above T_g using inelastic neutron scattering [2,3,6] and positron annihilation lifetime spectroscopy (PALS) [4,5]. In the neutron scattering measurements, we have evaluated the non-Gaussian parameter which is a measure of the heterogeneity. In addition, we have obtained the size of free volume and its distribution from the PALS experiments. Combining the neutron and PALS data, we proposed a new strategy to evaluate the spatial scale of heterogeneity or *CRR* [5]. In this report, the main results of polyisobutyrene (PIB) and polybutadiene (PB) with T_g =

FUNDAMENTAL MATERIAL PROPERTIES — Polymer Materials Science —

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 the 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 process and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.

Prof
KAJI, Keisuke
(D Eng)

Assoc Prof
KANAYA, Toshiji
(D Eng)

Instr
NISHIDA, Koji

Students
MATSUBA, Go (DC)
MIYAZAKI, Tsukasa (DC)
SAITO, Mitsuru (MC)
TAKAHASHI, Nobuaki (MC)
KITO, Takashi (MC)
KONISHI, Takashi (MC)
OKUYAMA, Tomohiro (MC)
MATSUBARA, Shinya (UG)
YAMANO, Hiroaki (UG)

200 and 170 K, respectively, are summarized.

Firstly we briefly explain about non-Gaussian parameter A_0. Under the so-called Gaussian approximation, an incoherent elastic neutron scattering intensity $I_{el}(Q)$ can be described by

$$I_{el}(Q) = \exp(-\alpha Q^2) \quad (1)$$

where α is the mean square displacement and Q is the length of scattering vector. If α has a Gaussian distribution $g_G(\alpha)$ due to the dynamic heterogeneity, $I_{el}(Q)$ is given by

$$I_{el}(Q) = \exp(-\bar{\alpha}Q^2 + \bar{\alpha}^2 A_0 Q^4 / 2) \quad (2)$$

$$A_0 = (\overline{\alpha^2} - \bar{\alpha}^2 / \bar{\alpha}^2) \quad (3)$$

Here, A_0 is a non-Gaussian parameter corresponding to the width of the distribution $g_G(\alpha)$, and hence a measure of the heterogeneity.

The observed incoherent elastic scattering intensities $I_{el}(Q)$ are plotted versus Q^2 in Fig. 1 for PIB, clearly showing non-linear or non-Gaussian behavior. The solid curves in the figure are the best fits of eq. (2) with the observed values, from which the non-Gaussian parameter A_0 and the mean square displacement α were extracted. It was found that the evaluated A_0 increases with decreasing temperature, suggesting PIB becomes more heterogeneous with decreasing temperature. The heterogeneity can be visualized as a normalized distribution of the mean square displacement α/α_{av} as shown in inset of Fig. 1.

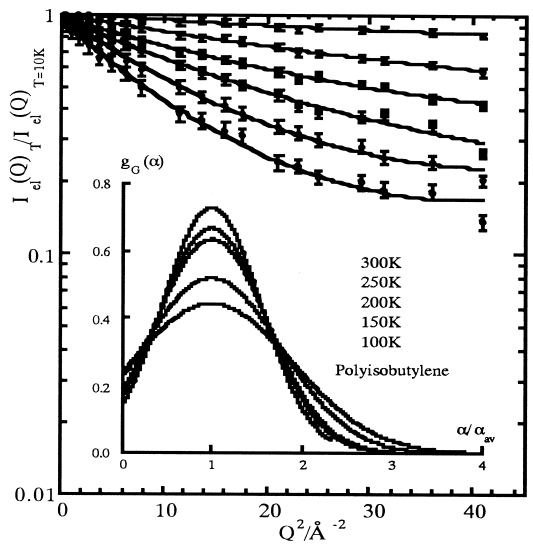

Figure 1. Incoherent elastic scattering intensity $I_{el}(Q)$ from PIB at various temperature, showing non-Gaussian behavior. Inset shows normalized distribution functions of mean square displacement α.

The behaviors of the mean square displacement are suggestive as well. Below T_g, α is proportional to temperature T, meaning that the motion observed here is approximately harmonic vibration, but above about T_g, it shows an excess value Δα, supporting the onset of relaxational motions above T_g.

The studies of the non-Gaussian parameter showed that the amorphous polymers are heterogeneous, but gave no information about the spatial scale of the heterogeneous domain or *CRR*. In order to evaluate the spatial scale we performed PALS measurements on PB and obtained the average size of free volume V_f as a function of temperature. It was found that the relation of the free volume and the viscosity can be well described by the free volume theory above T_g, meaning that the free volume observed here is related to the structural relaxation. In addition, this relaxational motion must be a cause of the excess mean square displacement Δα observed above T_g because the temperature dependence of Δα can be also well described by the free volume theory [4]. In the previous paper [5], we have derived a new formula to relate the free volume V_f to the excess mean square displacement Δα using the size (radius) ξ of *CRR* as a parameter and evaluated ξ as a function of temperature. It was found that the value ξ increases with decreasing temperature to reach 13 Å at T_g for PB, which is in good agreement with reported values [5]. It should be noted that ξ does not diverge at the Vogel-Fulcher temperature T_0 in contradiction to the fluctuation theory. This finding suggests that *CRR* is frozen in near T_g and the heterogeneity is sustained below T_g, leading to a new idea that the frozen heterogeneity is an origin of the famous Boson peak (localized mode) [5].

[1] Proc. Yukawa International Seminar (YKIS96): *Dynamics of Glass Transition and Related Topics*, ed Odagaki T, Hiwatari Y and Matsui J, 1996, Kyoto,

[2] Kanaya T, Tsukushi I and Kaji K, *Prog. Theor. Phys. Suppl.*, 126, 133 (1997).

[3] Kanaya T, Tsukushi I, Kaji K, Gabys B and Bennington S M, *J. Non-Cryst. Solids*, 235/237, 212 (1998).

[4] Kanaya T, Tsukushi I, Kaji K, Bartos J and Kristiak J, *Phys. Rev.*, E60, 1906 (1999).

[5] Kanaya T, Tsukushi I, Kaji K, Bartos J and Kristiak *J, J. Phys. IV France*, 10, Pr7-317 (2000).

[6] Kanaya T, Buchenau U, Koizumi S, Tsukushi I and Kaji K, *Phys. Rev.*, B61, R6451 (2000).